Activation of Carbon-Hydrogen Bonds by Some Derivatives of Bis(cyclopentadienyl)zirconium(IV)

Thesis by

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to my parents

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I have enjoyed my four years at Caltech. This is mainly due to the people I have worked with and the friends I have made.

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ABSTRACT

In the presence of D_2, bis(pentamethylcyclopentadienyl)zirconium(IV) dihydride $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ shows deuterium exchange with both the hydride and the thirty ring methyl hydrogen positions. At -78°C only the hydride ligands exchange with D_2 to yield H_2, HD, and D_2. At temperatures above 50°C the rate of D_2 incorporation (as determined by ^{1}H-nmr) into the ring methyl hydrogens is found to be first order in [Zr] and independent of D_2 pressure. Other bis(alkyltetramethylcyclopentadienyl)zirconium(IV) dihydrides show regioselective D_2 exchange. A mechanism for this intramolecular carbon-hydrogen activation and consistent with these data is presented involving a facile and reversible metal-to-ring hydride transfer. Results for solvent activation are also presented.

Furthermore, activation of olefin C–H bonds leads to formation of some zirconocyclopentane complexes $(\eta^5\text{-}C_5Me_5)_2\overline{ZrCH_2(CHRCHR)CH_2}$ where R is H, CH_3, and CH_3CH_2. These are synthesized from $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2$ with excesses of ethylene, propene, and 1-butene. Their pyrolysis and reactivity toward small molecules such as H_2, CO, and ethylene are presented. With one-to-one molar ratios of propene to the zirconium complex, a π-allyl hydride complex is obtained. It shows unique fluxional behavior in both ^{1}H- and ^{13}C-nmr spectra. Its reactivity and that of a π-methylallyl hydride complex are also presented.

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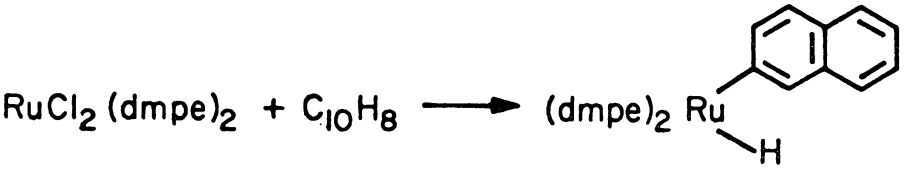
Chapter I

CARBON-HYDROGEN ACTIVATION BY HYDRIDE COMPLEXES OF PERALKYL ZIRCONOCENES

Introduction

Recently, many studies have been undertaken in the area of carbon-hydrogen bond activation by transition metal complexes. Applications to both homogeneous catalysis and synthesis have contributed to the impetus, as well as a need for mechanistic understanding. Basically two types--intramolecular and intermolecular carbon-hydrogen activation--have been reported involving a variety of Group V-VIII metal complexes.

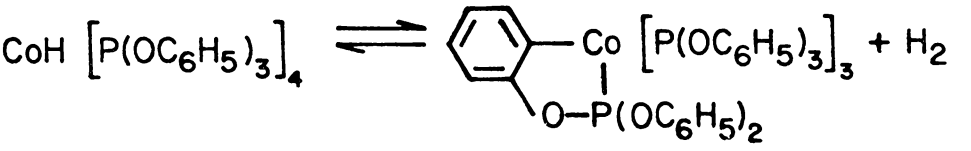
Activation of C–H bonds was first reported in the late 1930's by Farkas and Farkas[1] involving a platinum film catalyzing the exchange between gaseous benzene and D_2. Homogeneous activation was first observed by Chatt and Davidson.[2] They reported that the reduction product of $RuCl_2(dmpe)_2$ reacts with certain aromatic hydrocarbons to give an arylruthenum hydride complex (eq. 1).



(1)

Several years later, Shilov[3] reported activation of alkanes using $[PtCl_4]^{2-}$ in a mixture of D_2O and acetic acid. Garnett[4] reported in 1971 that this same system exhibited catalytic activation by producing deuterated benzenes from benzene and substituted benzenes.

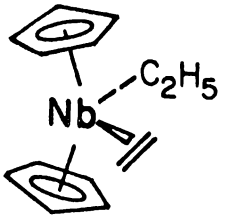
In addition, Parshall[5] has reported many systems involving intramolecular aromatic substitution in which a transition metal reacts with the C–H bond at the ortho position of an aryl donor ligand to form a carbon-metal bond (eq. 2).

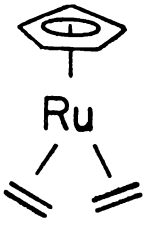


(2)

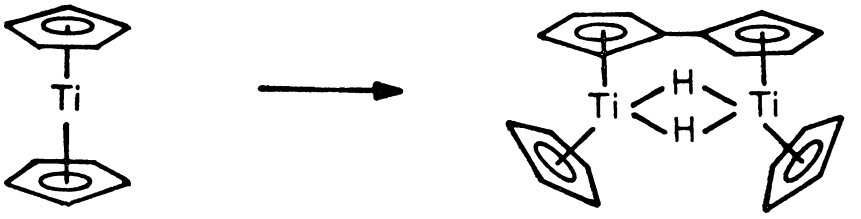
This type of activation has also been referred to as orthometallation and has included many aromatic and olefinic C–H bonds of N- and P-donor ligands.[6-12]

Other polyhydride catalysts including $TaH_3(C_5H_5)_2$[5], $IrH_5[P(CH_3)_3]_2$[5], $NbH_3(C_5H_5)_2$[13], $TaH_5(dmpe)_2$[14], and $ReH_5[P(C_6H_5)_3]_3$[15] have been shown to catalyze the intermolecular exchange of benzene with D_2. Besides these systems, several monohydride catalysts such as $RuHCl[P(C_6H_5)_3]_3$[5] which causes deuterium exchange at the ortho positions only in benzenes are known, as well as nonhydride catalysts including the two below, both of which incorporate deuterium into benzene.[5]



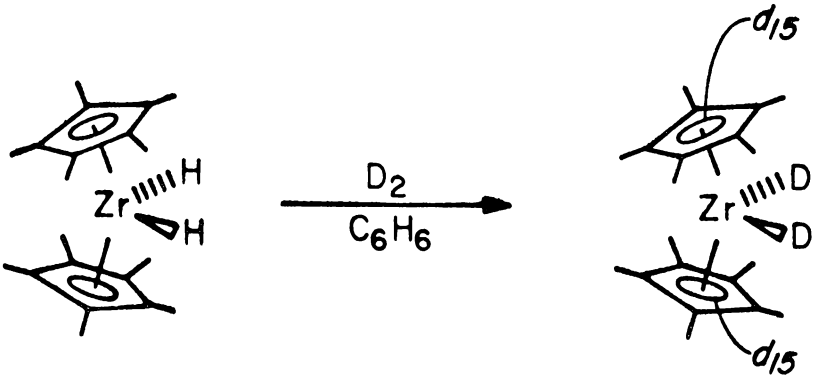


In addition to these systems, certain transition metal cyclopentadienyl complexes of Group IV undergo intramolecular insertion of the metal center into the C–H bonds of the cyclopentadienyl ligands (eq. 3).[16]



(3)

Similar results are known for zirconium which can also form polymeric species. More stable, soluble, and easily crystallizable complexes are obtained for Ti and Zr by employing pentamethylcyclopentadienyl ligands. And when the complex $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ is placed in solution in the presence of a D_2 atmosphere, the deuterium exchanges with all thirty-two hydrogens in the system (eq. 4).



(4)

Because of the apparent C–H activation, these results prompted an investigation of this H–D exchange between D_2 and the alkyl hydrogen positions of the rings and the hydride positions of bis(peralkylcyclopentadienyl)-zirconium(IV) dihydride complexes. This chapter presents those results.

Results

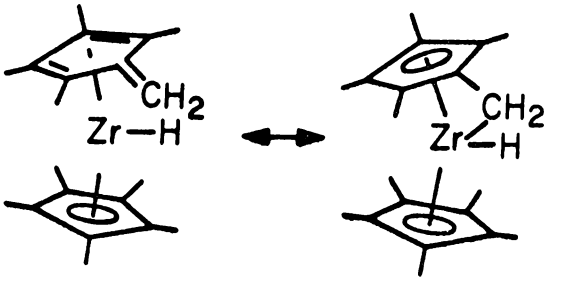
Synthesis and reactivity of bis(pentamethylcyclopentadienyl)-zirconium(IV) dihydride. A benzene or toluene solution of $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2$ (1) reacts with H_2 at room temperature to produce $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (2) quantitatively (eq. 5).

$$\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2 + 2H_2 \rightarrow 2(\eta^5\text{-}C_5Me_5)_2ZrH_2 + 3N_2 \qquad (5)$$

The reaction is stoichiometric yielding three moles of N_2 and consuming two moles of H_2 per dimer. The reaction proceeds from deep purple due to 1 through a dark blue to a pale yellow 2. The yellow crystals of 2 are very soluble in hydrocarbon and ether solvents. Its molecular weight (cryoscopically determined for 112 mg of 2 per g of benzene as 369; calculated as 364), analytical data, and spectra are entirely in accord with a monomeric pseudotetrahedral structure similar to $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$. The Zr-H bonds of 2 appear to be hydridic as exemplified by its readily reducing both HCl and CH_3I quantitatively (eq. 6).

$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 \xrightarrow{HCl} (\eta^5\text{-}C_5Me_5)_2ZrCl_2 + 2H_2$$
$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 \xrightarrow{CH_3I} (\eta^5\text{-}C_5Me_5)_2ZrI_2 + 2CH_4 \qquad (6)$$

Furthermore, 2 is very stable in solution and in the solid state, showing no apparent decomposition at 120°C *in vacuo* for days. But 2 is extremely oxygen and water sensitive decomposing to various Zr-O bonded species. Besides forming directly from 1, 2 can also be obtained by reacting H_2 with a solution of an intermediate formed when 1 is placed *in vacuo* and its N_2 is removed. The complex 3 that is formed appears to have a structure consistent with 3a or 3b but not simply permethylzirconocene.



3a 3b

This red complex is monomeric from molecular weight determinations (cryoscopically determined for 120 mg of 3 per g of benzene as 383; calculated as 362) and was characterized by analytical data and ^{1}H-nmr and ir spectral data. Structures 3a and 3b are invoked mainly based on ^{1}H-nmr data which suggest that one ring's motion is stopped. Indeed, proton signals for four methyls can be identified along with protons from a methylene. And a hydride signal is present in the nmr as well as in the ir. This complex is thermally unstable, decomposing within hours at room temperature. Its reactivity and kinetics with H_2 uptake do not appear to be straightforward. These results are presented in the Appendix. Besides

these methods, 2 can also be obtained by treating $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ with $Li^+[BH(C_2H_5)_3]^-$ in THF or with $Na^+[AlH_2(OCH_2CH_2OCH_3)_2]^-$ in benzene. However, its isolation from these reaction mixtures is extremely difficult. Consequently, in all cases 2 was prepared in situ from 1.

Hydride-D_2 exchange. In order to better understand the exchange between D_2 and all the hydrogen positions of 2, the study was divided into investigations of only the hydride exchange and then of the ring-methyl-hydrogen exchange. The hydride positions readily exchange with a deuterium atmosphere. This was followed by the disappearance of the ^1H-nmr signal at probe temperature when the complex was allowed to stand over D_2.

Selectivity of hydride exchange only was accomplished by allowing the reaction to occur at temperatures below zero degrees--temperatures at which no deuterium incorporation in the ring methyl hydrogens was occurring. A solution of 2 was exposed to a D_2 atmosphere at -78°C, and the gas phase above the solution was monitored for its H_2, HD, and D_2 content by mass spectrometry. After 15 minutes the gas above the toluene solution of 2 was completely scrambled into a statistical mixture of H_2, HD, and D_2. Allowing the reaction to occur at -105°C in isopentane with D_2 ($\sim$2 times the mole fraction of D as H present) and sampling the gas above the reaction at specific intervals permitted a rough determination of the rate of HD formation to be $6 \times 10^{-4} sec^{-1}$. By using the dideuteride with H_2 above the solution and repeating the procedure, the H–D isotope effect was determined to be 0.8 for k_H/k_D.

Ring methyl hydrogen exchange in bis(pentamethylcyclopenadienyl)-zirconium(IV) dihydride. At temperatures above 20°C all thirty methyl hydrogen positions of the two permethylcyclopentadienyl rings exchange with a deuterium atmosphere. The kinetic rate of this exchange was measured in benzene following the disappearance of the methyl hydrogen resonance in the ^{1}H-nmr spectrum relative to an internal standard of ferrocene. The D_2 atmosphere over $\underset{\sim}{2}$ in each case provided $\geq$ 80g atom excess of D allowing the exchange to proceed to $\geq$ 98% completion.

The observed kinetic rate of disappearance of the ring methyl proton signal in the nmr was that of a first order dependence on $\underset{\sim}{2}$. Further measurements at D_2 pressures ranging from 0.5 to 1.6 atmospheres indicated the rate to be independent of pressure. Thus, the rate of D_2 incorporation into the C–H bonds of $\underset{\sim}{2}$ can be expressed as follows:

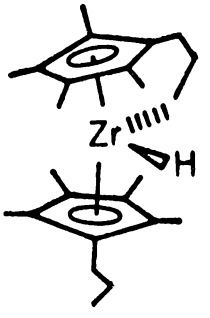
$$\text{rate} = k[Zr] \qquad k = 3.3 \times 10^{-5}\,\text{sec}^{-1} \text{ at } 50°C$$
$$k = 1.4 \times 10^{-4}\,\text{sec}^{-1} \text{ at } 64°C$$
$$k = 3.9 \times 10^{-4}\,\text{sec}^{-1} \text{ at } 80°C$$

From these data, and using the Arrhenius-Eyring equation, the activation energy $\Delta H^{\neq}$ was determined to be 19 kcal/mole and the $\Delta S^{\neq}$ was -23 eu.

Furthermore, the fact that the deuterium could be incorporated into all positions of the dihydride allowed for formation of the bis(perdeuteriopentamethylcyclopentadienyl)zirconium dideuteride. The same kinetic procedure was followed using H_2 in order to determine the isotope effect. The rate of deuterating the perprotio-complex was found to be $\sim$ 7 times faster than protonating the perdeuterio-complex.

Ring alkyl hydrogen exchange in bis(alkyltetramethylcyclopentadienyl)zirconium(IV) dihydride. In order to assess the regioselectivity of deuterium incorporation into the ring alkyl hydrogens, a systematic study of a series of bis(alkyltetramethylcyclopentadienyl)zirconium dihydrides was made. The synthetic route for alkyltetramethylcyclopentadienes[17] provided the means for obtaining the parent compound with pentamethylcyclopentadienyl rings, the ethyltetramethylcyclopentadienyl ring system, the n-propyltetramethylcyclopentadienyl ring system, and the neo-pentyltetramethylcyclopentadienyl ring system.

The synthesis of all of these dihydride complexes followed the procedures used to obtain the parent permethyl system. This consisted of first forming the dichloride $(\eta^5\text{-}C_5RMe_4)_2ZrCl_2$ from $ZrCl_4$ and $Li^+(C_5RMe_4)^-$ in DME followed by reduction in benzene under N_2 with sodium amalgam. In the ethyltetramethylcyclopentadiene case, the purple dinitrogen complex $(\eta^5\text{-}C_5EtMe_4)_2Zr(N_2)_2N_2$ was obtained which upon treatment with H_2 formed the dihydride (4). However, when the other two bis(alkyltetramethylcyclopentadienyl)zirconium dichlorides were reduced, they complexed no nitrogen. Instead, they formed complexes 5 and 6 as revealed by ^{1}H-nmr spectra and analysis.



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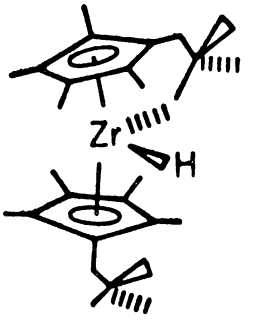
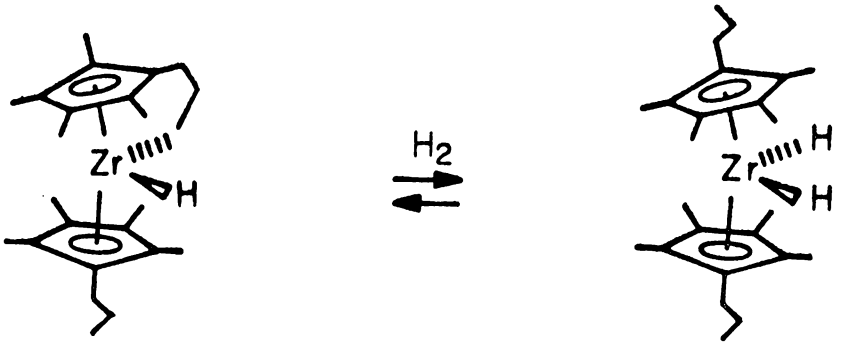
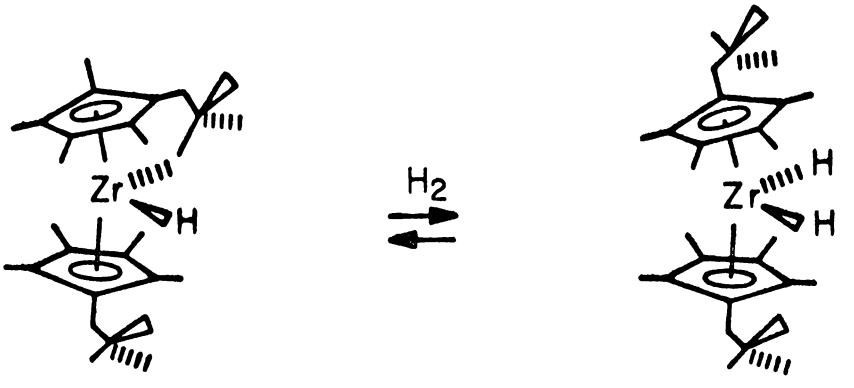


6

These yellow complexes were difficult to purify. They reversibly bind H_2. When solutions of 5 or 6 were placed under H_2 they formed the dihydrides, but when the H_2 atmosphere was removed 5 and 6 reformed (eq. 7).



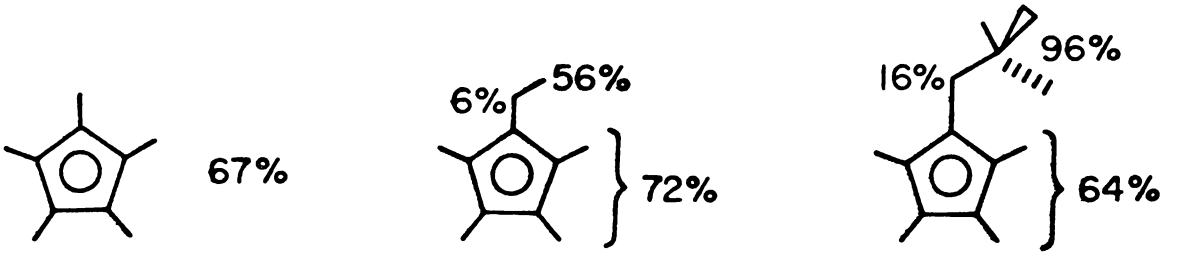
5 7 (7)



6 8

Because of the difficulty involved in purifying the n-propyl case 5 and because the ^{1}H-nmr spectrum of 7 did not clearly discern the various methylene hydrogens on the n-propyl groups, only 6 and 8 were studied further.

In each case the corresponding dihydride was allowed to exchange with a deuterium atmosphere for one hour at 70°C in benzene in the same manner as with 2. The comparative results are given below:



These percentages are based on the relative amount of deuterium incorporation with respect to ferrocene as compared to the fully deuterated complex. Within the experimental error (± 7%) the ring methyls are 68% deuterated. The methylene positions of the ethyl and neo-pentyl groups show considerably less deuterium incorporation. The methyl groups of the neo-pentyl, however, are nearly completely deuterated.

Activation of solvent with bis(pentamethylcyclopentadienyl)-zirconium dihydride. An investigation of the ability of these dihydrides to undergo intermolecular C—H activation led to 2 being heated to 120°C in a thick-walled vessel with benzene-d_6 and toluene-d_8 and with ∿ 4 atm of H_2. After one week the toluene-d_8 showed 54% protonation of the C_6D_5 group and 71% protonation of the CD_3 group. This was determined by ^{1}H-nmr using a ferrocene internal standard. No methylcyclohexane appeared. The benzene-d_6 showed 25% protonation and no cyclohexane formation. In each

case 2 showed corresponding degrees of deuterium incorporation.

Besides aryl solvents 2 was heated three days at 110°C with cyclohexane-d_{12} under ~ 4 atm of H_2. No protonation of the solvent occurred.

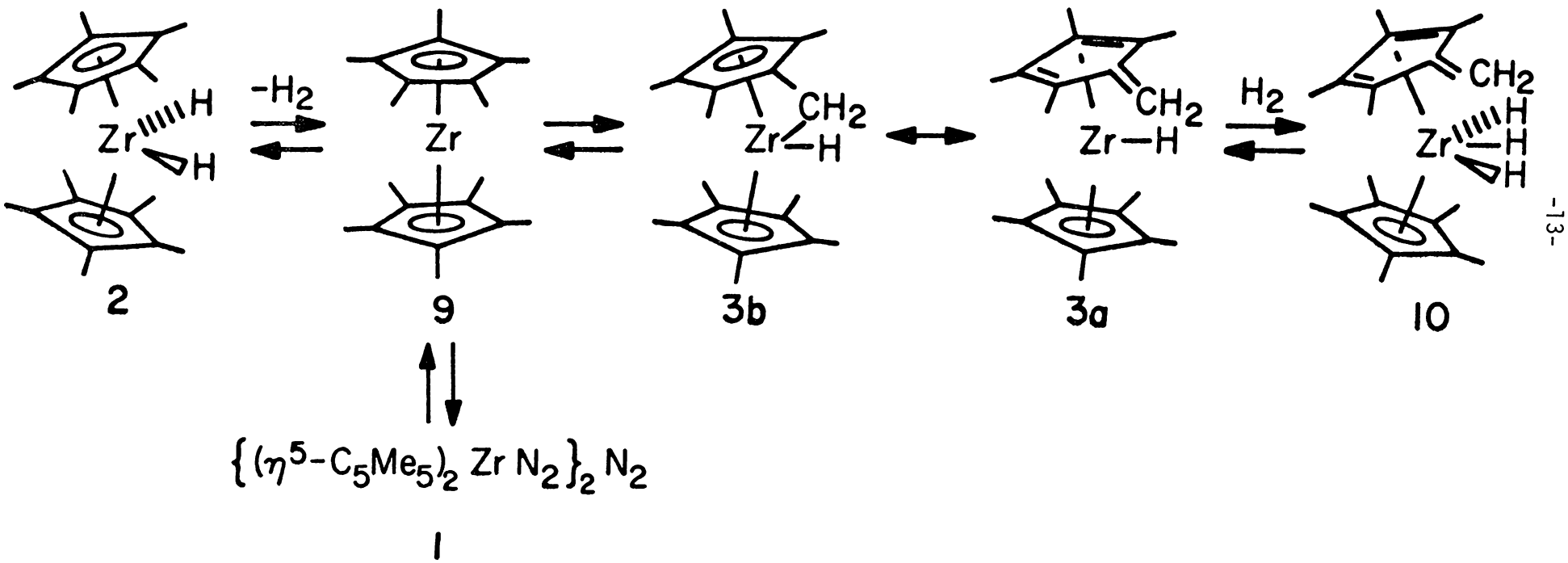
Discussion

In order for the ring methyl hydrogens to exchange with D_2 in these bis(peralkylcyclopentadienyl)zirconium dihydride complexes, some sort of C—H activation must be occurring. In addition, complex 3 appears to be an intermediate in this reaction pathway. These results suggest that one reasonable mechanism is that shown in Scheme I. This mechanism first involves a rapid preequilibrium between 2 and 9 leading to reductive elimination of H_2 to give permethylzirconocene. This can then slowly form 3 as 3a or 3b. Since 3a involves formally Zr(II), oxidative addition of H_2 or D_2 can occur. By reversing the steps, deuterium can be incorporated into the ring-methyl-hydrogen positions. This mechanism also allows for formation and decomposition of the dinitrogen complex 1.

Although initially plausible, this mechanism does not explain all of the results satisfactorily. Since the HD forms upon hydride-D_2 exchange, and since the mechanism implies reductive elimination of just H_2 or D_2, another additional step involving a rapid bimolecular exchange of hydride ligands would have to be occurring (eq. 8).

$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + (\eta^5\text{-}C_5Me_5)_2ZrD_2 \rightleftarrows 2(\eta^5\text{-}C_5Me_5)_2ZrHD \qquad (8)$$

The possibility of such a reaction was checked using 2 and perdeuterio bis(ethyltetramethylcyclopentadienyl)zirconium dideuteride, since the



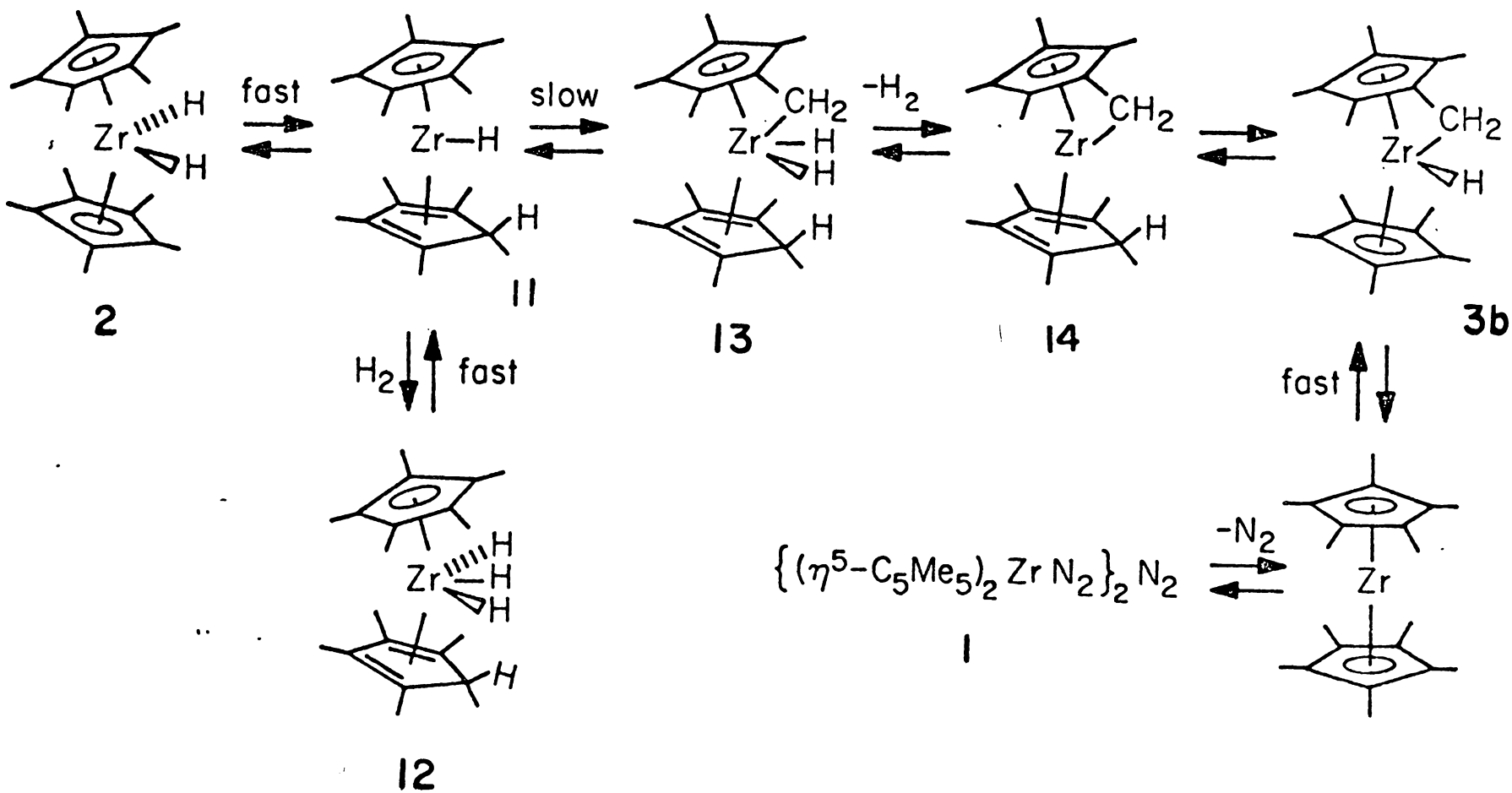
Scheme I

hydride peaks appeared to have different chemical shifts in the ^{1}H-nmr. The reaction did show exchange and incorporation of H and D into the corresponding systems at elevated temperatures. Certainly this process may be occurring, but it does require formation of the dideuteride. And since 2 shows high thermal stability with no loss of H_2 in vacuo, the fast preequilibrium 2 ⇄ 9 seems unlikely especially at -78°C.

Reversible addition of H_2 forming 10 demands the 3a species with its conjugation of the Zr-CH_2 moiety to the cyclopentadiene ring. Without invoking 3a an oxidative addition to Zr(IV) would be necessary but highly unlikely. This type of conjugated species should be apparent in the comparison of relative rates of deuterium incorporation in other bis(alkyltetramethylcyclopentadienyl)zirconium dihydrides. The results of this study show rather conclusively that the fulvene-type complex does not explain the activation. Indeed, in the ethyltetramethylcyclopentadienyl case, deuterium incorporation occurs readily into the methyl C–H bonds of the ethyl groups and to a much smaller extent into the methylene C–H positions. Certainly, with the neo-pentyltetramethylcyclopentadienyl ligand, the exchange is considerably faster for the terminal methyls of the neo-pentyl groups. Species 6 demonstrates the enhanced stability resulting from zirconium-carbon bond formation leading to a pseudo-five membered ring about the metal. Several other intramolecular C–H activated species have been reported to preferentially form five membered rings about the metal.[18,19] This stability is evidenced by 8 easily losing its H_2 and reforming 6 which shows no decomposition at room temperature unlike 3.

Because of these inconsistencies between the proposed mechanism and the observed results, Scheme II is proposed. This mechanism features a facile and reversible metal-to-ring hydride transfer forming (pentamethylcyclopentadienyl)(1-exo--methyltetramethylcyclopentadiene)hydridozirconium(II) $\underset{\sim}{2} \rightleftarrows \underset{\sim\sim}{11}$. Benfield and Green[20,21] have reported an analogous rearrangement of $(\eta^5\text{-}C_5H_5)_2Mo(C_2H_5)Cl$ to $(\eta^5\text{-}C_5H_5)$(1-exo-ethyl C_5H_5)-$Mo(PR_3)_2Cl$ by addition of phosphines to the starting material. In addition, a reversible hydride and/or alkyl transfer to a $(\eta^5\text{-}C_5H_5)$ ring has been proposed for the formation of a bis-mesityl derivative of tungstenocene when $(\eta^5\text{-}C_5H_5)_2WH_2$ is irradiated in mesitylene.[21,22] And a $(\eta^5\text{-}C_5H_5)Co(PMe_3)_2$ system shows facile transfer of an electrophile from the Co to the ring for electrophilic substitution.[23] In order to substantiate this intermediate the synthesis of bis(1,2,3-trimethylcyclopentadienyl)zirconium dihydride was attempted. Since hydride shifts are known for cyclopentadienyl systems, if the intermediate formed with a D being transferred to the ring it could undergo a hydride shift which would allow it to remain incorporated in the ring even after reforming the dihydride. The initial step in synthesizing the ligand, however, could not be achieved.

Indeed, intermediate $\underset{\sim\sim}{11}$ allows for oxidative addition of D_2 forming $\underset{\sim\sim}{12}$ which can reductively eliminate HD to explain the hydride exchange kinetics. It also provides for insertion of Zr into the C—H bonds of the ring alkyls forming $\underset{\sim\sim}{13}$ which can undergo reductive elimination of H_2. This then allows D_2 to oxidatively add, which upon reversal of the steps, incorporates deuterium into the ring alkyl positions. Furthermore, this scheme obeys the observed rate expression involving only [Zr]. Providing that $\underset{\sim\sim}{13} \rightleftarrows \underset{\sim\sim}{14}$ is much faster than $\underset{\sim\sim}{11} \rightleftarrows \underset{\sim\sim}{13}$, any H_2 pressure dependence drops


fast
slow
$-H_2$
H_2
fast
fast
$-N_2$
$\{(\eta^5-C_5Me_5)_2 Zr N_2\}_2 N_2$
1
2
11
12
13
14
3b

Scheme II

out of the rate expression. This mechanistic pathway satisfies the activation parameters including the $\Delta S^{\neq}$ of -23 eu assuming the slow step involves 13 in which all ring motion is stopped. And the isotope effect--in particular the kinetic isotope effect of ~ 5 for k_H/k_D--agrees with the necessary C–H bond breaking required in this scheme.

Scheme II accommodates the various alkyl ring derivatives and their exchange results. The pseudo-five membered ring provided by the neopentyl system certainly seems to be most desired, and those methyl hydrogens easiest to activate. This ease of exchange is also apparent with the ethyl case, although not to the same extent. The methylene positions are less likely to be activated since they are adjacent to the more desirable methyl hydrogens and possibly since they are secondary carbons which, according to several studies on intramolecular activation involving phosphines and intermolecular activation of alkenes, suggest that the rate of exchange follows the pattern of primary > secondary > tertiary.[18,24]

Further evidence for this mechanism is provided by a study of the reductive elimination of isobutane from bis(pentamethylcyclopentadienyl)-zirconium(IV) isobutyl hydride reported by Don McAlister.[25] The complexes $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$ (20), $(\eta^5\text{-}C_5Me_5)_2Zr(D)(CH_2CDMe_2)$ (21), and $[\eta^5\text{-}C_5(CD_3)_5]_2Zr(D)(CH_2CDMe_2)$ (22) were all obtained quantitatively from treatment of benzene solutions of $(\eta^5\text{-}C_5\text{-}Me_5)_2ZrH_2$, $(\eta^5C_5Me_5)_2ZrD_2$, and $[\eta^5\text{-}C_5(CD_2)_5]_2ZrD_2$ with isobutylene at 25°C (eq. 8).

$$[\eta^5\text{-}C_5(CX_3)_5]_2ZrY_2 + CH_2{=}{=}CMe_2 \rightarrow [\eta^5\text{-}C_5(CX_3)_5]_2Zr(Y)(CH_2CYMe_2)$$

(20) X = Y = H

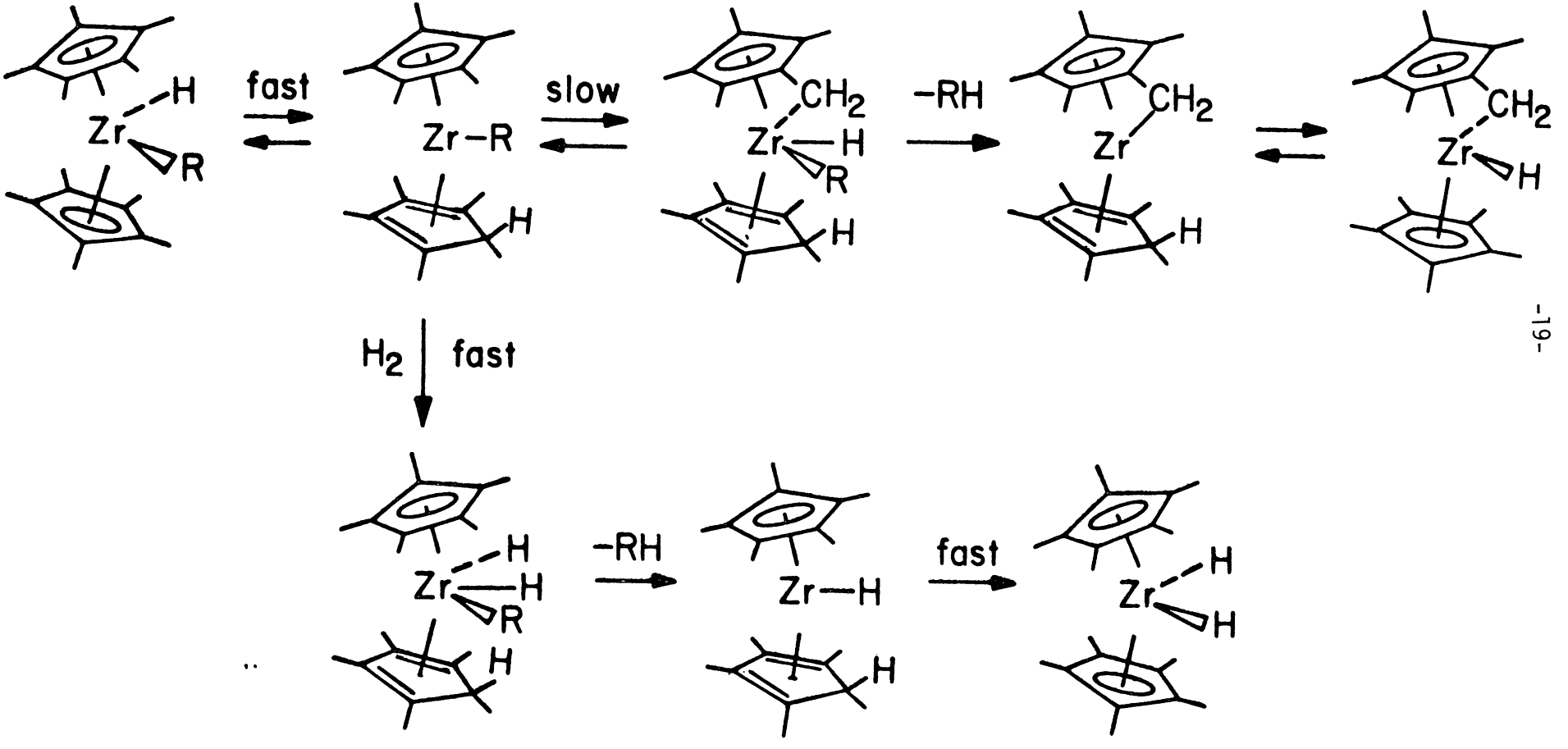
(21) X = H; Y = D (8)

(22) X = Y = D

Unlike other permethylzirconocene complexes, these compounds decompose readily at 75°C providing isobutane quantitatively. The isotopic distributions for these isobutanes show that pyrolysis of $\underset{\sim\sim}{20}$ gives isobutane, $\underset{\sim\sim}{21}$ gives 2-deuterio-2-methylpropane, $\underset{\sim\sim}{22}$ gives 1,2-dideuterio-2-methylpropane and a 1:1 mixture of $\underset{\sim\sim}{20}$ and $\underset{\sim\sim}{22}$ gives only isobutane and 1,2-dideuterio-2-methylpropane. The fourth result implies that no intermolecular process is occurring. The other three results point to an intramolecular coupling of the isobutyl group with a hydrogen or deuterium from a cyclopentadienyl methyl group.

The isobutyl hydride also reacts rapidly with H_2 at -15°C to give the dyhydride $\underset{\sim}{2}$ and isobutane. Both $\underset{\sim\sim}{21}$ and $\underset{\sim\sim}{22}$ react with H_2 to produce 2-deuterio-2-methyl-propane. But $\underset{\sim\sim}{20}$ reacts with D_2 to yield 1-deuterio-2-methyl-propane and $\underset{\sim\sim}{21}$ gives 1,2-dideuterio-2-methylpropane. These results support the mechanism outlined in Scheme II and its description of the hydride exchange. Consequently, this scheme can be expanded to include alkyl hydrides. This is shown in Scheme III. Certainly, this mechanism is by no means proven, but it does seem most reasonable in light of all observed data and results.

Finally, shifting from intramolecular to intermolecular activation, the bis(pentamethylcyclopentadienyl)zirconium dihydride shows some activation of solvents. Both benzene-$\underline{d}_6$ and toluene-$\underline{d}_8$ show protonation upon mixing with $\underset{\sim}{2}$ under H_2 at 120°C for several days. No cyclohexane or methylcyclohexane appear. And no activation of cyclohexane occurs. The activating conditions, however, are rather extreme. With the apparent ease by which the system is capable of activating its own bonds, similar



$R = CH_2CHMe_2$

Scheme III

bonds from external solvents would be expected to show similar activation unless possibly steric effects are operative. In any case this system exhibits some unique examples of carbon-hydrogen activation.

Experimental Section

General considerations. All manipulations were carried out using either glove box or high vacuum line techniques. Prior to use all solvents were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene."[26] All nmr solvents were purified over activated 4Å molecular sieves, followed by "titanocene." Hydrogen and deuterium (MCB) were passed over MnO on vermiculite[27] and activated 4Å molecular sieves.

^{1}H-nmr spectra were recorded on Varian A-60A and EM-390 spectrometers. Infrared spectra were obtained using a Beckman Ir-12 spectrophotometer. Mass spectrometry data were obtained using a DuPont spectrometer.

Procedures

(1) $(\eta^5\text{-}C_5Me_5)_2ZrH_2$. (a) Synthesis from 1. After transferring 0.0740 mmoles of 1 to a small round-bottomed flask, a calibrated volume was added (Figure 1). Then ∿15 ml of toluene was vacuum transferred at -78°C onto the solid. To the stirring solution was added 0.5950 mmoles of H_2 from the calibrated volume. Upon warming to room temperature the solution changed from purple to blue to yellow. Toepler pumping the gas through three -196°C cooled traps yielded 0.2150 mmoles of N_2 (2.91 mmoles N_2/mmoles 1) and showed that 0.1470 mmoles of H_2 (1.98 mmoles H_2/mmoles Zr) were consumed. The ^{1}H-nmr spectrum showed signals at 2.02δ (s,30,

$10CH_3$) and 7.46 δ (s,2,2H). The $\nu_{(Zr-H)}$ appeared at 1555 cm^{-1} in the ir spectrum.

(b) Synthesis from 3. About 25 ml of toluene were vacuum distilled onto 0.1239 mmoles of 1. The N_2 was pumped off slowly at room temperature under a dynamic vacuum. After about two hours 3 was formed. Its ^{1}H-nmr spectrum (C_7D_8) showed signals at 1.07δ(d,1,CH), 1.30δ(d,1,CH), 1.33δ(s,3,CH_3), 1.61δ(s,3,CH_3), 1.87δ(d,3,CH_3), 1.92δ(s,15,$5CH_3$), 2.10δ(s,3,CH_3), and 5.40δ(s,1,H). The ir spectrum (Nujol mull on KBr plates) showed $\nu_{(Zr-H)}$ 1525 cm^{-1}. Then ∿ 20 ml of toluene were distilled onto 3 and one atmosphere of H_2 was added. Within several minutes at room temperature 2 formed.

(c) Synthesis from $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ and $Li^+[BH(C_2H_5)_3]^-$. To a swivel frit assembly (Figure 2) was added 2 g of $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$. Toluene was vacuum distilled in, followed by addition at -78°C of 7.2 ml of a 1.3 M solution of $Li^+[BH(C_2H_5)_3]^-$ in THF with a counter flow of Ar. The mixture was stirred and allowed to warm to room temperature. After one hour the toluene was removed and 30-60 pet ether was added. The mixture was filtered and the pet ether removed. A clear oil was recovered which showed some $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ present along with other by-products in the ^{1}H-nmr spectrum.

(d) Synthesis from $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ and $Na^+[AlH_2(OCH_2CH_2OCH_3)_2]^-$. The procedure of (c) was followed except 1 g of $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ and 10 ml of a 70% solution of $Na^+[AlH_2(OCH_2CH_2OCH_3)]^-$ in benzene was used. Again the ^{1}H-nmr spectrum showed formation of 2 but with several other products present.

(e) Reaction of $\underset{\sim}{2}$ at high temperature . In an nmr tube was placed 55 mg (0.0681 mmoles) of $\underset{\sim}{1}$. Then benzene-d_6 was distilled in. Next, one atmosphere of H_2 was added until $\underset{\sim}{2}$ was formed. Then the H_2/N_2 mixture was removed and the tube was sealed off. Upon heating the tube in vacuo to 120° for 1 week, no change was observed.

(f) Reaction of $\underset{\sim}{2}$ with HCl . To a toluene solution at -196°C of 0.1490 mmoles of $\underset{\sim}{2}$ was added 0.8920 mmoles of anhydrous HCl which had been through one freeze-pump-thaw cycle. After warming to room temperature the solution was Toepler pumped. This gave 0.1380 mmoles of H_2 (0.93 H_2/Zr). The other product was $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$.

(g) Reaction of $\underset{\sim}{2}$ with CH_3I . To a toluene solution of 0.1830 mmoles of $\underset{\sim}{2}$ at -196°C was added 1.100 mmoles of CH_3I (dried over CaH_2). The solution was stirred and allowed to warm to room temperature. Toepler pumping yielded 0.3560 mmoles of CH_4 (1.95 CH_4/Zr). The other product was $(\eta^5\text{-}C_5Me_5)_2ZrI_2$.

(2) Hydride-D_2 exchange at low temperature. For the reaction at -78°C, 63.2 mg (0.0783 mmoles) of $\underset{\sim}{1}$ was placed in a 25 ml round-bottomed flask to which ∿15 ml of toluene was added in vacuo. Then one atmosphere of H_2 was added, and the solution was warmed to room temperature until the purple $\underset{\sim}{1}$ disappeared and the yellow $\underset{\sim}{2}$ appeared. At -78°C the H_2/N_2 mixture was pumped away in vacuo. Then 0.3494 mmoles of D_2 was added while the solution was stirring at -78°C. After 15 min the solution was cooled to -196°C, and the gas above the solution was Toepler pumped through three -196°C cooled traps. After a freeze-pump-thaw cycle the gas in the solution was also Toepler pumped. A fraction of the gas was added to a gas

bulb and the contents were analyzed by mass spectrometry to be 54% D_2, 38% HD, and 9% H_2 as compared with 48% D_2, 43% HD, and 10% H_2 for a statistical mixture.

For the -105°C reaction, 152.4 mg (0.1888 mmoles) of $\underset{\sim}{1}$ were placed in a special apparatus (Figure 3) to which 10 ml of isopentane was added in vacuo. After adding one atmosphere of H_2 and converting $\underset{\sim}{1}$ to $\underset{\sim}{2}$, the N_2/H_2 mixture was removed and 0.7558 mmoles of D_2 were added with the solution stirring at -105°C; this was maintained by passing dry N_2 through coils cooled to -196°C and blowing this gas on the reaction vessel. Then 0.0168 mmole samples of gas were periodically removed and allowed to fill gas bulbs whose contents were analyzed for H_2, HD, and D_2 by mass spectrometry.

A plot of the log of the final HD (statistical) percentage minus the initial HD percentage versus time was linear for greater than three half-lives. The first order rate constant was $6 \times 10^{-4} sec^{-1}$.

The same procedure was followed for the -105°C reaction using 150.0 mg (0.1858 mmoles) of $\underset{\sim}{1}$ and adding D_2 several times to convert $\underset{\sim}{1}$ to the dideuteride. Then 0.7450 mmoles of H_2 were added. Again the H_2, HD, and D_2 was analyzed. The first order rate constant was 7.5×10^{-4} sec^{-1} for HD formation.

(3) Kinetics of deuterium exchange with ring methyl hydrogens of bis(pentamethylcyclopentadienyl)zirconium dihydride. The extent of deuterium incorporation into the ring methyl hydrogens of $\underset{\sim}{2}$ was monitored by ^1H nmr. In a typical experiment (giving one data point) 60 mg (0.0743 mmoles) of $\underset{\sim}{1}$ and 50 mg (0.2688 mmoles) of ferrocene were placed

in a special reaction vessel (Figure 4). Then 15 ml of benzene were distilled into the apparatus at -78°C in vacuo. Next, one atmosphere of H_2 was added and the solution was warmed to room temperature in order to convert 1 to 2. The H_2/N_2 gas mixture was removed at -78°C and 43.6 mmoles of D_2 were added. The apparatus was placed in a constant temperature oil bath for the allotted time. Following this, the gas mixture and most of the solvent were removed and an nmr sample was prepared from the benzene.

In order to determine the percentage complete by nmr, a ratio of ratios was calculated. This involved first determining the ratio of the ring methyl proton integration to the ferrocene ring proton integration. Then the ratio of the calculated mole fraction of H in the ring methyl hydrogens present to the calculated mole fraction of H in the ferrocene ring hydrogens was determined. The ratio was then taken of these two ratios and the result was subtracted from one in order to express the amount deuterated. This result was then divided by the calculated mole fraction of D in the entire system (correcting for deuterium used being 98.7% D_2, 1% HD, and 0.3% H_2). The resulting fraction when multiplied by 100 gave the percentage complete.

A plot of the log of 100 minus the percentage complete versus time was linear. The first order rate constants were determined at 50°C, 64°C, and 80°C. The pressure (mmoles of D_2) was varied from 0.6 atm, 1.0 atm, and 1.6 atm. No dependence was observed. And the above procedure was used to obtain isotope effects by completely deuterating 2. This was accomplished by using the special vessel and changing the D_2 above the solution every three hours for six times. Then the H_2 was added

instead of D_2. The kinetic rate was $1.9 \times 10^{-5} sec^{-1}$ at 64°C.

(4) $(\eta^5\text{-}C_5Me_4Et)_2ZrH_2$. The preparation of this compound parallels closely the synthesis of 2. The ligand ethyltetramethylcyclopentadiene was prepared using the procedure of Threlkel and Bercaw.[17] The $(\eta^5\text{-}C_5Me_4Et)_2ZrCl_2$ was then prepared using analogous steps as outlined by Manriquez and Bercaw.[28] The ^{1}H-nmr spectrum ($CDCl_3$) showed peaks at 0.9 δ(t,6,$2CH_3$), 2.0 (s,24,$8CH_3$), and 2.4 δ(q,4,$2CH_2$). The infrared spectrum (Nujol mull on KBr plates) showed bands of 2720(w), 1630(w), 1430(s), 1375(s), 1160(m), 1070(w), 1060(s), 1025(s), 970(m), 950(m), 790(w), 760(w) cm^{-1}. Calculated for $C_{22}H_{34}Cl_2Zr$: C 57.36, H 7.44; found: C 57.08, H 7.19.

The corresponding dinitrogen complex was made. The dichloride was added to a special apparatus (Figure 5), then benzene was distilled in and 1% Na/Hg was added as a 10-fold excess. The mixture was then stirred at room temperature for three days under one atmosphere of N_2. Then after letting the Na/Hg settle, the purple solution was filtered, the benzene was removed in vacuo, and 30-60 pet ether was added with an N_2 atmosphere. Green metallic crystals formed and were filtered and washed. The ^{1}H-nmr spectrum (C_6D_6) showed signals at 1.00 δ(t,6,$2CH_3$), 2.00 δ(s,12,$4CH_3$), 2.03 δ(s,12,$4CH_3$), and 2.58 δ(q,4,$2CH_2$). The infrared spectrum (Nujol mull on KBr plates) showed bands of 2860(m), 2040(m), 2000(s), 1570(m), 1025(w) cm^{-1}. Calculated for $C_{44}H_{68}N_6Zr_2$: C 61.20, H 7.94; found: C 61.03, H 7.97.

Then, to a small flask was added 0.1543 mmoles of $\{(\eta^5\text{-}C_5Me_4Et)_2\text{-}ZrN_2\}_2N_2$. A calibrated volume (see Figure 1) was added and ~15 ml of

toluene were distilled on in vacuo. Next, 1.018 mmoles of H_2 were added. Toepler pumping the gases yielded 0.4655 mmoles of N_2 (1.3 N_2/Zr) and 0.7085 mmoles of H_2(0.9 H_2/Zr). The ^{1}H-nmr spectrum (C_6D_6) showed peaks at 1.02 δ(t,6,2CH_3,$^3J_{HH}$ = 7 Hz) 2.03 δ(s,12,4CH_3), 2.05 δ(s,12,4CH_3), 2.60 δ(q,4,2CH_2,$^3J_{HH}$ = 7 Hz), and 7.45 δ(s,2,2H). The infrared spectrum (Nujol mull on KBr plates) showed bands at 2720(w), 1560(m), 1310(w), 1150(w), 1080(m), 1030(m), 960(w), 750(m), 720(m), 650(s) cm^{-1}.

(5) $(\eta^5$-$C_5Me_4CH_2CH_2CH_3)_2ZrH_2$. This complex was prepared by a method similar to 2 and $(\eta^5$-$C_5Me_4Et)_2ZrH_2$. The ligand was made using the Threlkel and Bercaw[17] procedure. The $(\eta^5$-$C_5Me_5CH_2CH_2CH_3)_2ZrCl_2$ was synthesized in a manner identical with $(\eta^5$-$C_5Me_5)_2ZrCl_2$ and $(\eta^5$-$Cl_5Me_4Et)_2$-$ZrCl_2$. The reduction with Na/Hg was done the same as in (4) except no dinitrogen complex formed. Instead only 5 formed. Upon treating 5 with H_2 in solution the corresponding dihydride was formed. The ^{1}H-nmr spectrum consisted of the following: 2.00 δ(t,6,3CH_3), 1.60 δ(m,4,2CH_2), 2.02 δ(s,12,4CH_3), 2.06 δ(s,12,4CH_3), 2.20 δ(m,4,2CH_2), and 7.44 δ(s,2,2H). Calculated for 5 $C_{24}H_{38}Zr$: C 75.96, H 10.09; found: C 69.34, H 9.24.

(6) $(\eta^5$-$C_5Me_4CH_2CMe_3)_2ZrH_2$. This complex was prepared in a manner similar to that given in (5). The ligand was made using 3,3-dimethylbutyric chloride instead of ethyl acetate used in the pentamethyl case. The reduction gave 6. Calculated for $C_{28}H_{46}Zr$: C 70.97, H 9.78; found: C 70.73, H 9.67. Adding an H_2 atmosphere to the complex produced 8 . The ^{1}H-nmr (C_6D_6) showed signals at 0.95 δ(s,18,6CH_3), 20.2 δ(s,12,4CH_3), 2.08 δ(s,12,4CH_3), 2.65 δ(s,4,2CH_2), and 7.43 δ(s,2,2H). (See Figure 6).

(7) Kinetics of deuterium exchange with ring alkyl hydrogens of bis(alkyltetramethyl)cyclopentadienyl)zirconium dihydrides. The procedure of (3) was followed. The only exception was that the $(\eta^5\text{-}C_5Me_4CH_2CMe_3)_2ZrH_2$ was added directly to the reaction vessel since it did not form any dinitrogen complex. Each sample was run one hour at 70°C with one atmosphere of D_2. The data were treated the same as (3) except the final comparison with the calculated mode fraction of D in the entire system was eliminated. This gave only the relative percentages.

(8) Reaction of 2 with $[\eta^5\text{-}C_5(CD_3)_4(CD_2CD_3)]_2ZrD_2$. First the $(\eta^5\text{-}C_5Me_4Et)_2ZrH_2$ was completely deuterated using the special apparatus at a constant temperature of 70°C and changing the D_2 atmosphere seven times. Then in an nmr tube equal amounts (~ 50 mg) of 2 and $[\eta^5\text{-}C_5(CD_3)_4(CD_2CD_3)]_2ZrD_2$ were added. Benzene-d_6 was distilled on. After the initial spectrum was recorded the tube was heated to 70°C and checked periodically. In the initial spectrum two hydride peaks appeared. After heating they coalesced to one peak.

(a) Solvent activation with 2. Into a thick-walled reaction tube equipped with a teflon needle valve was added 38.8 mg (0.0481 mmoles) of 1 and 23.1 mg (0.1242 mmoles) of ferrocene. Then toluene-d_8 was vacuum distilled in. After addition of one atmosphere of H_2 and conversion of 1 to 2, the gas was pumped away. Then at -196°C, one atmosphere of H_2 was added. The mixture was heated with stirring for one week at 120°C.

The procedure was repeated with benzene-d_6 as the solvent. Then 3.70 mg of ferrocene and 418.8 mg of benezene-d_6 were used. The reaction was heated to 120°C for one week.

The same procedure was used for cyclohexane-d_{12}. No ferrocene was used. The reaction was heated to 110°C for three days.

In each case ^{1}H-nmr was used as in (3) to detect protonation of the solvent. No hydrogenation products were observed and no proton incorporation into the cyclohexane-$\underline{d}_{12}$ was detected.

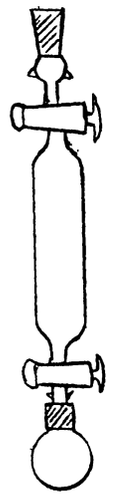


Figure 1

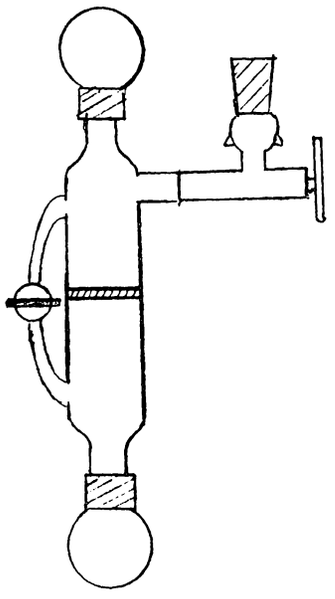


Figure 2

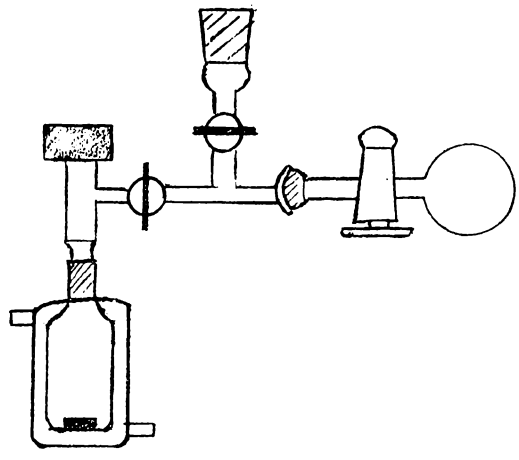


Figure 3

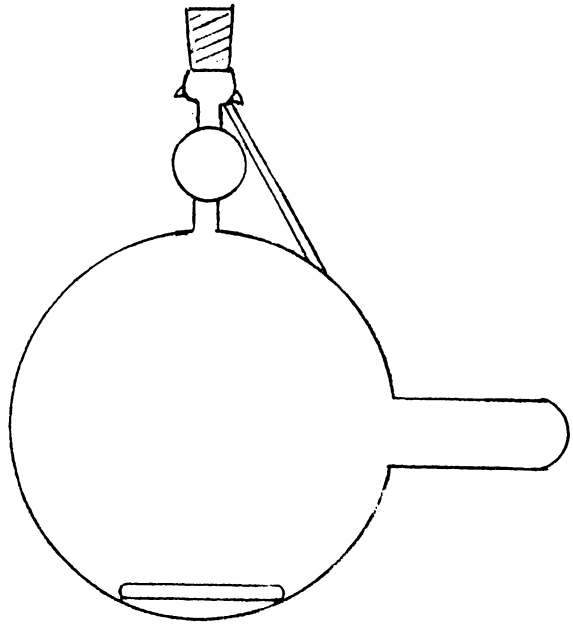


Figure 4

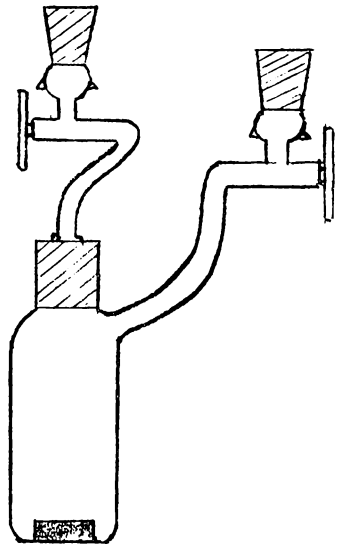


Figure 5

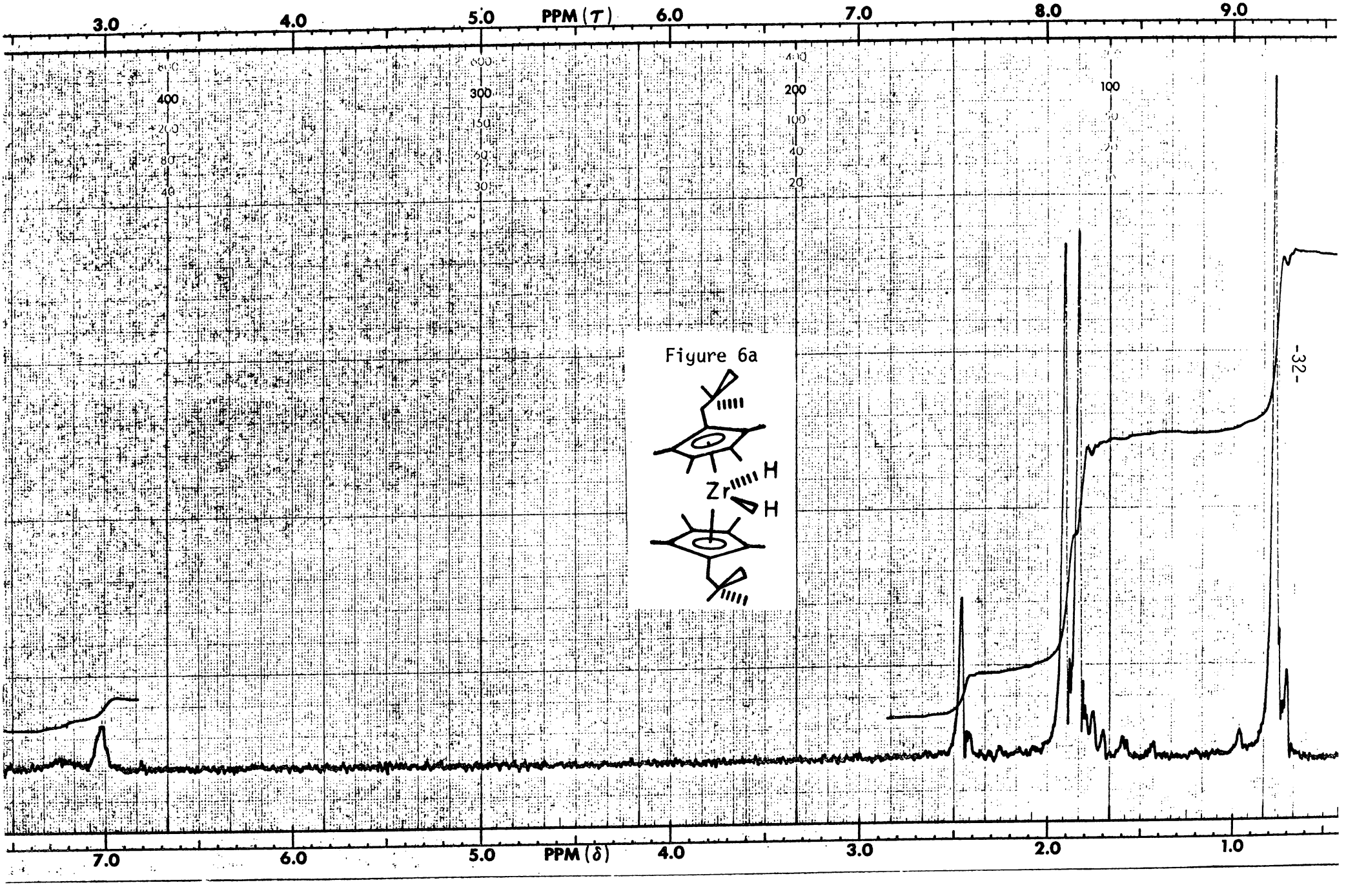


Figure 6a

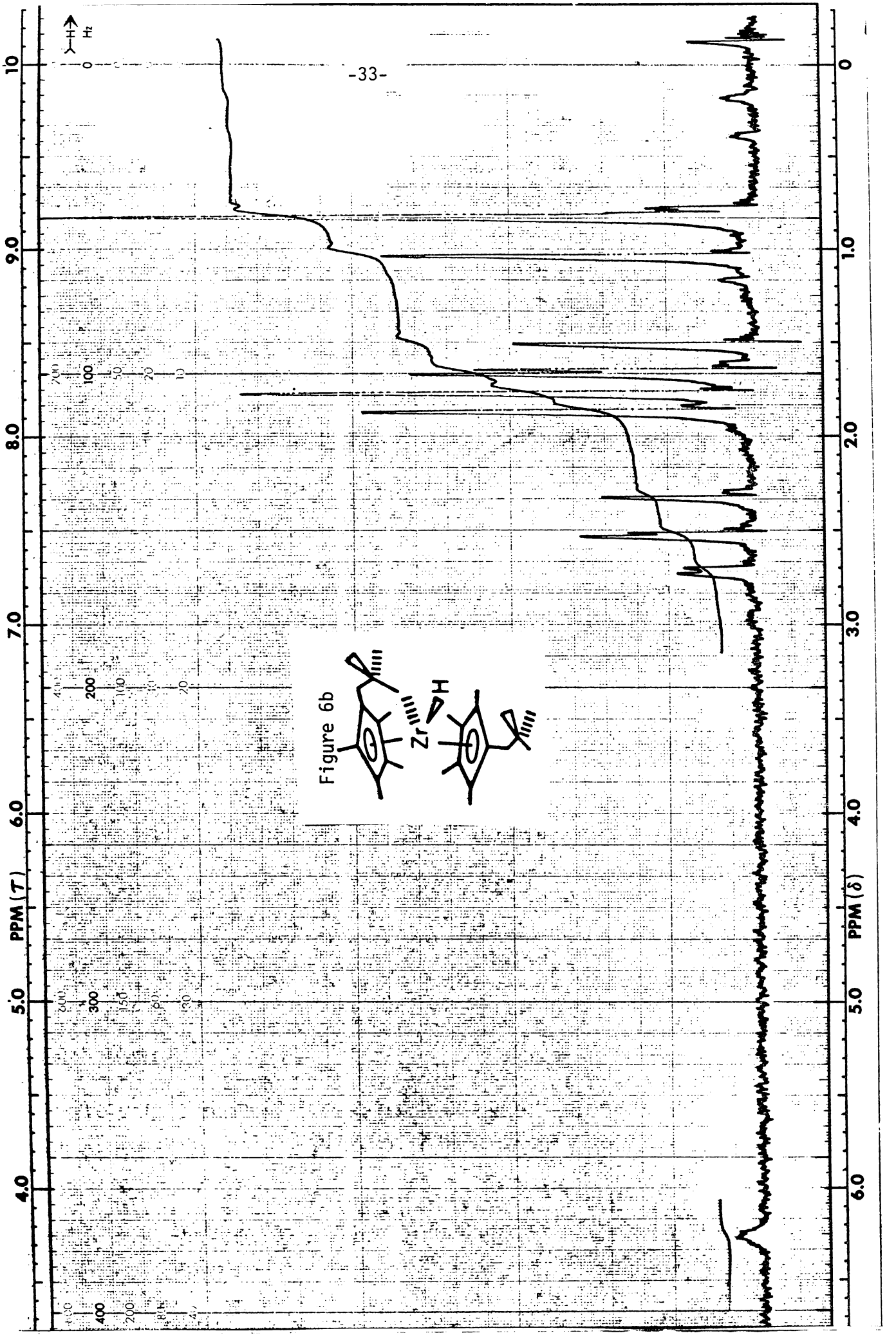
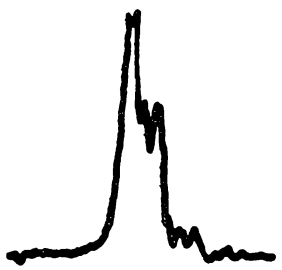
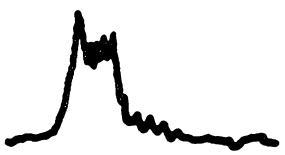


Figure 6b

$$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + D_2 \xrightarrow[C_6H_6]{64^\circ C}$$



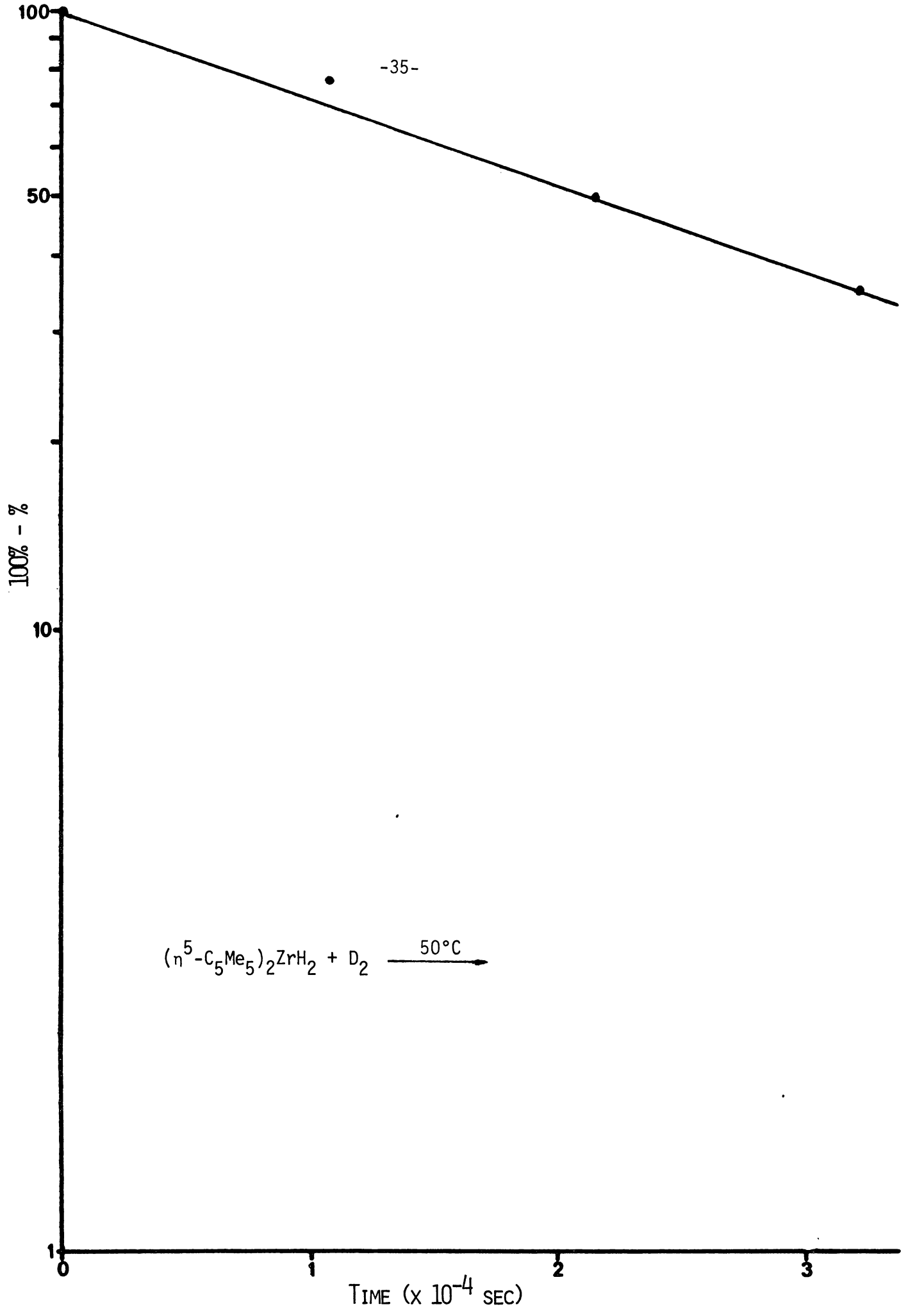
33.0% Deuterated

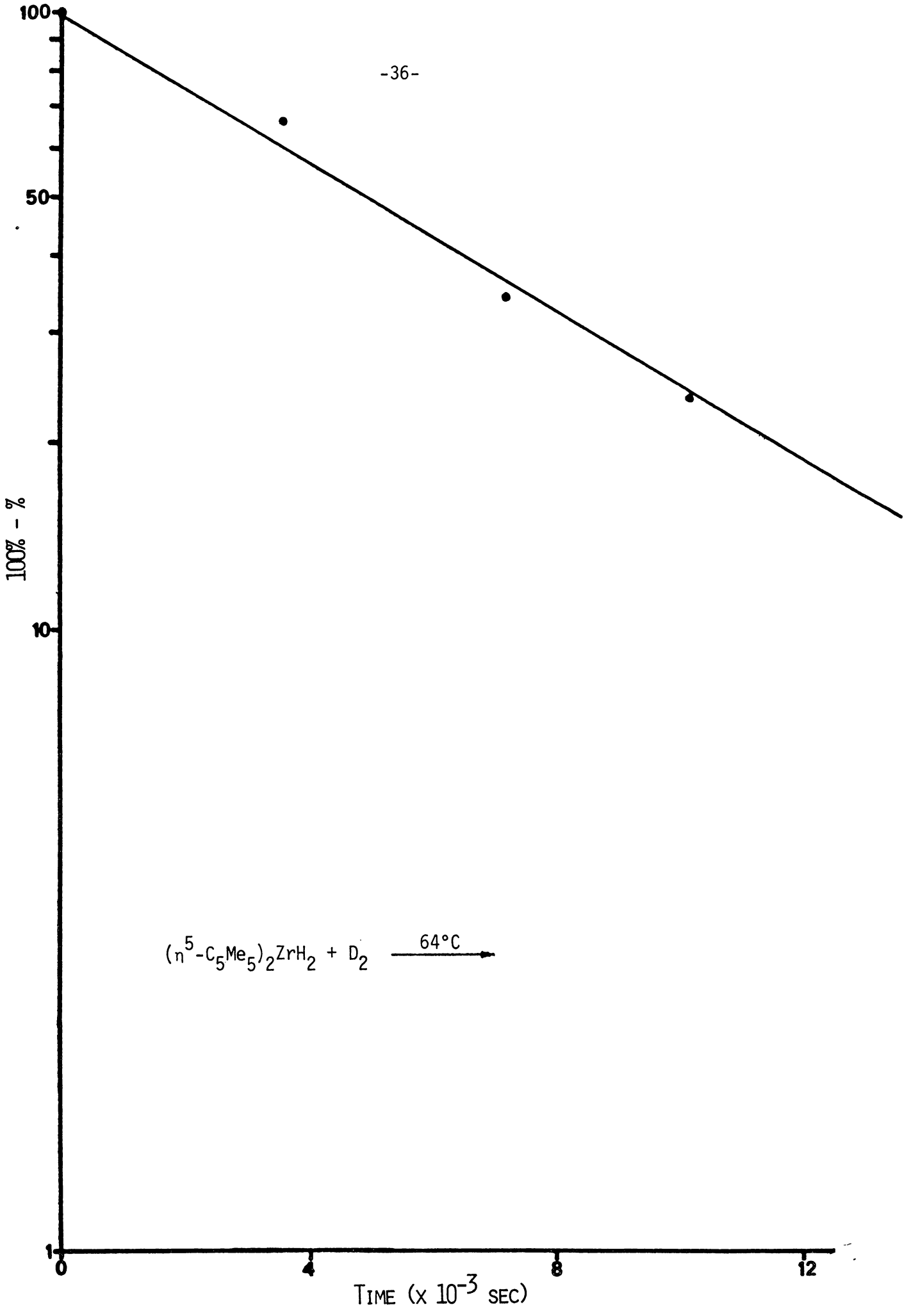


68.4% Deuterated

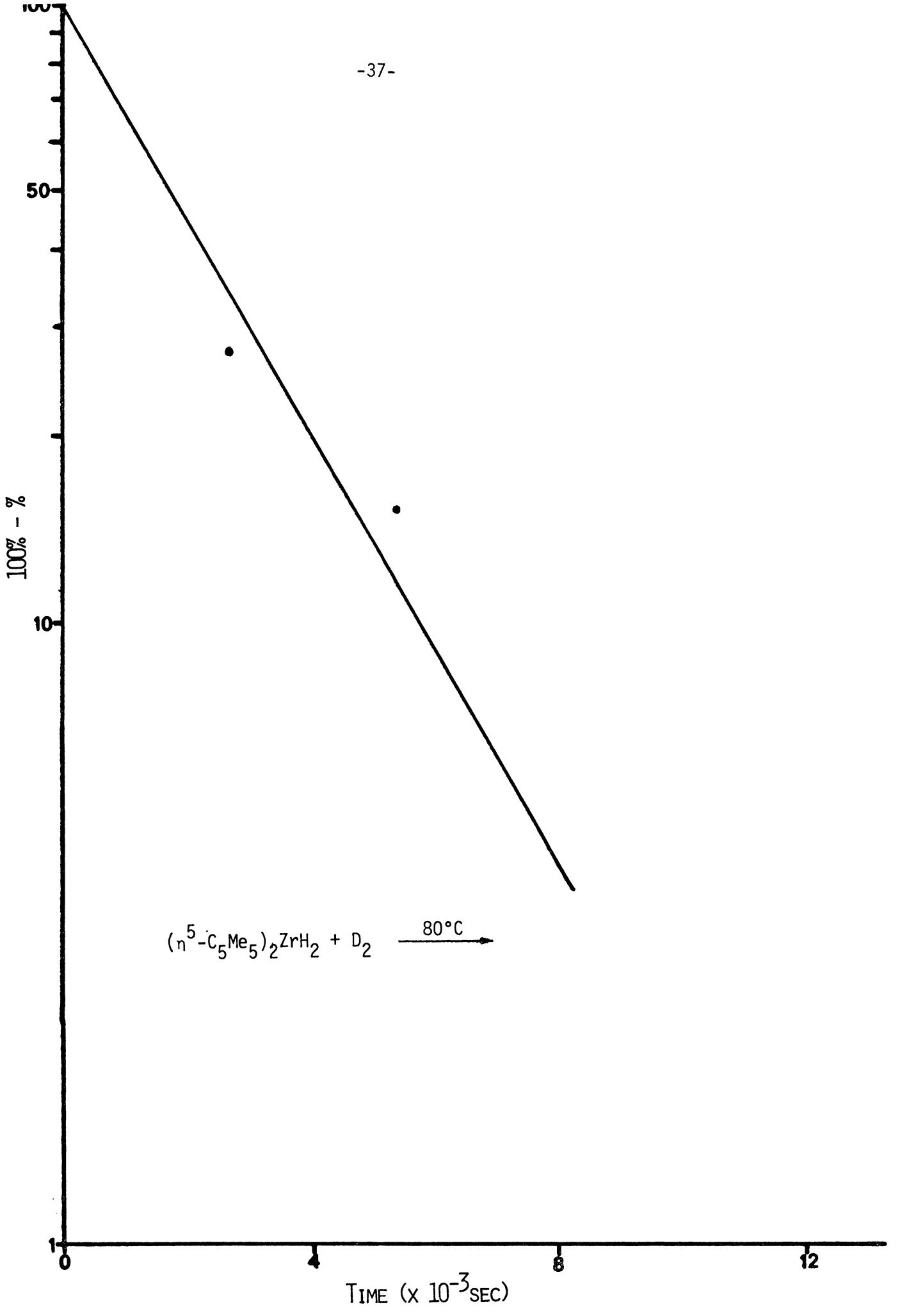
76.4% Deuterated

These peaks correspond to the ^1H-nmr spectra of the permethyl peak after deuteration.


100
50
10
1
100% - %
0
1
2
3
TIME (x 10^{-4} SEC)
$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + D_2 \xrightarrow{50°C}$



$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + D_2 \xrightarrow{64°C}$


100
50
10
1
100% - %
0
4
8
12
TIME (X 10^{-3} SEC)
$(\eta^5\text{-}C_5Me_5)_2ZrH_2 + D_2$
80°C

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Chapter II

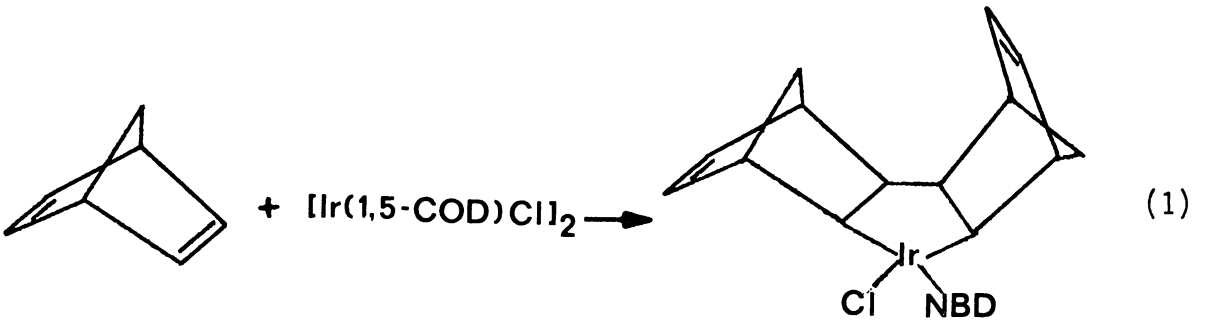
METALLOCYCLE AND π-ALLYL HYDRIDE COMPLEXES OF PERMETHYL ZIRCONOCENE

Introduction

Olefin complexes of transition metals have been under investigation since the isolation of Zeise's salt. Studies of these compounds have included their attack by both nucleophiles[1] and electrophiles,[2] carbonylation[3] as with hydroformylation, polymerization,[4] oligomerization,[5] cyclooligomerization,[6] and hydrogenation.[7] Furthermore, much recent work has centered on olefin isomerization[8] and olefin metathesis.[9] In each of these cases metal-olefin complexes have been implicated as intermediates or catalysts and represent important potential uses in organic synthesis.

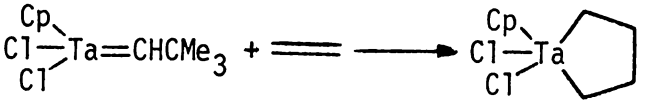
Many of these intermediate complexes involve or imply metallocycles and/or π-allyl-hydride-metal derivatives of the olefins. Consequently, many recent studies have been directed toward the synthesis, characterization, and mechanistic understanding of these species.

The first metallocycle systems isolated involved activated olefins such as cyclopropane and norbornadiene reacting with metals (eq. 1).[10]



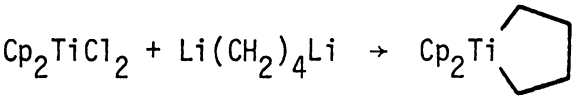
(1)

Not until Schrock[11] reported metallocycle formation from ethylene were unactivated olefins involved (eq. 2).

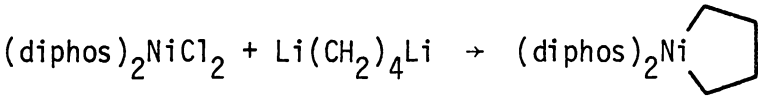


(2)

Most of these studies deal with synthesis and characterization. Whitesides[12] and Grubbs[13] have reported studies of thermal and photochemical decompositions including reaction pathways of Ti (eq. 3) and Ni (eq. 4) metallocyclopentanes synthesized from lithium reagents rather than from olefins directly.

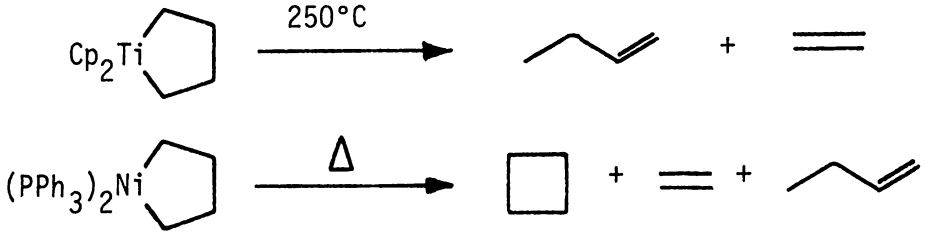


(3)



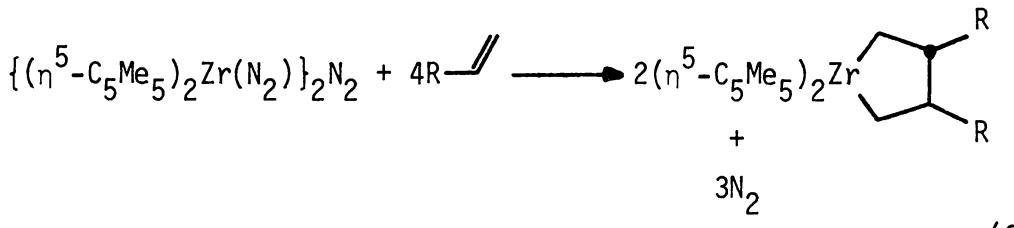
(4)

Their findings show that metallocycles are much more stable than their acyclic analogs. The decompositions yielded products resulting from C–C bond cleavage and formation as well as β-hydrogen elimination (eq. 5).



(5)

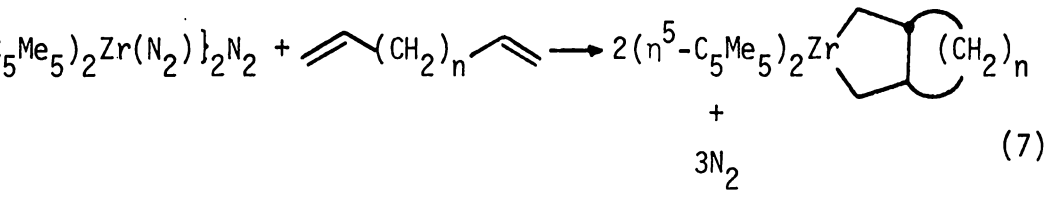
Sanner[15] has reported the synthesis and reactivity of some metallocycles resulting from bis(pentamethylcyclopentadienyl)zirconium(IV) complexes of olefins. His results indicate that metallocycles can be formed stoichiometrically from the reaction of $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2$ with ethylene, propene, and 1-butene (eq. 6).



(6)

where R = H, CH_3, or C_2H_5 .

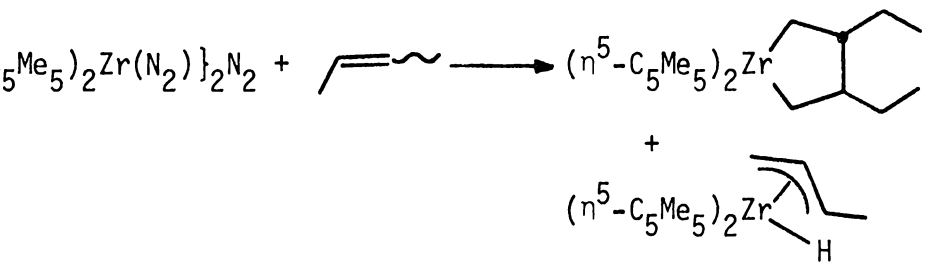
Furthermore, terminal dienes are found to form metallocycles (eq. 7)



(7)

where n = 3,4 .

Besides these terminal olefins, Sanner has reported reactions with cis- and trans-2-butene yielding two major products--metallocycle and a π-methylallyl hydride complex (eq. 8).



(8)

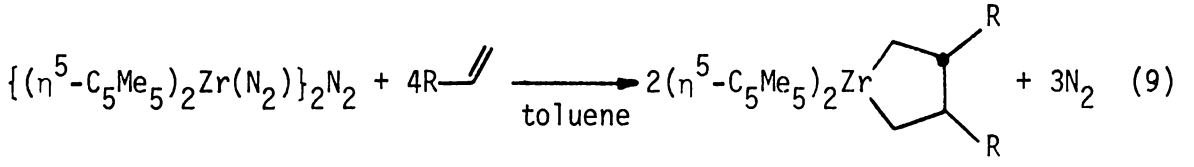
He found that cis-2-butene would form some π-methylallyl hydride but mainly metallocycle while trans-2-butene could be forced to form π-methylallyl hydride exclusively. The π-methylallyl hydride complex was characterized by ^{1}H-nmr, ir, and reaction products. This type of complex has few peers--the only other such isolated compounds being $(\eta^3\text{-}C_3H_5)Ni(H)(PPh_3)$[15] stable only below -30°C, $(\eta^3\text{-}C_3H_5)Mo(H)(diphos)_2$[16] stable to >110°C, a ruthenium(II) π-allyl hydride,[17] and $Ir(Cl)(H)(\eta^3\text{-}C_3H_4Ph)(PPh_3)_2$[18] which is very stable and which has been characterized by x-ray structural determination.

These initial findings involving both the π-methylallyl hydride complex and the metallocycle complexes of bis(pentamethylcyclopentadienyl)zirconium(IV) warrant further investigation. This chapter reports such studies.

Results and Discussion

Bis(pentamethylcyclopentadienyl)zirconium(IV) metallocyclopentanes.

Synthesis of the metallocyclopentanes follows reported procedures[14] involving the reaction of $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)_2\}_2N_2$ (1) with excesses of either ethylene, propene, or 1-butene in toluene at room temperature (eq. 9).

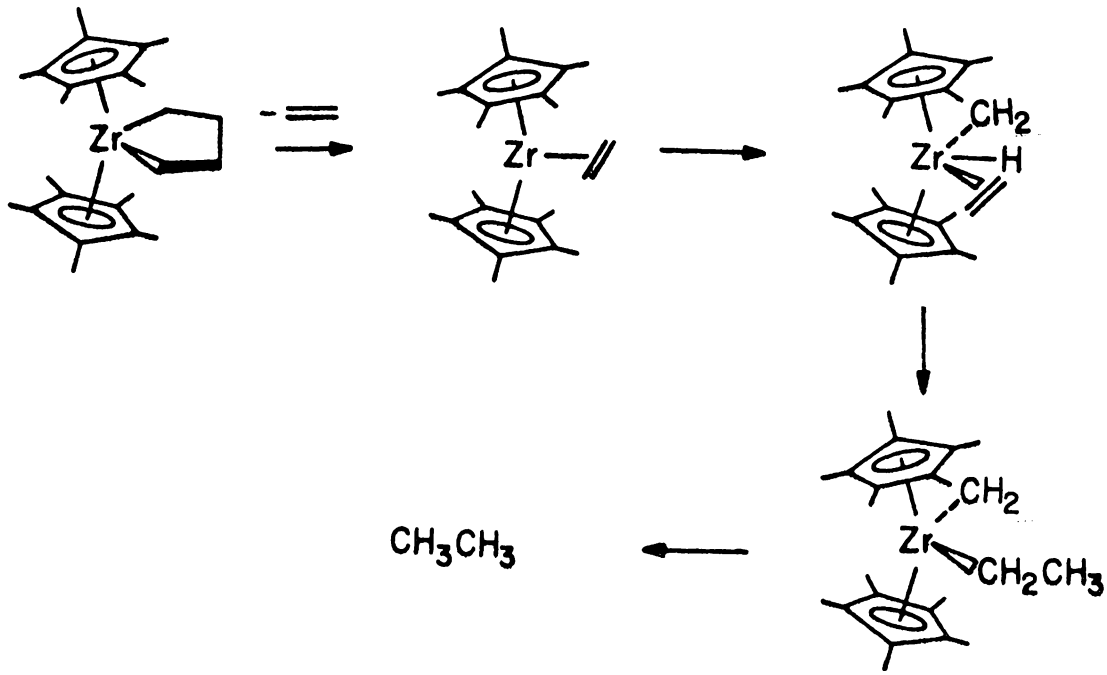


(9)

R = H (2), CH_3 (3), C_2H_5 (4)

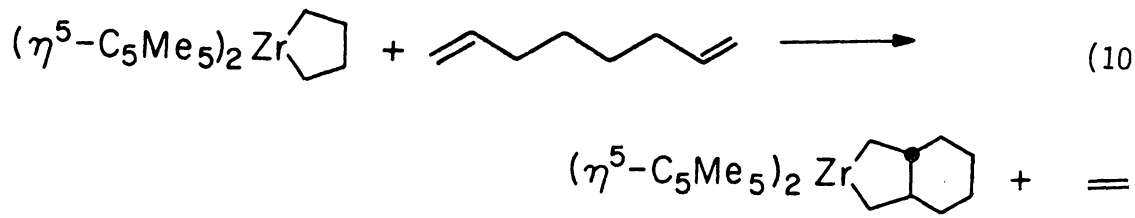
These yellow metallocycles are stable to 100°C in vacuo for days. The parent metallocycle $(\eta^5\text{-}C_5Me_5)_2\overline{ZrCH_2(CH_2)_2CH_2}$ (2) upon heating to > 120°C for several hours in toluene in vacuo yields ethylene (24%), cyclobutane (26%), 1-butene (12%), and ethane (39%) as major gas products. The organozirconium product resembles the decomposition products observed when permethylzirconocene is heated. Upon photolyzing both 2 and 3 with a 1000 watt medium pressure Hg lamp for 24 hours at 0°C through Pyrex glass, no gas or new products were produced. The ^{1}H-nmr spectra showed the corresponding metallocycles to be unreacted.

The thermal properties of these metallocyclopentanes closely parallel those found by Grubbs[13] in his Ni systems and Whitesides[12,19] in his Pt and Ti systems. Indeed, these cyclic complexes are much more stable than their acyclic analogs. Complexes of $(\eta^5\text{-}C_5Me_5)_2Zr(Bu)_2$ and $(\eta^5\text{-}C_5Me_5)_2Zr(Et)_2$ β-hydrogen eliminate forming olefins at room temperature[20] where as the metallocycles show no decomposition below 100°C implying considerable suppression of this β-hydrogen elimination pathway for decomposition as has been proposed by Whitesides.[12] The products obtained from the 120°C pyrolysis represent three major reaction types competitively occurring: reductive elimination forming cyclobutane, β-carbon-carbon bond cleavage accounting for the ethylene which is not seen in acyclic counterparts, and β-hydrogen elimination yielding 1-butene. Each of these pathways leaves the metal as Zr(II) formally resulting in permethylzirconocene which is not thermally stable. This product may form the carbon-hydrogen activation intermediate[21] which could, by a process similar to Scheme 1, yield ethane.



Scheme 1

Certainly, both formation of ethylene and ethane suggest carbon-carbon bond breaking as an important decomposition alternative. This has been further evidenced by reactions of the metallocycles with dienes (eq. 10).[14]

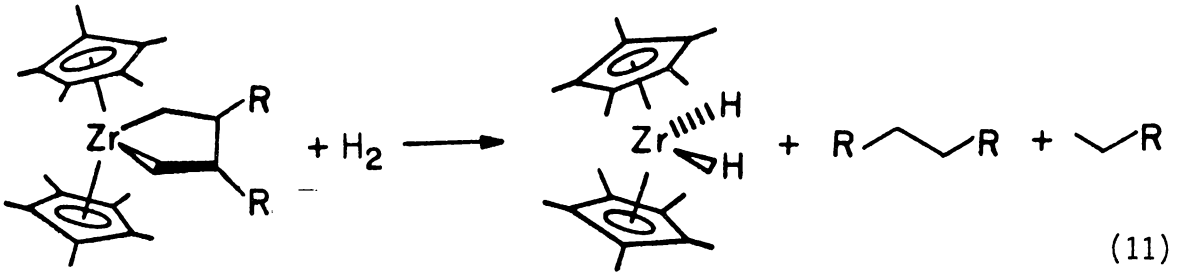


(10)

Upon heating the parent metallocycle 2 with a tenfold excess of ethylene in toluene to 80°C, the products obtained were mixtures of mainly C_4 hydrocarbons--butane, 1-butene, cis- and trans-2-butene, and

1,3-butadiene. In addition, ethane was formed. These gases suggest dimerization and disproportionation of ethylene as viable pathways besides those already stated. The reaction of excess ethylene with the other metallocyclopentanes produces 2 quantitatively implying that this system is the most stable.

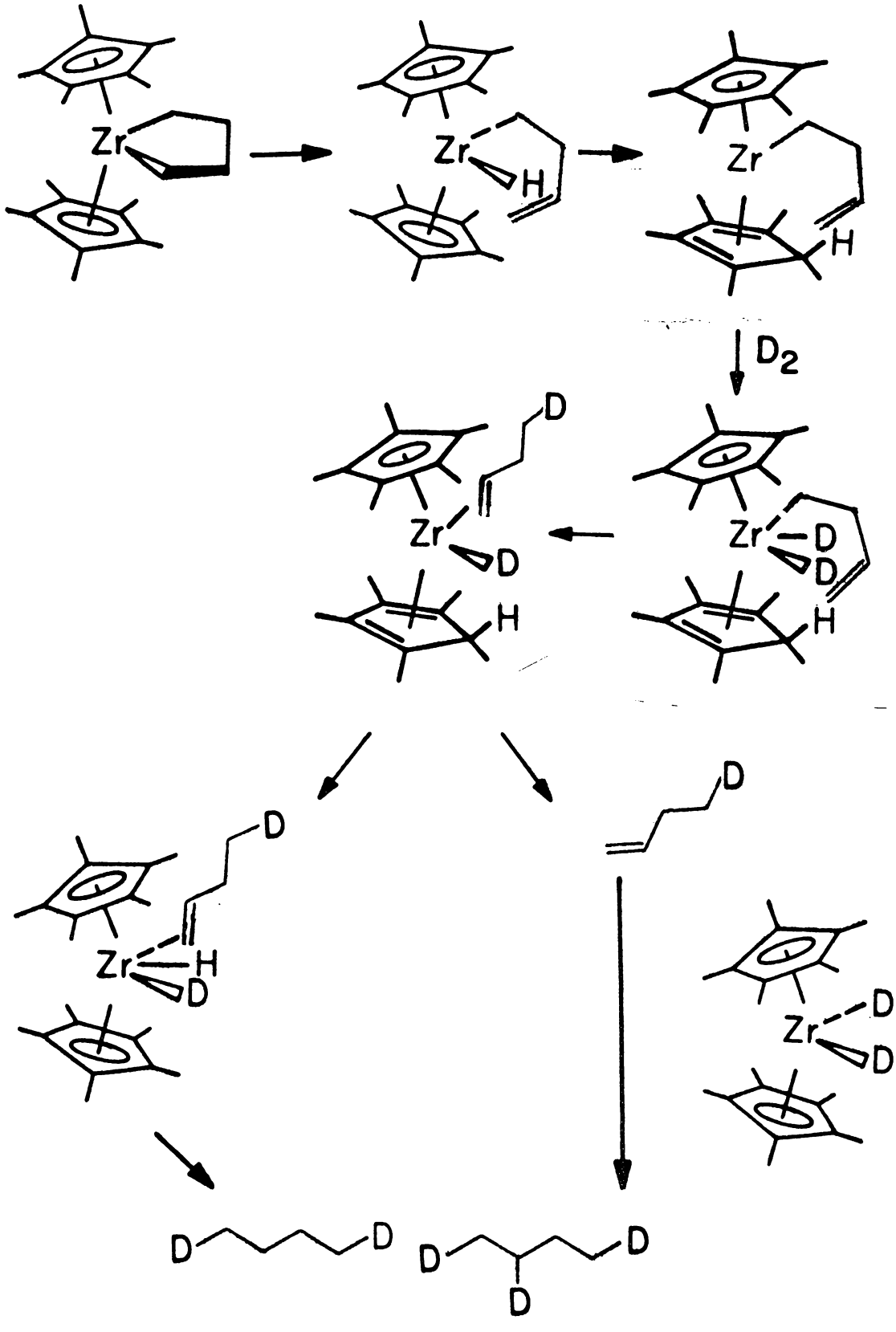
Reaction of metallocycles with H_2 at room temperature in toluene produces $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ cleanly and quantitatively with formation of C_2 and C_4 hydrocarbons (eq. 11).



(11)

R=H, CH_3

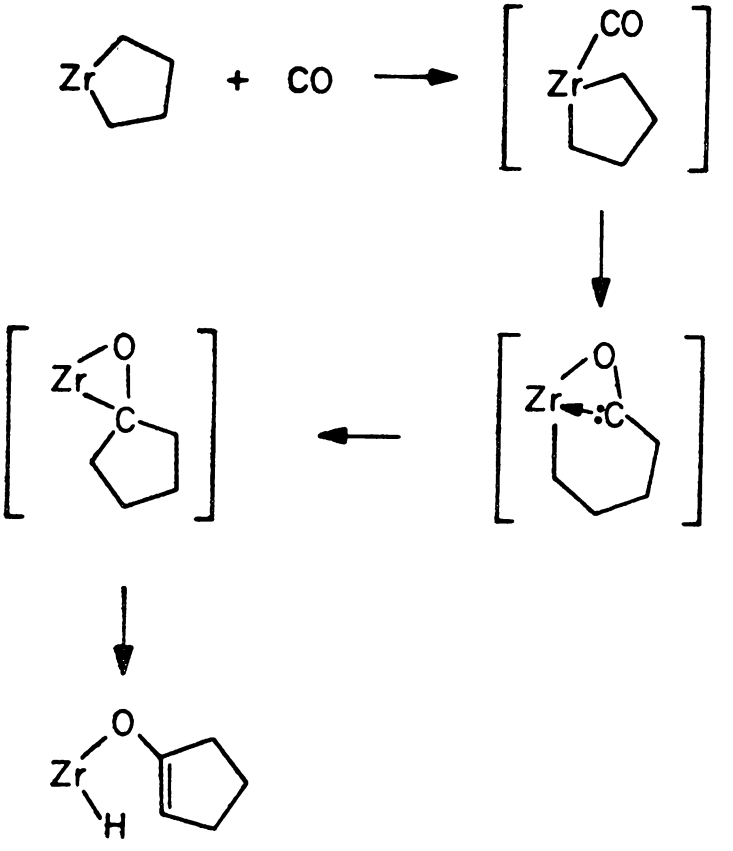
With an excess (∿ 5-fold) of H_2 above the solution, the reaction takes several minutes. Toepler pump analysis showed 1.8 hydrogen molecules consumed per metallocycle. The major gas products for 2 were butane and ethane (2:1) while for 3 were 2,3-dimethylbutane and butane (2:1). Using D_2 instead of H_2 afforded 1,4-diduteriobutane, 1,2,4-trideuteriobutane, and 1,2-dideuterioethane for 2. These deuterated butane products are indicative of a mechanism such as in Scheme 2. This scheme invokes β-H elimination to form an alkenyl hydride. Then the hydride transfers from the metal to the ring as seen in both $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CMe_3)$ cases.[21] This allows for oxidative addition



Scheme 2

of D_2. The butene can then π-bond to the Zr. At this point either the hydrogen can move back to the Zr and hydrogenate the butene giving 1,4-dideuteriobutane or D_2 can oxidatively add and hydrogenate the butene leaving 1,2,4-trideuteriobutane. The ethane products can be generated by the metallocycle undergoing C—C bond cleavage forming coordinated ethylene which can then be hydrogenated.

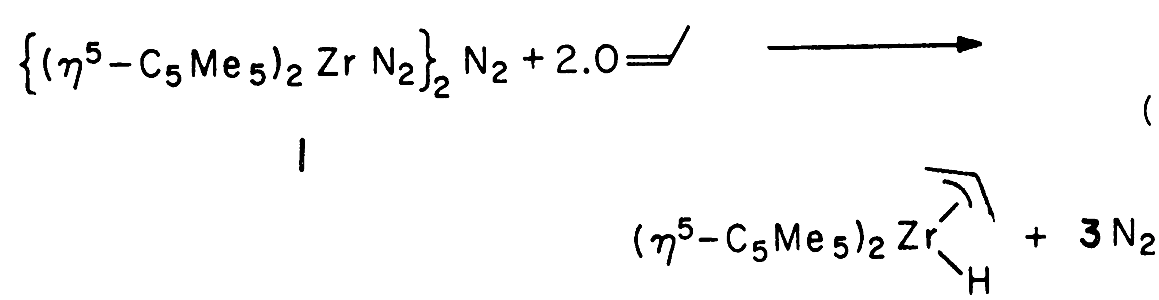
Other reactions of the metallocyclopentanes include addition of anhydrous HCl to a toluene solution. This produces $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ and butane using 2. The reaction of 2 in toluene with carbon monoxide has been reported earlier[14] and proceeds as in Equation 12.



(12)

In an attempt to promote catalytic olefin isomerization, the 1-butene metallocycle 4 was heated with excess 1-butene to 110°C in toluene and aliquots were sampled for gas distribution. The rate of disappearance of 1-butene was first order in 1-butene concentration with a rate constant of $4 \times 10^{-5} sec^{-1}$ and with probable formation of cis- and trans-2-butene. But the resulting organozirconium solid was no longer the metallocycle. Formation of the 2-butenes was encouraging except that only a small amount could be produced before metallocycle destruction. Thus, the kinetics are only approximate and only serve to give a handle on the order of magnitude of such a reaction. Although this system is not suited for such an in-depth study of olefin isomerization, the corresponding Ti system seems to lend itself to such an investigation. This study is in progress.

Bis(pentamethylcyclopentadienyl)zirconium(IV) π-allyl hydrides. The reaction of $\{(\eta^5\text{-}C_5\text{-}Me_5)_2Zr(N_2)\}_2N_2$ with exactly two molar equivalents of propene (a one-to-one molar ratio of propene to Zr) produces a yellow π-allyl hydride complex of bis(pentamethylcyclopentadienyl)zirconium (eq. 13)(Figure 1).



(13)

5

Figure 1

The reaction is quantitative and stoichiometric as determined by Toepler pump analysis of the released N_2. The amount of propene used is critical since in excess it will lead to formation of the trans-dimethyl metallocyclopentane 3. The synthesis of this π-allyl hydride may also be achieved using $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and allene in toluene at room temperature (eq. 14).

$$(\eta^5\text{-}C_5Me_5)_2\,Zr\,H_2 + ==\!= \longrightarrow (\eta^5\text{-}C_5Me_5)_2\,Zr\!\!<\!\!\begin{matrix}\diagup\!\!=\\ H\end{matrix} \quad (14)$$

The exact amount of allene used as starting material does not seem to be important. Toepler pump analysis in 1,2,4-trimethylbenzene showed the

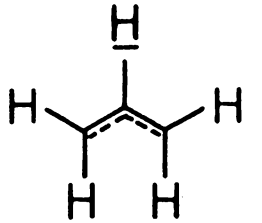
reaction to be stoichiometric consuming 0.93 allene per Zr.

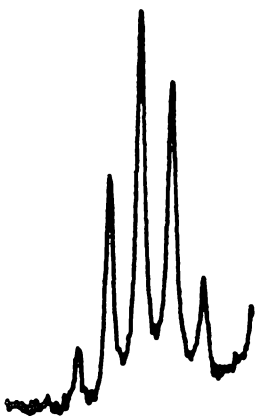
The π-allyl hydride nature of the complex is confirmed by elemental analysis data, ir spectrum exhibiting a band at 1580 cm^{-1}--a region where other metal hydrides appear--and ^{1}H- and ^{13}C-nmr spectral data. The ^{1}H-nmr spectrum (Figure 2) in toluene-$\underline{d}_8$ at 40°C shows a binomial quintet at 3.53δ. This five-line pattern has a $^{3}J_{H-H}$ of 12 Hz and corresponds to the central hydrogen of the π-allyl group. This assignment agrees closely with 3.72δ given for the central hydrogen in the π-allyl system $(diphos)_2Mo(H)(\eta^3\text{-}C_3H_5)$[16]. Its integration relative to the ring methyl hydrogens which appear as a singlet at 1.70δ is one to thirty. No other resonances are present in the ^{1}H-nmr spectrum. The quintet implies four equivalent hydrogens. These should appear as a doublet. One conjecture was that this resonance might be hidden under the ring-methyl singlet. This was shown, however, not to be the case by reacting the bis(perdeuteriopentamethylcyclopentadienyl)zirconium dihydride with allene to produce $[\eta^5\text{-}C_5(CD_3)_5]_2Zr(H)(\eta^3\text{-}C_3H_5)$. Only the quintet appeared.

Varying the probe temperature for the ^{1}H-nmr reveals much more detail. At -10°C the ^{1}H-nmr spectrum shows the ring methyl hydrogens coalescing; at lower temperature they appear as two singlets, one for each ring, whereas at higher temperature they show only a singlet. At -33°C the ^{1}H-nmr spectrum (C_7D_8) (Figure 3) shows a doublet at 4.09δ with a $^{3}J_{H-H}$ of 10 Hz and corresponding to one methylene hydrogen of the π-allyl system, a multiplet at 3.63δ being the one central hydrogen, a doublet at 2.32δ having a $^{3}J_{H-H}$ of 8 Hz and corresponding to one π-allyl methylene hydrogen, a singlet at 1.88δ having 15 hydrogens and being one ring's methyl protons, another singlet at 1.79δ also having 15 hydrogens and being the other

Figure 2

^{1}H nmr $(\eta^5\text{-}C_5Me_5)_2ZrH(\eta^3\text{-}C_3H_5)$;
toluene-d_8, 34°C





$[\eta^5\text{-}C_5(C\underline{H}_3)_5]$

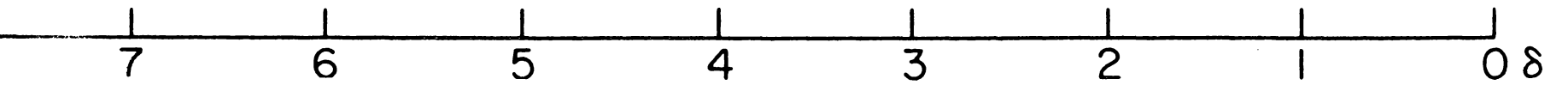
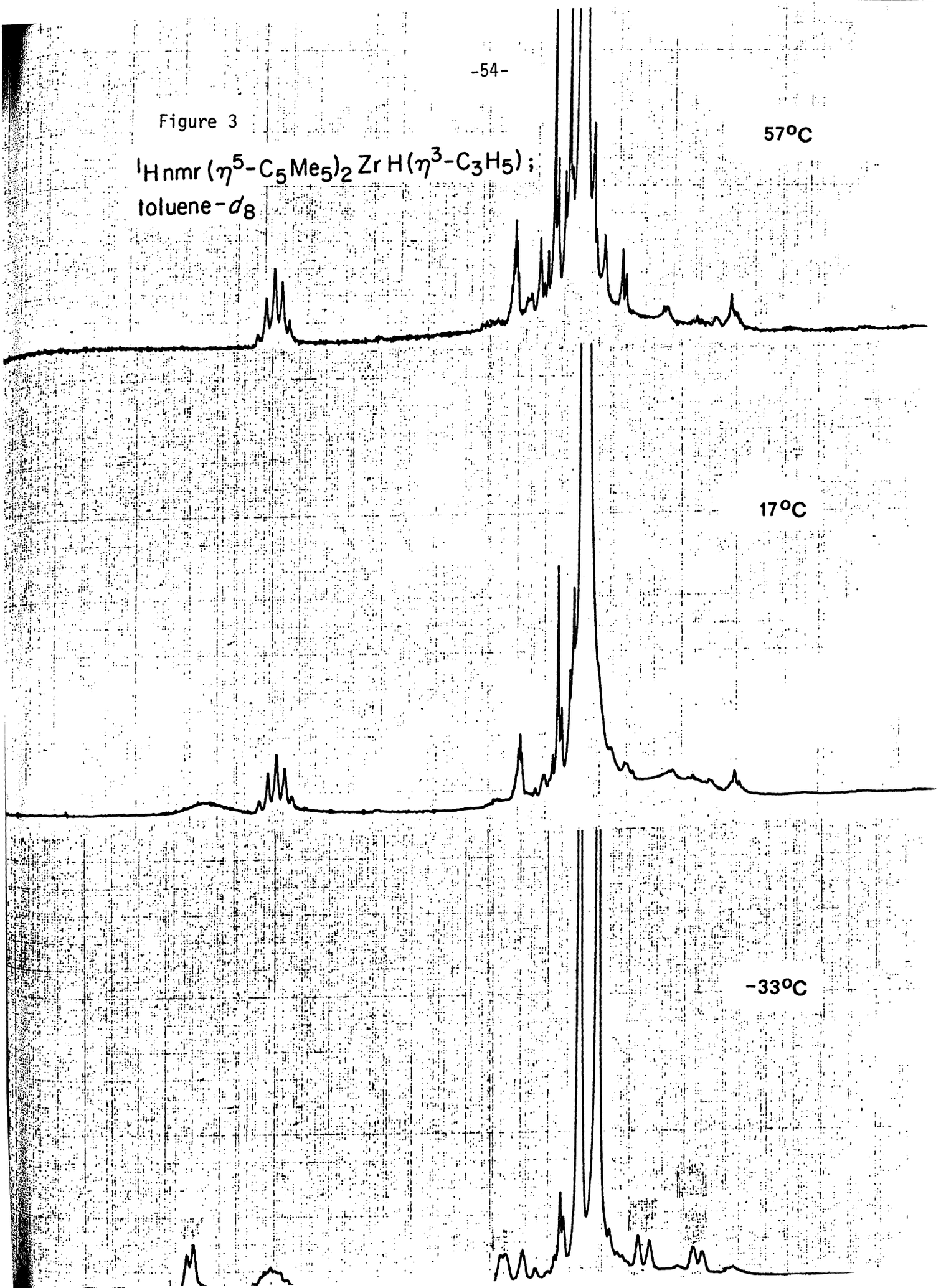


Figure 3

^1H nmr $(\eta^5\text{-}C_5Me_5)_2ZrH(\eta^3\text{-}C_3H_5)$; toluene-$d_8$



ring's methyl protons, a doublet at 1.52 with a $^{3}J_{H-H}$ of 18 Hz and corresponding to another methylene hydrogen, and finally a doublet at 1.22δ with a $^{3}J_{H-H}$ of 15 Hz and being the last methylene hydrogen. At the +66°C another coalescence occurs in the ^{1}H-nmr spectrum (Figure 4). At this temperature the quintet with its coupling constant of 12 Hz coalesces to a binomial sextet with a coupling constant of 9 Hz.

The ^{13}C-nmr spectra (C_7D_8) show similar behavior (Figure 5). At +65°C the proton decoupled spectrum shows only four singlets at 21.0 ppm, 26.2 ppm, 79.4 ppm, and 125.0 ppm (upfield of the C_1 resonance of toluene-$\underline{d}_8$). As the temperature is lowered to room temperature the broad peak at 79.4 ppm becomes two peaks at 67.1 ppm and 86.9 ppm. Lowering the probe temperature to -40°C allows both the proton decoupled and proton undecoupled spectra to be interpreted. These results show a singlet at 21.4 ppm which splits into a doublet with $^{1}J_{C-H}$ of 150 Hz and corresponding to the central carbon of the π-allyl group. The two peaks at 26.6 ppm and 27.4 ppm correspond to the carbons of the ring cyclopentadienyl systems which are inequivalent at this temperature. The singlet at 71.2 ppm which splits into a triplet with a $^{1}J_{^{13}C-H}$ of 155 Hz corresponds to the carbon of one of the methylenes on the π-allyl group. And the singlet at 87.7 ppm which also splits into a triplet with $^{1}J_{^{13}C-H}$ of 150 Hz is the other methylene carbon on the π-allyl system. The two singlets at 125.4 ppm and 125.8 ppm which split into quartets with $^{1}J_{^{13}C-H}$ of 130 Hz correspond to the methyl carbons of two inequivalent rings. The coupling constants of the π-allyl carbon system are indicative of their sp^2 character.

The nmr spectral results imply that intramolecular motions leading to exchanges and fluxionality in the allyl group are occurring. Indeed,

Figure 4

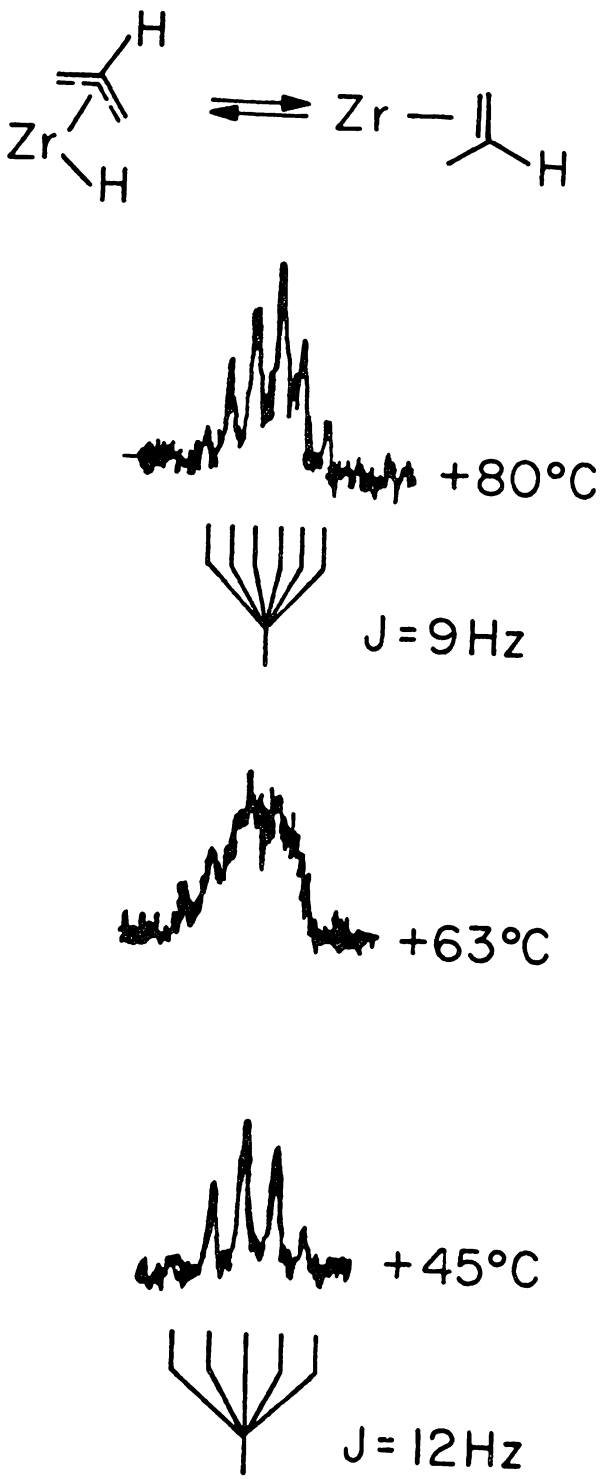
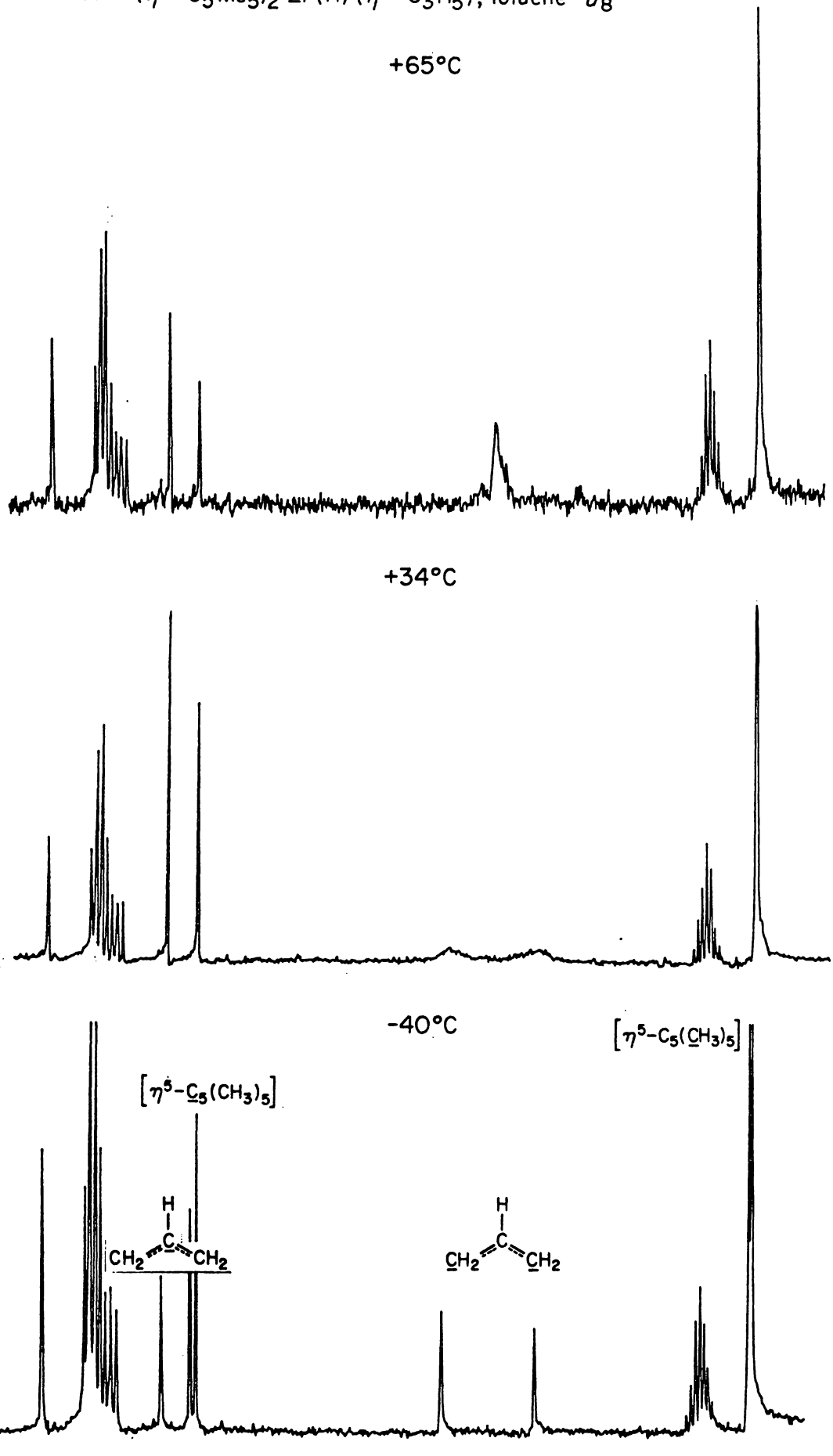
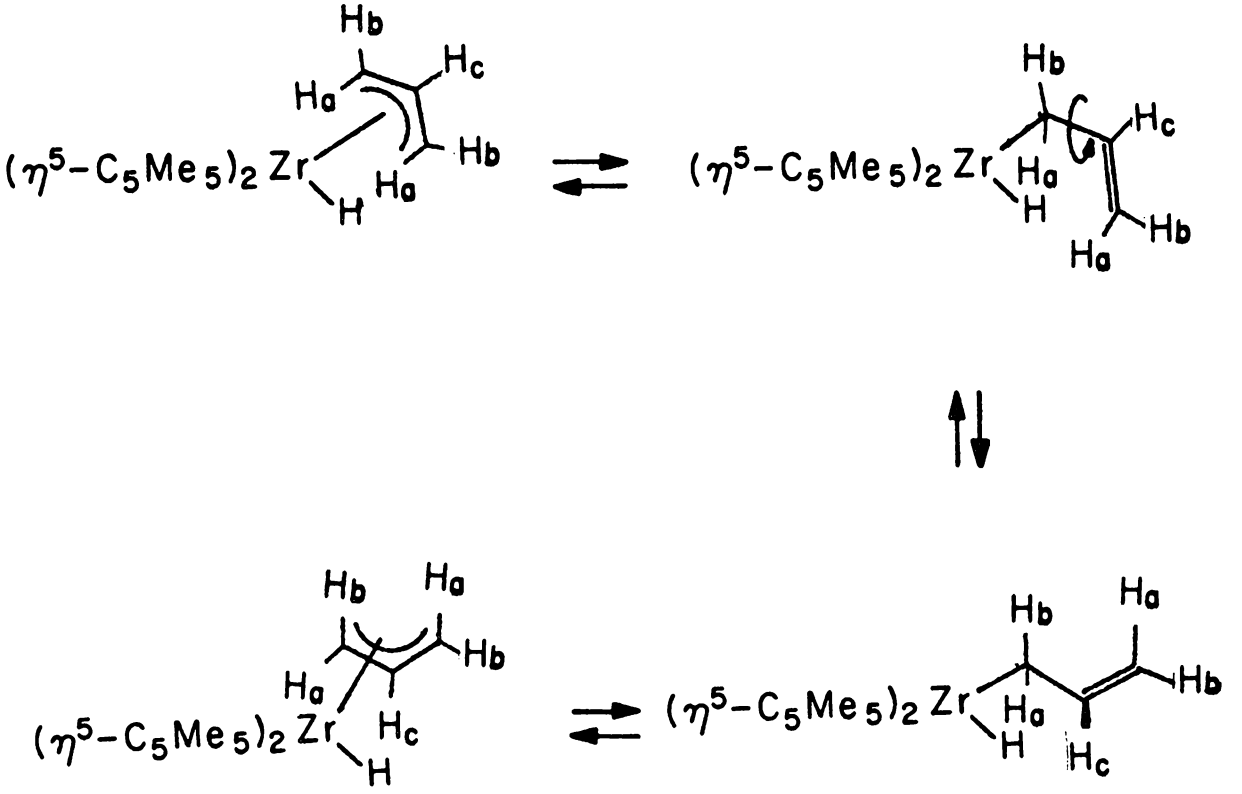


Figure 5 ^{13}C nmr $(\eta^5\text{-}C_5Me_5)_2\,Zr(H)(\eta^3\text{-}C_3H_5)$; toluene-$d_8$

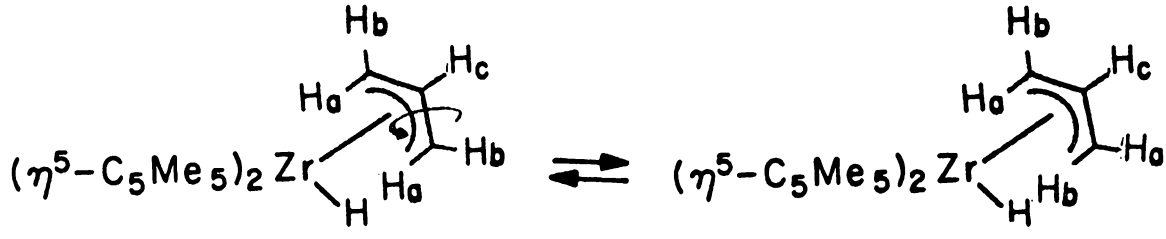


the quintet for the central hydrogen in the ^{1}H-nmr spectrum must result from the terminal methylene hydrogens both <u>syn</u> and <u>anti</u> being equivalent as well as both ends experiencing the same environment. This can be accomplished in part by a <u>syn</u>-<u>anti</u> isomerization involving a σ-π equilibrium which is quite common in π-allyl systems and which is illustrated in Scheme 3.



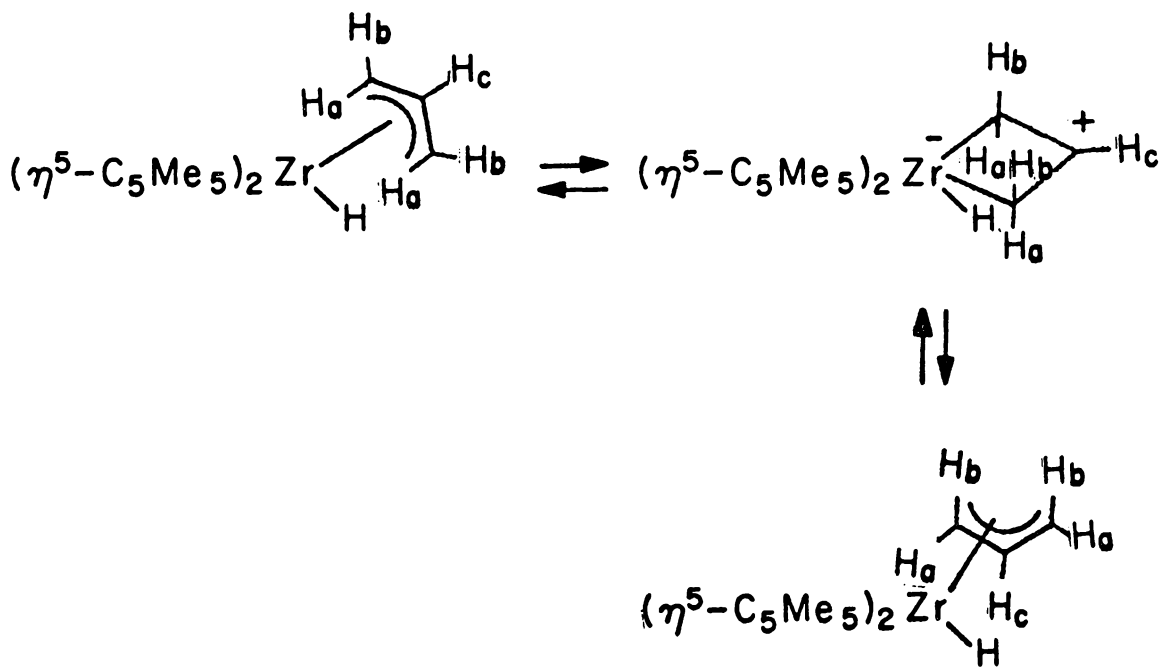
Scheme 3

The σ-allyl intermediate in this scheme allows the two geminal hydrogens to become equivalent by rotation about the C–C single bond followed by reformation of the π-bonded complex. This process is possible at either end. Other possible processes include rotation of the terminal CH_2 groups about the carbon-carbon bond in which the allyl group essentially maintains its π-configuration (Scheme 4). This type of process is favored by Becconsall and O'Brien[22-24] for several of their π-allyl systems.



Scheme 4

Another possibility involves a flip motion in which the allyl group is σ-σ bonded and rotates backwards with the central carbon moving away from the metal (Scheme 5).



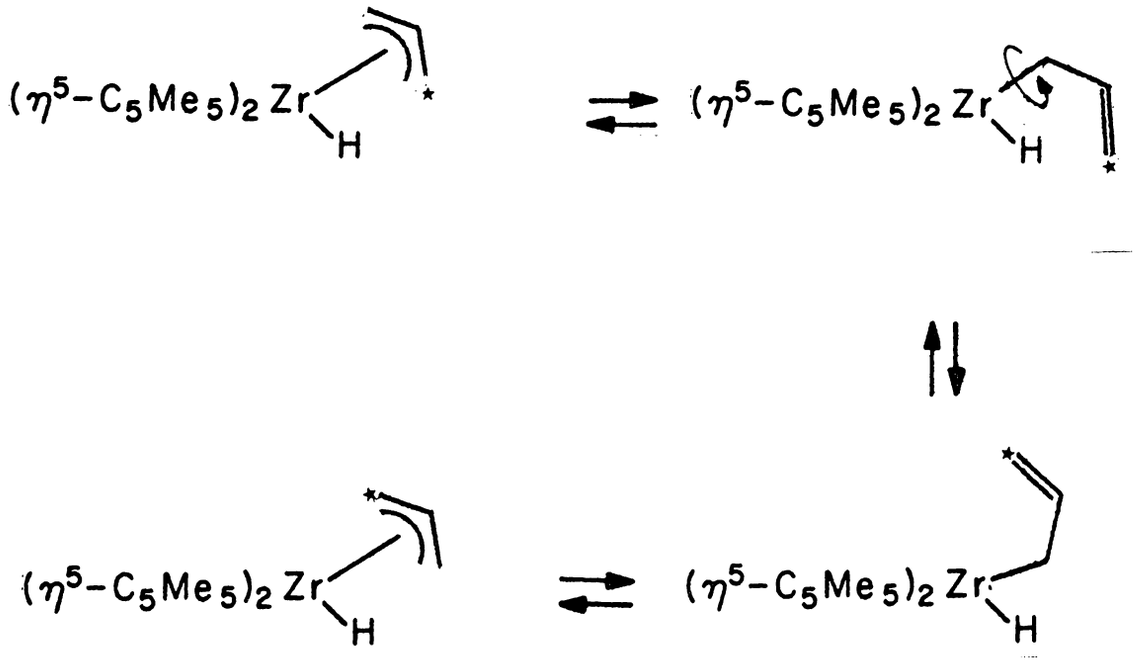
Scheme 5

The axis of the rotation lies in the plane of the allyl group and passes through the terminal carbons. This pathway is proposed by Whitesides[25] to best correlate calculated line shapes in $(\eta^3\text{-}C_3H_5)_4Zr$.

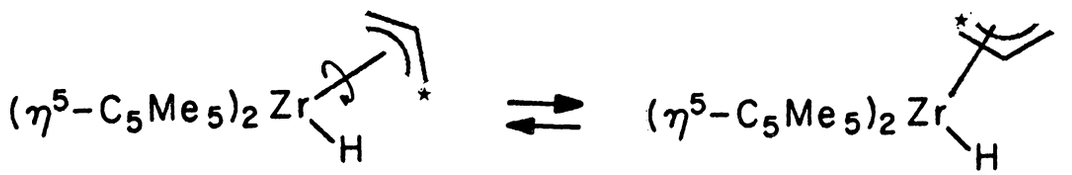
The second and third schemes seem less likely. The second has been shown to be impossible for certain palladium compounds and has been suggested to be unlikely for any compounds with interactions between metal d orbitals and allyl orbitals.[26] Since this complex involves Zr(IV) which has no d electrons for backbonding, it may still be possible, but it seems unlikely to be occurring at 40°C. The third mechanism involving the flip has been ruled out by Vrieze et al.[27] for most π-allyl complexes based on evidence for asymmetric π-allyl compounds and seems unlikely if any bonding is to be maintained. Besides, the variation in charge distribution required for this process is less than satisfying.

In the π-allyl hydride configuration, all of the methylene hydrogens should not be equivalent, since one end is in closer proximity to the hydride than the other. In order to effect both ends of the system experiencing similar environments as the spectrum requires, one of two processes must be occurring (Schemes 6 and 7). Scheme 6 requires a rotation of the σ-allyl group about the carbon-metal bond and reformation of the π-system at a slightly different coordination site. The orbital lobes involved in this bonding should be diffuse enough to accommodate such a shift. Scheme 7 also agrees with the data but involves rotation of the allyl group in a plane normal to the metal-allyl group bond axis destroying much of the bonding interaction. Faller[28] has recently reported studies implicating this pathway in which a π-allyl group rotates between two or four possible minima above the equatorial plane formed by three carbonyls and one phosphorous atom in the complex $(\eta^3\text{-}C_3H_5)Mo(CO)_3(diphos)_2PF_6$. Scheme 6, however, coupled with the σ-π equilibrium for <u>syn</u>-<u>anti</u> isomerization certainly seems most reasonable since once the metal-carbon bond is formed either rotation would be likely.

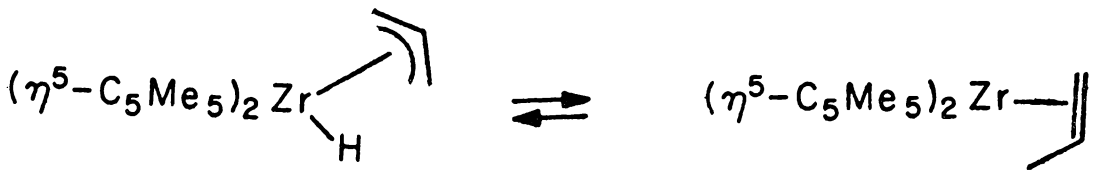
In order to complete the observed ^{1}H-nmr spectral data, another process must be occurring which broadens the methylene hydrogens and the hydride resonances at 40°C and changes the splitting pattern of the central hydrogen at higher temperatures. This is illustrated in Scheme 8.



Scheme 6



Scheme 7



Scheme 8

This scheme requires an equilibrium between the π-allyl hydride and a complexed propene. Such a process allows for equivalence of the terminal methylene hydrogens and the hydride. On the ^{1}H-nmr time scale at 40°C this process is somewhere between one moiety and the other as are the chemical shifts. At elevated temperatures the quintet with its coupling constant of 12 Hz is converted into a sextet with a coupling constant of 9 Hz. This suggests that indeed the hydride is being made equivalent with the other four methylene hydrogens explaining the sextet. Assuming the hydride has a nominal coupling constant, the 12 Hz coupling for the four hydrogens expanded to five hydrogens would imply a new coupling of $\sim$ 9 Hz which is what is observed. Upon cooling, the process of Scheme 8 is the first to be frozen out.

Further cooling freezes the π-allyl group into one orientation, stopping the other processes and causing all of the hydrogens to be inequivalent. This, then, explains the ^{1}H-nmr spectrum at -33°C which shows all four methylene hydrogens with different coupling constants which are consistent with <u>syn</u> and <u>anti</u> configurations about the central hydrogen which appears as a multiplet. The hydride resonance still is not apparent.

The ^{13}C-nmr spectra show similar results. At high temperature the two methylene carbons of the π-allyl are exchanging ends fast enough to average their chemical shifts. Lowering the temperature reveals the two independent resonances. The undecoupled spectrum shows these carbons as triplets, but they may be two sets of overlapping doublet of doublets, since the <u>syn</u> and <u>anti</u> hydrogens are in different environments.

The π-allyl hydride is further characterized by its reactivity. When $\underset{\sim}{5}$ is reacted with excess CH_3I in toluene, a yellow π-allyl methyl complex $\underset{\sim}{6}$ forms along with $(\eta^5\text{-}C_5Me_5)_2ZrI_2$, propene, and methane--further evidence for a hydride species (eq. 15).

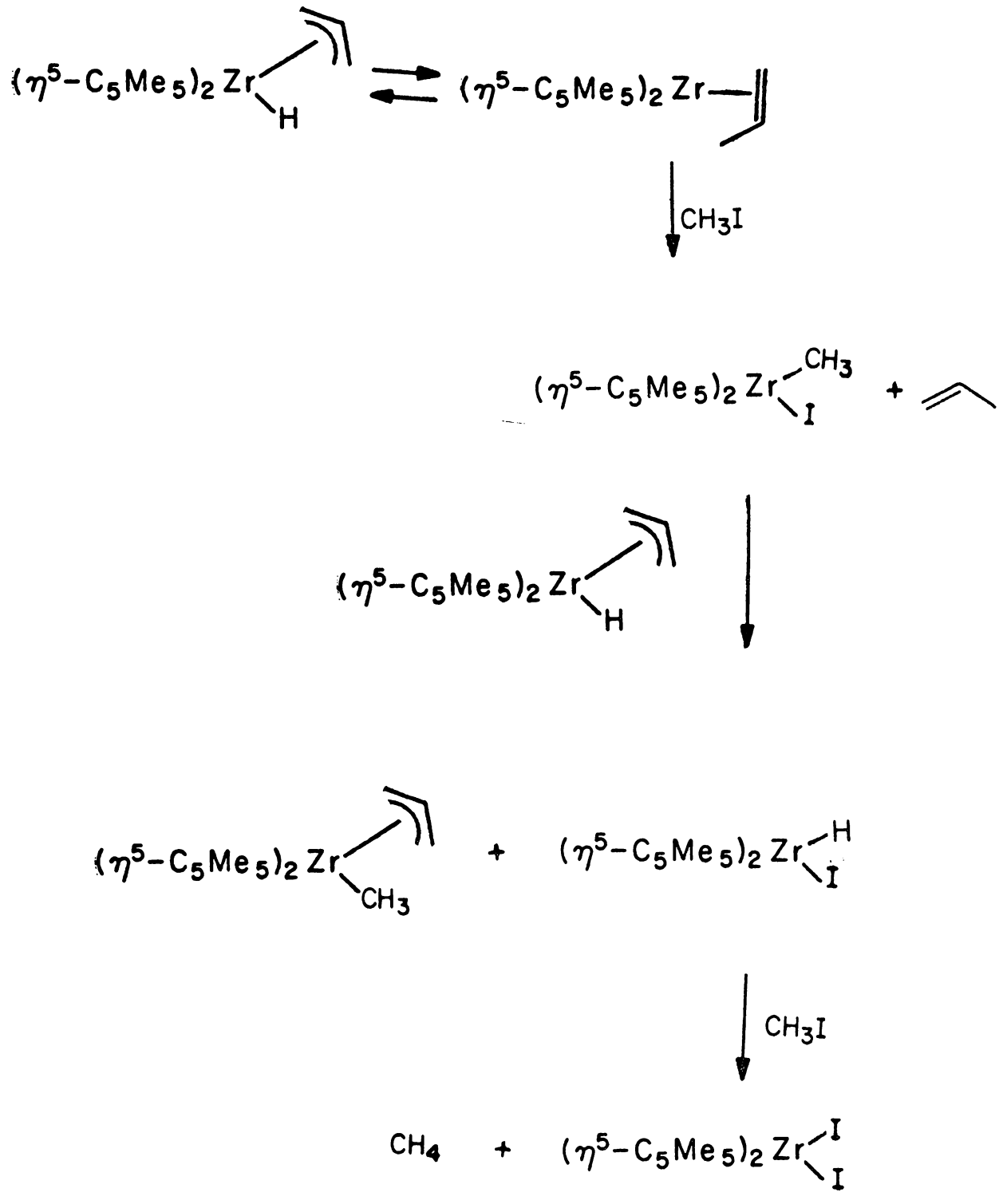
$$2(\eta^5\text{-}C_5Me_5)_2Zr(H)(\eta^3\text{-}C_3H) + 2CH_3I \xrightarrow[\text{toluene}]{} (\eta^5\text{-}C_5Me_5)_2ZrI_2 + (\eta^5C_5Me_5)_2Zr(CH_3)(\eta^3\text{-}C_3H_5) + CH_4 + C_3H_6 \quad (15)$$

By Toepler pump analysis and ^{1}H-nmr spectral data, this reaction is stoichiometric. The $(\eta^5\text{-}C_5\text{-}Me_5)_2ZrI_2$ has been previously characterized.

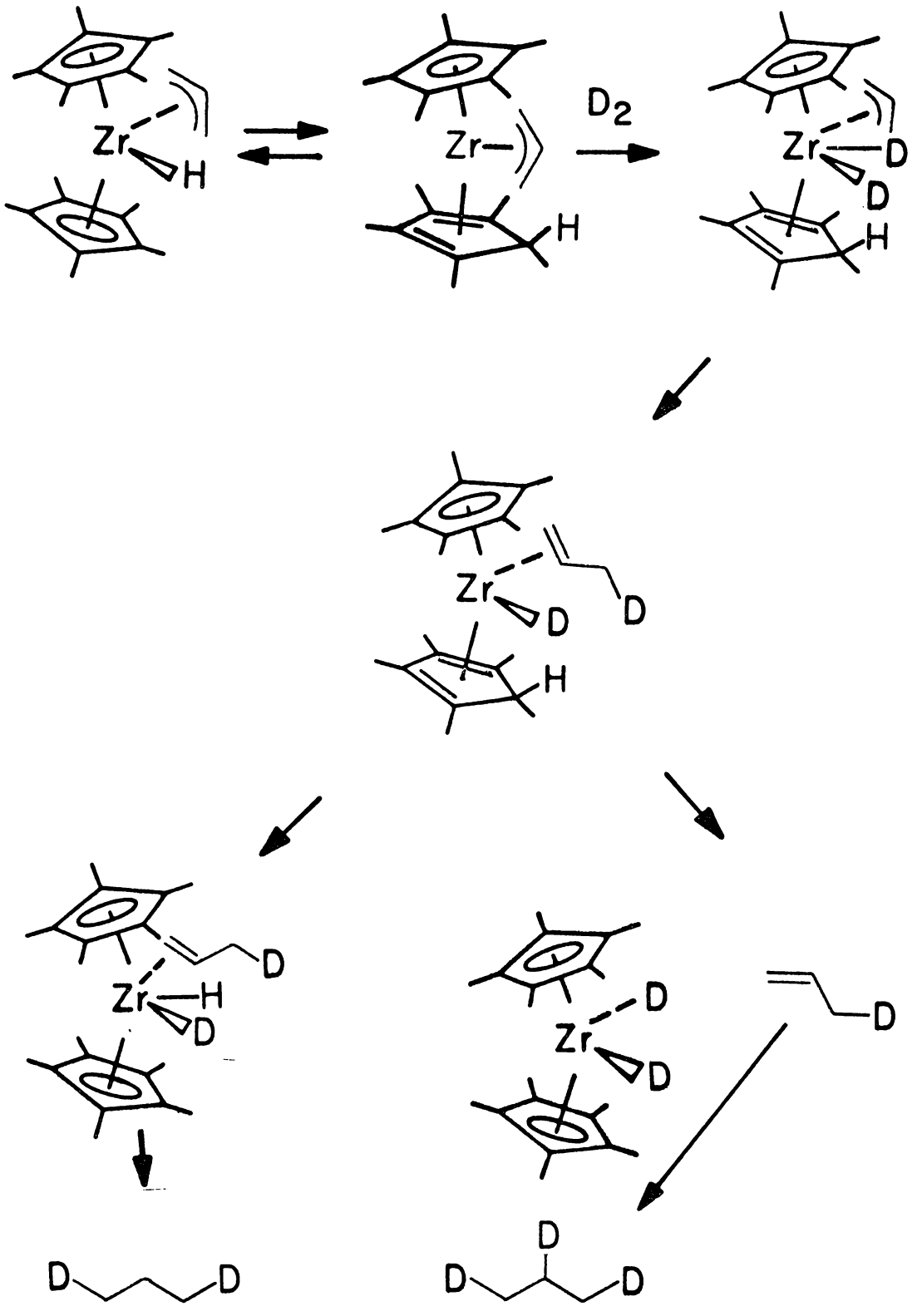
The $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)(\eta^3\text{-}C_3H_5)$ shows resonances in the ^{1}H-nmr spectrum at 5.36δ as a quintet ($^3J_{H-H}$ = 12 Hz) for the central hydrogen of π-allyl, at 2.66δ as a doublet ($^3J_{H-H}$ = 12 Hz) for the methylene hydrogens of the π-allyl, at -0.04δ as a singlet for the methyl's hydrogens on the zirconium, and at 2.00δ as a singlet for the thirty hydrogens on the ring methyls. This complex does not have a hydride which should and does shut down formation of propene as in Scheme 8. The methylenes are still equivalent and syn-anti isomerization is still occurring. Thus Schemes 3 and 6 are operative.

The mechanism for this reaction, however, is unclear. One possibility is shown in Scheme 9. This scheme involves the π-allyl hydride reductively eliminating propene in the presence of CH_3I to form the methyl iodide complex which undergoes a ligand exchange with more π-allyl hydride forming the π-allyl methyl and the iodohydride complex. This iodohydride then reacts with more CH_3I to produce the methane and diiodide complex which is isolated.

Besides reacting with CH_3I, 5 reacts with other small molecules. With H_2 in toluene the complex forms $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and a gas mixture of propene and propane (1:2). The Toepler pump analysis showed 1.1 mmoles of H_2/mmole of Zr and 0.8 mmoles of gas/mmole of Zr for this reaction in 1,2,4-trimethylbenzene. When D_2 is substituted for H_2, the same ratios are obtained with gases being propene-$\underline{d}_1$ and a mixture of propane-$\underline{d}_2$ and propane-$\underline{d}_3$. These results may be explained by the mechanism of Scheme 10. This is similar to Scheme 2 again involving the hydride transfer from the metal to the ring allowing D_2 to oxidatively add releasing propene-$\underline{d}_1$ or



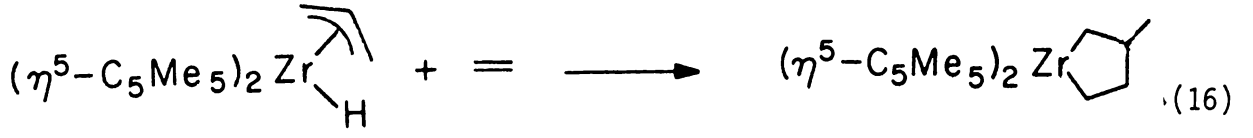
Scheme 9



Scheme 10

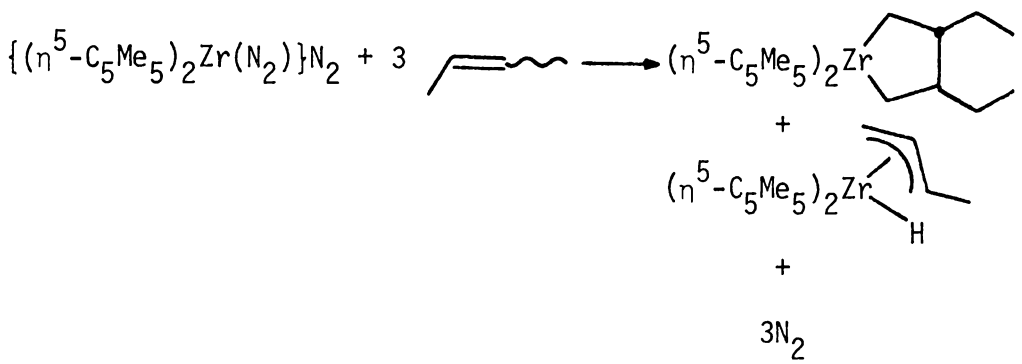
further hydrogenating the propene-$\underline{d}_1$ to propane-$\underline{d}_2$ or propane-$\underline{d}_3$.

Upon reaction of the π-allyl hydride with excess CO in toluene the products obtained are $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ and propene. The Toepler pump analysis in 1,2,4-trimethylbenzene showed this reaction to be stoichiometric. Both H_2 and CO promote reductive elimination in this system. Ethylene, on the other hand, reacts with the complex to form the mixed metallocycle (eq. 16).



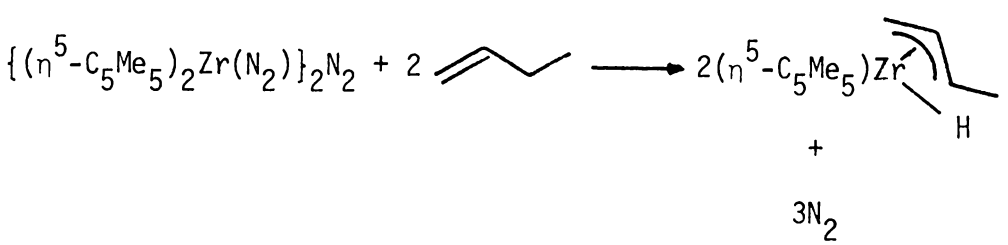
(16)

In addition to the parent π-allyl hydride, similar complexes can be synthesized from the dinitrogen complex $\underset{\sim}{1}$ and other olefins. The reaction with cis- and trans-2-butene gives two products--one of which is the π-methylallyl hydride of bis(pentamethylcyclopentadienyl)zirconium ($\underset{\sim}{7}$) (eq. 17).



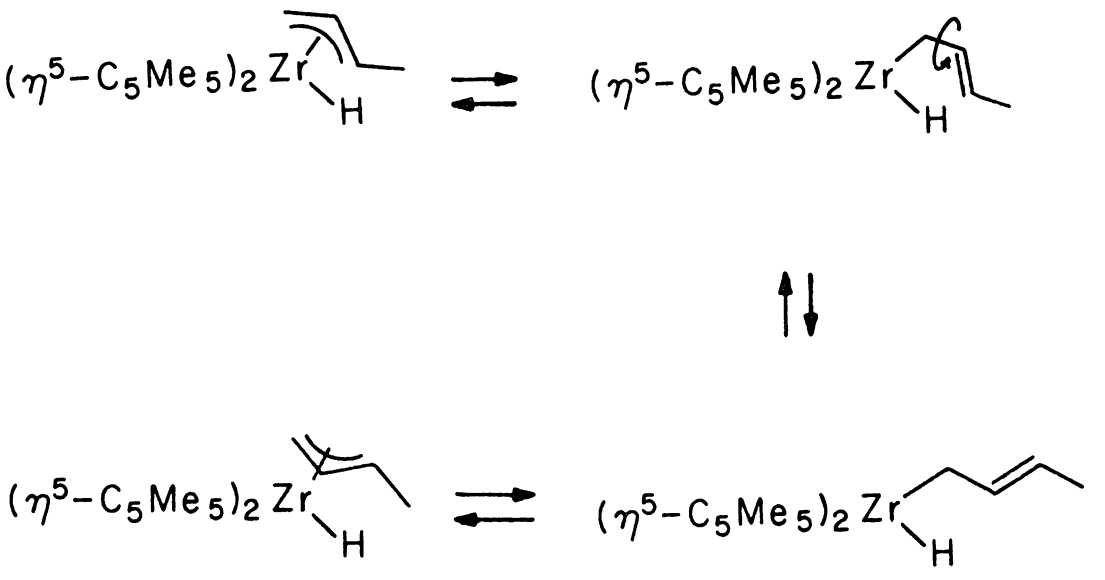
(17)

As previously reported, cis-2-butene can be converted completely to the metallocycle by heating at 40°C for ∿ 12 hours and trans-2-butene can be converted solely to the π-methylallyl hydride by heating to 40°C for several minutes followed by immediate removal of all excess olefin. Furthermore, 1-butene will also form the π-methylallyl hydride complex if reacted with $\underset{\sim}{1}$ on a one-to-one molar ratio with Zr (eq. 18).



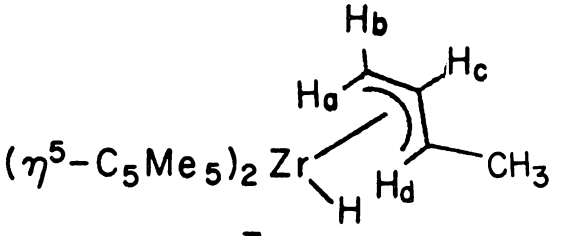
(18)

Again with this system, the nmr spectra warrant further discussion. The central hydrogen of the π-allyl shows a six-line pattern at 3.81δ in the ^{1}H-nmr spectrum (C_6D_6) at 40°C. This appears to be two overlapping triplets which is in agreement with a syn-anti isomerization exemplified in Scheme 11 and similar to Scheme 2.



Scheme 11

Again the geminal hydrogens become equivalent by going to the σ-allyl intermediate. The triplet resulting from this is then split due to the methyne hydrogen. The coupling constants are in agreement with this explanation. For the structure 7, $^{3}J_{H_a,H_b-H_c}$ is 10 Hz which is an average of cis- and trans- vicinal coupling, and $^{3}J_{H_c-H_d}$ is 15 Hz which is trans vicinal coupling only. The ^{1}H-nmr spectrum also shows a singlet at 1.81δ corresponding to the ring methyl hydrogens. But the rest of the



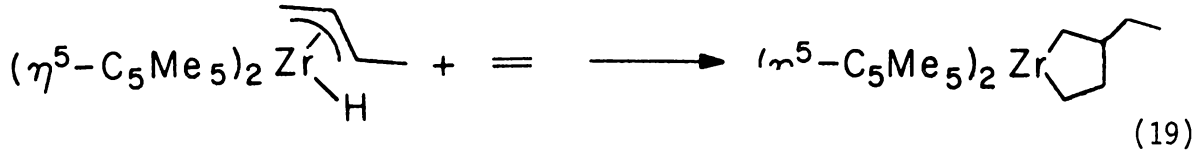
7

spectrum is only undefinable multiplets. No hydride resonance is discernible.

The ^{13}C-nmr spectrum in benzene-d_6 is similar to the parent system. Relative to TMS is a singlet in the decoupled spectrum at 117.1 ppm which splits into a doublet with a $^{1}J_{^{13}C-H}$ of 144 Hz and corresponds to the central carbon with H_c. At 111.4 ppm are the carbons of the cyclopentadienyl rings. The carbon with H_d shows a singlet at 91.5 ppm in the proton decoupled spectrum and a doublet in the gated spectrum with $^{1}J_{^{13}C-H}$ of 144 Hz. At 42.0 ppm is the carbon with H_a and H_b. It appears as a singlet and triplet in the two respective spectra and has a $^{1}J_{^{13}C-H}$ of 146 Hz. The methyl carbon of the π-allyl group shows a singlet at 20.2 ppm in the proton decoupled spectrum and a quartet with $^{1}J_{^{13}C-H}$ of 120 Hz in the undecoupled spectrum. Finally, the ring methyl carbons appear at 11.9 ppm and show a $^{1}J_{^{13}C-H}$ of 126 Hz.

The low temperature ^{1}H-nmr shows nothing significant except that the π-methylallyl system can be frozen out at -7°C. This is at a higher temperature than the parent π-allyl, suggesting that the fluxional behavior requires less energy for the parent and consequently is harder to freeze out.

The π-methylallyl hydride complex reacts in a manner similar to the parent π-allyl hydride. With H_2 in toluene, the complex is converted to $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and a mixture of 1-butene and butane (1:2). And with D_2 the gaseous products are butane-$\underline{d}_2$, butane-$\underline{d}_3$, and 1-butene-$\underline{d}_1$. Addition of excess CO produces $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ and 1-butene. Ethylene (in a one-to-one molar ratio) reacts to form the mixed metallocycle (eq. 19) and in excess forms the parent metallocyclopentane.



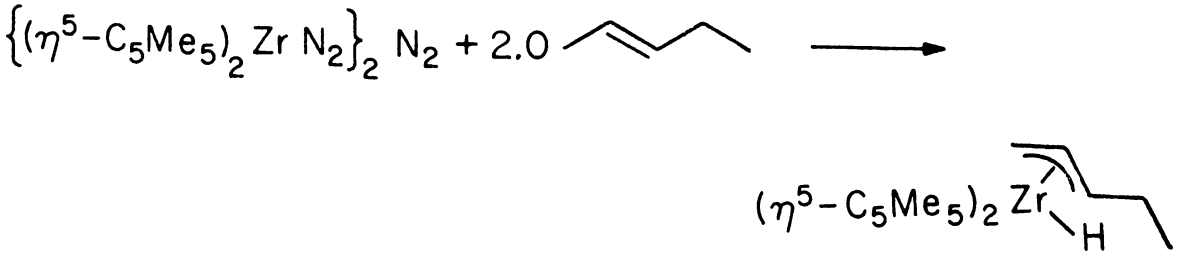
(19)

Reactions of both propyne and 2,6-dimethylphenylisocyanide with $\underset{\sim}{7}$ gave no discernible products. The reaction with CH_3I is not clean, but gives a mixture of products including $(\eta^5\text{-}C_5Me_5)_2ZrI_2$ and some Zr-CH_3 bonded

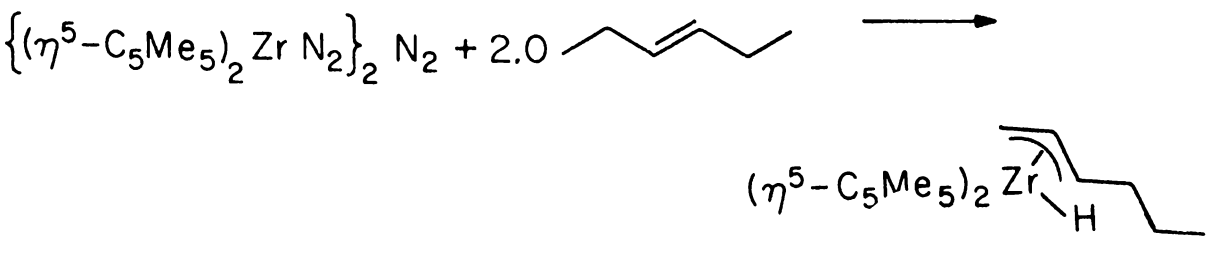
species. No π-allyl complex appeared to be present by ^{1}H-nmr.

The reaction of 1 with 2-fluoropropene in molar ratios from 1:2 to 1:6 gives some indeterminant compound or compounds. The ^{1}H-nmr spectrum suggests the possibility of a π-allyl hydride with a fluorine in the central position of the π-allyl. The spectrum implies that the π-allyl system is frozen in one position and no fluxional behavior is occurring. But when the complex is treated with CH_3I, no reaction occurs. Work on this system was not pursued further.

Besides reactions with C_3 and C_4 olefins, 1 reacts with trans-2-pentene and trans-3-hexene. Both reactions give corresponding π-allyl hydride complexes (eq. 20).

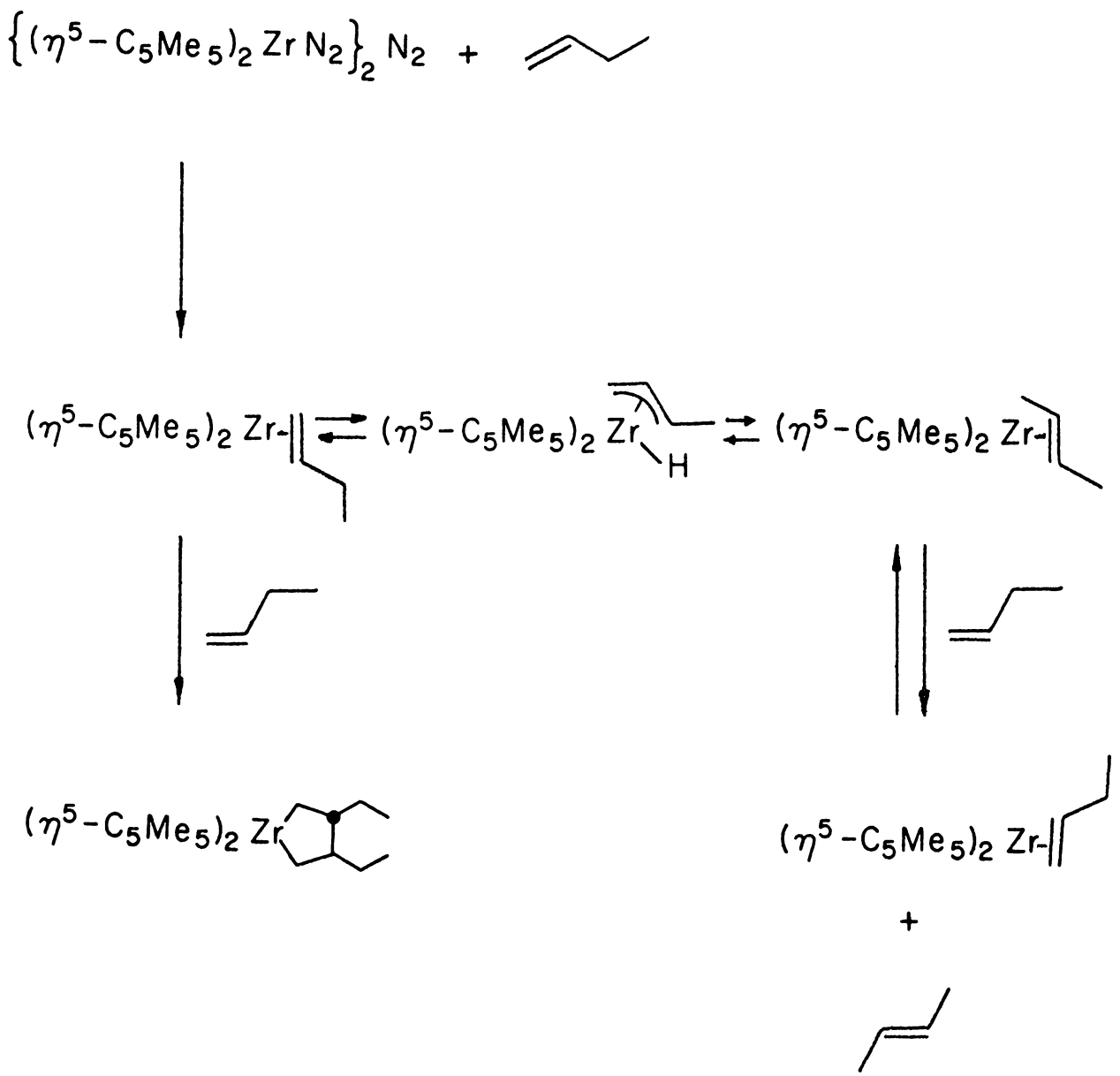


(20)



Again, both exhibit the six-line pattern in the ^{1}H-nmr spectra. This means that the trans-2-pentene forms a π-ethylallyl hydride complex and the trans-3-hexene forms a π-propylallyl hydride complex. This latter result implies that the internal olefins are converted to terminal allyl systems. This is similar to results found by Schwartz[29] in his reactions of olefins with $Cp_2Zr(H)(Cl)$. He sees internal olefins converted to terminal species in the formation of $Cp_2Zr(R)(Cl)$.

Certainly many reaction mechanisms involving olefins and transition metals and in particular involving olefin isomerization have been postulated to involve metal-π-allyl hydride complexes. These bis(pentamethylcyclopentadienyl)zirconium(IV) systems provide isolable compounds of this type. And these seem to be part of the total scheme linking the observed olefin isomerization and metallocycle formation in the zirconium system. This is illustrated for butenes in Scheme 12. This scheme shows the olefins reacting with the dinitrogen complex to coordinate the olefin and form the π-allyl hydride which is in equilibrium with the π-bound olefin complexes. The π-bound olefins can either exchange with other olefins or react to form metallocyclopentanes. Indeed, the study of these olefin, π-allyl hydride, and metallocycle reactions may better explain and aid in the understanding of other olefin isomerizations and conversions.


{(η5-C5Me5)2 Zr N2}2 N2 +
(η5-C5Me5)2 Zr-
(η5-C5Me5)2 Zr
H
(η5-C5Me5)2 Zr-
(η5-C5Me5)2 Zr
(η5-C5Me5)2 Zr-
+

Scheme 12

Experimental Section

General considerations. All manipulations were carried out using glove box or high vacuum line techniques. Prior to use all solvents were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene."[30] All nmr solvents were purified over activated 4Å molecular sieves followed by "titanocene." Hydrogen and deuterium (MCB) were passed over MnO on vermiculite[31] and activated 4Å molecular sieves. Other gases, ethylene, propene, 1-butene, cis- and trans-2-butene, were purified by freezing at -196°C and pumping followed by distillation from -78°C to -196°C traps. $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2$ was prepared by previously reported methods.[32]

^{1}H-nmr spectra were recorded using Varian A-60A and EM-390 spectrometers and a Bruker HS-270 nmr spectrometer[33] which was interfaced with a Nicolet 1080 computer at the University of Chicago. ^{13}C-nmr spectra were obtained on a Varian XL-100 spectrometer and a Bruker nmr spectrometer[34] at the Francis N. Bitter National Magnet Laboratory in Cambridge, Massachusetts. Infrared spectra were obtained using a Beckman Ir-12 and Ir-4240 spectrophotometers. Mass spectrometry data were obtained using a DuPont mass spectrometer.

Hydrocarbon gases were analyzed by gas chromatography on a Varian 940 gas chromatograph equipped with a thermal detector using a 20 foot 13% DBT (dibutyltetrachlorophthalate) on Chromosorb W column.

Procedures

(1) $(\eta^5\text{-}C_5Me_5)_2\overline{ZrCH_2(CH_2)_2CH_2}$ (a) Preparation. At -196°C, 0.9900 mmoles of ethylene were added to a solution of 100 mg (0.1239 mmoles) of

1 in toluene. The solution was allowed to warm to room temperature and stirred for 1 hour. A bright yellow compound was formed which was isolated by removing the toluene and recrystallized with 30-60 pet ether. The ^{1}H-nmr spectrum (C_6D_6) showed peaks at 0.50δ (m,4,$2CH_2$), 1.82δ (s,30, $10CH_3$), and 1.95δ (m,4,$2CH_2$).

(b) Reaction with HCl. To 60 mg (0.1439 mmoles) of 2 in 10 ml of toluene were added 0.8634 mmoles of anhydrous HCl at -196°C. After warming to room temperature and stirring for 1.5 hours, the gas and solvent were removed. The gas was identified as butane by ir and mass spectrometry. The remaining solid was $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$.

(c) Reaction with H_2. After adding 41 mg (0.0983 mmoles) of 2 to a flask, 15 ml of 1,2,4-trimethylbenzene were added. Then 0.4199 mmoles of H_2 were added. The mixture was stirred for ∿ 1 hour at room temperature. Toepler pumping the gas through three -196°C cooled traps revealed that 0.0703 mmoles of H_2 were used (1.8 H_2/Zr). Warming the traps to 0°C and continuing to Toepler pump gave a mixture of butane and ethane (2:1).

(d) Reaction with D_2. The procedure of (c) was followed. 45 mg (0.1085 mmoles) of 2 were used and 0.6800 mmoles of D_2 were added. 0.1939 mmoles of D_2 were consumed (1.79 D_2/Zr). Deuterated butanes (1,4-dideuteriobutane and 1,2,4-trideuteriobutane) and dideuterioethane (2:1) were also obtained.[35]

(e) Pyrolysis of 2 in vacuo. Into a thick-walled glass vessel equipped with a Teflon needle valve were placed 80 mg (0.1920 mmoles) of 2. Then 15 ml of 1,2,4-trimethylbenzene were added. The solution was

stirred at 120°C for three days. The color of the solution changed from yellow to brown to red-orange. Toepler pumping through three 0°C cooled traps yielded 0.2061 mmoles of gas which analyzed by gas chromotography and mass spectrometry to be 24% ethylene, 26% cyclobutane, 12% 1-butene, and 39% ethane.

(f) Pyrolysis of 2 with excess ethylene. Into a thick-walled glass vessel equipped with a Teflon needle valve were placed 51 mg (0.1219 mmoles) of 2. Then 15 ml of 1,2,4-trimethylbenzene were added as was 0.5062 mmoles of ethylene. The solution was stirred at 80°C for three days. The gases were collected by Toepler pumping and analyzed by gas chromatography to be a mixture of ethane, butane, 1-butene, cis- and trans-2-butene, and 1,3-butadiene.

(g) Photolysis of 2 in vacuo. Into two small flasks were placed 60 mg (0.140 mmoles) of 2. Then ∿ 10 ml of toluene were added and the samples were placed in an ice water bath in front of a 1000 watt medium pressure Hg lamp. One sample was wrapped in aluminum foil. Both samples were irradiated for 24 hours. No gases were found to evolve and the starting material remained unchanged.

(2) $(\eta^5\text{-}C_5Me_5)_2\overline{ZrCH_2(CHCH_3CHCH_3)CH_2}$.

(a) Preparation. To a solution of 100 mg (0.1239 mmoles) of 1 in toluene was added 1.0 mmole of propene at -196° C. The solution was allowed to warm to room temperature and stirred for one hour. A yellow compound was formed which was isolated by removing the toluene and recrystallized from 30-60 pet ether. The ^{1}H-nmr spectrum (C_6D_6) showed peaks at -0.04δ (dd,2,2CH), 0.89δ(t,2,2CH), 1.09δ (d,6,2CH_3), 138δ (m,2,2CH), and 1.83δ (s,30,10CH_3)

(b) Reaction with H_2. After adding 48 mg (0.1079 mmoles) of 3 to a small flask, 15 ml of toluene were added. Then 0.4316 mmoles of H_2 were added. The mixture was stirred at room temperature for ∿ 1 hour. Toepler pumping the unused H_2 through three -196°C cooled traps showed that 0.1942 mmoles of H_2 were used (1.8 H_2/Zr). The toluene solution contained 2,3-dimethylbutane and butane (2:1).

(c) Reaction of 3 with D_2. The procedure of (b) was followed using 40 mg (0.0899 mmoles) of 3 and 0.3590 mmoles of D_2. Toepler pumping showed that 0.1591 mmoles of D_2 were consumed (1.77 D_2/Zr). The toluene contained both tri- and dideuterio-2,3-dimethylbutane and dideuteriobutane.[35]

(d) Reaction with ethylene. Following addition of 44 mg (0.0989 mmoles) of 3 to a flask, 10 ml of toluene were added. Then at -196°C, 0.4000 mmoles of ethylene were added. After warming to room temperature the solution was allowed to stir for 2 hours. The solid was isolated and found to be 2.

(3) $(\eta^5\text{-}C_5Me_5)_2\overline{ZrCH_2(CHEtCHEt)CH_2}$.

(a) Preparation. After distilling 20 ml of toluene onto 100 mg (0.1239 mmoles) of 1 at -196°C, 1.000 mole of 1-butene was added. The solution was allowed to warm and stir at room temperature for 2 hours. The yellow product was recrystallized using 30-60 pet ether. The ^{1}H-nmr spectrum (C_6D_6) showed signals at -0.10δ (dd,2,2CH), 0.79δ (t,2,2CH), 1.08δ (m,10,2Et), 1.54δ (m,2,2CH), and 1.84δ (s,30,10CH_3).

(b) Reaction with ethylene. After adding 35 mg (0.0740 mmoles) of 4 to a small flask, toluene was distilled in. Then at -196°C, 0.2951 mmoles of ethylene were added. After the solution warmed to room temperature and stirred for 2 hours, the solid was isolated and characterized to

be 2.

(c) Pyrolysis with excess 1-butene. Into a thick-walled glass tube equipped with a Teflon needle valve were placed 89.8 mg (0.1113 mmoles) of 1. Toluene was added. Then 0.4450 mmoles of 1-butene were added at -196°C and the reaction mixture was allowed to warm to room temperature and stir for 1 hour. Then the excess 1-butene was pumped off as was the toluene. More toluene was added with 0.0777 mmoles of 1-butene and 0.0958 mmoles of propane (internal standard). The reaction mixture was heated to 110°C and the gas phase was sampled while hot with a 5 ml gas-tight syringe. The gas chromotograph showed propane, 1-butene, and some cis- and/or trans-2-butene.

(4) $(\eta^5\text{-}C_5Me_5)_2Zr(H)(\eta^3\text{-}C_3H_5)$.

(a) Preparation from 1. To a solution of 85 mg (0.1053 mmoles) of 1 in toluene were added 0.2105 mmoles of propene at -196°C. After warming to room temperature, the reaction was allowed to stir for 2 hours. The color changed from deep purple to yellow. Toepler pumping the gas through three -196°C cooled traps gave 0.3064 mmoles of N_2(2.91 N_2/Zr_2). The π-allyl hydride was recrystallized from cold 30-60 pet ether giving a beige solid. The ir spectrum (Nujol mull on KBr plates) shows bands at 1600(m), 1580(m), 1540(s), 1380(s), 1265(w), 1220(2), 1025(m), 1005(m), 1000(m), 840(s), 700(m), 740(w), 690(m), 650(w), and 400(m) cm^{-1}. Calculated for $C_{23}H_{36}Zr$: C 68.42, H 8.99; found: C 68.23, H 8.84.

(b) Preparation from $(\eta^5\text{-}C_5Me_5)_2ZrH_2$. After distilling 1,2,4-trimethylbenzene onto 60 mg (0.1653 mmoles) of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ in a small flask, 0.4900 mmoles of allene were condensed in at -196°C. After warming

to room temperature and stirring for 1 hour, the excess allene was Toepler pumped through three 0°C cooled traps. From this, 0.1537 mmoles of allene were used (0.93 allene/Zr). The solid was recrystallized from cold 30-60 pet ether.

(c) Reaction with CH_3I. After forming 0.1362 mmoles of 5 from 1 in situ, toluene was added. Then 0.5450 mmoles of CH_3I were added at -196°C. The mixture was allowed to warm to room temperature and stirred for 3 hours until a bright yellow color developed. Then the gas was Toepler pumped first through three -196°C cooled traps yielding 0.0831 mmoles of CH_4 (0.61 CH_4/Zr) and then through -78°C cooled traps yielding 0.0572 mmoles of propene (0.42 propene/Zr). The resulting solid was a mixture of $(\eta^5\text{-}C_5Me_5)_2ZrI_2$ and $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)(\eta^3\text{-}C_3H_5)$. Upon attempted recrystallization the two could not be completely separated either by cold pet ether or sublimation.

(d) Reaction with H_2. To a small round-bottomed flask equipped with a calibrated volume were added 44 mg (0.0545 mmoles) of 1. Then 15 ml of toluene were vacuum distilled in at -78°C. Then 0.1090 mmoles of propene were added at -196°C. After warming to room temperature with stirring, the solvent was removed and 15 ml of 1,2,4-trimethylbenzene were added at -78°C. Then 0.6540 mmoles of H_2 were added via the calibrated volume. After stirring for 3 hours at room temperature the mixture was Toepler pumped through three -196°C cooled traps giving 0.1196 mmoles of H_2 (1.1 H_2/Zr) consumed. Warming the three traps to 0°C allowed 0.0872 mmoles of propene and propane (1:2) to be collected. The product remaining was $(\eta^5\text{-}C_5Me_5)_2ZrH_2$.

(e) Reaction with D_2. The procedure of (c) was followed using 37.2 mg (0.0461 mmoles) of 1 and 0.0921 mmoles of propene. Then upon conversion to 5, 0.5649 mmoles of D_2 were added. The Toepler pumping revealed that 0.1011 mmoles of D_2 (1.1 D_2/Zr) were used and 0.0728 mmoles of a 1:2 mixture of propene-d_1 and 1,3-dideuteriopropane and 1,2,3-trideuteriopropane were collected.[35]

(f) Reaction with CO. To a solution of 76.0 mg (0.0942 mmoles) of 1 in toluene were added 0.1883 mmoles of propene at -196°C. After forming 5 the toluene and N_2 were removed and 1,2,4-trimethylbenzene was added *in vacuo*. Then using the calibrated volume, 0.5892 mmoles of CO were added to the stirring, room temperature solution. After ~6 hours and a color change from yellow to brown, the excess CO was Toepler pumped through three -196°C cooled traps. This showed that 0.2543 mmoles of CO were used (1.8 CO/Zr). Warming the traps to 0°C and continuing to Toepler pump revealed that 0.0972 mmoles of propene (0.9 propene/Zr) were released. The resulting solid was $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$.

(g) Reaction with ethylene. After adding 37.8 mg (0.0468 mmoles) of 1 and 15 ml of toluene to a flask, 0.0936 mmoles of propene were added *in vacuo*. The solution was warmed to room temperature and stirred until 5 formed. Then the solvent/gas mixture was removed. More toluene was added *in vacuo* and 0.0936 mmoles of ethylene were condensed into the flask at -196°C. Warming to room temperature and stirring for 3 hours caused a color change from pale yellow to bright yellow. The solvent was removed and the solid was isolated. The solid was the mixed metallocycle $(\eta^5\text{-}C_5Me_5)_2\overline{ZrCH_2(CHCH_3CH_2)CH_2}$. The ^{1}H-nmr spectrum (C_6D_6) showed signals

at -0.03δ (dd,2,2CH), 0.90δ (dd,2,2CH), 1.07δ (d,3,CH_3), 1.43δ (m,1,CH), 1.52δ (m,2,CH_2), and 1.80δ (s,30,10CH_3).

(h) Reaction of $(\eta^5\text{-}C_5Me_5)_2ZrD_2$ with allene. The procedure outlined in (b) was followed using 55 mg (0.1515 mmoles) of $(\eta^5\text{-}C_5Me_5)_2ZrD_2$ in toluene and 0.4540 mmoles of allene. The solid was recrystallized from 30-60 pet ether. The ^{1}H-nmr spectrum (C_6D_6) showed only one singlet at 2.00δ for the ring methyl protons.

(i) Reaction of $[\eta^5\text{-}C_5(CD_3)_5]_2ZrH_2$ with allene. The procedure of (h) was followed after first obtaining the $[\eta^5\text{-}C_5(CD_3)_5]_2ZrH_2$ from successive (7 times) deuteration of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ with D_2 at 70°C. Then at -78°C H_2 was added to a solution of $[\eta^5\text{-}C_5(CD_3)_5]_2ZrD_2$ three times to make the dihydride. The allene was added in a three-fold excess. The solid product was recrystallized from cold 30-60 pet ether. The ^{1}H-nmr spectrum showed only the π-allyl quintet centered at 3.53δ.

(j) Reaction of $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)(\eta^3\text{-}C_3H_5)$ with CO. A reaction flask with a calibrated volume was charged with 65 mg (0.0805 mmoles) of 1. Toluene was added in vacuo at -78°C. Then 0.1610 mmoles of propene were condensed onto the solution at -196°C. After warming to room temperature and conversion to 5, the solvent/N_2 was removed in vacuo. More toluene was added. Next, 0.6440 mmoles of CH_3I were condensed at -196°C into the reaction flask. After 3 hours of stirring at room temperature the solvent was removed with the excess CH_3I, propene, and CH_4. Then more solvent was added and 0.6813 mmoles of CO were added via the calibrated volume to the stirring reaction mixture. After 12 hours the gas was Toepler pumped. The results showed that 0.0860 mmoles of CO

(0.53 CO/Zr) were used. Assuming before addition of CO that the reaction mixture was 50:50 $(\eta^5\text{-}C_5Me_5)_2ZrI_2$ and $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)(\eta^3\text{-}C_3H_5)$, then one CO per $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)(\eta^3\text{-}C_3H_5)$ was used. The solid formed was a mixture of $(\eta^5\text{-}C_5Me_5)_2ZrI_2$ and other indistinguishable products.

(5) $(\eta^5\text{-}C_5Me_5)_2Zr(H)(\eta^3\text{-}C_4H_7)$.

(a) Preparation from trans-2-butene. To 65.0 mg (0.0805 mmoles) of 1 were added 10 ml of toluene at -78°C. Then 0.4830 mmoles of trans-2-butene were condensed in at -196°C. The mixture was warmed slowly to 40°C with stirring. Following a color change from purple to red-orange, the solvent/N_2 mixture was immediately pumped off. The product was recrystallized from 30-60 pet ether. The ^{1}H-nmr spectrum (C_6D_6) showed clear peaks at 1.81δ (s,30,10CH_3) and 3.81δ (dt,1,CH). The ir spectrum (Nujol mull on KBr plates) showed bands at 1575(m), 1530(m), 1025(s), 1000(m), 970(m), 845(s), 775(m), and 670(m) cm^{-1}.

(b) Preparation from 1-butene. To a solution of 53.8 mg (0.0666 mmoles) of 1 and 10 ml of toluene was added 0.1332 mmoles of 1-butene at -196°C. After warming to room temperature and stirring for 2 hours the reaction changed colors from purple to red-orange. The solvent/gas mixture was removed and the solid was recrystallized from 30-60 pet ether.

(c) Reaction with H_2. Toluene (10 ml) was added to 0.0564 mmoles of 1 at -78°C. Then 0.3380 mmoles of trans-2-butene were added at -196°C. After conversion to 7 and removal of the gas/solvent mixture, 10 ml of 1,2,4-trimethylbenzene were added at -78°C. Next, 0.3386 mmoles of H_2 were added via a calibrated volume. The solution was stirred for 2 hours at room temperature. Then Toepler pumping the H_2 through -196°C cooled

traps revealed that 0.1184 mmoles of H_2 were consumed (1.05 H_2/Zr). Then warming the traps to 0°C and Toepler pumping the remaining gas showed that 0.0902 mmoles of gas (2:1 butane to 1-butene) were obtained. The remaining solid was $(\eta^5\text{-}C_5Me_5)_2ZrH_2$.

(d) Reaction with D_2. The procedure of (c) was followed using 0.0785 mmoles of 1 which was converted to 7. Toepler pump analysis showed 0.1727 mmoles of H_2 (1.1 H_2/Zr) were used and 0.1115 mmoles of gas--a 1:2 mixture of 1-butene-d_1 and deuterated butanes (1,4-dideuteriobutane and 1,2,4-trideuteriobutane)--were obtained.[35]

(e) Reaction with CO. The procedure of (a) was followed to make 7 using 0.1072 mmoles of 1 and 0.9196 mmoles of trans-2-butene. Then after removing the solvent/gas mixture, 10 ml of toluene and 0.6976 mmoles of CO via a calibrated volume were added. Toepler pumping the mixture through three -196°C coded traps showed that 0.3613 mmoles of CO (1.69 CO/Zr) were used. The remaining solid was $(\eta^5\text{-}C_5\text{-}Me_5)_2Zr(CO)_2$.

(f) Reaction with ethylene. To a solution of 0.1370 mmoles of 7 and 10 ml of toluene were added 0.1456 mmoles of ethylene at -196°C. Upon warming to room temperature and stirring for 3 hours, the reaction mixture changed from red-orange to yellow. The product was recrystallized from 30-60 pet ether. It was the mixed metallocycle $(\eta^5\text{-}C_5Me_5)_2\overline{ZrCH_2(CHEtCH_2)CH_2}$. The ^{1}H-nmr spectrum (C_6D_6) showed resonances at -0.07δ (dd,2,2CH), 0.70δ (dd,2,2CH), 1.03δ (m,5,Et), 1.27δ (m,1,CH), 1.43δ (m,2,CH_2), and 1.80δ (s,30,10CH_3).

(g) Reaction with propyne. To 0.1239 mmoles of 7 were added 15 ml of toluene in vacuo at -78°C. Then 0.5514 mmoles of propyne were condensed in at -196°C. Upon warming to room temperature the reaction mixture changed color from orange to yellow. The resulting solid appeared to be a complex mixture of products by ^{1}H-nmr spectroscopy.

(h) Reaction with 2,6-dimethylphenylisocyanide. To a solution of 0.1300 mmoles of 7 and 15 ml of toluene were added 60 mg (0.4580 mmoles) of 2,6-dimethylphenylisocyanide. The mixture was allowed to stir for 24 hours at room temperature. The ^{1}H-nmr spectrum (C_6D_6) of the isolated solid contained a multitude of peaks.

(i) Reaction with CH_3I. After adding 0.6084 mmoles of CH_3I to a solution of 0.1516 mmoles of 7 in 15 ml of toluene at -196°C, the solution was warmed to room temperature and stirred for 3 hours. Then the gas was Toepler pumped through three -196°C cooled traps. This gave 0.0864 mmoles of CH_4 (0.58 CH_4/Zr). The ^{1}H-nmr spectrum (C_6D_6) of the solid showed a complex mixture of products--none of which involved a π-allyl group.

(6) Reaction of 1 with 2-fluoropropene. To a solution of 0.0768 mmoles of 1 and 15 ml of toluene were added 0.1537 mmoles of 2-fluoropropene at -196°C. The solution was warmed to room temperature and stirred for 2 hours. The solid was isolated. The ^{1}H-nmr spectrum (C_6D_6) showed resonances at 1.80δ (s), 4.40δ (m), 5.07δ (m), 5.80δ (m), and 6.03δ (m).

Reacting 1 (0.0684 mmoles) with a three-fold excess (0.4102 mmoles) of 2-fluoropropene gave the same ^{1}H-nmr spectrum.

Reacting 1 (0.0629 mmoles) with 0.1258 mmoles of 2-fluoropropene and that product in toluene with 0.5033 mmoles of CH_3I gave the same ^{1}H-nmr

spectrum for the resulting solid.

(7) Reaction of $\underset{\sim}{1}$ with trans-2-pentene. To a solution of 0.0466 mmoles of $\underset{\sim}{1}$ and 15 ml of toluene were added 0.1 ml of trans-2-pentene (dried over Na) at -196°C. The solution was warmed to room temperature and stirred for 1 hour. Toepler pumping the gas through three -196°C cooled traps gave 0.1260 mmoles of N_2 (2.70 N_2/Zr_2). The ^{1}H-nmr spectrum (C_6D_6) showed resonances at 1.20δ (m), 1.71δ (s), 1.97δ (m), 2.55δ (m), and 3.72δ (dt).

(8) Reaction of $\underset{\sim}{1}$ with trans-3-hexene. To a solution of 0.0756 moles of $\underset{\sim}{1}$ and 15 ml of toluene were added 0.1 ml of trans-3-hexene (dried over Na) at -196°C. The solution was warmed to room temperature and stirred for 1 hour. Toepler pumping the gas through three -196°C cooled traps gave 0.2264 mmoles of N_2 (3.00 N_2/Zr). The ^{1}H-nmr spectrum (C_6D_6) showed signals at 1.10δ (m), 1.60δ (m), 1.80δ (s), 2.55δ (m), and 3.80δ (dt).

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33. Thanks to Ayusman Sen for running the low temperature ^{1}H-nmr spectra of π-allyl hydride complex.

34. Thanks to Clayton Wood and R. R. Schrock for running ^{13}C-nmr spectrum of π-methylallyl hydride complex.

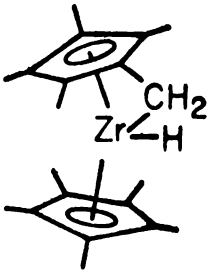
35. Assignments are based upon mass spectral data compared to data given in A. Cornu and R. Massot, "Compilation of Mass Spectral Data," Vol. 1, Heyden, New York (1975).

APPENDIX

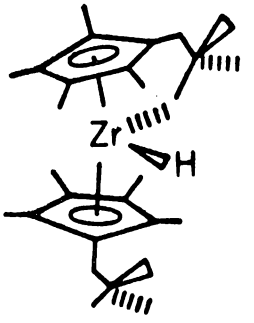
APPENDIX

Introduction

The purpose of this appendix is to include additional data about complexes 3 and 6 from Chapter 1.



3



6

Both are isolable intermediates in carbon-hydrogen activation and play important roles in the mechanistic schemes described previously. Consequently, reactions of 3 and 6 with hydrogen (kinetic uptake of H_2) and with other small molecules are presented here. Most of the results, however, remain unclear.

Results and Discussion

Kinetics. The method for forming 3 was the same as outlined in Chapter I. This involved pumping off the N_2 from a toluene solution of $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2N_2$. With the solution of 3 at -78°C the H_2 was added at several different pressures. The data initially seemed to illustrate a first order rate expression. Closer examination, however, showed that a better fit of the data was provided by a one-half order rate dependence. These results are shown in Table I.

Furthermore, for 6 similar results were obtained. With 6, the H_2 uptake could be repeatedly measured using the same sample, since it reversibly binds H_2. In addition, it took up H_2 at a slower rate, allowing the reaction kinetics to be measured at 0°C, 12°C, and 24°C. Again the best fit results in a one-half order rate. These results are shown in Table II.

Both Table I and Table II show interesting features. For 3 the rate was unaffected by H_2 pressure, whereas for 6 there was a proportional change. Furthermore, H_2 uptake of 6 appears to depend on concentration but shows no significant isotope effect. This includes all possibilities--6 with H_2, 6 with D_2, perdeuterio 6 with D_2, and perdeuterio 6 with H_2.

The one-half order kinetics are the most difficult to explain. Besides the first-order dependence not fitting, an autocatalytic system was considered in which the production of the dihydride complex might accelerate the rate with time. But, upon mixing $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ with both 3 and 6, no change was produced in the rates observed. Thus, the rate seems to be one-half order. This could be explained by a dimer-monomer equilibrium:

D = dimer of 3 or 6

M = 3 or 6

P = dihydride complex of 3 or 6

$$D \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2M \qquad K_1 = \frac{M^2}{D}$$

$$M + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} P$$

Table I

Pressure (Torr)	Temperature	1st Order $k(x10^{-2}sec^{-1})$	r	1/2 Order $k(x10^{-1}sec^{-1})$	r
101.5	-78°	1.95	0.4771	1.35	0.9929
497	-78°	2.09	0.0240	1.35	0.9576
101.5	-78°	1.29	0.9723	1.29	0.9699

Table II

Gas	Pressure (Torr)	Temperature	Conc.	$k(x10^{-3}sec^{-1})$	r
H_2	748	0°	1.0	5.2	0.9990
H_2	564	0°	1.0	3.5	0.9997
H_2	373	0°	1.0	2.5	0.9991
H_2	745	12°	1.0	5.7	0.9983
H_2	748	24°	1.0	7.0	0.9910
H_2	749	0°	0.5	3.3	0.9990
H_2	745	0°	2.0	6.0	0.9986
D_2	747	0°	1.0	3.9	0.9979
D_2	747	0°	1.0	4.0	0.9955
H_2	741	0°	1.0	4.9	0.9993

$$\frac{d[P]}{dt} = k_2[M][H_2]$$

For a rapid K_1 , $[M] = [K_1D]^{1/2}$

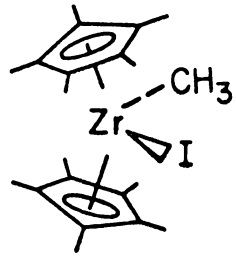
Thus, $\frac{d[P]}{dt} = k_2[H_2][K_1D]^{1/2}$

And since $\frac{d[P]}{dt} = -\frac{d[H_2]}{dt}$

$$-\frac{d[H_2]}{dt} = k_2[H_2][K_1D]^{1/2}$$

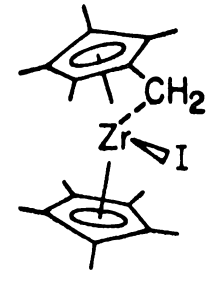
The problem with this mechanism is that the molecular weight of 3 was determined in benzene to be a monomer. One possible explanation may be that some small impurity is controlling the kinetics.

Reactions of 3. When a toluene solution of 3 was reacted with a five-fold excess of CH_3I, the solution turned orange in color. The Toepler pump analysis showed that methane was released (0.43 CH_4/Zr) and the ^{1}H-nmr spectrum revealed three species in percentages shown in Figure 1.



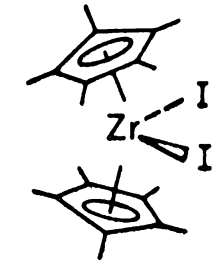
I

56%



II

40%



III

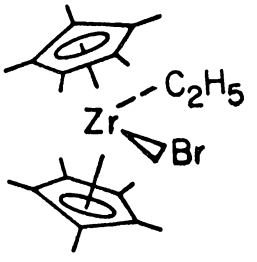
4%

Figure 1

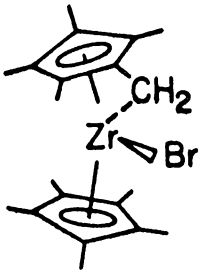
Isolation of the individual products proved unsuccessful in that a yellow pet-ether insoluble powder and orange solution could be separated, but the yellow solid contained a mixture of II and III. And recombination of

the yellow and orange mixture did not regenerate the initial ^{1}H-nmr spectrum.

In addition, 3 reacted with CH_3CH_2Br in toluene to produce ethane (0.5 ethane/Zr) and IV and V.



IV



V

No dibromide complex appeared in the ^{1}H-nmr spectrum, but neither IV nor V could be isolated.

Besides alkyl halides, 3 reacted with excess ethylene to produce $(\eta^5\text{-}C_5Me_5)_2\overline{ZrCH_2(CH_2)_2CH_2}$ and with CO to produce $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$. Due to the complexity of the ^{1}H-nmr spectrum, these reactions with 6 were difficult to interpret.

Experimental Section

(1) Kinetics of 3 with H_2. To a 10 ml round-bottomed flask were typically added 75 mg of $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2$ which was then connected to the special manometer apparatus (Figure 2). Then 5 ml of toluene were added in vacuo and the N_2 was pumped off. After the solution turned red, 5 ml of toluene were added in vacuo. The solution was cooled to -78°C and the desired H_2 was added. The change in the manometer was recorded with time.

(2) Kinetics of $\underset{\sim}{6}$ with H_2. To a 10 ml round-bottomed flask were added 92.2 mg of $\underset{\sim}{6}$, and this was connected to the special manometer apparatus (Figure 2). Then 5 ml of toluene were added in vacuo. The solution was cooled to the desired temperature and the H_2 was added. The change in the manometer readings was recorded with time.

(3) Reaction of $\underset{\sim}{3}$ with CH_3I. To a 124.7 mg (0.1544 mmoles) of $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2$ were added 15 ml of toluene. The N_2 was pumped off in vacuo. After the solution turned red, another 10 ml of toluene were added. Then 1.552 mmoles of CH_3I were added in vacuo. The solution was allowed to warm to room temperature with stirring. The Toepler pump analysis through three -196°C traps gave 0.1050 mmoles of CH_4.

(4) Reaction of $\underset{\sim}{3}$ with CH_3CH_2Br. The procedure of (3) was followed except 103.6 mg (0.1283 mmoles) of $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2$ and 1.549 mmoles of CH_3CH_2Br were used. The Toepler pump analysis showed 0.1185 mmoles of ethane were produced.

(5) Reaction of $\underset{\sim}{3}$ with ethylene. The procedure of (3) was followed except 57.5 mg (0.0712 mmoles) of $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2$ and 1.139 mmoles of ethylene were used. The reaction mixture turned yellow after stirring for one hour at room temperature. The product was $(\eta^5\text{-}C_5Me_5)_2\overline{ZrCH_2(CH_2)_2CH_2}$.

(6) Reaction of $\underset{\sim}{3}$ with CO. The procedure of (3) was followed except 42.8 mg (0.0530 mmoles) of $\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2N_2$ and 1.383 mmoles of CO were used. The solution turned brown upon stirring at room temperature. The Toepler pump analysis showed 0.2086 mmoles of CO used (1.97 CO/Zr). The other product was $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$.

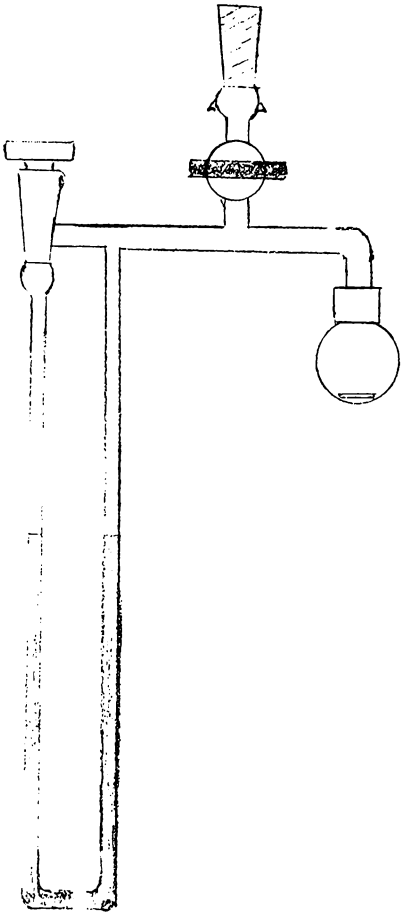


Figure 2