Ministry of Education, Republic of Korea, for their generous support of this work.

Registry No. KIPBH, 42278-67-1; $RBO_2(CH_2)_3$ (R = 2,3-dimethyl-1-butyl), 98303-39-0; $RBO_2(CH_2)_3$ (R = 2-ethyl-1-pentyl), 98303-40-3; $RBO_2(CH_2)_3$ (R = (*trans*-2-methylcyclopentyl)methyl), 98303-41-4; $RBO_2(CH_2)_3$ (R = (*trans*-2-methylcyclohexyl)methyl), 98303-42-5; $RBO_2(CH_2)_3$ (R= *exo*-norbornylmethyl), 98303-43-6; $RBO_2(CH_2)_3$ (R = (*trans*-2-phenylcyclopentyl)methyl), 98303-44-7; $LiCHCl_2$, 2146-67-0; $BHBr_2$, 13709-65-4; $RBO_2(CH_2)_3$ (R = 1,2-dimethyl-1-propyl), 98303-38-9; $RBO_2(CH_2)_3$ (R = 1-ethyl-1-butyl), 86290-28-0; $RBO_2(CH_2)_3$ (R = *trans*-2-methylcyclopentyl), 86290-31-5; $RBO_2(CH_2)_3$ (R = *trans*-2-methylcyclohexyl), 98392-60-0; $RBO_2(CH_2)_3$ (R = *exo*-norbornyl), 30154-25-7; $RBO_2(CH_2)_3$ (R = *trans*-2-phenylcyclopentyl), 98392-61-1; $RBO_2(CH_2)_3$ (R = *endo*-norbornylmethyl), 98303-45-8; $RBO_2(CH_2)_3$ (R = *cis*-2-methylcyclopentyl)methyl), 98303-46-9; norbornene, 498-66-8; 2-methyl-1-methylene cyclopentane, 41158-41-2; 2-methylenenorbornane, 497-35-8; 1,3-propanediol, 504-63-2; 1-methyl cyclopentene, 693-89-0; (*trans*-2-phenylcyclopentyl)methanol, 98392-62-2; 2,3-dimethyl-1-butanol, 19550-30-2; 2-ethyl-1-pentanol, 27522-11-8; (*trans*-2-methylcyclopentyl)methanol, 63241-06-5; (*trans*-2-methyl cyclohexyl)methanol, 3937-46-0; methyl di-2-butylborinate, 32705-45-6; methyl di-3-methyl-2-butyl borinate, 43209-69-4; tri-*n*-butylborane, 122-56-5; tri-2-butylborane, 1113-78-6; B-*n*-butyl-9-borabicyclo[3.3.1]nonane, 23532-74-3; 2-methyl-1-butanol, 137-32-6; *n*-pentyl alcohol, 71-41-0; *cis*-5-hydroxymethylcyclooctanol, 98303-47-0.

Thermolysis, Photolysis, and Deuterium Exchange Studies of Dinuclear Zirconocene Hydride Complexes

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Parallel thermolysis (at 75 °C in solution) and photolysis (20 °C) studies of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$, **1**, and $\{[SiR_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2$ (R = CH_3, **2a**; R = C_2H_5, **2b**; R = *n*-C_3H_7, **2c**) have shown that these dinuclear zirconocene hydride complexes reductively eliminate H_2. In each case, this process is accompanied by the initial formation of a paramagnetic zirconocene hydride species, which exhibits a hydride doublet with $A(^1H)$ = 6.8 G in the corresponding solution EPR spectrum. The results from a low temperature gas chromatographic analysis of the gas mixture containing H_2, HD, and D_2 generated during the thermolysis of **1** in the presence of a large excess of D_2 are consistent with deuterium incorporation into the methylcyclopentadienyl rings and the hydride positions. Further evidence for the involvement of the methylcyclopentadienyl rings during the thermolysis of **1** is provided by the fact that 3 equiv of H_2 are eliminated per equivalent of **1**. Comparable experiments conducted on **2**, however, clearly reveal that the chelating $[SiR_2(C_5H_4)_2]^{2-}$ ligand significantly restricts the chemical participation of the rings. Linking the rings with a dialkylsilyl bridge reduces the number of equivalents of H_2 evolved per equivalent of **2** to ca. two upon prolonged thermolysis and stabilizes the corresponding paramagnetic zirconocenophane hydride species produced during the initial reductive elimination step. A series of consecutive solution EPR experiments have demonstrated that this Zr(III)–H intermediate undergoes reversible H/D exchange at the hydride position. Complementary NMR measurements have further confirmed that deuterium incorporation is restricted to only the hydride positions of **2**. The role of paramagnetic zirconocene hydride species in these H/D exchange reactions is discussed.

Introduction

The reactivity patterns associated with zirconocene hydrides have attracted considerable interest due to the hydridic nature of the $Zr^{\delta+}\text{–}H^{\delta-}$ bond(s) in these compounds.[1-7] Bercaw and co-workers[1] have studied extensively the chemistry of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$, which generally is initiated by nucleophilic attack at the vacant valence orbital of this 16-electron species. In contrast the dinuclear structure of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$,[8] **1**, requires that all nine metal hybrid orbitals of each Zr be involved in bonding. Consequently, to provide a vacant coordination site a suitable pathway leading to the degradation of its dinuclear structure must be available for **1**. The involvement of a dimer ⇄ monomer equilibrium process, however, appears to be minimal on the basis that **1** is stereochemically rigid at 25 °C on a NMR time scale. An alternative possibility involves the reductive elimination of H_2 with concomitant formation of reduced zirconocene hydride species. Preliminary results, as communicated earlier,[9] indicate that both photolysis (at 20 °C) and the

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heating (at 75 °C) of benzene solutions containing 1 similarly proceed with the loss of H_2 and the initial formation of a paramagnetic zirconocene hydride species ($g = 1.9854$, $A(^1H) = 6.8$ G). A quantitative determination of the H_2 evolved during thermolysis surprisingly revealed that ca. 3 mol of H_2 are collected per mole of 1. The origin of this third mole presumably requires the direct involvement of the methylcyclopentadienyl rings in the overall H_2 elimination process. Further efforts to investigate the reactivity of 1, however, have been hindered by its limited solubility and by the possible participation of the methylcyclopentadienyl rings. The former limitation precludes the use of NMR methods to monitor reactions in noncoordinating solvents whereas the inherent mobility of the methylcyclopentadienyl rings complicates the interpretation of the spectroscopic and thermolysis data by providing additional competitive pathways for the formation of several reduced zirconocene species.

To address these problems, we have prepared a series of zirconocenophane hydrides, $\{[SiR_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2$ (R = CH_3, **2a**; R = C_2H_5, **2b**; R = $n\text{-}C_3H_7$, **2c**), in which the cyclopentadienyl rings are linked by a dialkylsilyl bridge. We have found that modification of the alkyl substituent provides a simple way to enhance the solubility of these compounds without significantly perturbing their dinuclear structure. In addition, recent studies[10] of the reduced species generated from the electrochemical reduction or chemical reduction of $[Si(CH_3)_2(C_5H_4)_2]ZrCl_2$ have shown that the presence of the dialkylsilyl bridge significantly enhances the stability of the Zr(III) oxidation state. This feature should aid our efforts to investigate the role of any paramagnetic Zr(III)–hydride species in the reactivity of 2. Finally, the restricted ring mobility introduced by the bridge should significantly reduce the chemical participation of the cyclopentadienyl rings.

On the basis of these considerations, parallel thermolysis and photolysis studies of 2 were undertaken to investigate the influence of a chelating bis(cyclopentadienyl) ligand on these reactions. Quantitative measurements of the H_2 evolved during the photolysis or thermolysis of these compounds were performed. Complementary NMR, EPR, and visible spectroscopy experiments were carried out to provide spectroscopic information about the organozirconium species produced upon reductive elimination of H_2 from 2 as well as to monitor these reactions. Finally, NMR and EPR methods were employed to investigate the susceptibility of 2 to H/D exchange and to evaluate the possible role of any paramagnetic zirconium(III) hydride species in this process. The collective results from these studies are discussed herein and are compared when possible with those obtained for 1.

Experimental Section

General Considerations. All manipulations were conducted under a prepurified argon or N_2 atmosphere in oven-dried glassware equipped with solvent seal joints on an all-glass high-vacuum line fitted with high-vacuum Teflon stopcocks. Solid reagents were weighed and handled in a nitrogen-filled Vacuum Atmospheres drybox. Solvents (reagent grade) were purified and dried by standard methods[11] and then vacuum-distilled into solvent storage flasks containing $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}Cl)_2]_2Zn$[12] (THF, benzene, pentane) prior to use. Benzene-d_6 (Aldrich, 99.5%) and THF-d_8 (Stohler, 99%) were dried over $LiAlD_4$ and vacuum-distilled. $LiAl(t\text{-}BuO)_3H$,[13] 1,[8] and $[SiR_2(C_5H_4)_2]ZrCl_2$ (R = CH_3, C_2H_5, $n\text{-}C_3H_7$)[10] were prepared according to published procedures. Elemental analyses of 2 were performed by Dornis and Kolbe Microanalytical Laboratory, West Germany.

Table I. Summary of ^{1}H NMR[a] and IR[b] Spectral Data for 2

	^{1}H NMR			
compd	C_5H_4	R	Zr–H	IR $\nu_{Zr\text{-}H}$, cm^{-1}
2a[c]	6.68 (m, 2 H)		−3.41 (t, H[e])	1585
	6.45 (m, 2 H)	0.65 (s, CH_3, 6 H)		1355
	6.02 (m, 2 H)		2.85 (t, H)	
	5.93 (m, 2 H)			
2b[d]	6.53 (m, 4 H)		−3.10 (t, H[f])	1545
	5.95 (m, 2 H)	0.6–1.1 (m, C_2H_5, 10 H)		
	5.02 (m, 2 H)		3.40 (t, H)	1355
2c[c]	6.63 (m, 2 H)		−3.52 (t, H[e])	1555
	6.38 (m, 2 H)	1.0–1.7 (m, C_3H_7, 14 H)		
	5.96 (m, 2 H)		2.80 (t, H)	1355
	5.85 (m, 2 H)			

[a] Chemical shifts (δ) in ppm from Me_4Si. [b] Spectra measured in KBr disks. [c] Recorded in THF-d_8 at 25 °C. [d] Recorded in benzene-d_6 at 25 °C. [e] $J_{H\text{-}H} = 7.5$ Hz. [f] $J_{H\text{-}H} = 7.7$ Hz.

Instrumentation. ^{1}H NMR spectra were recorded by using a Varian CFT-20 NMR spectrometer operating in the FT mode. Spectra were measured in THF-d_8 or benzene-d_6 with the residual ^{1}H resonance (δ 1.80, 3.65 (THF), or 7.24 (benzene) ppm from Me_4Si)[14] as the internal standard. IR spectra were recorded on either a Beckman IR-20A or IR-8 spectrometer and were calibrated relative to polystyrene film. EPR spectra were measured with an IBM/Bruker ER200-SRC EPR spectrometer controlled by an ASPECT computer system. The microwave frequency was monitored with a Hewlett-Packard 5340A frequency counter. The magnetic field of the spectrometer was calibrated by an internal NMR gaussmeter (±0.01 G). In situ visible spectroscopy measurements were made by using a Varian Cary-219 spectrometer equipped with a thermostated cell holder assembly. The photolysis reactions were conducted with a 450-W Hanovia medium-pressure mercury vapor photochemical lamp located in a quartz water-cooled immersion well. Gas chromatographic analyses were performed with a Perkin-Elmer Sigma 1 gas chromatograph that is equipped with thermal conductivity and flame ionization detectors.

Synthesis and Characterization of 2. These zirconocenophane complexes were prepared by the metathesis reaction of 2 equiv (20 mmol) of $LiAl(t\text{-}BuO)_3H$ with 1 equiv (10 mol) of $[SiR_2(C_5H_4)_2]ZrCl_2$ (R = CH_3, C_2H_5, $n\text{-}C_3H_7$). Stoichiometric amounts of these reagents were placed in a 100-mL pear-shaped flask fitted with a solvent seal joint to a fritted-filter assembly. Approximately 25 mL of THF was vacuum distilled into the flask, and the reaction mixture was warmed to room temperature with stirring. Stirring was continued for an additional 2 h under a H_2 atmosphere, and the light blue supernatant liquid was removed by filtration. The crude product was washed twice with small portions of cold THF, dried in vacuo, and then recrystallized from THF to yield white microcrystals of the desired product in 75–95% yield.

$\{[Si(CH_3)_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2$, 2a. Anal. Calcd for $C_{12}H_{16}SiZr$ (empirical formula): C, 51.56; H, 5.77. Found: C, 51.55; H, 5.78.

$\{[Si(C_2H_5)_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2$, 2b. Anal. Calcd for $C_{14}H_{20}SiZr$ (empirical formula): C, 54.66; H, 6.55. Found: C, 54.56; H, 6.52.

$\{[Si(n\text{-}C_3H_7)_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2$, 2c. Anal. Calcd for $C_{16}H_{24}SiZr$ (empirical formula): C, 57.25; H, 7.20. Found: C, 57.24; H, 7.26.

The infrared spectra of 2 were measured in KBr discs. The observed $\nu_{Zr\text{-}H}$ for these hydrides are listed in Table I, and their values are comparable to those reported for $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_x$ ($\nu_{Zr\text{-}H}$ (KBr disk) 1520, 1300 cm^{-1})[15] and for $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$

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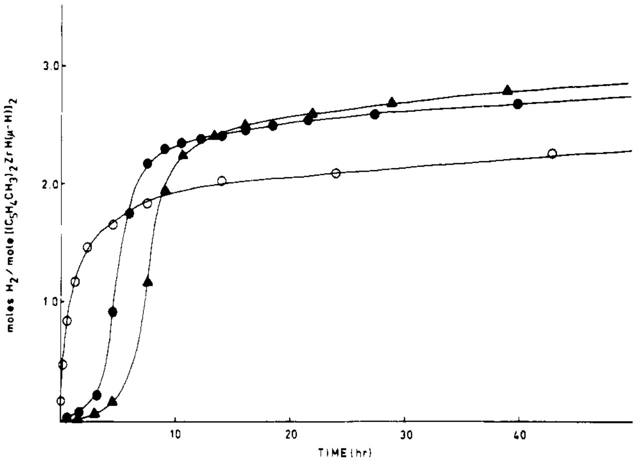

Figure 1. Plots of the moles of H_2 evolved per mole of 1 vs. time for the thermolysis or photolysis of 1 (●, thermolysis at 75 °C in benzene; ▲, thermolysis at 75 °C in octane; ○, photolysis (20 °C) in benzene).

(ν_{Zr-H} (KBr disk) 1565, 1330 cm^{-1}).[8] The corresponding ^{1}H NMR spectra for **2a**, **2b**, and **2c** were measured in THF-d_8, benzene-d_6, and THF-d_8, respectively. The peak assignments for the ^{1}H NMR resonances are summarized in Table I. Each spectrum contains two characteristic triplets consistent with the presence of two bridging, H_b, and two terminal, H_t, hydrido ligands and a complex set of four multiplets in the aromatic region for the cyclopentadienyl ring protons. Their similarity to the corresponding resonance patterns observed in the ^{1}H NMR spectrum[8] of 1 leads one to conclude that these zirconcenophane hydrides exist as discrete dimers (with a comparable dinuclear structure) in solution at 25 °C.

Quantitative Determination of H_2. Quantitative measurements of the amount of H_2 evolved during the photolysis or the thermolysis of 1 and 2 were performed. Solvents were vacuum distilled into a reaction flask containing a weighed amount of the hydride. To monitor the course of these reactions, the reaction flask was periodically placed in a liquid-nitrogen-filled Dewar and the H_2 was pumped through two liquid-nitrogen-cooled traps into a calibrated volume by means of a Toepler pump. To ensure that all of the H_2 was removed each time from the frozen reaction, the solution was repeatedly thawed, frozen, and then pumped until no additional amount of H_2 was collected. The thermolysis experiments were performed in several different noncoordinating solvents (benzene, octane, and cyclohexane), and the results provide no indication of any solvent dependence or participation (via H atom abstraction). In the case of benzene as the solvent, after the conclusion of the corresponding thermolysis reaction the organic volatiles were collected in a liquid-nitrogen trap and then analyzed by gas chromatography. Benzene was found to be the sole component, and no biphenyl was observed.

For each reaction the amount of accumulated hydrogen (relative ratio of moles of H_2 evolved per mole of dimer) was plotted vs. time. The corresponding results for 1 and 2 are depicted in Figures 1 and 2, respectively. From the thermolysis experiments it is apparent that rapid loss of H_2 does not occur until after an initial induction period. During this time the solution remains colorless and no detectable amount of H_2 is collected until after a purple color appears. In contrast, the photolyses of 1 and 2 proceed with immediate loss of H_2 and formation of the corresponding deep purple solutions.

Low-Temperature Gas Chromatographic Analysis. Low-temperature gas chromatographic methods were employed to analyze the H_2, HD, and D_2 gaseous mixture produced during the thermolysis of 1 under a D_2 atmosphere. The gases were quantitatively spearated at −196 °C on the 12 ft × 0.25 in. (o.d.) copper column packed with 150–200 mesh alumina which had been treated with ferric chloride according to the method published by Ward and Moore.[18] Helium was used as the carrier gas with a flow rate of 120 mL/min. The effluent gases were converted to their corresponding oxides by a copper oxide furnace at 350 °C in order to increase their sensitivity at the thermal conductivity detector which was maintained in 110 °C. Prior to its use the column was charged with CO_2 for 30 min at room temperature to partially deactivate the column packing and thereby reduce peak tailing.

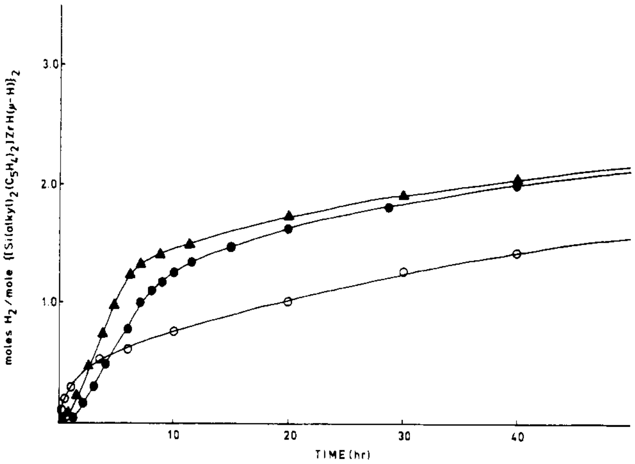

Figure 2. Plots of the moles of H_2 evolved per mole of 2 vs. time during the thermolysis or photolysis of 2 (●, thermolysis of **2a** at 75 °C in benzene; ▲, thermolysis of **2b** at 75 °C in cyclohexane; ○, photolysis (20 °C) of **2b** in benzene).

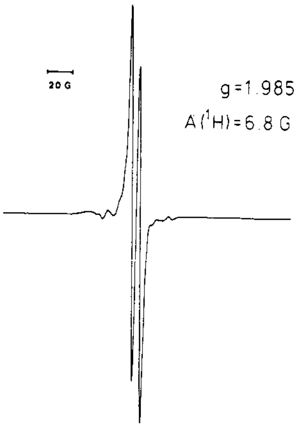

Figure 3. Solution EPR spectrum measured after 3 min of photolysis of 1 in benzene.

Spectroscopic Studies of the Thermolysis and Photolysis Reactions. a. EPR Analysis. Solution EPR measurements were conducted periodically to monitor the formation and evaluate the stability of any paramagnetic intermediates that are generated during the photolysis and thermolysis of 1 and 2. In general, the thermolysis reactions proceed more slowly (at least initially) than the photolysis reactions. The EPR samples were prepared by adding 5–10 mg of the appropriate hydride to a quartz EPR tube (previously flame dried under vacuum) that is equipped with a high vacuum Teflon stopcock. Benzene was introduced by vacuum distillation, the sample was freeze–pump–thawed, and the EPR tube was then sealed under vacuum. The samples used for the thermolysis experiments were heated in an oil bath at 75 °C. The corresponding photolysis experiments were conducted at ca. 20 °C. In each case the photolysis and thermolysis reactions proceed initially with the formation of a paramagnetic zirconocene hydride species. The corresponding solution EPR spectra generated upon photolysis of **1** and **2a** are illustrated in Figures 3 and 4, respectively, and are each characterized by a distinct hydride doublet. Comparable EPR spectra are obtained upon thermolysis of these compounds. Extended photolysis or thermolysis of 1 is accompanied by the gradual introduction of other unidentifiable spectral lines and a deterioration of the intensity of the central line. By comparison, the intensity of the corresponding EPR

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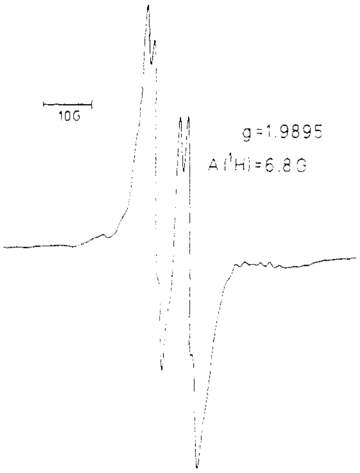

Figure 4. Solution EPR spectrum of the photolysis reaction of **2a** in benzene after fifteen minutes.

spectrum in Figure 4 continually increases upon further photolysis or thermolysis without appreciable deterioration or loss of resolution over a period of nearly 3 h.

The values of the isotropic magnetic parameters given in Figures 3 and 4 were determined from the measured field positions and the microwave frequency, ν_0. The additional splitting resolved on each line in Figure 4 presumably is due to the hyperfine coupling of the unpaired electron with the ring protons of the $[Si(CH_3)_2(C_5H_4)_2]^{2-}$ ligand. The fact that the doublet spectrum is not symmetrical with respect to inversion suggests that two paramagnetic hydride species with slightly different g-values may be present. Geometrical isomers that differ in their relative orientation of the hydride and chelating bis(cyclopentadienyl) ligands could certainly account for this spectral feature.

b. NMR Measurements. Previous EPR experiments clearly demonstrate that a paramagnetic zirconocene hydride species is generated upon thermolysis or photolysis of benzene solutions containing 1 or 2. To monitor the loss of the starting hydride as well as the possible formation of any new diamagnetic products, parallel NMR experiments were undertaken. Of these dinuclear hydrides only **2b** is sufficiently soluble to carry out this study in a noncoordinating solvent, such as benzene. The samples were prepared by dissolving 10–15 mg of **2b** in benzene-d_6, degassed, and then sealed under vacuum. Upon heating or irradiation of these samples, periodic ^1H NMR measurements showed a rapid reduction of the intensities for the proton resonances of the hydride and ring protons. The hydride triplets disappear within a few hours. After 24 h the intensities of the remaining resonances are reduced to only a small fraction of their original values. No evidence for the formation of any new diamagnetic product(s) is observed. The loss in the intensity of the ^1H NMR signals is clearly consistent with the loss of H_2 from **2b** and subsequent formation of a reasonably stable paramagnetic zirconocenophane hydride species.

c. Visible Spectroscopic Measurements. The EPR and NMR spectra obtained during the photolysis and thermolysis of 2 indicate that these reactions proceed with the initial formation of highly colored solutions containing a paramagnetic species. Since this compound should exhibit a characteristic visible absorption spectrum, electronic spectroscopic measurements were performed to monitor its formation and to probe the nature of the thermolysis reaction. A similar experiment was carried out with 1 for comparison purposes.

Approximately 2–4 mg of the appropriate dinuclear zirconocene hydride was added to a rectangular quartz cell (path length = 1.000 cm) equipped with a high-vacuum Teflon stopcock. After adding benzene via vacuum distillation, the cell was placed into the thermostated cell compartment of the spectrometer and heated at 70 °C for nearly 24 h. The visible spectrum within the range of 400–700 nm was recorded every 30 min. The original solutions containing these dinuclear zirconocene hydrides do not absorb in this region of the visible spectrum. However, upon heating, these solutions develop a purple color which continues to darken with the appearance of an appropriate absorption spectrum (Figures 5 and 6).

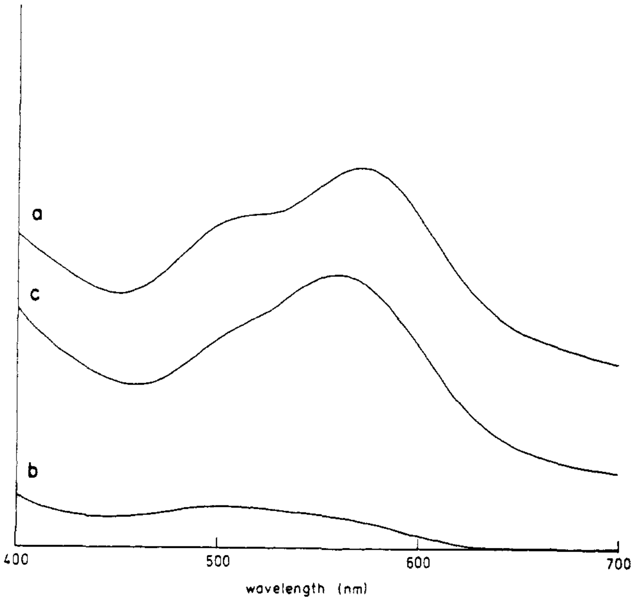

Figure 5. Visible absorption spectra measured during the thermolysis of **2b** in benzene after (a) 23 h of thermolysis, (b) the addition of excess H_2, and (c) removal of H_2 followed by 18 h of thermolysis.

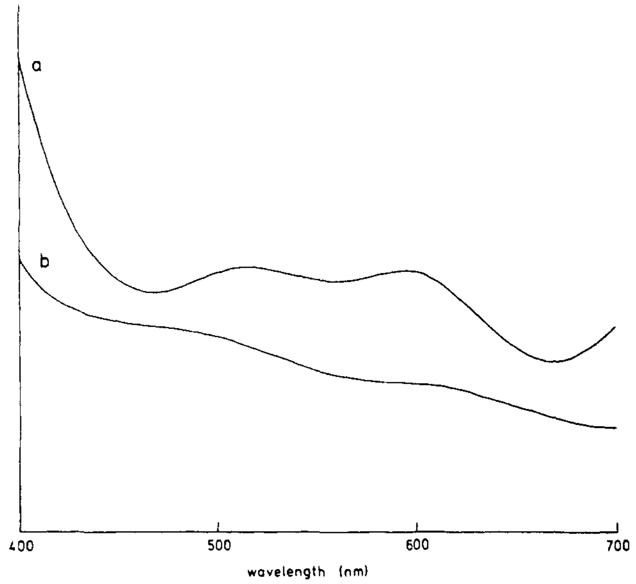

Figure 6. Visible absorption spectra measured during the thermolysis of 1 in benzene after (a) 17 h of thermolysis and (b) the addition of excess H_2.

For the species produced upon reductive elimination of H_2 from **2b**, its principal visible absorption band is observed at 570 nm with a small shoulder at 500 nm (Figure 5a). To examine the reversibility of the reductive elimination process, the purple solution was placed under a H_2 atmosphere and stirred for several hours. The resultant fading of the solution's purple color was accompanied by nearly complete loss of the visible spectrum (Figure 5b). Upon removal of the H_2, subsequent thermolysis led to the regeneration of the purple species and its associated absorption spectrum (Figure 5c).

Thermolysis of 1 similarly generates a purple solution, which in this case exhibits two bands ca. 510 and 600 nm of nearly equal intensity and indicates the existence of a third band above 700 nm (Figure 6a). Upon stirring the solution under a H_2 atmosphere for several hours, the amplitude of this latter band diminishes more rapidly than the others (Figure 6b). This result coupled with the fact that the purple color of the solution persists suggests that more than one species is produced during the thermolysis of 1.

H/D Exchange Studies of $[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2$, 1. Since more than 2 mol of H_2 are evolved per mole of 1 during the

Table II. Summary of Subambient GC Data for Thermolysis of 1 under a D_2 Atmosphere

expt	time of heating, h	mol of H/mol of dimer from H_2	mol of H/mol of dimer from HD	total, mol of H/mol of dimer
1	3.25	3.68 (41)[a]	1.95 (25)	5.63 (33)
2	26	4.06 (19)	6.65 (12)	10.7 (16)

[a] Numbers in parentheses are estimated standard deviations based on 10 consecutive runs.

thermolysis of this compound, it is evident that the methylcyclopentadienyl rings are involved somehow in these reactions. To provide further experimental evidence supporting this remark, the thermolysis of 1 was repeated under a D_2 atmosphere. This experiment was performed twice, and the composition of the gas above the solution was analyzed by low-temperature gas chromatography. This analytical technique permits the separation of the H_2 and HD (that is generated during the H/D exchange reaction) from the D_2 and thereby the determination of their molar amounts. The first sample containing 0.843 g (1.675 mmol) of 1 in 50 mL of benzene was stirred under excess D_2 (127.3 mmol) for 3.25 h at 85 °C, and the composition of the gas mixture above the solution was then determined. The second sample containing 0.665 g (1.323 mmol) of 1 in 50 mL of benzene was similarly analyzed after 26 h of stirring the reaction mixture of 85 °C under D_2 (86.2 mmol). The corresponding ratios of mol of H/mol of dimer as determined from the collected moles of H_2 and HD are summarized in Table II. Presumably, the majority of the H_2 was generated by the reductive elimination of H_2 from the original dimer. The presence of significant amounts of HD indicates that H/D exchange has occurred. Finally the fact that the ratio of the total mol of H/mol of dimer is greater than four in each case substantiates the participation of both the hydrides and methylcyclopentadienyl rings in the overall exchange process.

To investigate the possible role of the paramagnetic zirconocene hydride species (initially produced upon the thermolysis or photolysis of 1) in this process, a sample of 1 was photolyzed under an atmosphere of D_2. The initial hydride doublet is replaced by an apparent singlet centered at 1.9856 due to H/D exchange of the Zr–H bond. The magnitude of $A(^2D)$, ca. $^1/_6$ of $A(^1H)$, is sufficiently small in this case to prevent resolution of any ^2D ($I = 1$) hyperfine coupling. The reversibility of this exchange process was examined by a series of consecutive EPR experiments. The appropriate solution EPR spectra are depicted sequentially in Figure 7. To perform these experiments the EPR tube was modified by the attachment of a gas storage bulb. After a benzene solution of 1 was photolyzed for several minutes, a large excess of D_2 (>100-fold) was introduced into the storage bulb of the EPR tube. Upon mixing, the initial hydride doublet (Figure 7a) was replaced by a weak "apparent" singlet (Figure 7b). Subsequent removal of the D_2 followed by irradiation of the sample for several minutes led to a substantial increase in the concentration of the paramagnetic zirconocene deuteride species (Figure 7c). Admission of a similarly large excess of H_2 quenched the singlet leaving behind a weak doublet (Figure 7d). Finally, removal of H_2 followed by further irradiation regenerated the EPR spectrum of the original hydride doublet (Figure 7e). The fact that the purple color of the solution persists throughout these experiments (even when D_2 or H_2 are in large excess) supports our previous contention that other zirconocene species are present in solution.

H/D Exchange Studies of $\{[SiR_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2$, 2. To investigate the chemical consequences of linking the cyclopentadienyl rings with regard to the susceptibility of the cyclopentadienyl ring hydrogens and the hydride ligands of 2 toward H/D exchange and to evaluate the reversibility of this process, the following EPR and NMR experiments were performed.

a. EPR Experiments. A 3–10-mg sample of **2a** was added to the reaction bulb of a modified EPR tube, and benzene was added via vacuum distillation. A purple solution containing a parmagnetic zirconocenophane hydride species was generated by either photolysis or thermolysis. The evolved H_2 was removed periodically by repeated freeze–pump–thawing of the solution, and a solution EPR spectrum comparable to that in Figure 4 was recorded. A large excess of D_2 was admitted, and the solution was stirred for several hours until its color completely faded. The D_2 was removed. Upon subsequent photolysis or thermolysis, the purple color returned. The solution EPR spectrum (Figure 8) reveals that the previously observed hydride doublet ($g = 1.9895$, $A(^1H) = 6.8$ G) is now been replaced by an "apparent" singlet ($g = 1.9897$) due to H/D exchange of the Zr–H bond. The additional lines that are symmetrically disposed on this central line are attributed to hyperfine coupling of the unpaired electron with the ring protons of the $[Si(CH_3)_2(C_5H_4)_2]^{2-}$ ligand. A series of EPR experiments (analogous to those described previously for 1) have further shown that this exchange process is reversible. The fact that the purple color of the solution containing the paramagnetic zirconocenophane hydride disappears upon exposure to excess H_2 or D_2 suggests that no other reduced species are present in significant concentrations.

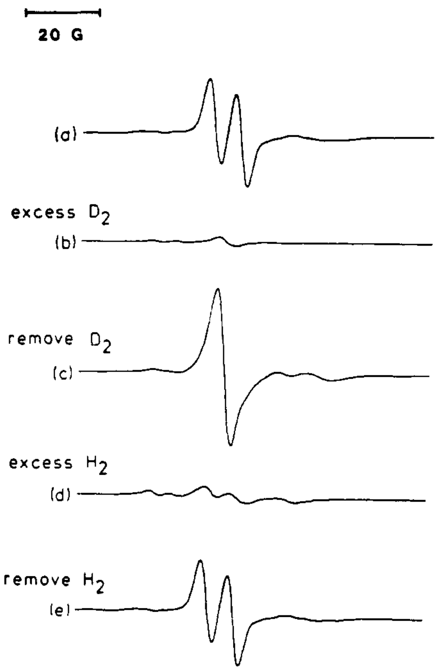

Figure 7. Series of solution EPR spectra depicting reversible deuterium exchange for the paramagnetic zirconocene hydride generated initially during the photolysis of 1.

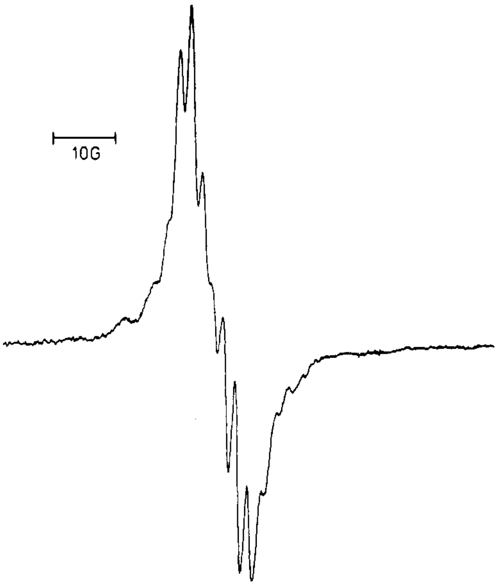

Figure 8. Solution EPR spectrum of the paramagnetic zirconocenophane deuteride species.

b. ^1H NMR Analysis. Although these EPR studies provide evidence for deuterium incorporation at the hydride position(s), complementary NMR studies were conducted to determine the extent that the cyclopentadienyl ring hydrogens participate in a similar H/D exchange reaction. Due to its greater solubility in benzene, **2b** was selected for these NMR studies. A 25-mg sample of **2b** was dissolved in 10 mL of benzene and then heated in an oil bath at 75 °C for 24 h. The evolved H_2 was removed periodically. An atmosphere of D_2 was admitted to the reaction vessel, and the solution was stirred for several days until a nearly colorless solution was obtained. The solvent was removed, and the white microcrystalline residue was dried in vacuo. A solution of 10 mg of the product in benzene-d_6 was prepared and then sealed in an NMR tube. The ^1H NMR spectrum of this solution exhibits three resonances of relative intensity 2:1:1 in the cyclopentadienyl region and one multiplet signal in the alkyl region. Their chemical shifts and integrated intensity are identical with the corresponding values for the ring and alkyl protons of the parent hydride. The ^1H NMR spectrum of this deuterated species also contains very weak signals at the original positions of the hydride resonances. The relatively low but measurable intensity observed for these signals indicates that not all of the hydride positions in **2b** have been completely deuterated. However, on the basis of the observed decrease in their intensity, the H/D exchange appears to be greater than 90% complete. The fact that the relative intensities for the cyclopentadienyl ring and ethyl protons of **2b** remains unchanged during the course of this reaction provides strong evidence to conclude that the cyclopentadienyl ring protons do not participate in a deuterium exchange process in this case.

Discussion of Results

General Comments. Parallel photolysis and thermolysis studies of 1 and 2 were performed to investigate their susceptibility to reductive elimination of H_2. Quantitative measurements of the evolved H_2 have revealed that these dinuclear hydrides eventually lose 3 and 2 mol of H_2/mol of dimer, respectively, upon prolonged thermolysis in solution at 75 °C. Similar behavior is observed for these hydrides during the corresponding photolysis reactions except that as the solutions become more opaque to the transmission of light, the relative rate at which H_2 is produced significantly diminishes. This observed reduction in loss of H_2 may further reflect a lower susceptibility of intermediate zirconocene species to eliminate more H_2 under these photochemical conditions and thereby suggests that the latter stages of this process are primarily thermally driven. The data provided in Figures 1 and 2 show that H_2 is eliminated immediately upon photolysis of these hydrides. In contrast, the initial rate for H_2 evolution is much slower for the thermolysis reactions with no detectable amount of H_2 observed until after the solution's color begins to become purple. The rapid loss of H_2 that occurs following this induction period suggests that the reductive elimination process may be autocatalytic and depends on the presence of a minimum concentration of some reduced species that catalyzes the further loss of H_2. From Figures 1 and 2 it is readily apparent that linking the cyclopentadienyl rings significantly reduces the number of moles of H_2 collected per mole of dimer.

Reductive Elimination of H_2 and the Generation of Paramagnetic Zirconocene Hydrides. Several different elimination pathways are needed to rationalize the amount of H_2 obtained from these dinuclear zirconocene hydrides. In both systems that have been examined, the first mole of H_2 most likely arises from reductive elimination of two of the hydride ligands as H_2 and proceeds with the concomitant formation of a paramagnetic zirconocene hydride species (eq 1 and 2). Although the precise identity or composition of these hydride species remains to be determined, their presence in each case was verified by solution EPR measurements. The corresponding solution EPR spectra in Figures 3 and 4, respectively, similarly exhibit a distinct doublet with a hyperfine coupling constant for the one hydride ligand of $A(^1H) = 6.8$ G. The g values being significantly less than 2.0023 are consistent with the unpaired electron residing in a metal-based orbital. The magnitude of $A(^1H)$ is comparable to that reported for other paramagnetic early transition metal hydrides, including $(\eta^5\text{-}C_5H_5)_2NbH_2$,[17] $(\eta^5\text{-}C_5H_5)_2TiH$ (solvate),[18] and the paramagnetic Zr hydrides produced during the photolysis of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$[19] and $(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)_2$.[20] In general, these parramagnetic zirconocene hydrides appear to be reasonably stable over a period of several days since no significant reduction in the intensity of the corresponding EPR signal is observed. Upon further photolysis or thermolysis these signals grow to a more-or-less steady-state intensity consistent with the equilibrium processes 1 and 2. However, under analogous conditions the initial paramagnetic species generated from 1 is substantially less stable than the comparable species generated from 2. Upon continued thermolysis or photolysis the EPR spectrum of the latter remains essentially unchanged, whereas that of the former deteriorates with the appearance of several less recognizable resonances. Although the reductive elimination of H_2 from 1 and 2 initially proceeds in a similar manner, the greater stability of the paramagnetic zirconocenophane hydride species is consistent with the ability of the chelating bis(cyclopentadienyl) ligand to stabilize the Zr(III) oxidation state.[10]

$$[(\eta^5\text{-}C_5H_4CH_3)_2ZrH(\mu\text{-}H)]_2 \overset{h\nu\text{ or }\Delta}{\rightleftharpoons} 2\text{“}(\eta^5\text{-}C_5H_4CH_3)_2ZrH\text{”} + H_2 \quad (1)$$

$$\{[SiR_2(C_5H_4)_2]ZrH(\mu\text{-}H)\}_2 \overset{h\nu\text{ or }\Delta}{\rightleftharpoons} 2\text{“}[SiR_2(C_5H_4)_2]ZrH\text{”} + H_2 \quad (2)$$

Since **2b** is reasonably soluble in benzene, parallel ^1H NMR studies were undertaken to monitor the formation of any new diamagnetic compounds during photolysis or thermolysis. As these reactions proceed, a continual decay in the intensities for all of the proton resonances of **2b** occurs. The fact that no new species are observed strongly suggests that the paramagnetic zirconocenophane hydride species detected in solution by EPR is the principal organozirconium product generated during the initial stages of this reductive elimination reaction. This remark as well as the reversibility of reaction 2 is further supported by the visible spectroscopic spectra (Figure 5) that were measured during the thermolysis of **2a**. In contrast, the results from comparable visible spectroscopic studies for 1 indicate that more than one zirconocene species is produced during the thermolysis of this dinuclear hydride. One of the species, which is characterized by an absorption band above 700 nm, readily adds H_2 while the other(s) react significantly more slowly with H_2 (Figure 6). The more complex behavior observed in this case is consistent with the tendency of 1 to eliminate one additional equivalent of H_2 and in the process produce other zirconocene products.

Although reactions 1 and 2 account for the first equivalent of H_2 obtained from the respective dinuclear zirconocene hydrides, alternative pathways are needed to rationalize the origin of the remaining H_2 observed in each case. For the zirconocenophane hydrides one possibility may involve an intermolecular pathway that involves the formation of a dinuclear hydride intermediate that subsequently eliminates H_2 to produce a dinuclear zirconocenophane product (eq 3). The availability of a vacant valence orbital in the paramagnetic zirconocenophane hydride provides a means to accommodate the formation

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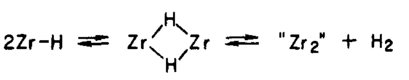


$$2Zr{-}H \rightleftharpoons Zr(\mu{-}H)_2Zr \rightleftharpoons \text{"}Zr_2\text{"} + H_2 \qquad (3)$$

of the hydrido bridges. This bimolecular reaction presumably depends on a reasonably high concentration of this Zr–H species in solution and a low H_2 pressure. Since the samples used for our spectroscopic studies were sealed, a finite H_2 pressure from the first reductive elimination step was always maintained above the solutions. Consequently, under these conditions it appears unlikely that reaction 3 leading to the loss of a second equivalent of H_2 can occur to the extent necessary to observe appreciable formation of any new dinuclear zirconocenophane products. However, by continually removing the H_2 during thermolysis or photolysis, one should be able to drive reaction 3 to the right and ultimately isolate the resultant zirconocenophane product.

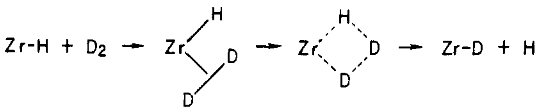
A similar intermolecular reaction to (3) is probably operative as well for 1. However, the analysis is further complicated by the participation of the methylcyclopentadienyl rings in the overall H_2 elimination process. The demonstrated ability of methyl substituents to undergo a facile, reversible ring methyl-to-metal hydride transfer[21] coupled with the potential of various electron-deficient intermediates to activate a C–H bond of the methylcyclopentadienyl ring could potentially provide several pathways leading to the formation of ring-bridged or ring-coupled dinuclear zirconocene hydride species similar to those observed in titanocene[22] and molybdenocene[23] chemistry. Subsequent reductive elimination of H_2 from these or related species would account for the third mole of H_2 observed as well as the insoluble (presumably oligomeric) zirconocene products isolated in this case.

H/D Exchange Studies. A series of deuterium exchange studies were performed for these dinuclear zirconocene hydrides to determine the extent of deuterium incorporation and to examine the possible role of the corresponding paramagnetic zirconocene hydride intermediate in any H/D exchange process. For 1 low-temperature gas chromatographic methods were employed to monitor the amount of H_2 and HD produced upon heating 1 under a D_2 atmosphere. Since our thermolysis data does not suggest H abstraction from the solvents that were used is significant, any H_2 and HD presumably arises from reductive elimination of H_2 from 1 and from H/D exchange due to the involvement of zirconocene intermediates present in solution.

The progress of the D_2 exchange reaction for 1 was examined for two separate, yet analogous experiments. The analytical data (Table II) indicates that after 3.25 h of heating, 5.63 mol of H atoms were obtained per mole of 1. The majority, 3.68 or nearly 4 mol of H, was obtained as H_2 rather than HD. As the thermolysis proceeds, the amount of evolved H_2 remains essentially unchanged (within experimental error) while a substantial increase in the relative amount of HD is observed after 26 h of heating.

This variation in the H_2/HD composition during the course of the thermolysis reaction can be rationalized on the basis of the following arguments. Since 1 is coordinatively saturated, it is unlikely that any deuterium exchange will occur until after some H_2 has been eliminated. Presumably at least half of the H_2 observed after the initial 3.25 h of heating results from reaction 1. As this reaction proceeds, the concentration of the initial paramagnetic species increases and eventually is sufficient to initiate either reaction 3 or an intramolecular hydride migration reaction that proceeds with reductive elimination of more H_2. In excess D_2 the electron-deficient zirconocene species are likely to undergo oxidative addition of D_2 and subsequently participate in the overall H/D exchange process. Since more than 4 mol of H atoms can be accounted for after the initial 3.25 h of thermolysis, deuteration most likely occurs at the hydride positions and the methyl hydrogens (vide infra) of the methylcyclopentadienyl rings. On the other hand, since less than 16 mol of H atoms/mol of the original dimer were observed after 26 h of heating, deuterium incorporation into the methyl groups is far from complete.

Several different exchange mechanisms can be employed to rationalize the deuterium exchange data. For the hydride ligand the formation of HD may involve a four-centered intermediate.[24] The EPR data have shown that reductive elimination of H_2 from 1 is accompanied by the formation of a coordinatively unsaturated, paramagnetic zirconocene hydride with a vacant orbital for interacting with D_2. Subsequent reductive elimination of HD (eq 4)



$$Zr{-}H + D_2 \rightarrow Zr(H)(D)(D) \rightarrow [Zr\cdots H\cdots D\cdots D] \rightarrow Zr{-}D + HD \qquad (4)$$

from this four-centered intermediate produces the corresponding paramagnetic zirconocene deuteride. Another possibility may involve a series of bimolecular exchanges such as those shown by reactions 5–7.[25]

$$Zr{-}H + ZrD_2 \rightarrow ZrHD + ZrD \qquad (5)$$

$$Zr{-}H + ZrD \rightarrow ZrHD \qquad (6)$$

$$ZrHD \rightarrow Zr + HD \qquad (7)$$

Deuterium incorporation into the methyl hydrogen positions, however, is considerably more complicated. Bercaw and co-workers[21] have observed that above 50 °C the two hydride and all 30 methyl hydrogen positions of the two C_5Me_5 rings in $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ exchange with a D_2 atmosphere. To assess the regioselectivity of deuterium incorporation into the C_5Me_5 rings, they conducted a systematic study of bis(η^5-alkyltetramethylcyclopentadienyl)zirconium(IV) dihydrides. For the methyl, ethyl, and *tert*-butyl derivatives, deuterium is readily incorporated into the methyl C–H bonds. This process presumably relies on the ability of these alkylated cyclopentadienyl species to form "tucked-in" complexes[26] in which a methylene bridge between the σ-bonded framework of the cyclopentadienyl ring and the metal exists. However, further insight into this process as it pertains to compounds containing *methyl*-substituted cyclopentadienyl rings has been provided by Bercaw and co-workers[27] from their kinetic and mechanistic study of the thermolysis of $(\eta^5\text{-}C_5Me_5)_2Ti(CH_3)_2$. The results of a series

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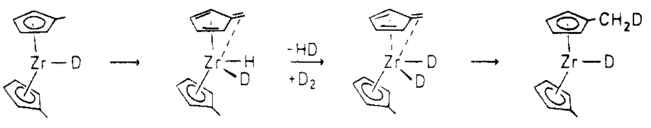

Figure 9. Intramolecular mechanism for the H/D exchange of the methyl hydrogens.

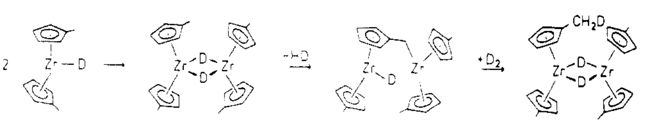

Figure 10. Intermolecular mechanism for the H/D exchange of the methyl hydrogens.

of labeling and crossover experiments indicate that the thermal decomposition of $(\eta^5\text{-}C_5Me_5)_2Ti(CH_3)_2$ occurs primarily by a pathway in which one of the titanium–methyl groups obtains a hydrogen from its neighboring Ti–CH_3 group to form CH_4 and $[(\eta^5\text{-}C_5Me_5)_2Ti{=}CH_2]$. This reactive carbene intermediate rearranges by hydrogen migration from a ring methyl group to the methylidene ligand to produce $(\eta^5\text{-}C_5Me_5)(C_5Me_4CH_2)TiCH_3$. Although the structure of this titanium compound remains to be determined, infrared and ^1H and ^{13}C NMR data suggest that the $C_5Me_4CH_2$ group probably interacts with the titanium as a methyl-substituted fulvene ligand. On the basis of these results, one could envision that deuterium incorporation into the methyl hydrogen positions of 1 may involve the intermediate participation of a comparable Zr–fulvene species. A plausible intramolecular pathway (starting with the paramagnetic zirconocene deuteride generated by (4)) is illustrated in Figure 9. However, in light of the lower steric bulk of $C_5H_4CH_3$ as compared to C_5Me_5, the involvement of intermolecular processes, which rely on the formation of a dinuclear methylene-bridged intermediate, such as shown in Figure 10, cannot be ruled out. Considering the number of possible zirconocene species that could be generated during the thermolysis of 1, the simultaneous participation of several competitive H/D exchange processes seems likely.

Since deuterium incorporation into the methyl groups of 1 depends largely on the inherent mobility of the methylcyclopentadienyl rings to move along the frontier molecular orbital surface of the metal, any constraints that restrict this motion should significantly curtail this secondary exchange process. Conclusive evidence for this effect has been provided by complementary deuterium exchange studies of **2b**. The NMR spectrum measured after heating **2b** with D_2 contains the same resonance patterns due to the cyclopentadienyl ring and ethyl protons of **2b**. Their chemical shifts and relative intensities in these two spectra are identical. The significant loss in intensity for the hydride resonances provides strong evidence to conclude that deuterium incorporation occurs at only the hydride positions in this case. This result further suggests that the corresponding deuterated zirconocenophane complexes $\{[SiR_2(C_5H_4)_2]ZrD(\mu\text{-}D)\}_2$ are accessible. Therefore, bridging the cyclopentadienyl rings provides an effective method to block deuterium incorporation into the rings. This constraint provides an opportunity to control deuteration and thereby prepare dinuclear zirconocenophane deuterides, which could be potentially valuable for further mechanistic studies.

The participation of the paramagnetic zirconocene hydride species generated by reactions 1 and 2 in the deuterium exchange process has been substantiated by complementary EPR studies. The corresponding solution EPR spectra show that the original hydride doublet observed upon photolysis or thermolysis of 1 or 2 disappears upon exposure to a large excess of D_2. The fact that the purple color of the solution persists in the former case is consistent with visible spectroscopic data that indicate at least one other zirconocene species is present. In contrast, for each paramagnetic zirconocenophane hydride the solution's color slowly fades with loss of the EPR signal as well as the corresponding visible absorption spectrum. Subsequent removal of D_2 followed by irradiation or heating in either case leads to the observation of an "apparent" singlet with an isotropic g value analogous to that calculated for the hydride doublet and thereby verifies that the hydride position has been deuterated. The observation of additional hyperfine structure superimposed on the "apparent" singlet for the paramagnetic zirconocenophane deuteride (Figure 8) provides further evidence that the rings of the $[SiR_2(C_5H_4)_2]^{2-}$ ligand are not involved in the deuterium exchange process. Admission of a similarly large excess of H_2 again quenches the EPR signal. Finally, removal of H_2 followed by irradiation or heating regenerates the initial hydride doublet.

These deuterium exchange studies have shown that the protons of the chelating bis(cyclopentadienyl) ligand in 2 are resistant to H/D exchange. Smith and Brintzinger[28] observed similar behavior for the reduced species generated during the chemical reduction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and $[(CH_2)_2(C_6H_4)_2]TiCl_2$. Whereas the reduced titanocene compound obtained from the former readily incorporates deuterium into the cyclopentadienyl rings, the corresponding reduced titanocenophane species does not. The presence of the dialkylsilyl bridge not only inhibits ring participation but noticeably enhances the stability of the paramagnetic zirconocenophane hydride generated during the thermolysis or photolysis of 2. This Zr(III) species is resistant to further loss of H_2 as long as it is kept under a partial pressure of H_2.

Concluding Remarks

From these studies it is evident that bridging the cyclopentadienyl rings introduces two significant effects relevant to the chemical behavior of 2. The chelating $[SiR_2(C_5H_4)_2]^{2-}$ ligand stabilizes the paramagnetic Zr–H species produced initially upon reductive elimination of H_2 from 2. Further, linking the rings restricts their chemical participation as demonstrated by the fact that deuterium incorporation occurs at only the hydride positions. Current efforts are underway to take advantage of these features to investigate further the reactivity of 2 and the Zr(III)–H derivatives.

Acknowledgment. We thank the National Science Foundation (Grant No. ISP-8011453), Research Corp., and the West Virginia Energy Research Center for financial support of various aspects of this research. Funds to purchase an IBM/Bruker ER200D-SRC EPR spectrometer were provided in part by NSF (PRM-8011453). We further express our appreciation to Professors E. A. Mintz for the use of a photolysis apparatus and Ken Showalter for the use of a Cary 219 spectrophotometer.

Registry No. 1, 77965-67-4; **2a**, 98088-28-9; **2b**, 98088-29-0; **2c**, 98088-30-3; $[Si(CH_3)_2(C_5H_4)_2]ZrCl_2$, 86050-32-0; $[Si(C_2H_5)_2(C_5H_4)_2]ZrCl_2$, 96688-72-1; $[Si(n\text{-}C_3H_7)_2(C_5H_4)_2]ZrCl_2$, 96666-17-0; $LiAl(t\text{-}BuO)_3H$, 17476-04-9.

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