$Fe_2(CO)_9$, 15321-51-4; $Fe(CO)_5$, 13463-40-6; $LiHB(Et)_3$, 22560-16-3; (*E*)-cyclooctene, 931-89-5.

Supplementary Material Available: Detailed information on the crystal structure determination of 1 and 3 including tables of final atomic positional parameters, final anisotropic thermal parameters, interatomic distances, and bond angles (10 pages); lists of observed and calculated structure factors for 1 and 3 (24 pages). Ordering information is given on any current masthead page.

Activation of Benzene Carbon–Hydrogen Bonds via Photolysis or Thermolysis of $(\eta^5\text{-}C_5Me_5)_2Zr(alkyl)H$. Isolation of $(\eta^5\text{-}C_5Me_5)_2Zr(C_6H_5)H$ and Its Conversion to a Complex Containing a Tetramethylfulvene Ligand

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A new high-yield synthesis of $Cp^*_2ZrH_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) is described, and olefin insertion into its Zr–H bond is used to prepare several new $Cp^*_2Zr(alkyl)H$ complexes. Photolysis or thermolysis of $Cp^*_2Zr(alkyl)H$ in benzene yields the respective alkane by intramolecular reductive elimination of the cis alkyl and hydride ligands, as well as the benzene C–H bond activation product $Cp^*_2Zr(C_6H_5)H$. Photochemically induced reductive elimination is also observed for $Cp^*_2Zr(C_6H_5)H$ and $Cp^*_2ZrH_2$. Deuterium-labeling experiments show that hydrogen exchange between the hydride and Cp* methyl groups occurs in both $Cp^*_2Zr(H)CH_2CH(CH_3)_2$ and $Cp^*_2Zr(C_6H_5)H$. An additional exchange process in $Cp^*_2Zr(C_6H_5)H$ involves the hydride ligand and an ortho phenyl hydrogen atom. Thermolysis of $Cp^*_2Zr(C_6H_5)H$ in benzene causes quantitative evolution of dihydrogen and reversibly forms the tetramethylfulvene complex $Cp^*(\eta^6\text{-}C_5Me_4CH_2)Zr(C_6H_5)$. Reaction of this compound with iodine produces the Cp* ring substituted phenyl iodide $Cp^*(\eta^5\text{-}C_5Me_4CH_2I)Zr(C_6H_5)I$. Several of the transformations involving $Cp^*_2Zr(C_6H_5)H$ are believed to proceed via β-hydrogen elimination from the phenyl group to yield a benzyne dihydride intermediate.

Introduction

In recent years, the activation of carbon–hydrogen bonds has attracted considerable interest.[2] Early work in this area, notably Green's studies with tungstenocene complexes,[3] demonstrated the utility of transition-metal compounds in the activation of aromatic C–H bonds. Bergman's preparation[4] of iridium alkyl hydride complexes via intermolecular oxidative addition of aliphatic carbon–hydrogen bonds was an important discovery since this is a crucial step in the functionalization of saturated hydrocarbons. Further work by Bergman,[4,5] Jones,[6] and Graham[7] has broadened the scope of this oxidative addition reaction to include other metals such as rhodium and rhenium.

In addition to these intermolecular hydrocarbon reactions, transition metals are also known to insert into the C–H bonds of coordinated ligands; phosphines are notably prone to such behavior.[8] Even the usually inert cyclopentadienyl group is susceptible to attack, especially in its early-transition-metal complexes.[9] However, use of the pentamethylcyclopentadienyl ligand ($\eta^5\text{-}C_5Me_5$, usually called Cp*) can often circumvent this problem[10] although a few reports of metal–ligand reactions have appeared. The most common pathway for these reactions involves intramolecular insertion of the transition metal into a methyl C–H bond on the Cp* ring, which results in conversion of $\eta^5\text{-}C_5Me_5$ into $\eta^6\text{-}C_5Me_4CH_2$. (In this paper we will refer to this ligand as "tetramethylfulvene" although this is not meant to imply a particular resonance form or bonding mode for the $\eta^6\text{-}C_5Me_4CH_2$ moiety.) Such reversible transformations have been proposed to explain the reactions of some early-transition-metal compounds[11,12] and

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a few tetramethylfulvene complexes have been isolated.[10,13]

In this paper, we report our work in the area of carbon–hydrogen bond activation using permethylzirconocene complexes. We have observed the activation of hydrocarbon solvents and coordinated Cp* ligands and have isolated and fully characterized the products of both these processes. Furthermore, the choice of inter- or intramolecular activation is dependent on whether light or heat is used as the reaction stimulus.

Results and Discussion

Synthesis of $Cp^*_2ZrH_2$ and $Cp^*_2Zr(R)H$. $Cp^*_2ZrH_2$ was first reported in 1976 and was prepared in 50–60% yield by the two-step reaction shown below (eq 1 and 2).[14]

$$2Cp^*_2ZrCl_2 \xrightarrow[N_2]{Na/Hg} (Cp^*_2ZrN_2)_2N_2 + 4NaCl \tag{1}$$

$$(Cp^*_2ZrN_2)_2N_2 \xrightarrow{H_2} 2Cp^*_2ZrH_2 + 3N_2 \tag{2}$$

We report herein a new high-yield synthesis of $Cp^*_2ZrH_2$ utilizing the high pressure hydrogenation of the known $Cp^*_2ZrMe_2$[15] (eq 3 and 4). Similar reactions have been

$$Cp^*_2ZrCl_2 + 2MeLi \rightarrow Cp^*_2ZrMe_2 + 2LiCl \tag{3}$$

$$Cp^*_2ZrMe_2 \xrightarrow{H_2\ (50\text{–}100\ atm)} Cp^*_2ZrH_2 + 2CH_4 \tag{4}$$

used successfully in the preparation of other metal hydrides,[16] and in the present case 85–90% yields of the dihydride were realized on the basis of $Cp^*_2ZrCl_2$. Hydrogenation with 1 atm of dihydrogen is unsuccessful, leading only to slow conversion of $Cp^*_2ZrMe_2$ to an unidentified product.

The alkyl hydrides $Cp^*_2Zr(R)H$ were prepared by olefin insertion into a Zr–H bond of $Cp^*_2ZrH_2$. This method, using isobutene, has previously been employed to prepare $Cp^*_2Zr(H)CH_2CH(CH_3)_2$ (**1a**)[15] which (to date) is one of only two reported alkyl hydrides of permethylzirconocene.[17] Even in the presence of excess isobutene, reaction with a second equivalent is not observed, apparently for steric reasons. In contrast, the corresponding reaction with excess ethene yields ethane and a zirconacyclopentane.[15] However, we have found that addition of only 1 equiv of ethene to a $Cp^*_2ZrH_2$ solution leads to quantitative formation of $Cp^*_2Zr(CH_2CH_3)H$ (**1b**) within minutes at 25 °C (eq 5). Interestingly, while the ethyl and

$$\begin{aligned} Cp^*_2ZrH_2 + CH_2{=}C(R)R' \rightarrow\ & Cp^*_2Zr[CH_2CH(R)R']H \\ & \textbf{1a},\ R = R' = CH_3 \\ & \textbf{1b},\ R = R' = H \\ & \textbf{1c},\ R = CH_3,\ R' = H \end{aligned} \tag{5}$$

isobutyl hydrides are stable in benzene solutions at 25 °C, the *n*-propyl hydride is thermally unstable under these conditions, slowly decomposing to a 1:1 mixture of $Cp^*_2ZrH_2$ and an unidentified organometallic product[19] with concomitant evolution of propane (products identified by NMR). The rate of this decomposition was found to increase with temperature, and in a sealed NMR tube experiment (benzene-d_6) the reaction was two-thirds complete after 46 h at 45 °C. Upon continued thermolysis to force the reaction to completion, decomposition into a mixture of secondary products was observed.

Photoreactions. Upon blacklight photolysis in benzene solution, the permethylzirconocene alkyl hydrides evolve their respective alkanes. In the case of the isobutyl hydride, the gas was quantitatively collected by means of a Toepler pump, yielding 0.996 mmol of isobutane/mmol of $Cp^*_2Zr(H)CH_2CH(CH_3)_2$. The major organometallic product (greater than 90% yield by NMR) produced in these reactions is $Cp^*_2Zr(C_6H_5)H$ (**2**) which may be isolated as a pale yellow solid in 65% purified yield (eq 6). An

$$\underset{\textbf{1a–c}}{Cp^*_2Zr(R)H} \xrightarrow[benzene]{h\nu} \underset{\textbf{2}}{Cp^*_2Zr(C_6H_5)H} + RH \tag{6}$$

$$R = Et,\ Pr,\ i\text{-}Bu$$

alternate preparation of **2** utilizes the metathesis reaction (eq 7); a similar procedure has been reported for the hafnium analogue[20] Analytical, mass spectral, and ^1H

$$Cp^*_2ZrH_2 + C_6H_5Li \rightarrow Cp^*_2Zr(C_6H_5)H + LiH \tag{7}$$

NMR data are entirely consistent with the formulation of **2** as the phenyl hydride complex of permethylzirconocene. Further support for this formulation is given by its conversion to $Cp^*_2Zr(C_6H_5)I$ with evolution of methane upon treatment with methyl iodide. Apparently light is required to induce alkane formation in these reactions since benzene solutions of the alkyl hydrides remain unchanged in the dark.[21] If the photochemical reactions are performed under vacuum, the resultant solutions are yellow-brown in color. If, however, a benzene solution of the isobutyl hydride is photolyzed in the presence of excess dinitrogen (1 atm), a permanganate colored solution is formed. NMR analysis indicates the presence of $Cp^*_2Zr(C_6H_5)H$ (**2**) and the known dinitrogen complex $(Cp^*_2ZrN_2)_2N_2$[14] as well as several other unidentified products. The reaction shown in eq 6 represents, to our knowledge, the first example of photochemically induced reductive elimination of alkane from solutions of a monomeric alkyl hydride complex. Puddephatt[22] has previously reported photochemical elimination of methane from the "A-frame" species $[Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$, and Perutz[23] has described the photolysis of $Cp_2W(CH_3)H$ at 20 K in an Ar matrix wherein Cp_2W and methane were detected. Finally, Green[24] has noted that photolysis of $Cp_2W(C_6H_5)H$ in C_6D_6 did *not* lead to H/D exchange, suggesting that no reductive elimination took place.

We have also found that the phenyl hydride complex **2** undergoes reductive elimination photochemically. Thus, a sample of **2** in benzene-d_6 solution is quite stable, and

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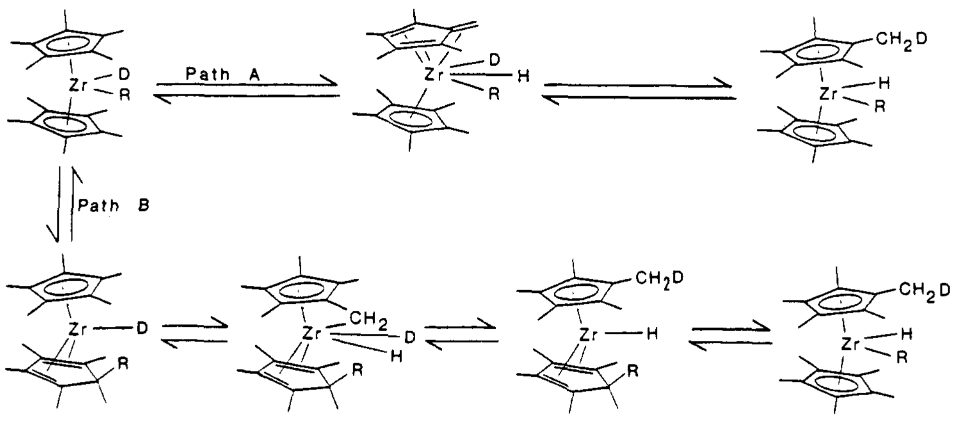
Scheme I



no evidence of H/D exchange with the solvent is seen even after 6 days at 25 °C. However, if the sample is blacklight photolyzed, nearly complete exchange of C_6H_6 (supplied by reductive elimination from the zirconium complex) for solvent C_6D_6 occurs within 43 h as indicated by a substantial decrease in the phenyl and hydride resonances and a concomitant appearance of C_6H_6 in the ^1H NMR. If the solvent is replaced with fresh C_6D_6 and the photolysis continued, complete conversion to $Cp^*_2Zr(C_6D_5)D$ occurs, as identified by the resonance of its Cp* rings in the ^1H NMR. Further evidence for this deuteriated species is supplied by shifts in the absorption bands of the infrared spectrum (Nujol): phenyl ν(C–H) 3052, ν(C–D) 2255 cm^{-1}; ν(Zr–H) 1563, ν(Zr–D) 1128 cm^{-1}. These results show that the phenyl hydride, like the alkyl hydrides, also undergoes photochemically induced reductive elimination.

Finally, we have observed photochemically induced reductive elimination of H_2 from $Cp^*_2ZrH_2$. In sealed NMR tube reactions, blacklight photolysis of benzene-d_6 solutions of $Cp^*_2ZrH_2$ proceeded very slowly with only 10% conversion to $Cp^*_2Zr(C_6D_5)D$ after 32 h (the alkyl hydrides 1 are completely converted to 2 in ca. 30 h under identical conditions); no other photoproducts were observed (eq 8).

$$Cp^*_2ZrH_2 \xrightarrow[\text{benzene-}d_6]{h\nu} Cp^*_2Zr(C_6D_5)D + H_2 \qquad (8)$$

In an attempt to increase the rate of the reaction, a sample was photolyzed with an unfiltered medium pressure Hg lamp: though the rate was increased significantly, the reaction was still only 30% complete after 20 h. The slower rate of the dihydride photochemical reactions compared to the alkyl hydride is consistent with the known trend of greater stability for cis dihydride complexes via-ã-vis their cis alkyl hydride analogues.[12,25] Another possible explanation for the slower reaction rate of the dihydride, as compared to the alkyl hydrides, is a back-reaction between the evolved dihydrogen and the phenyl hydride product to re-form $Cp^*_2ZrH_2$. However, this hydrogenation is quite slow at 25 °C even under 1 atm of hydrogen ($t_{1/2} \approx 6$ days).

Thermal and Photoreactions of $Cp^*_2Zr(D)CH_2CD(CH_3)_2$. Quantitative evolution of alkane upon photolysis of the permethylzirconocene alkyl hydrides suggests clean reductive elimination of the cis alkyl and hydride ligands. To obtain proof of this pathway the deuteriated species $Cp^*_2Zr(D)CH_2CD(CH_3)_2$ was prepared, and the labeled isobutane evolved upon photolysis was analyzed. The results of these studies listed in Table I show that the hydrogen incorporated into the isobutane is abstracted from the hydride position. Additionally, the crossover experiment reported in the table indicates that isobutane is liberated via *intramolecular* reductive elimination of the cis alkyl and hydride ligands. These results support the intermediacy of the coordinatively unsaturated Zr(II) species, Cp^*_2Zr, in the activation of benzene C–H bonds. Traces (<10%) of two isobutane-d_1 isomers were also observed and could have been produced in several ways, the most likely being the use of nonisotopically pure $Cp^*_2Zr(D)CH_2CD(CH_3)_2$, but slow exchange between the deuteride and the methyl hydrogens of the Cp* ligands cannot be overlooked in the formation of $CH_3CD(CH_3)_2$ (vide infra).

Table I. Deuterium-Labeling Experiments[a]

compound	gas evolved
$Cp^*_2Zr(D)CH_2CD(CH_3)_2$	$(CH_2D)CD(CH_3)_2$[b]
$Cp^*_2Zr(H)CH_2CH(CH_3)_2$	$CH_3CH(CH_3)_2$
+	+
$Cp^*_2Zr(D)CH_2CD(CH_3)_2$	$(CH_2D)CD(CH_3)_2$[b]

[a] The compound was photolyzed in toluene at 0 °C. [b] Traces (<10%) of $CH_3CD(CH_3)_2$ and $(CH_2D)CH(CH_3)_2$ were also present.

It should be noted that the thermal decomposition (74 °C) of $Cp^*_2Zr(D)CH_2CD(CH_3)_2$ has previously been reported.[12] Since only $CH_3CD(CH_3)_2$ was evolved upon thermolysis, the authors proposed that the hydrogen incorporated into the isobutane was removed preferentially from the Cp* ligands via reductive elimination from a tautomer of the parent compound. Differences in the isobutane-labeling patterns observed in the photochemical and thermochemical reactions led us to reinvestigate the thermolysis. These studies revealed that slow exchange between the deuteride in $Cp^*_2Zr(D)CH_2CD(CH_3)_2$ and the 30 hydrogens of its Cp* ligands occurs at 25 °C, with 12% hydrogen incorporation after 4 days (NMR, benzene-d_6). (H/D exchange between the deuteride and the isobutyl group is ruled out by the results of Bercaw et al.[12]) At elevated temperature (35–40 °C) the rate of exchange increases with 30% hydrogen incorporation after only 3 days. The rate of this exchange would be expected to increase still further at higher temperatures, and thus at 74 °C, the temperature used in the previous thermal decomposition experiments, the deuteride was perhaps replaced by hydride (to form $(Cp^*\text{-}d_1)Cp^*Zr(H)CH_2CD(CH_3)_2$) prior to loss of isobutane. Therefore, we propose an alternate mechanism for the thermal decomposition of the isobutyl hydride involving fast H/D exchange of the deuteride with the Cp* hydrogen atoms followed by reductive elimination of isobutane as is observed for the photochemical reaction. (To reduce the effect of this H/D scrambling, our photochemical labeling experiments were performed at 0 °C.) Two possible pathways for this H/D exchange are shown

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(25) See ref 8, p 243.

in Scheme I. In path A exchange occurs by reversible cyclometalation of a Cp* methyl group. Path B invokes reversible metal-to-ring alkyl transfer[26] to reduce the formal oxidation state to Zr(II), allowing oxidative addition of a Cp* methyl C–H bond. Of these pathways, we prefer path B since it is analogous to the mechanism proposed for H/D exchange in $Cp^*_2ZrH_2$.[11]

The organometallic products formed upon thermolysis of $Cp^*_2Zr(H)CH_2CH(CH_3)_2$ (**1a**) are also of interest, and it is reasonable to assume that the thermal reaction would also initiate C–H bond activation of the solvent (as found in the photochemical studies). In the previous thermolysis study,[12] several products were observed but only $Cp^*_2ZrH_2$ was clearly identified. However, these experiments were performed in toluene that would be expected to produce a mixture of ortho, meta, and para C–H bond activation species. Indeed, this may have been why these workers were unable to identify the products. To simplify the analysis we repeated the thermolysis in benzene. In a typical sealed NMR tube experiment, a sample of **1a** was thermolyzed at 75–80 °C and the progress of the reaction monitored over time. After 22 h, nearly complete disappearance of **1a** was observed with accompanying formation of $Cp^*_2Zr(C_6H_5)H$ (**2**) and $Cp^*_2ZrH_2$ in a 2:1 ratio; in addition, several minor products (<10%) were present. Continued thermolysis showed slow conversion of $Cp^*_2ZrH_2$ to **2** as well as a decrease in the amount of the minor products. These results clearly indicate that C–H bond activation of benzene also occurs thermally with the isobutyl hydride although we are unsure of the mechanism for the formation of $Cp^*_2ZrH_2$.[27]

Synthesis, Characterization, and Reactions of $Cp^*(\eta^6\text{-}C_5Me_4CH_2)Zr(C_6H_5)$. Thermolysis of $Cp^*_2Zr(C_6H_5)H$ (**2**) at 150 °C in benzene effects quantitative evolution of dihydrogen (0.952 mmol/mmol of **2**) and the formation of the tetramethylfulvene complex **3** in greater than 95% yield (eq 9). This compound may be isolated

$$\underset{\mathbf{2}}{Cp^*_2Zr(C_6H_5)H} \xrightleftharpoons{\text{benzene}} \underset{\mathbf{3}}{Cp^*(\eta^6\text{-}C_5Me_4CH_2)Zr(C_6H_5)} + H_2 \quad (9)$$

as orange crystals by removal of dihydrogen during the course of the reaction and recrystallization from petroleum ether at −78 °C. The ^1H and ^{13}C NMR spectra provide evidence for the tetramethylfulvene nature of **3**, and the mass spectrum shows the expected parent ion at *m/e* 436. (Concurrent with our work, Marks et al.[28] found an alternate route to **3** via thermolysis of $Cp^*_2Zr(C_6H_5)_2$ and an X-ray crystal structure was reported which delineates the bonding mode of the tetramethylfulvene ligand.)

The reversible nature of eq 9 is supported by the following experiments. A sealed NMR tube containing **2** under vacuum in benzene solution was heated to 150 °C for 5 h; an NMR spectrum taken immediately after cooling to room temperature revealed that 90% of **2** had been converted to **3**. Repeated NMR scans showed that **3** gradually reverted to **2** until no **3** remained after 3 h at room temperature. A pure sample of **3** in petroleum ether reacted with H_2 (1 atm) to cleanly yield **2** after 15 min. Reaction of **3** with D_2 under the same conditions leads to the phenyl deuteride as indicated by the disappearance of the hydride resonance in the NMR. Though it is assumed that the other deuterium atom was incorporated into a Cp* methyl group, no experimental evidence was obtained to support this conclusion. Additionally, a strong deuterium isotope effect is present since the reaction with D_2 occurs at approximately half the rate of the H_2 reaction. The temperature dependence of this reaction is indicated by the fact that thermolysis of a sealed NMR tube sample of **2** in benzene at 70 °C shows only traces of **3** after 12 h. With increasing temperature, the reaction is shifted further to the right until nearly complete conversion to **3** is seen at 150 °C.

While the thermal conversion of **2** to **3** is straightforward and produces good yields, a route to **3** utilizing more abundant starting materials was desirable. Such a route involves thermolysis of $Cp^*_2ZrH_2$ at 150 °C in benzene solution with removal of H_2 during the course of the reaction (eq 10). This presumably proceeds by reversible

$$Cp^*_2ZrH_2 \xrightleftharpoons[+H_2,\ -C_6H_6]{-H_2,\ +C_6H_6} \underset{\mathbf{2}}{Cp^*_2Zr(C_6H_5)H} \xrightleftharpoons[H_2]{-H_2} \underset{\mathbf{3}}{Cp^*(\eta^6\text{-}C_5Me_4CH_2)Zr(C_6H_5)} \quad (10)$$

loss of H_2 from $Cp^*_2ZrH_2$ and oxidative addition of a benzene C–H bond to Cp^*_2Zr to form **2** in situ (vide supra). Subsequent loss of H_2 leads to the desired product **3**. Collection of the gas evolved by means of a Toepler pump yields 1.84 mmol of H_2/mmol of $Cp^*_2ZrH_2$. An added advantage of this synthetic route is that **3** can be prepared in greater than 80% yield based on $Cp^*_2ZrCl_2$ (>95% based on $Cp^*_2ZrH_2$).

The reactivity of tetramethylfulvene complexes of the early transition metals has not been studied in detail; therefore investigations into the reactivity of **3** were undertaken. The initial experiments consisted of adding two-electron donor ligands to benzene solutions of **3** in an attempt to form an 18-electron adduct, as has been observed for a titanium bis(fulvene) complex,[29] or possibly induce a change of the tetramethylfulvene ligand from η^6 to η^4 coordination. In this regard, a sixfold excess of PMe_3 was added to a benzene solution of **3**, but no reaction was observed even after 6 days. In a similar experiment, 1 atm of CO was placed over a solution of **3**, and within 30 min the solution had become brown in color, but NMR analysis revealed a profusion of unidentifiable products. It is assumed that these products are derived from CO insertion into Zr–phenyl or possibly Zr–methylene bonds. The most intriguing result, however, was obtained upon reaction of **3** with iodine: this led to the ring-substituted phenyl iodide complex **4** as the major product, characterized by its mass spectrum and ^1H NMR (eq 11).

$$\underset{\mathbf{3}}{Cp^*(\eta^6\text{-}C_5Me_4CH_2)Zr(C_6H_5)} + I_2 \rightarrow \underset{\mathbf{4}}{Cp^*(\eta^5\text{-}C_5Me_4CH_2I)Zr(C_6H_5)I} \quad (11)$$

A question remains to be answered in the formation of the tetramethylfulvene complex **3**: what is the source of the dihydrogen evolved in its formation from $Cp^*_2Zr(C_6H_5)H$ (**2**)? In this regard, deuterium-labeling experiments were attempted, but severe scrambling did not allow definitive results to be obtained. For example, thermolysis of **2** at 150 °C in C_6D_6 showed exchange of C_6H_6 for C_6D_6 as indicated by the appearance of C_6H_6 in the NMR. To overcome this exchange problem $Cp^*_2Zr(C_6D_5)D$ was

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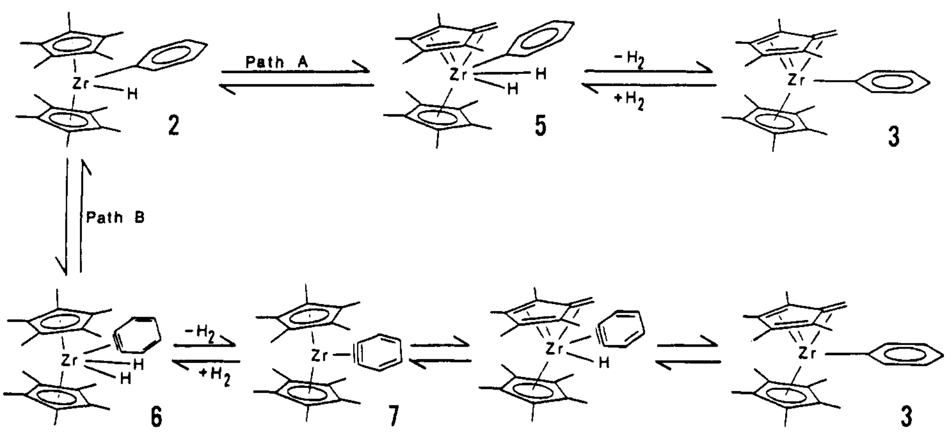
Scheme II



thermolyzed in C_6D_6, but partial hydrogen incorporation into the phenyl and deuteride positions of **2** as well as observation of $C_6D_{6-n}H_n$ in the solvent clearly demonstrated that H/D exchange with the Cp* ligands was occurring. This is probably initiated by scrambling of the hydride and Cp* hydrogens in **2**, possibly as shown in Scheme I. Although this H/D exchange is not observed after 50 h at 25 °C, it apparently occurs readily at elevated temperatures.

While a clear determination of the mechanism for conversion of the phenyl hydride **2** into the tetramethylfulvene complex **3** is not possible due to the scrambling of deuterium labels just outlined, two reasonable pathways are proposed in Scheme II. (We have represented **3** as the π-bonded Zr(II) resonance form although it can also be considered as a ring-metalated Zr(IV) σ,η^5 complex.[28]) The key step in path A is reversible cyclometalation of a Cp* methyl group forming a Zr(IV) dihydride (**5**) which reductively eliminates H_2 to produce **3**. An analogous cyclometalation has been proposed to account for H/D exchange in the isobutyl hydride (Scheme I). An alternate route via path B proceeds through a benzyne dihydride complex (**6**), followed by elimination of H_2 to yield **7**. Subsequent cyclometalation of a Cp* methyl group followed by hydrometalation of the benzyne produces **3**. It should be noted that the H/D scrambling observed for this system can be accounted for by either pathway. A slight modification[30] of path B would be required if the benzyne complexes (e.g. compound **6**) were instead considered as *o*-phenylene species.[31,32] Thus, **6** would be Zr(VI), an unacceptable formal oxidation state. A variation of path B proceeds directly from **2** to **7** via a four-center transition state involving zirconium, hydride, and the ortho phenyl carbon and hydrogen. Direct loss of H_2 in this way would lead to **7** without the need to invoke the the (potentially) Zr(VI) species **6**. This is analogous to the mechanism proposed for the reaction of some scandium alkyl and hydride complexes.[33] Additionally, **7** may go directly to **3** (without the zirconium hydride intermediate shown in Scheme II) by insertion of a Cp* C–H bond into the strained metallacyclopropane ring[28] of the *o*-phenylene moiety.

Of these two mechanisms (paths A and B), we prefer path B for several reasons. First, the ^1H NMR spectrum of **2** reveals an upfield shift of one of its aryl hydrogens (δ 6.37 versus δ 7.00–7.36), suggesting an agostic interaction[34] between an ortho phenyl hydrogen and the zirconium.[35] This would facilitate the formation of the benzene complex **6** or its four-center transition-state alternative. Further support for path B is gleaned from the deuterium-labeling experiments of $Cp^*_2Zr(C_6H_5)D$ described below. Thus benzene-d_6 solutions of $Cp^*_2Zr(C_6H_5)D$ show nearly complete disappearance of the ortho hydrogen resonance (δ 6.37) and appearance of a strong resonance for the hydride (δ 6.32) in the ^1H NMR after only 21 h at 25 °C. (Benzene solutions of $Cp^*_2Zr(C_6D_5)D$ show no sign of exchange of the deuteride or phenyl deuteriums with the solvent or methyl hydrogens of the Cp* ligands, even after 50 h at 25 °C.) This clearly shows that the majority of the deuterium is in the ortho phenyl position rather than bound to zirconium after 21 h as would be expected since heavy isotopes normally concentrate in those positions where they are bound most strongly.[36] These results clearly demonstrate that H/D exchange occurs at 25 °C between the deuteride and the phenyl ortho hydrogen involved in the agostic interaction. One possible mechanism for this exchange is given in Scheme III which involves initial formation of the benzyne complex **6a**. Reversible metal-to-ring deuterium transfer via complex **8** is then invoked to exchange the hydride and deuteride ligands as shown in **6b**. Finally, transfer of the deuteride to the benzyne ligand produces the correctly labeled product. As mentioned in the discussion for Scheme II, species **6a** and **6b** could be alternately represented as Zr(VI) *o*-phenylene complexes. A possible variation[30] of Scheme III to bypass this potential problem with **6** would invoke a four-center transition state consisting of zirconium, deuteride (or hydride), and the ortho phenyl carbon and hydrogen (or deuterium). For example, $Cp^*_2Zr(C_6H_5)D$ would proceed to **8** via metal-to-ring deuterium transfer mediated by this transition state, eliminating **6a** from the mechanism. Finally, although not shown in Scheme III, we cannot rule out the possible intermediacy of an η^2-benzene complex[6] in this H/D exchange reaction. Returning to Scheme II, additional support for path B is given by the proposed intermediacy of a benzyne complex

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[30] We are grateful to a reviewer for this suggestion.

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[35] Strong evidence for ortho hydrogen agostic interactions in another Zr aryl compound is given by the NMR spectrum of $Cp^*_2Zr(2,5\text{-}C_6H_3Me_2)H$. 400.1-MHz ^1H NMR (99.96% benzene-d_6): δ 7.23, 6.94 (both d, both 1 H, $^3J_{HH}$ = 7.4 Hz, $C_6H_3Me_2$), 5.42 (d, 1 H, J_{HH} = 3.5 Hz, $C_6H_3Me_2$, ortho hydrogen), 5.12 (d, 1 H, J_{HH} = 3.5 Hz, ZrH). Gated-decoupled, 100.6-MHz ^{13}C NMR (cyclohexane-d_{12}): δ 131.6, 140.5, 187.6 (all s, $C_6H_3Me_2$), 127.6, 130.8 (both d, $^1J_{CH}$ = 154–155 Hz, $C_6H_3Me_2$), 100.1 (d, $^1J_{CH}$ = 127 Hz, $C_6H_3Me_2$, ortho carbon). See ref 27.

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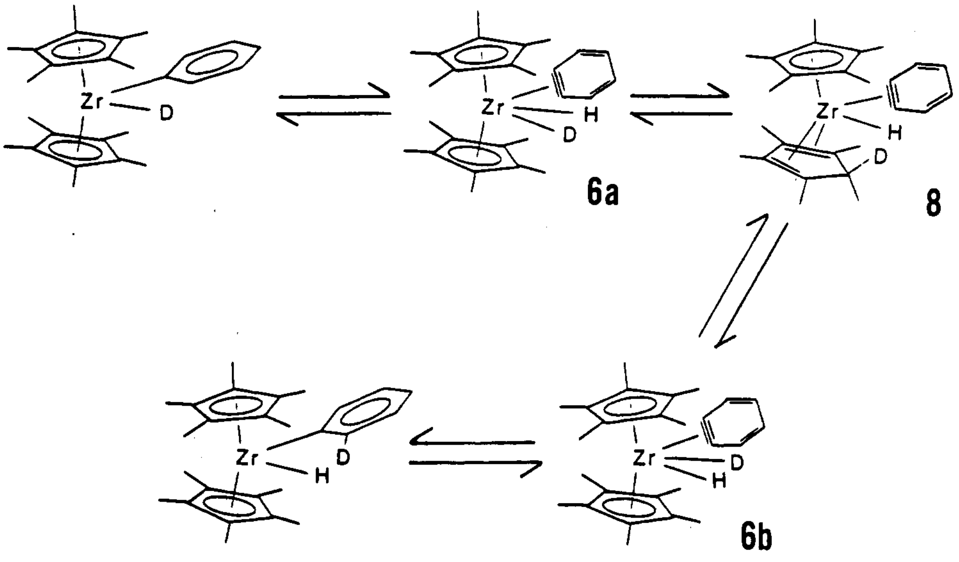
Scheme III



in the thermal reactions of $Cp_2Zr(C_6H_5)_2$ and $Cp^*_2Zr(C_6H_5)_2$. In these reactions, the benzyne intermediate may be trapped in the presence of olefins to yield zirconabenzocyclopentenes.[28,37] Further evidence for a benzyne intermediate is provided by the recent isolation and X-ray crystal structure determination of the zirconium benzyne complex $Cp_2Zr(C_6H_4)PMe_3$.[31] Therefore, for the above reasons we believe that a benzyne intermediate (Scheme II, path B) is indicated in the thermal conversion of $Cp^*_2Zr(C_6H_5)H$ (2) to the tetramethylfulvene complex 3.

The mechanism for the formation of $Cp^*(\eta^5\text{-}C_5Me_4CH_2I)Zr(C_6H_5)I$ (4) must also be considered, and one possible pathway involves oxidative addition of I_2 at the Zr center of 3, followed by migration of an iodine atom to the methylene group. However, we cannot rule out other pathways such as a concerted mechanism involving a four-center transition state containing the Zr, iodine atoms, and the methylene carbon.

Conclusion

Our results suggest that photochemically induced intramolecular reductive elimination of alkanes or arenes from $Cp^*_2Zr(R)H$ complexes results in the in situ generation of the highly reactive Cp^*_2Zr fragment. This coordinatively unsaturated species can activate benzene carbon-hydrogen bonds to yield the phenyl hydride 2. Thermal reactions of $Cp^*_2Zr(R)H$ are more complex. Thus, activation of benzene C–H bonds to yield 2 is observed although other products (notably $Cp^*_2ZrH_2$) are also formed. In addition, H/D exchange between the hydride and Cp* hydrogens in 1 is found even at room temperature.

The phenyl hydride (2) exhibits an exchange process whereby the hydride and an ortho phenyl hydrogen are interchanged at 25 °C. At elevated temperatures 2 liberates dihydrogen to reversibly form the tetramethylfulvene complex 3. We believe the key step in these reactions is β-hydrogen elimination from the phenyl group to yield a benzyne dihydride intermediate. Subsequent elimination of H_2 and metal-mediated transfer of a hydrogen atom from a Cp* methyl group to the benzyne ligand leads to 3 (Scheme II). Our H/D exchange results can also be explained by postulating the intermediacy of a benzyne dihydride species (Scheme III). A minor modification of Schemes II and III yields an alternate mechanism: this approach substitutes a four-center transition state for the benzyne dihydride 6, thereby bypassing the formally Zr(VI) species that would result if 6 is considered as an *o*-phenylene dihydride species. We are currently examining the activation of other aromatic and aliphatic C–H bonds using photochemically generated Cp^*_2Zr. In addition, we are probing the thermal reactions of alkyl and aryl hydrides of permethylzirconocene to better understand their mechanisms.

Experimental Section

General Considerations. All manipulations were performed under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or on a high vacuum line. Schlenk techniques under argon were utilized when appropriate. Benzene, toluene, petroleum ether (30–60 °C), diethyl ether, benzene-d_6, and cyclohexane-d_{12} were dried over 4-Å molecular sieves and subsequently vacuum distilled from "titanocene".[38] Ar, H_2, and CO (Liquid Air) were purified by passing over 4-Å molecular sieves and MnO on vermiculite.[39] D_2 (Linde) was used without purification. Ethene, propene, and anhydrous HCl (Matheson) were freeze–pump–thawed prior to use. Isobutene (Matheson) was freeze–pump–thawed and then distilled from a –40 °C cold trap (CH_3CN/LN_2). MeI was first distilled and then washed with several portions of $Na_2S_2O_3$ solution, H_2O, Na_2CO_3 solution, and finally H_2O. It was subsequently dried over $CaSO_4$ and stored over molecular sieves. Iodine was sublimed in vacuo prior to use, and MeLi (Alfa) was used directly. PMe_3,[40] $Cp^*_2ZrCl_2$,[41] and $Cp^*_2Zr(H)CH_2CH(CH_3)_2$[15] were prepared according to literature procedures.

NMR spectra were recorded on Varian T-60A (^1H), Bruker WH-90 (^1H), Varian XL-100 (^1H), and Bruker AM-400 (^1H, ^{13}C) spectrometers and reported in parts per million versus TMS at 0.00 ppm. IR spectra were taken on a Nicolet MX-1 FT spectrophotometer. Mass spectrometry was performed on a double-focusing Finnigan MAT 312 spectrometer with an S2000 data system. Elemental analysis was done by Galbraith Laboratories. The photochemical experiments were performed by using two 15-W General Electric blacklights (Model no. F15T8 BLB) with output primarily at 355 nm or with a 450-W Hanovia medium-pressure Hg lamp in a water-cooled quartz immersion well. The low-temperature photochemical experiments were conducted in a specially constructed Dewar. This consisted of a Dewar with

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two unsilvered sections 180° apart. Attached to the inside of the Dewar, behind the unsilvered sections, were hemispherical reaction vessel holders (sealed with silicone cement to prevent leakage of the coolant medium). One of these was designed for 5-mm tubes and the other for a cylindrical reaction vessel (30-mm o.d., 40-mL capacity). The apparatus was cooled by circulating an antifreeze mixture by means of a Forma Scientific constant temperature bath and circulator (Model 2095/2100), through a coil of copper tubing immersed in an antifreeze solution within the Dewar.

All photochemical and thermochemical experiments were run under vacuum unless otherwise specified. Some preliminary reactions as well as those monitored by NMR were conducted in sealed NMR tubes.

Collection and Analysis of Gases. Gases were quantitatively collected through a series of cold traps by means of a Toepler pump. H_2 was collected through LN_2 traps (−196 °C) and characterized by burning to H_2O by cycling (via a Toepler pump) over a CuO column at 315 °C. Isobutane was collected through dry ice/acetone traps (−78 °C) and identified by its IR spectrum. Ethane and propane were characterized by NMR in sealed NMR tube reactions. The labeled isobutanes obtained in the labeling experiments were analyzed by a combination of MS and IR spectroscopy as reported previously.[12]

Procedures. $Cp^*_2ZrMe_2$. This was prepared by using the following variation of a literature procedure.[15] To a suspension of $Cp^*_2ZrCl_2$ (6.00 g, 13.9 mmol) in 150 mL of diethyl ether was added a 1.6 M diethyl ether solution of MeLi (18.1 mL, 29.0 mmol) via syringe under Ar purge. The mixture was stirred for 6 h, the solvent removed under vacuum, and the product extracted with 150 mL of petroleum ether. The solvent volume was reduced until some of the product had precipitated. It was then cooled to −78 °C and filtered to yield 4.68 g (86.0%) of white crystalline product.

$Cp^*_2ZrH_2$. Approximately half (2.4 g) of the $Cp^*_2ZrMe_2$ prepared above was dissolved in 25 mL of toluene and placed in a 75-mL stainless-steel bomb. The bomb was pressurized with 50–100 atm of H_2 directly from the tank. After the valve was closed, the bomb was placed in a rocking mechanism and gently agitated for 7 days. (Shorter reaction times have been used, but the product is usually not as pure.) The bomb was depressurized, the solution transferred to a flask, and the solvent removed in vacuo to give a quantitative yield of pure $Cp^*_2ZrH_2$. The procedure was repeated with the remainder of the $Cp_2^*ZrMe_2$ to give an overall yield of 4.3 g of $Cp_2^*ZrH_2$ (85% yield based on $Cp^*_2ZrCl_2$).

$Cp^*_2Zr(CH_2CH_3)H$ (1b). Ethane (1.10 mmol), measured with a calibrated gas bulb, was condensed at −196 °C into a solution of $Cp^*_2ZrH_2$ (400 mg, 1.10 mmol) in 25 mL of petroleum ether contained in a 100-mL flask fitted with a needle valve. The needle valve was closed and the mixture warmed to room temperature. After the solution was stirred for 1 h, a quantitative yield of the yellow product is obtained upon removal of the solvent. The mass spectrum shows the parent ion at *m/e* 390. 90-MHz ^1H NMR (benzene-d_6, referenced to C_6D_5H at δ 7.15): δ 1.82 (s, 30 H, Cp*), 0.06 (q, 2 H, $^3J_{HH}$ = 8.6 Hz, CH_2), −0.70 (t, 3 H, $^3J_{HH}$ = 8.6 Hz, CH_3), 3.51 (s, 1 H, ZrH).

$Cp^*_2Zr(CH_2CH_2CH_3)H$ (1c). Propene (8.3×10^{-2} mmol), measured with a calibrated gas bulb, was condensed at −196 °C into a solution of $Cp^*_2ZrH_2$ (30 mg, 8.2×10^{-2} mmol) in 0.5 mL of benzene-d_6 contained in an NMR tube fitted with a needle valve. The tube was torch sealed and warmed to room temperature. The quantitative reaction was complete in several minutes as shown by NMR, which was the only characterization obtained due to thermal instability of the compound. 100-MHz ^1H NMR (benzene-d_6): δ 1.90 (s, 30 h, Cp*), 1.15 (m, 3 H, CH_3), 0.10–0.92 (m, 4 H, CH_2CH_2), 5.65 (s, 1 H, ZrH).

$Cp^*_2Zr(D)CH_2CD(CH_3)_2$. This compound was prepared by using a variation of a published procedure.[11,15] In a 100-mL flask was placed 300 mg of $Cp^*_2ZrH_2$ and 25 mL of petroleum ether. The sample was degassed and cooled to 0 °C, and 1 atm of D_2 (200-mL total volume) was placed over the solution. After the solution was stirred for 1 h, the sample was cooled to −78 °C and degassed. After the solution was warmed to 0 °C, 1 atm of D_2 was again placed over the solution. After the solution was stirred for another hour, the D_2 was exchanged once more and the solution stirred for an additional hour and then degassed at −78 °C. An excess of isobutene was condensed into the solution, and the mixture was warmed to 0 °C and stirred for 2.5 h. Finally, the petroleum ether was vacuum distilled from the flask at 0 °C to yield the product.

$Cp^*_2Zr(C_6H_5)H$ (2). Method A. In each of two 100-mL flasks fitted with needle valves was placed $Cp^*_2Zr(H)CH_2CH(CH_3)_2$ (600 mg, 1.43 mmol) and 30 mL of benzene. The samples were thoroughly degassed and photolyzed with two blacklights for 10 days. The long photolysis time was used to ensure complete reaction. The samples were then combined, and the solvent was removed to yield a brown tar. The product was purified by the addition to 10 mL of −78 °C petroleum ether, followed by stirring the mixture at −78 °C for several hours until the solid broke up to yield a finely divided yellow solid. The suspension was filtered while cold and washed with minimal −78 °C petroleum ether yielding 825 mg (65.6%) of yellow product. It may be further purified by recrystallization from −78 °C petroleum ether. Anal. Calcd for $C_{26}H_{36}Zr$: C, 71.01; H, 8.25. Found: C, 70.91; H, 8.35. MS shows parent ion at *m/e* 438. 90-MHz ^1H NMR (99.96% benzene-d_6): δ 1.76 (s, 30 H, Cp*), 7.36–7.00 (m, 4 H, C_6H_5), 6.37 (d, 1 H, $^3J_{HH}$ = 9 Hz, C_6H_5), 6.32 (s, 1 H, ZrH).

Method B. The compound may also be prepared by the reaction of $Cp^*_2ZrH_2$ with 1 equiv of C_6H_5Li (>90% yield by NMR) as reported previously for its hafnium analogue.[20] Only preliminary experiments with this synthetic route have been attempted.

$Cp^*_2Zr(C_6H_5)I$. A solution of $Cp^*_2Zr(C_6H_5)H$ (113 mg, 0.257 mmol) in 25 mL of benzene was cooled to −78 °C, and a large excess of MeI was vacuum distilled into the flask. The mixture was warmed to room temperature and stirred in the dark (to prevent photodecomposition of the methyl iodide) for 0.5 h. The volatiles were removed to quantitatively yield the yellow product. The mass spectrum shows the parent ion at *m/e* 564. 90-MHz ^1H NMR (99.96% benzene-d_6): δ 1.78 (s, 30 H, Cp*), 7.80–7.68 (m, 1 H, C_6H_5), 7.23–7.00 (m, 3 H, C_6H_5), 6.62–6.52 (m, 1 H, C_6H_5).

$Cp^*(\eta^6\text{-}C_5Me_4CH_2)Zr(C_6H_5)$ (3). Method A. In a 40-mL thick walled glass ampule sealed to a Teflon needle valve was placed 100 mg of $Cp^*_2Zr(C_6H_5)H$ and 15 mL of benzene. After degassing, the sample was thermalyzed (150 °C) for 4 h. It was then quickly cooled to −196 °C and the evolved H_2 pumped off. This procedure was repeated until no more H_2 was produced (four to five times). The solution was transferred to a flask and the solvent vaccum distilled from the sample to yield an orange oil. Several 10-mL portions of petroleum ether were added and then removed under vaccum to eliminate the last traces of benzene, allowing the product to be isolated as orange crystals. A nearly quantitative yield of reasonably pure 3 was obtained in this manner and used directly in the reactions described herein. Greater purity may be achieved by recrystallization from −78 °C petroleum ether. (This reduces the yield to 90%.) MS shows parent ion at *m/e* 436. 400.1-MHz ^1H NMR (99.5% cyclohexane-d_{12}): δ 1.75 (s, 15 H, Cp*), 1.86, 1.81, 1.55, 0.68 (all s, all 3 H, $C_5Me_4CH_2$), 1.98, 1.86 (both d, both 1 H, $^2J_{HH}$ = 6.6 Hz, C_5MeCH_2), 6.97–6.81 (m, 4 H, C_6H_5), 5.76 (d, 1 H, $^3J_{HH}$ = 6.9 Hz, C_6H_5). Gated-decoupled, 100.6-MHz ^{13}C NMR (99.5% cyclohexane-d_{12}): δ 11.5 (q, $^1J_{CH}$ = 126 Hz, C_5Me_5), 13.1, 12.0, 10.7, 10.5 (all q, $^1J_{CH}$ = 126–127 Hz, $C_5Me_4CH_2$), 63.3 (t, $^1J_{CH}$ = 145 Hz, $C_5Me_4CH_2$), 118.2 (s, C_5Me_5), 126.2, 125.2, 122.1, 119.2, 117.5 (s, $C_5Me_4CH_2$), 134.3, 127.1, 125.9, 125.3, 122.5 (all d, $^1J_{CH}$ = 152, 156, 155, 157, 147 Hz, C_6H_5), 194.0 (s, C_6H_5).

Method B. The compound may also be prepared directly from $Cp^*_2ZrH_2$ by using a procedure similar to method A. In a typical reaction, 225 mg of $Cp^*_2ZrH_2$ in 20 mL of benzene was placed in the thick walled reaction vessel described in method A above. After degassing, the sample was thermalyzed (150 °C) for 4 h. It was then quickly cooled to −196 °C and the evolved H_2 pumped off. This procedure was repeated until no more H_2 was produced (six to seven times). Workup was then performed as in method A.

$Cp^*(\eta^5\text{-}C_5Me_4CH_2I)Zr(C_6H_5)I$ (4). Benzene (15 mL) was vacuum distilled into a flask containing I_2 (29 mg, 0.114 mmol) and a twofold excess of $Cp^*(\eta^6\text{-}C_5Me_4CH_2)Zr(C_6H_5)$ (3) (100 mg, 0.228 mmol). The presence of excess 3 inhibited the formation of side products. The mixture was stirred at room temperature for 19 h. After removal of the solvent, 5 mL of petroleum ether was added. The solution was cooled to −78 °C and the bright yellow solid quickly filtered before 3 reprecipitated. It was washed once with −78 °C petroleum ether (5 mL) to yield 31.7% (25 mg) of product based on I_2. The product contained traces of impurities. MS showed parent ion at m/e 690. 400.1-MHz ^1H NMR (99.5% cyclohexane-d_{12}): δ 2.16 (s, 15 H, Cp*), 2.14, 2.19 (both s, both 6 H, $C_5Me_4CH_2I$), 4.01 (s, 2 H, $C_5Me_4CH_2I$), 7.22–6.87 (m, 5 H, C_6H_5).

Photolysis of 1a under a Nitrogen Atmosphere. In an NMR tube attached to a Teflon needle valve via a ground-glass joint was placed $Cp^*_2Zr(H)CH_2CH(CH_3)_2$ (25 mg) and 0.5 mL of benzene-d_6. One atmosphere of N_2 (excess) was placed over the solution, the needle valve closed, and the sample photolyzed (blacklight) for 24 h. The sample was then cooled to −196 °C, the tube was torch sealed under slightly reduced pressure, and the contents were analyzed by NMR.

H_2 (D_2) and 3. One atmosphere of H_2 (D_2) was placed over a petroleum ether (10 mL) solution of **3** (40 mg) contained in a 50-mL flask. Conversion to $Cp^*_2Zr(C_6H_5)H$ was complete in 15 min (D_2 complete in 30–40 min).

HCl and 3. One atmosphere of anhydrous HCl (excess) was placed over a solution of **3** (60 mg) in 10 mL of benzene. Within minutes the reaction was complete and $Cp^*_2ZrCl_2$ was recovered upon removal of the solvent.

PMe_3 and 3. In an NMR tube attached to a needle valve was placed benzene-d_6 and **3**. A sixfold excess of PMe_3 was then condensed into the sample at −196 °C and the tube sealed. An NMR spectrum recorded after 6 days showed no sign of reaction.

CO and 3. One atmosphere of CO was placed over a benzene (10 mL) solution of **3** (30 mg). After 24 h an NMR revealed a profusion of products.

MeI and 3. Excess MeI was condensed at −78 °C into 15 mL of benzene containing **3** (40 mg). After 24 h, the volatiles were removed and an NMR revealed that no reaction had occurred.

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Registry No. **1a**, 67108-86-5; **1b**, 112532-21-5; **1c**, 112532-22-6; **2**, 112532-20-4; **3**, 105501-02-8; **4**, 112532-25-9; $Cp^*_2ZrMe_2$, 67108-80-9; $Cp^*_2ZrCl_2$, 54039-38-2; $Cp^*_2ZrH_2$, 61396-34-7; $Cp^*_2Zr(D)CH_2CD(CH_3)_2$, 67108-87-6; $Cp^*Zr(C_6H_5)I$, 112532-23-7; $Cp^*_2Zr(C_6D_5)D$, 112532-24-8; ethene, 74-85-1; propene, 115-07-1; isobutene, 115-11-7; benzene, 71-43-2.

Chiral 1-[1-(Dimethylamino)ethyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene and 1-[(Dimethylamino)methyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene Derivatives

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A series of chiral 1-[1-(dimethylamino)ethyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene and 1-[(dimethylamino)methyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene derivatives, (R,S)-$C_5H_5FeC_5H_3(CHMeNMe_2)(SCSNR_2)$ and $C_2H_5FeC_5H_3(CH_2NMe_2)(SCSNR_2)$ (R = Me, Et), have been prepared by reaction of (R,R)-1-[1-(dimethylamino)ethyl]-2-lithioferrocene and 1-[(dimethylamino)methyl]-2-lithioferrocene, respectively, with tetraalkylthiuram disulfide. The derivatives were characterized by ^1H NMR, ^{13}C NMR, IR, and MS techniques. Rotation around the C–N carbamate bond was studied by dynamic ^1H NMR, and the approximate barriers to rotation for the methyl and ethyl derivatives **1**, **2**, **4**, and **5** are 15.83, 16.18, 15,36, and 15.81 kcal/mol, respectively, and are correlated with the "thioureide" band in the infrared.

Introduction

The dithiocarbamate ligand has played a major role in the chemistry of transition-metal sulfide complexes.[1,2] In the bid to introduce chirality to these dithiocarbamate ligands, we have prepared a series of chiral 1-[1-(dimethylamino)ethyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene and 1-[(dimethylamino)methyl]-2-[(dialkylthiocarbamoyl)thio]ferrocene derivatives, where the dithiocarbamate is attached to the ferrocene through a thioester linkage at the 2-position. The former contains both planar and central elements of chirality while the latter contains only a chiral plane.

Tetraalkylthiuram disulfides undergo nucleophilic attack at the disulfide linkage by cyanide ions, amines, and Grignard reagents.[3] Cava also reported that aryllithium derivatives react with tetraisopropylthiuram disulfide to give dithiocarbamate esters that were precursors to aromatic thiols.[4] Recently, a series of mono- and bis[(dialkylthiocarbamoyl)thio]ferrocene derivatives was synthesized in our laboratory.[5]

Experimental Section

Air-sensitive reagents were manipulated in a prepurified argon or nitrogen atmosphere by using Schlenck techniques or in a glovebox. Solvents were dried and distilled by standard methods.[6]

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