

Thermally Induced Rearrangement of α -Zirconocenyl Thioethers: Carbon-Carbon Bond Formation via a Transition-Metal Hydroxymethyl or Metalloxirane Analogue

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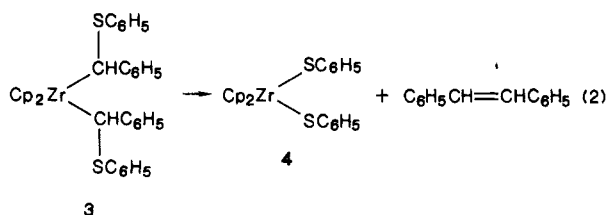
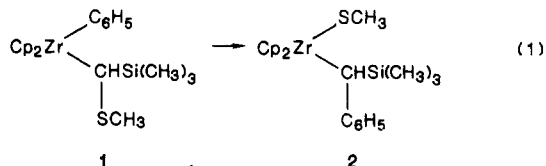
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The thermal rearrangement of α -zirconocenyl thioethers (η^5 -C₅H₅)₂Zr(Ar)[CH(SC₆H₅)(Si(CH₃)₃)] (Ar = C₆H₅, *p*-C₆H₄CH₃, *p*-C₆H₄OCH₃, *p*-C₆H₄Cl) and (η^5 -C₅H₅)₂ZrC₆H₅[CH(SCH₃)(Si(CH₃)₃)] in toluene solution follows clean first-order kinetics to produce (η^5 -C₅H₅)₂Zr(SC₆H₅)[CH(Ar)(Si(CH₃)₃)] and (η^5 -C₅H₅)₂Zr-(SCH₃)[CH(C₆H₅)(Si(CH₃)₃)]. Labeling studies using (η^5 -C₅H₅)₂Zr(*p*-C₆H₄CH₃)[CH(SC₆H₅)(Si(CH₃)₃)] and (η^5 -C₅H₅)₂ZrC₆H₅[CD(SC₆H₅)(Si(CH₃)₃)] show this rearrangement to be intramolecular. Activation parameters for the rearrangement of (η^5 -C₅H₅)₂ZrC₆H₅[CH(SC₆H₅)(Si(CH₃)₃)] were found to be $\Delta H^\ddagger = 20.30$ (43) kcal/mol and $\Delta S^\ddagger = -19.0$ (2) eu. It is proposed that this rearrangement proceeds by intramolecular nucleophilic attack (migration) of the aryl group to the methylene carbon with commensurate breaking of the C-S bond. A Hammett plot of log (k_{obsd}) for the rearrangement of (η^5 -C₅H₅)₂Zr(Ar)[CH(SC₆H₅)(Si(CH₃)₃)] versus σ_p produces a straight line ($\rho = -2.22$ (9)), supporting this mechanism.

Introduction

The chemistry of hydride and alkyl complexes of the group 4 transition metals and actinides have been the subject of extensive study in recent years as model systems to investigate carbon-carbon bond-forming reactions as may be occurring in the reductive homologation of CO which occurs in the Fischer-Tropsch and related reactions. The reactivity of these metal systems with CO has been attributed in large part to the high oxygen affinity of these metal systems.^{1,2} Transition-metal α -hydroxyalkyl and metalloxirane complexes have been proposed as key catalytic intermediates in the Fischer-Tropsch and related reactions.^{3,4} With this in mind we were interested in

examining the thermolysis of α -zirconocenyl thioethers to gain insight into the basic reactivity patterns of α -heteroatom-substituted alkyl groups in highly oxophilic transition-metal complexes. In recent preliminary reports, we have shown that α -zirconocenyl thioethers undergo carbon-carbon bond-forming reactions 1⁵ and 2⁶, which are



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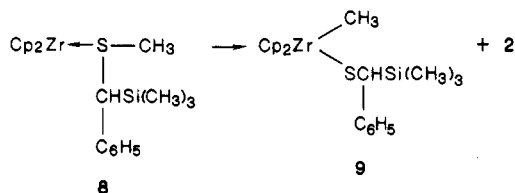
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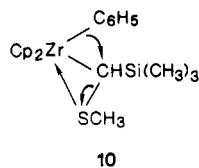
potentially good models for carbon-carbon bond formation via a hydroxymethyl metal or metalloxirane complex. We report here detailed studies into the mechanism of reaction 1.

Results and Discussion

Preliminary thermolysis experiments on $\text{Cp}_2\text{ZrC}_6\text{H}_5\text{-[CH(SCH}_3\text{)(Si(CH}_3\text{)}_3\text{)]}$ (1) at 95 °C for 22 h produces benzyltrimethylsilane in greater than 80% yield and as yet an unidentified insoluble organometallic complex (5).⁵ The formation of the benzyltrimethylsilane was of particular interest to us as it was clearly the product of a novel desulfurization and carbon-carbon bond-forming reaction. In contrast to complex 1, $\text{Cp}_2\text{ZrCH}_2\text{C}_6\text{H}_5\text{[CH(SCH}_3\text{)(Si(CH}_3\text{)}_3\text{)]}$ (6) and $\text{Cp}_2\text{ZrCH}_2\text{C}_6\text{H}_5\text{[CH(SCH}_3\text{)(Si(CH}_3\text{)}_3\text{)]}$ (7) exhibit remarkable thermal stability. Complexes 6 and 7 were recovered in over 90% yield after thermolysis in toluene at 82 °C for 1 week in the dark. Thermolysis of 1 was carried out in the dark in $\text{C}_6\text{D}_5\text{CD}_3$ in an NMR tube at 82 °C, and ^1H NMR spectra were recorded periodically during the course of the reaction. Under these conditions we observed two new cyclopentadienyl resonances that we attribute to 2 *vide infra*, initially appearing at approximately the same rate as the disappearance of the cyclopentadienyl resonances of 1, and then the resonances due to 2 disappeared at a slower rate while resonances due to benzyltrimethylsilane increased with the simultaneous formation of 5. On the basis of this NMR scale experiment a preparative thermolysis of 1 was carried out in toluene at 82 °C for 5 days, producing complex 2 in 58% isolated yield. Thermolysis of 2 in toluene at 82 °C produces benzyltrimethylsilane and 5. One could envision two potential mechanisms for the conversion of 1 to 2: (1) Complex 1 could undergo thermally induced reductive elimination, analogous to that which has been observed for $\text{Cp}_2\text{Zr(H)(R)}$ or $\text{Cp}_2\text{Zr(C}_6\text{H}_5\text{)[C(O)C}_6\text{H}_5\text{]}$ in the presence of Lewis bases, and could produce species such as 8 which



could then undergo oxidative addition to a C-S bond to give complex 2 or complex 9.^{7,8} (2) Complex 1 could undergo intermolecular or intramolecular nucleophilic attack (migration) of the phenyl group to the methylene carbon with commensurate C-S bond cleavage to produce complex 2. Anchimeric activation of the methylthio group in 1 by the neighboring Cp_2Zr group via an η^2 structure such as in 10 may be important in this process.^{5,6,9,10}



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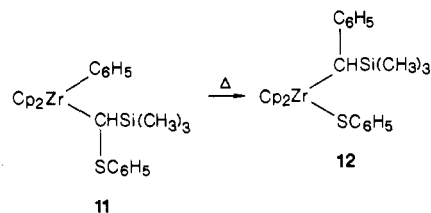
Table I. Summary of Rate Constants for the Rearrangement of α -Zirconocenyl Thioethers^c

compd	temp, °C	k_{obsd} , s ⁻¹
1 ^a	82.0	8.14 (41) $\times 10^{-6}$
11 ^a	72.0	2.57 (12) $\times 10^{-5}$
11 ^a	81.9	5.59 (27) $\times 10^{-5}$
11 ^a	92.0	1.38 (9) $\times 10^{-4}$
13 ^a	81.9	1.15 (6) $\times 10^{-4}$
13 ^b	81.9	1.12 (6) $\times 10^{-4}$
14 ^a	81.9	1.36 (2) $\times 10^{-5}$
15 ^a	81.9	1.78 (9) $\times 10^{-4}$
15 ^b	81.9	1.79 (9) $\times 10^{-4}$

^aBased on loss of starting material. ^bBased on appearance of product. ^cThe entry in parentheses is the error limit estimated to be one standard deviation based on repetitive experiments.

In the belief that the active hydrogens of the S-CH₃ group in complex 2 are responsible for its facile thermal decomposition, we have prepared the corresponding phenylthio derivatives $\text{Cp}_2\text{Zr(Ar)[CH(SC}_6\text{H}_5\text{)(Si(CH}_3\text{)}_3\text{)]}$ and examined their thermolysis, to evaluate possible mechanistic pathways for thermal rearrangement of α -zirconocenyl thioethers.

Thermolysis of $\text{Cp}_2\text{Zr(C}_6\text{H}_5\text{)[CH(SC}_6\text{H}_5\text{)(Si(CH}_3\text{)}_3\text{)]}$ (11) in toluene solution at 82 °C produces $\text{Cp}_2\text{Zr(SC}_6\text{H}_5\text{)[CH(C}_6\text{H}_5\text{)(Si(CH}_3\text{)}_3\text{)]}$ (12) in 83% isolated yield. In contrast



to complex 2, complex 12 is stable at the reaction conditions under which complex 11 undergoes thermolysis, thus allowing detailed examination of the thermally induced rearrangement of 11. The thermolysis of complex 11 in toluene-*d*₈ in sealed NMR tubes was followed by ^1H NMR at 72.0, 81.9, and 92.0 °C and found to be virtually quantitative. The reaction kinetics, as measured by loss of the starting complex 11 relative to ferrocene, added as an internal reference, with time, were consistently found to be first-order, and the observed rate constants are summarized in Table I. An Arrhenius plot of the data obtained from the thermolysis of 11 gives the expected straight line, yielding at 82 °C $\Delta H^\ddagger = 20.30$ (43) kcal mol⁻¹ and $\Delta S^\ddagger = -19.0$ (9) eu.

A study of the effect of substituents on the migrating phenyl group in this rearrangement has been carried out by preparing $\text{Cp}_2\text{ZrAr[CH(SC}_6\text{H}_5\text{)(Si(CH}_3\text{)}_3\text{)]}$ (Ar = *p*-C₆H₄CH₃ (13), *p*-C₆H₄Cl (14), and *p*-C₆H₄OCH₃ (15)) and measuring the rate of rearrangement in $\text{C}_6\text{D}_5\text{CD}_3$ at 81.9 °C. The kinetics for the thermally induced rearrangement of complexes 13 and 15 were followed by ^1H NMR measuring the loss of starting material and formation of the rearrangement product relative to internal ferrocene or toluene reference with time. The measured rate constants for

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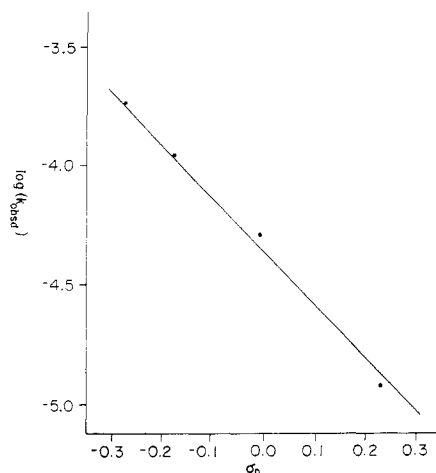
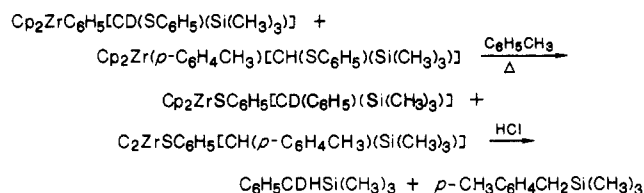


Figure 1. Hammett plot for the thermal rearrangement of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(p\text{-C}_6\text{H}_4\text{X})[\text{CH}(\text{SC}_6\text{H}_5)(\text{Si}(\text{CH}_3)_3)]$ ($\text{X} = \text{H}, \text{CH}_3, \text{OCH}_3, \text{Cl}$) at 81.9 °C in toluene- d_6 .

Scheme I



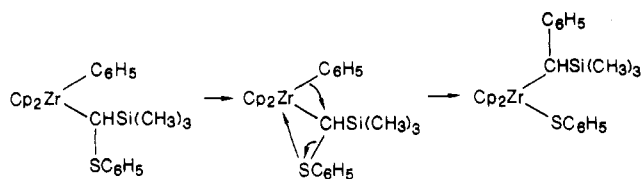
disappearance of starting material and the appearance of product for complexes 13 and 15 were found to be within experimental error (Table I), indicating the quantitative nature of this rearrangement in these complexes. In the case of complex 14 only the loss of starting material could be measured due to an apparent slow degradation of the primary reaction product. A Hammett plot of σ_p for the phenyl substituent versus $\log(k_{\text{obsd}})$ at 81.9 °C, for the rearrangement of complexes 11, 13, 14, and 15, produces a linear plot with good fit (Figure 1), yielding $\rho = -2.22$ (9).¹¹ The negative value of ρ observed for this rearrangement is consistent with a nucleophilic attack of the phenyl group to the methylene carbon via a cyclic transition state.

The intramolecular nature of the thermally induced rearrangement of 11 was verified by a crossover experiment. Thermolysis of a toluene solution, 0.1 M in $\text{Cp}_2\text{Zr}(p\text{-C}_6\text{H}_4\text{CH}_3)[\text{CH}(\text{Si}(\text{CH}_3)_3)(\text{SC}_6\text{H}_5)]$ (13) and 0.1 M in $\text{Cp}_2\text{ZrC}_6\text{H}_5[\text{CD}(\text{Si}(\text{CH}_3)_3)(\text{SC}_6\text{H}_5)]$ (11a) at 82.0 °C for 48 h followed by hydrolysis with HCl produced only benzyltrimethylsilane- d_1 and (*p*-methylbenzyl)trimethylsilane- d_0 with no observed crossover products (less than 2%) (Scheme I).

The "reductive elimination" mechanism (1) can account for the production of 2 and the retention of stereochemistry; however it would also be expected to lead to complexes such as 9. However, we have not observed any organometallic complexes or hydrolysis product corresponding to 9.

The labeling and crossover experiments and the kinetic data presented above clearly demonstrate that the rearrangement of these aryl α -zirconocenyl thioethers proceeds in an intramolecular fashion. The linear free energy relationship determined for this reaction and the retention

Scheme II



of stereochemistry of the arene ring are consistent with the intramolecular nucleophilic attack (migration) of the phenyl group to the methylene carbon with commensurate breaking of the C-S bonds as depicted in Scheme II. The failure of complexes 6 and 7 to undergo thermally induced rearrangement under conditions which readily cause the rearrangement of aryl α -zirconocenyl thioethers can be understood in terms of the greater migratory aptitude of a phenyl group, relative to the methyl and benzyl groups in nucleophilic migrations.¹¹ The intramolecular nucleophilic attack with anchimeric activation of the thiophenyl group by the neighboring Cp_2Zr depicted in Scheme II requires that the phenylthio group be in the "outside" position in the ground state with the (phenylthio)(trimethylsilyl)methyl group functioning as an η^2 four-electron ligand or that this "outside" η^2 conformation is accessible in a thermally excited state.¹² It has previously been well-established that the (methylthio)methyl group can serve as an η^2 four-electron ligand in organometallic systems.¹⁰ Recently Erker et al. have shown that the methoxydiphenylmethyl group in $\text{Cp}_2\text{ZrCl}[\text{C}(\text{OCH}_3)(\text{C}_6\text{H}_5)_2]$ serves as an η^2 four-electron ligand; however, it was shown that the OCH_3 group is in the "inside position" in the ground state; however, the OCH_3 outside conformation is proposed to be close enough in energy to be chemically significant.^{4a} The dynamic behavior of α -zirconocenyl thioethers has recently been demonstrated and the chemical availability of the SC_6H_5 "outside" conformation is clearly possible.¹⁶ We believe that the results of our current study on the thermal rearrangement of aryl α -zirconocenyl thioethers support an intramolecular rearrangement pathway as shown in Scheme II.

We believe that the intramolecular carbon-carbon-bond forming reaction observed in aryl α -zirconocenyl thioethers may serve as a possible molecular model for the fate of hydroxymethyl metal complexes and metallaioxirane complexes proposed as intermediates in the Fischer-Tropsch and related reactions.

Experimental Section

All operations were performed under vacuum or an atmosphere of dry nitrogen or argon on a double manifold, high vacuum line or in a Vacuum Atmospheres glovebox under a nitrogen atmo-

(12) The ground-state structure for (η^2 -acyl)zirconocene complexes have been shown to have the oxygen in the inside position;^{1a,7,9c,13} however, the oxygen atom outside conformation has been shown to be close enough in energy to be chemically significant^{3b,14} and in (η^2 -iminoacyl)zirconocene complexes the nitrogen inside and outside conformations are close enough in energy to coexist at 25 °C.¹⁵

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sphere. Solvents were prepurified by distillation from Na/K alloy under nitrogen. Solvents used on the high vacuum line were vacuum distilled into flasks containing $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-Cl})_2\text{Zn}]^{17}$ and redistilled under vacuum prior to use. Bis(cyclopentadienyl)zirconium dichloride (Alfa), *n*-butyllithium (Aldrich), methylmagnesium bromide (Aldrich), phenylmagnesium bromide (Aldrich), and benzylmagnesium chloride (Alfa) were used as received, $\text{C}_6\text{H}_5\text{SCH}_2\text{Si}(\text{CH}_3)_3$,¹⁸ $\text{CH}_3\text{SCH}_2\text{Si}(\text{CH}_3)_3$,¹⁹ and complexes 1, 6, 7, and 11¹⁶ were prepared by published procedures.

¹H NMR spectra were recorded at 60 MHz on a Varian EM-360 NMR spectrometer or at 270 MHz on a JEOL GX 270 NMR spectrometer. ¹³C NMR spectra were recorded at 20 MHz on a Varian CFT-20 NMR spectrometer or at 67.5 MHz on a JEOL GX 270 NMR spectrometer. Spectra were measured in C_6D_6 or $\text{C}_6\text{D}_5\text{CD}_3$ by using residual solvent peaks or tetramethylsilane as an internal standard. Melting points were determined on a Mel-Temp apparatus in sealed tubes under nitrogen and are uncorrected. GC/MS data was collected on a Finnigan Model GC/MS 4021 mass spectrometer fitted with a Finnigan 9610 GC using a 30-m SE-30 capillary column. Elemental analyses were performed by E-R Microanalytical Laboratory, Inc., Corona, NY, or Microlytics, S. Deerfield, MA.

Initial thermolysis experiments and kinetic experiments were performed on 0.2 M solutions of the α -zirconocenyl thioethers in sealed NMR tubes. A small amount of toluene or ferrocene was added when kinetic experiments were performed. The tubes were then attached to a high vacuum line. After freezing the solutions in the NMR tubes, the tubes were sealed under vacuum. The tubes were then placed in a thermostated bath calibrated with a Precision thermometer and ¹H NMR spectra periodically recorded on a Varian EM-360 NMR spectrometer at room temperature by quenching the sample tubes in an ice bath and then allowing them to warm to room temperature before taking the spectra, or the sealed NMR tube was placed into the thermostated probe of the JEOL GX-270 and ¹H NMR taken by using standard accumulation parameters using a locally written program. In the later case the reaction temperatures were maintained by the JEOL probe temperature controller. The resonance due to the methyl group of the added toluene or cyclopentadienyl group of ferrocene was used as an internal integration standard when kinetic experiments were performed. All data reduction was accomplished by using nonweighted linear least squares.

Preparative thermolyses were performed in tubes fitted with a high vacuum stopcock and a side arm with a ground-glass joint used to attach the tube to a high vacuum line. The α -zirconocenyl thioethers were added to the tubes in a drybox, and the tubes were evacuated. Toluene or benzene was vacuum transferred into the tubes, and the stopcocks were closed. The tubes were placed into a thermostated bath for the appropriate time period. Individual workups are described below.

Preparation of Bis(η^5 -cyclopentadienyl)*p*-tolyl[(phenylthio)(trimethylsilyl)methyl]zirconium, ($\eta^5\text{-C}_5\text{H}_5$)₂Zr(*p*-CH₃C₆H₄)[CH(SC₆H₅)(Si(CH₃)₃)] (13). *p*-Tolylmagnesium bromide in 15 mL of ether, prepared from 4-bromotoluene (1.0 mL 8.2 mmol) and excess magnesium in 15 mL of ether, was added dropwise to a suspension of 2.00 g (4.05 mmol) of ($\eta^5\text{-C}_5\text{H}_5$)₂ZrCl[CH(Si(CH₃)₃)SC₆H₅] in 25 mL of ether at room temperature. The reaction mixture was allowed to stir overnight in the absence of light. The solvents were removed under vacuum, and the reaction vessel was taken into a drybox, fitted with a pressure-equalizing fritted filter assembly, and attached to a high vacuum line via horizontal pivoting arm. The residue was then extracted twice with pentane and the pentane removed under vacuum to give 1.70 g (83% yield) of 13 as a light yellow microcrystalline solid: mp 50 °C dec; ¹H NMR (60 MHz, C_6D_6) δ 0.30 (9 H, s, Si(CH₃)₃), 1.85 (1 H, s, CH), 2.40 (3 H, SiCH₃), 5.55 (5 H, s, Cp), 5.70 (5 H, s, Cp), 6.6–7.7 (9 H, m, Ar); ¹³C{¹H} NMR (20 MHz, C_6D_6) δ 2.05 (Si(CH₃)₃), 21.19 (CH₃), 61.55 (CH), 108.40 (Cp), 108.54 (Cp), 126.8 (*o*-Ar), 127.14 (*p*-Ar), 128.4 (*m*-Ar), 129.67 (*m*-Ar), 139.68 (*i*-Ar), 141.90 (*o*-Ar), 148.0 (*i*-Ar), 172.00 (*i*-Ar).

Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{SiSiZr}$: C, 63.85; H, 6.35. Found: C, 63.73; H, 6.48.

Preparation of Bis(η^5 -cyclopentadienyl)(*p*-chlorophenyl)[(phenylthio)(trimethylsilyl)methyl]zirconium, ($\eta^5\text{-C}_5\text{H}_5$)₂Zr(*p*-ClC₆H₄)[CH(SC₆H₅)(Si(CH₃)₃)] (14). In a manner similar to that described for 13, (*p*-chlorophenyl)magnesium bromide, prepared from 4-bromochlorobenzene (1.57 g, 8.2 mmol) and excess magnesium in 30 mL of ether, was added dropwise to a suspension of 2.00 g (4.05 mmol) of ($\eta^5\text{-C}_5\text{H}_5$)₂ZrCl[CH(SC₆H₅)(Si(CH₃)₃)] in 25 mL of ether at room temperature. The reaction mixture was allowed to stir overnight in the absence of light. Upon removal of the solvent under vacuum workup as described for 13 gave 1.5 g (68% yield) of 14 as a light yellow microcrystalline solid: mp 126–130 °C; ¹H NMR (60 MHz, C_6D_6) δ 0.21 (9 H, s, Si(CH₃)₃), 1.84 (1 H, s, CH), 5.51 (5 H, s, Cp), 5.74 (5 H, s, Cp), 6.95–7.72 (9 H, m, Ar); ¹³C{¹H} NMR (67.5 MHz, C_6D_6) δ 2.0 (Si(CH₃)₃), 27 (CH, br), 108.7 (Cp), 126.3 (*o*-Ar), 127.1 (*p*-Ar), 128.8 (*m*-Ar), 129.3 (*m*-Ar), 129.9 (*i*-Ar), 139.2 (*i*-Ar), 143.1 (*o*-Ar), 173.9 (*i*-Ar).

Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{ClSiSiZr}$: C, 58.12; H, 5.44. Found: C, 58.37; H, 5.32.

Preparation of Bis(η^5 -cyclopentadienyl)*p*-anisyl[(phenylthio)(trimethylsilyl)methyl]zirconium, ($\eta^5\text{-C}_5\text{H}_5$)₂Zr(*p*-C₆H₄OCH₃)[CH(SC₆H₅)(Si(CH₃)₃)] (15). In a manner similar to that described for 13, (*p*-methoxyphenyl)magnesium bromide, prepared from 4-bromoanisole (1.0 g, 5.3 mmol) and excess magnesium in 30 mL of ether, was added dropwise to a suspension of 2.00 g (4.05 mmol) of ($\eta^5\text{-C}_5\text{H}_5$)₂ZrCl[CH(SC₆H₅)(Si(CH₃)₃)] in 25 mL of ether at room temperature. The reaction mixture was allowed to stir overnight in the absence of light. Upon removal of the solvent under vacuum workup as described for 13 gave 1.0 g (47% yield) of 15 as a yellow oil, mixed with a small amount of the rearrangement product: ¹H NMR (60 MHz, C_6D_6) δ 0.41, 0.47 (9 H, s, Si(CH₃)₃), 1.82 (1 H, s, CH), 3.42, 3.70 (3 H, s, OCH₃), 5.63, 5.84 (10 H, s, Cp), 6.8–7.8 (9 H, m, Ar).

Preparation of Bis(η^5 -cyclopentadienyl)phenyl[deuterio(phenylthio)(trimethylsilyl)methyl]zirconium, ($\eta^5\text{-C}_5\text{H}_5$)₂ZrC₆H₅[CD(SC₆H₅)(Si(CH₃)₃)] (11a). Complex 11a was prepared by the procedure reported for ($\eta^5\text{-C}_5\text{H}_5$)₂ZrC₆H₅[CH(Si(CH₃)₃)SC₆H₅] except that $\text{C}_6\text{H}_5\text{SCD}_2\text{Si}(\text{CH}_3)_3$ was used in place of $\text{C}_6\text{H}_5\text{SCH}_2\text{Si}(\text{CH}_3)_3$. The $\text{C}_6\text{H}_5\text{SCD}_2\text{Si}(\text{CH}_3)_3$ was prepared by treating $\text{C}_6\text{H}_5\text{SCH}_2\text{Si}(\text{CH}_3)_3$ with *n*-butyllithium in THF followed by quenching with D₂O. This process was repeated three times and the product distilled. By ¹H NMR the sample was greater than 98% d₂.

Thermolysis of Cp₂ZrC₆H₅[CH(SCH₃)(Si(CH₃)₃)] (1). A 0.2 M solution of 1 was prepared in a sealed NMR tube and thermolyzed at 82 °C. The reaction was followed by ¹H NMR. As the two cyclopentadienyl resonances for 1 disappeared, two new cyclopentadienyl resonances "grew in" at approximately the same rate. These new resonances disappeared at a slower rate with the simultaneous formation of a yellow precipitate. After 1 week at 82 °C, the peaks corresponding to 1 had disappeared completely.

Another tube containing a 0.2 M solution of 1 was sealed and thermolyzed at 95 °C for 22 h. The tube was broken and the volatile organic materials were separated by vacuum distillation, leaving a pale yellow residue. The major organic product was identified as benzyltrimethylsilane, $\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{CH}_3)_3$, which was characterized by ¹H NMR and GC/MS comparison with an authentic sample.²⁰

A preparative thermolysis of 1 was performed by dissolving 2.00 g of 1 in 15 mL of toluene as described above. The tube was thermolyzed at 82 °C for 5 days. The sample tube was taken into a drybox, fitted with a pressure-equalizing fritted filter assembly, and attached to a high vacuum line. The toluene was removed under vacuum, and 50 mL of pentane was vacuum transferred into the tube. The resulting solution was filtered, and the pentane was removed under vacuum to yield 1.16 g (58% yield) of ($\eta^5\text{-C}_5\text{H}_5$)₂Zr(SCH₃)[CH(C₆H₅)(Si(CH₃)₃)] (2): ¹H NMR (60 MHz, C_6D_6) δ 0.10 (9 H, s, Si(CH₃)₃), 2.18 (3 H, s, SCH₃), 2.24 (1 H, s, CH), 5.65 (5 H, s, Cp), 5.88 (5 H, s, Cp), 6.8–7.2 (5 H, m, C₆H₅); ¹³C{¹H} NMR (20 MHz, C_6D_6) δ 3.19 (Si(CH₃)₃), 20.93 (SCH₃), 62.09 (CH), 101.15 (Cp), 111.06 (Cp), 120.67 (*p*-Ar), 128.15 (*o*-m-Ar), 152.32 (*i*-Ar).

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Anal. Calcd for $C_{21}H_{28}SSiZr$: C, 58.14; H, 6.54. Found: C, 58.06, H, 6.51.

Thermolysis of $Cp_2Zr(SCH_3)[CH(C_6H_5)(Si(CH_3)_3)]$ (2). A tube containing a 0.2 M solution of 2 was sealed and thermolyzed at 100 °C for 24 h. The tube was broken in a drybox, and the solution was transferred to a flask. The flask was attached to a high vacuum line, and the volatiles were vacuum transferred into another flask. Benzyltrimethylsilane was identified as the major organic product by NMR and GC comparison with authentic sample. The yield was 80% as determined by GC using an internal standard.

Thermolysis of $Cp_2ZrCH_3[CH(SCH_3)(Si(CH_3)_3)]$ (6). Complex 6 (1.011 g, 2.74 mmol) was dissolved in 14 mL of toluene and heated to 82.0 °C for 1 week in the dark. Upon cooling to room temperature the solvent was removed under vacuum and the residue extracted with two 10-mL portions of hexane. The hexane was removed under vacuum to give 0.924 g (91% yield) of 6 which was found by 1H and ^{13}C NMR to be identical with an authentic sample.¹⁶

Thermolysis of $Cp_2ZrCH_2C_6H_5[CH(SCH_3)(Si(CH_3)_3)]$ (7). Complex 7 (1.024 g, 2.3 mmol) was dissolved in 12 mL of toluene and heated to 82.0 °C for 1 week in the dark. Upon cooling to room temperature the solvent was removed under vacuum and the residue extracted with two 20-mL portions of hexane. This hexane solution was concentrated under vacuum and cooled to 0 °C to precipitate 7. The hexane was decanted and the solid dried under vacuum to give 0.929 g of 7 (91% yield) which was found by 1H and ^{13}C NMR to be identical with an authentic sample.¹⁶

Thermolysis of $Cp_2ZrC_6H_5[CH(SC_6H_5)(Si(CH_3)_3)]$ (11). A 0.2 M solution of 11 was prepared in a sealed NMR tube and thermolyzed at 82 °C. The reaction was followed by 1H NMR, and after 25 h at 82 °C the NMR peaks corresponding to 11 had disappeared completely.

A preparative thermolysis of 11 was performed by dissolving 0.30 g (0.61 mmol) of 11 in 10 mL of toluene. The tube was thermolyzed at 82 °C for 2 days. The sample tube was taken into a drybox, fitted with a pressure-equalizing fritted filter assembly, and attached to a high vacuum line. The volatiles were removed under vacuum, and 30 mL of pentane was vacuum transferred into the tube. The resulting solution was washed with 10 mL of pentane, and the pentane was removed under vacuum to yield 0.25 g (83% yield) of $(\eta^5-C_5H_5)_2Zr(SC_6H_5)[CH(C_6H_5)(Si(CH_3)_3)]$ (12): mp 128 °C; 1H NMR (270 MHz, C_6D_6) δ 0.28 (9 H, s, $Si(CH_3)_3$), 2.26 (H, s, CH), 5.52 (5 H, s, Cp), 6.02 (5 H, s, Cp), 6.9–7.2 (10 H, m, Ar); $^{13}C\{^1H\}$ (67.5 MHz, C_6D_6) δ 3.13 ($Si(CH_3)_3$), 62.61 (CH), 112.75 (Cp), 112.85 (Cp), 121.78 (*p*-Ar), 125.84 (*p*-Ar),

128.3 (*m*-Ar), 129.06 (*o*-Ar), 129.79 (*o*-Ar), 133.19 (*m*-Ar), 147.71 (*o*-Ar), 153.22 (*i*-Ar).

Anal. Calcd for $C_{26}H_{30}SSiZr$: C, 63.23; H, 6.12. Found: C, 63.02; H, 6.37.

Thermolysis of $Cp_2Zr(p-CH_3C_6H_4)[CH(SC_6H_5)(Si(CH_3)_3)]$ (13). A 0.2 M solution of 13 was prepared in a sealed NMR tube and thermolyzed at 82 °C. The reaction was followed by 1H NMR, and after 12 h at 82 °C the peaks corresponding to 13 had completely disappeared. As the peaks for 13 disappeared, peaks corresponding to $(\eta^5-C_5H_5)_2Zr(SC_6H_5)[CH(p-C_6H_4CH_3)(Si(CH_3)_3)]$ "grew in" at the same rate. The tube was then broken, and 1.0 mL of concentrated HCl was added. After the aqueous and organic layers were mixed and the layers allowed to separate, the organic layer was transferred into a flask. The volatiles were then separated from the nonvolatiles by vacuum distillation. The major product was identified by NMR and GC/MS as *p*-xylyltrimethylsilane, *p*- $CH_3C_6H_4CH_2Si(CH_3)_3$.

Thermolysis of an Equimolar Mixture of $Cp_2Zr(p-CH_3C_6H_4)[CH(SC_6H_5)(Si(CH_3)_3)]$ (13) and $Cp_2ZrC_6H_5[CD_3(C_6H_5)(Si(CH_3)_3)]$ (11a). A solution that was 0.1 M in both 11a and 13 was prepared by dissolving 1.5×10^{-4} mol of 11a and 13 in a total volume of 1.5 mL of $C_6D_5CD_3$. The tube was sealed and thermolyzed at 82 °C for 48 h. The tube was broken, and 1.0 mL of concentrated HCl was added to the solution. After the organic and aqueous layers were mixed, the NMR tube was placed in a centrifuge. The organic layer was then transferred into a flask, and the volatiles were separated from the nonvolatiles by vacuum distillation. The major organic products were identified by GC/MS as benzyltrimethylsilane-*d*₁, $C_6H_5CHDSi(CH_3)_3$, and *p*-xylyltrimethylsilane, *p*- $CH_3C_6H_4CH_2Si(CH_3)_3$. There was less than 2% benzyltrimethylsilane, $C_6H_5CH_2Si(CH_3)_3$, or *p*-xylyltrimethylsilane-*d*₁, *p*- $CH_3C_6H_4CHDSi(CH_3)_3$, as determined by GC/MS.

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Registry No. 1, 96445-77-1; 2, 96445-78-2; 6, 96445-79-3; 7, 96445-80-6; 11, 102493-96-9; 11a, 111005-10-8; 12, 111005-11-9; 13, 111005-12-0; 14, 111005-13-1; 15, 111005-14-2; $(\eta^5-C_5H_5)_2ZrCl[CH(Si(CH_3)_3)SC_6H_5]$, 102493-94-7; 4-bromotoluene, 106-38-7; 4-bromochlorobenzene, 106-39-8; 4-bromoanisole, 104-92-7.