Organometallics 1986, *5*, 1585–1589 1585

Preparation and Properties of α-Zirconocenyl Thioethers

A. Steven Ward, Eric A. Mintz,* and Mike R. Ayers

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

Received November 13, 1985

Treatment of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ with 1 equiv of α-lithio thioethers produces the corresponding α-zirconocenyl thioethers $(\eta^5\text{-}C_5H_5)_2ZrCl[CH(SR)R']$ (R = CH_3, C_6H_5; R′ = $SiMe_3$, C_6H_5) in good yield. These α-zirconocenyl thioethers are conveniently alkylated with Grignard reagents to produce the corresponding alkyl and aryl complexes $(\eta^5\text{-}C_5H_5)_2ZrR''[CH(SR)R']$ (R″ = CH_3, C_6H_5, $CH_2C_6H_5$) in moderate yield. Treatment of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ with 2 equiv of $Li[CH(SC_6H_5)(C_6H_5)]$ or $LiCH_2SC_6H_5$ produces the corresponding bis(α-alkylthio) complexes $(\eta^5\text{-}C_5H_5)_2Zr[CH(SC_6H_5)(C_6H_5)]_2$ and $(\eta^5\text{-}C_6H_5)_2Zr(CH_2SC_6H_5)_2$ in moderate yield. NMR evidence is presented which suggests that the (methylthio)methyl and (phenylthio)methyl groups in these complexes serve as η^2 four-electron ligands.

Introduction

We have recently reported preliminary studies on the synthesis and thermal reactivity of the α-zirconocenyl thioethers $(\eta^5\text{-}C_5H_5)_2ZrCl[CH(Si(CH_3)_3)SCH_3]$ (**1**) and $(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)[CH(Si(CH_3)_3)SCH_3]$ (**2**).[1] The α-zirconocenyl thioethers **1** and **2** were found to be indefinitely stable in the dark at room temperature in an inert atmosphere, in sharp contrast to the analogous α-zirconocenyl ether $(\eta^5\text{-}C_5H_5)_2ZrCl[C(C_6H_5)_2OCH_3]$ which Erker et al.[2,3] have reported to be unstable with a half-life of 48 h at room temperature.

Although complex **1** proved to be extremely robust, having a half-life of greater than 1 month in toluene at 100 °C, the phenyl analogue **2** was found to undergo thermally induced rearrangement at 82 °C to give $(\eta^5\text{-}C_5H_5)_2Zr(SCH_3)[CH(Si(CH_3)_3)(C_6H_5)]$ (**3**) (eq 1) with a first-order

$$(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)[CH(Si(CH_3)_3)SCH_3] \xrightarrow[C_6H_5CH_3,\ 22\ h]{82\ °C} (\eta^5\text{-}C_5H_5)_2Zr(SCH_3)[CH(Si(CH_3)_3)(C_6H_5)] \quad (1)$$

rate constant of $8.14 \times 10^{-6}\ s^{-1}$. The stability and reactivity patterns of complexes **1** and **2** suggest that the (methylthio)(trimethylsilyl)methyl group in these complexes serves as a η^2 four-electron donor ligand analogous to that reported in $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_2SCH_3)$,[4] $Ni(PPh_3)(Cl)(\eta^2\text{-}CH_2SCH_3)$,[5] $Pd(PPh_3)_2(\eta^2\text{-}CH_2SCH_3)X$,[6] $Fe(PMe_3)_3(\eta^2\text{-}CH_2SCH_3)Cl$,[7] $[(CH_3)_2Ga(N_2C_3H_3)(OCH_2CH_2N(CH_3)_2)]Mo(CO)_2(\eta^2\text{-}CH_2SCH_3)$, and $[(CH_3)_2Ga(N_2C_5H_7)(OCH_2CH_2N(CH_3)_2)]Mo(CO)_2(\eta^2\text{-}CH_2SCH_3)$.[8] This bonding mode would be analogous to that found for acyl– and iminoacyl–zirconocene complexes $(\eta^5\text{-}C_5H_5)_2Zr(X)(\eta^2\text{-}COR)$[9] and $(\eta^5\text{-}C_5H_5)_2Zr(X)[\eta^2\text{-}C(NR)R']$,[10] in contrast to the more sterically hindered (diphenylphosphino)- and (dimethylphosphino)methyl groups in $(\eta^5\text{-}C_5H_5)_2ZrX[CH_2PR_2]$.[11,12]

As part of our ongoing studies on the effect of α-heteroatom substitution in alkyl complexes of the early transition metals, we report here the preparation and properties of α-zirconocenyl thioethers.

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 atmosphere. Solvents were prepurified by distillation from Na/K alloy under nitrogen. Solvents used on the high vacuum line were vacuum distilled into flasks containing $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}Cl)_2]_2Zn$[13] and redistilled under vacuum prior to use. Bis(cyclopentadienyl)zirconium dichloride (Alfa), *n*-butyllithium (Aldrich), methylmagnesium bromide (Aldrich), phenylmagnesium bromide (Aldrich), benzylmagnesium chloride (Alfa), benzyl phenyl sulfide (Aldrich), and methyl phenyl sulfide (Aldrich) were used as purchased. [(Methylthio)methyl]trimethylsilane, $CH_3SCH_2Si(CH_3)_3$,[14] and [(phenylthio)methyl]trimethylsilane, $C_6H_5SCH_2Si(CH_3)_3$,[15] were prepared by published procedures.

^1H spectra were recorded at 60 MHz on a Varian EM-360 NMR spectrometer or at 270 MHz on a JEOL GX 270 NMR spectrometer. ^{13}C 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 at ambient temperature unless otherwise noted in C_6D_6 or $C_6D_5CD_3$ by using residual peaks or tetramethylsilane as an internal standard. Melting points were determined on a Mel-Temp apparatus in sealed tubes under nitrogen and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or E+R Microanalytical Laboratory, Inc., Corona, NY.

Preparation of Bis(η^5-cyclopentadienyl)chloro[(methylthio)(trimethylsilyl)methyl]zirconium, $(\eta^5\text{-}C_5H_5)_2ZrCl[CH(SCH_3)(Si(CH_3)_3)]$ (1). To a 100-mL three-necked flask equipped with a nitrogen inlet adaptor and a septum-capped, pressure-equalizing addition funnel was added 7.1 mL (54 mmol) of $CH_3SCH_2Si(CH_3)_3$ and 30 mL of THF. Hexane (25 mL) and 26 mL (54 mmol) of 2.1 M *n*-butyllithium in hexane were added to the addition funnel. The *n*-butyllithium solution was then added dropwise at room temperature, and the resulting solution was allowed to stir for 4 h at room temperature. This solution was then added dropwise over 2 h to a stirred suspension of 15.0 g (51.4 mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in 100 mL of THF in a 250-mL flask fitted as above at −74 °C (ethyl acetate/liquid-nitrogen slush

---

[1] Mintz, E. A.; Ward, A. S.; Tice, D. S. *Organometallics* **1985**, *4*, 1308–1310.

[2] Erker, G.; Rosenfeldt, F. *Tetrahedron Lett.* **1981**, *22*, 1379–1382.

[3] Erker, G.; Rosenfeldt, F. *Tetrahedron* **1982**, *38*, 1285–1291.

[4] (a) de Gil, E. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3751–3756. (b) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 486–493.

[5] Davidson, J. G.; Borefield, E. K.; Van Derkeer, D. G. *Organometallics* **1985**, *4*, 1178–1184.

[6] (a) Yoshida, G.; Kurosawa, H.; Okawara, R. *J. Organomet. Chem.* **1976**, *113*, 85–89. (b) McPherson, H. M.; Wardell, J. L. *Inorg. Chim. Acta* **1983**, *74*, 37–43. (c) Miki, K.; Kai, Y.; Yasuka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3639–3647. (d) Miki, K.; Kai, Y.; Yasuka, N.; Kasai, N. *J. Organomet. Chem.* **1979**, *165*, 79–91. (e) Yoshida, G.; Matsumura, Y.; Okawara, R. *J. Organomet. Chem.* **1975**, *92*, C53–C56.

[7] Karsch, H. H. *Chem. Ber.* **1977**, *110*, 2699–2711.

[8] Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1980**, *58*, 1080–1090.

[9] (a) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–1950. (b) Erker, G.; Rosenfeldt, F., *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605–606. (c) Erker, G.; Rosenfeldt, F., *J. Organomet. Chem.* **1982**, *224*, 29–42. (d) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *120*, 1747–1748. (e) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103–109. (f) Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596–5598.

[10] Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. C. *J. Organomet. Chem.* **1979**, *174*, C35–C37.

[11] (a) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251–4253. (b) Schore, N. E.; Young, S. J.; Olmstead, M. M. *Organometallics* **1983**, *2*, 1769–1780.

[12] Karsch, H. H.; Muller, G.; Kruger, C. *J. Organomet. Chem.* **1984**, *273*, 195–212.

[13] Sekutowski, D. G.; Stucky, G. D. *J. Chem. Educ.* **1976**, *53*, 110.

[14] Peterson, D. J. *J. Org. Chem.* **1967**, *32*, 1717–1720.

[15] Ager, D.; Cookson, R. *Tetrahedron Lett.* **1980**, 1677–1680.

0276-7333/86/2305-1585$01.50/0 © 1986 American Chemical Society

bath). After addition was complete, the reaction mixture was allowed to warm to room temperature and stirring was continued overnight at room temperature. The solvents were removed under vacuum, and the reaction vessel was taken into a drybox and fitted with a pressure-equalizing fritted filter assembly and attached to a high vacuum line via a horizontal pivoting arm. Next, 100 mL of toluene was vacuum transferred onto the residue and the resulting solution filtered. The toluene was removed under vacuum, and 100 mL of pentane was then vacuum transferred onto the toluene-soluble product. The resulting suspension was filtered, and the pentane was removed under vacuum to give 16.1 g (80.3% based on $(\eta^5\text{-}C_5H_5)_2ZrCl_2$) of 1 as a white microcrystalline solid: mp 113–114 °C dec; ^{1}H NMR (270 MHz, $C_6D_5CD_3$) δ 0.28 (9 H, s, $Si(CH_3)_3$), 1.14 (1 H, s, CH), 1.86 (3 H, s, SCH_3), 5.80 (5 H, s, Cp), 5.83 (5 H, s, Cp); $^{13}C\{^1H\}$ NMR (67.5 MHz, $C_6D_5CD_3$, 50 °C) δ 2.16 ($Si(CH_3)_3$), 25.87 (SCH_3), 47.45 (CH), 110.40 (Cp), 112.32 (Cp).

Anal. Calcd for $C_{15}H_{23}ClSSiZr$: C, 46.18; H, 5.94. Found: C, 46.07; H, 5.84.

Preparation of Bis(η^5-cyclopentadienyl)phenyl[(methylthio)(trimethylsilyl)methyl]zirconium, $(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)[CH(SCH_3)(Si(CH_3)_3)]$ (2). To a solution of 5.00 g (12.8 mmol) of 1 in 150 mL of ether was added dropwise at room temperature in the absence of light 4.70 mL (14.1 mmol) of 3.0 M C_6H_5MgBr in ether. The resulting solution was allowed to stir at room temperature overnight. The solvents were removed under vacuum, and the flask was fitted with an apparatus as described for 1. After extraction with two 50-mL portions of pentane, the solution was concentrated under vacuum to 10 mL. The solution was then decanted to yield 4.55 g (82.2% based on 1) of a white microcrystalline solid: mp 84–85 °C; ^{1}H NMR (60 MHz, C_6D_6) δ 0.15 (9 H, s, $Si(CH_3)_3$), 0.80 (1 H, s, CH), 1.60 (3 H, s, SCH_2), 5.45 (5 H, s, Cp), 5.60 (5 H, s, Cp), 7.1–7.4 (3 H, m, Ar), 7.6–7.9 (2 H, m, Ar); $^{13}C\{^1H\}$ NMR (67.5 MHz, C_6D_6) δ 2.06 ($Si(CH_3)_3$), 25.72 (SCH_3), 36.29 (CH), 107.35 (Cp), 108.73 (Cp), 123.73 (*p*-Ar), 127.16 (*m*-Ar), 143.20 (*o*-Ar), 175.81 (ipso Ar).

Anal. Calcd for $C_{21}H_{28}SSiZr$: C, 58.14; H, 6.54. Found: C, 58.18; H, 6.53.

Bis(η^5-cyclopentadienyl)chloro[(phenylthio)(trimethylsilyl)methyl]zirconium, $(\eta^5\text{-}C_5H_5)_2ZrCl[CH(SC_6H_5)(Si(CH_3)_3)]$ (4). To a solution of 3.7 mL (18 mmol) of $C_6H_5SCH_2Si(CH_3)_3$ in 10 mL of THF was added dropwise at room temperature 12 mL (18 mmol) of 1.55 M *n*-butyllithium in hexane which had been diluted with an additional 10 mL of hexane. The resulting solution was allowed to stir at room temperature for 5 h and was then added dropwise over a 40-min period to a suspension of 5.00 g (17.1 mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in 35 mL of THF at –74 °C. The reaction mixture was then allowed to warm to room temperature and to stir overnight. The solvents were removed under vacuum, and the flask was fitted with an apparatus as described for 1. The product was extracted with one 50-mL portion of toluene. The toluene was removed under vacuum, and the residue was washed with two 50-mL portions of hexane to yield 4.75 g (61.4% based on $(\eta^5\text{-}C_5H_5)_2ZrCl_2$) as an orange microcrystalline solid: mp 102–103 °C dec; ^{1}H NMR (270 MHz, C_6D_6) δ 0.35 (9 H, s, $Si(CH_3)_3$), 2.20 (1 H, s, CH), 5.63 (5 H, s, Cp), 5.79 (5 H, s, Cp), 6.92 (1 H, d, P–Ar), 7.00 (2 H, t, *m*-Ar), 7.28 (2 H, d, *o*-Ar), 7.5 (5 H, m, Ar); $^{13}C\{^1H\}$ NMR (67.5 MHz, C_6D_6) δ 1.71 ($Si(CH_3)_3$), 30.52 (CH), 110.90 (Cp), 111.49 (Cp), 127.01 (*o*-Ar), 127.17 (*p*-Ar), 129.20 (*m*-Ar), 138.69 (ipso Ar).

Anal. Calcd for $C_{20}H_{25}ClSSiZr$: C, 53.12; H, 5.57. Found: C, 53.36; H, 5.69.

Preparation of Bis(η^5-cyclopentadienyl)chloro[phenyl(phenylthio)methyl]zirconium, $(\eta^5\text{-}C_5H_5)_2ZrCl[CH(SC_6H_5)(C_6H_5)]$ (5). To a solution of 11.8 g (59.0 mmol) of $C_6H_5CH_2SC_6H_5$ in 50 mL of THF was added dropwise at room temperature 38.1 mL (59.0 mmol) of 1.55 M *n*-butyllithium in hexanes. The resulting solution was allowed to stir at room temperature overnight and was then added dropwise to a suspension of 15.0 g (51.4 mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in 150 mL of ether at 0 °C and was then allowed to stir for 1 h. The solvents were removed under vacuum, and the flask was fitted with an apparatus as described for 1. The product was extracted with one 100-mL portion of toluene. The toluene was removed under vacuum, and the residue was washed with six 75-mL portions of cold ether to yield 10.4 g (45% based on $(\eta^5\text{-}C_5H_5)_2ZrCl_2$) of 5 as a yellow microcrystalline solid: mp 121–123 °C dec; ^{1}H NMR (270 MHz, C_6D_6) δ 4.58 (2 H, s, CH), 5.33 (0.7 H, s, Cp), 5.62 (5 H, s, Cp), 5.67 (0.7 H, s, Cp), 5.68 (5 H, s, Cp), 6.84 (1 H, t, *p*-Ar), 6.89 (2 H, t, *m*-Ar), 6.95 (1 H, t, *p*-Ar), 7.23 (2 H, t, *m*-Ar), 7.37 (2 H, d, *o*-Ar), 7.58 (2 H, d, *o*-Ar); $^{13}C\{^1H\}$ NMR (67.5 MHz, C_6D_6) δ 50.50 (CH), 60.63 (CH), 110.32 (Cp), 110.27 (Cp), 112.87 (Cp), 113.10 (Cp). 123.47 (Ar), 125.77 (Ar), 126.20 (Ar), 127.26 (Ar), 127.76 (Ar), 128.34 (Ar), 128.68 (Ar), 129.11 (Ar), 129.49 (Ar), 129.63 (Ar), 139.85 (ipso Ar), 149.04 (ipso Ar).

Anal. Calcd for $C_{23}H_{21}ClSZr$: C, 60.56; H, 4.64. Found: C, 60.69; H, 4.82.

Preparation of Bis(η^5-cyclopentadienyl)methyl[(methylthio)(trimethylsilyl)methyl]zirconium, $(\eta^5\text{-}C_5H_5)_2ZrCH_3[CH(SCH_3)(Si(CH_3)_3)]$ (6). To a suspension of 5.00 g (12.8 mmol) of 1 in 150 mL of ether was added dropwise at room temperature 4.4 mL (14 mmol) of 3.2 M CH_3MgBr in ether which had been diluted with 50 mL of ether. The reaction mixture was allowed to stir overnight in the absence of light. The solvents were removed under vacuum, and the flask was fitted with an apparatus as described for 1. The product was extracted with two 50-mL portions of hexanes. The solution was then concentrated under vacuum to 10 mL and was cooled to 0 °C. The solvent was decanted to yield 2.88 g (60.9% based on 1) of a red-brown viscous liquid: ^{1}H NMR (60 MHz, C_6D_6) δ 0.05 (3 H, s, $ZrCH_3$), 0.10 (9 H, s, $Si(CH_3)_3$), 1.20 (1 H, s, CH), 1.40 (3 H, s, CH_3), 5.45 (5 H, s, Cp), 5.55 (5 H, s, Cp); $^{13}C\{^1H\}$ NMR (270 MHz, $C_6D_5CD_3$, 50 °C) δ 2.36 ($Si(CH_3)_3$), 15.59 ($ZrCH_3$), 24.66 (SCH_3), 36.06 (CH), 107.64 (Cp), 108.99 (Cp).

Anal. Calcd for $C_{16}H_{26}SSiZr$: C, 51.98; H, 7.09. Found: C, 51.74; H, 6.88.

Preparation of Bis(η^5-cyclopentadienyl)benzyl[(methylthio)(trimethylsilyl)methyl]zirconium, $(\eta^5\text{-}C_5H_5)_2Zr(CH_2C_6H_5)[CH(SCH_3)(Si(CH_3)_3)]$ (7). In a manner similar to that described for 6, 10.8 mL (14.1 mmol) of 1.3 M $C_6H_5CH_2MgCl$ in THF was diluted with 50 mL of THF and was added to 5.00 g (12.8 mmol) of 1 in 150 mL of ether; the reaction mixture was allowed to stir overnight in the absence of light. The solvents were removed under vacuum, and the flask was fitted with an apparatus as described for 1. Extraction with two 50-mL portions of pentane yielded 3.93 g (69.0% based on 1) of a yellow microcrystalline solid: mp 93–94 °C; ^{1}H NMR (60 MHz, C_6D_6) δ 0.10 (9 H, s, $Si(CH_3)_3$), 0.45 (1 H, s, CH), 1.35 (3 H, s, SCH_3), 2.05 (1 H, d, CH_2), 2.55 (1 H, d, CH_2), 5.40 (5 H, s, Cp), 5.45 (5 H, s, Cp), 7.1–7.9 (5 H, m, Ar); $^{13}C\{^1H\}$ NMR (20 MHz, C_6D_6) δ 1.44 ($Si(CH_3)_3$), 23.94 (SCH_3), 30.21 (CH), 38.25 (CH_2), 107.18 (Cp), 108.64 (Cp), 120.09 (*p*-Ar), 126.28 (*m*-Ar), 127.99 (*o*-Ar), 156.60 (ipso Ar).

Anal. Calcd for $C_{22}H_{30}SSiZr$: C, 59.27; H, 6.78. Found: C, 58.95; H, 6.75.

Preparation of Bis(η^5-cyclopentadienyl)phenyl[(phenylthio)(trimethylsilyl)methyl]zirconium, $(\eta^5\text{-}C_5H_5)_2ZrC_6H_5[CH(SC_6H_5)(Si(CH_3)_3)]$ (8). In a manner similar to that for preparing 6, 1.6 mL (4.8 mmol) of 3.0 M C_6H_5MgBr in ether which had been diluted with an additional 10 mL of ether was added to 2.00 g (4.43 mmol) of 4 in 25 mL of ether. The reaction mixture was allowed to stir overnight in the absence of light. Solvents were removed under vacuum, and the flask was fitted with an apparatus as described for 1. Extraction with two 50-mL portions of pentane yielded upon removal of the solvent under vacuum 1.63 g (75% based on 4) of 8 as a yellow microcrystalline solid: mp 124 °C dec; ^{1}H NMR (270 MHz, C_6D_6) δ 0.45 (9 H, s, $Si(CH_3)_3$), 1.99 (1 H, s, CH), 5.69 (5 H, s, Cp), 5.91 (5 H, s, Cp), 6.98 (1 H, t, Ar), 7.05 (2 H, t, Ar), 7.23 (5 H, Ar), 7.75 (2 H, d, Ar); $^{13}C\{^1H\}$ NMR (67.5 MHz, C_6D_6, 50 °C) δ 2.53 ($Si(CH_3)_3$), 28.06 (CH), 109.10 (Cp), 109.33 (Cp), 124.10 (*p*-Ar), 127.10 (*m*-Ar), 127.62 (*p*-Ar), 127.91 (*o*-Ar), 129.70 (*m*-Ar), 140.20 (ipso Ar), 142.40 (*o*-Ar), 176.39 (ipso Ar).

Anal. Calcd for $C_{26}H_{30}SSiZr$: C, 63.23; H, 6.12. Found: C, 63.49; H, 6.30.

Preparation of Bis(η^5-cyclopentadienyl)bis[(phenylthio)methyl]zirconium(IV), $(\eta^5\text{-}C_5H_5)_2Zr(CH_2SC_6H_5)_2$ (9). A 7.6-mL sample of 1.8 M phenyllithium (13.7 mmol) in 75:25 benzene/ether which had been diluted with an additional 20 mL of THF was added dropwise at 0 °C to a solution of 1.6 mL (13.6 mmol) of thioanisole in 10 mL of THF. The resulting solution was allowed to stir at room temperature for 16 h. The resulting solution was then added dropwise to a suspension of 2.00 g (6.8

mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in 20 mL of THF at −74 °C. The reaction mixture was allowed to warm to room temperature and to stir overnight. The solvents were removed under vacuum, and the flask was fitted with an apparatus as described for **1**. The product was extracted with three 15-mL portions of toluene. The resulting toluene solution was concentrated under vacuum, the product was precipitated with pentane, and the product was filtered and washed with two 10-mL portions of pentane to give 1.30 g (41%) of **9** as on an off-white microcrystalline solid: mp 109–111 °C. ^1H NMR (270 MHz, C_6D_6) δ 2.23 (4 H, s, CH_2), 5.50 (10 H, s, Cp), 7.01 (2 H, t, *p*-Ar), 7.18 (4 H, t, *m*-Ar), 7.60 (4 H, d, *o*-Ar); $^{13}C\{^1H\}$ NMR (67.5 MHz, C_6D_6) δ 28.65 (CH_2), 108.31 (Cp), 125.45 (*p*-Ar), 126.65 (*m*-Ar), 129.40 (*o*-Ar), 143.36 (ipso Ar).

Anal. Calcd for $C_{24}H_{24}S_2Zr$: C, 61.62; H, 5.17. Found: C, 61.35; H, 5.28.

Preparation of Bis(η^5-cyclopentadienyl)bis[phenyl(phenylthio)methyl]zirconium(IV), $(\eta^5\text{-}C_5H_5)_2Zr[CH(SC_6H_5)(C_6H_5)]_2$ (10). To a solution of 7.2 g (36 mmol) of $C_6H_5CH_2SC_6H_5$ in 50 mL of THF was added dropwise at room temperature 23 mL (36 mmol) of 1.55 M *n*-butyllithium in hexane. The resulting solution was allowed to stir at room temperature for 4 h and was then added dropwise over a 2-h period to a suspension of 5.00 g (17.1 mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in 50 mL of THF at −74 °C. The reaction mixture was allowed to warm to room temperature and to stir overnight. The solvents were removed, and the flask was fitted with an apparatus as described for **1**. The product was extracted with three 50-mL portions of toluene, the toluene was then removed under vacuum, and the residue was washed with two 50-mL portions of hexane to yield 6.90 g of **10** (65% based on $(\eta^5\text{-}C_5H_5)_2ZrCl_2$) as a yellow, microcrystalline solid, contaminated with a small amount of $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2$: mp 125–130 °C; ^1H NMR (60 MHz, C_6D_6) δ 4.20 (1 H, s, CH), 5.40 (5 H, s, Cp), 5.74 (5 H, s, Cp), 6.8–7.7 (10 H, m, Ar); $^{13}C\{^1H\}$ NMR (67.5 MHz, C_6D_6) δ 49.41 (CH), 109.78 (Cp), 110.25 (Cp), 122.97 (*p*-Ar), 175.65 (*p*-Ar), 127.23, 127.62, 128.43, 128.97 (*o*- and *m*-Ar), 140.97 (ipso Ar), 151.23 (ipso Ar).

Anal. Calcd. for $C_{36}H_{32}S_2Zr$: C, 69.74; H, 5.20. Found: C, 67.56; H, 5.45.

Thermolysis of Bis(η^5-cyclopentadienyl)bis[phenyl(phenylthio)methyl]zirconium(IV), $(\eta^5\text{-}C_5H_5)_2Zr[CH(SC_6H_5)(C_6H_5)]_2$ (10). Thermolysis of **10** was performed by dissolving 1.00 g (1.6 mmol) of **10** in 15 mL of toluene. A sealed tube containing the reaction mixture was then placed in a thermostated bath at 70 °C for 24 h. 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 the product was washed with two 50-mL portions of pentane to yield 0.67 g (95%) of $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2$: ^1H NMR (60 MHz, C_6D_6) δ 5.97 (10 H, s, Cp), 7.3 (6 H, m, Ar), 8.1 (4 H, m, Ar).

Anal. Calcd for $C_{22}H_{20}S_2Zr$: C, 60.09; H, 4.58. Found: C, 60.06; H, 4.40.

Also isolated was 0.26 g (90% yield) of stilbene identified by ^1H NMR and GC.

Results and Discussion

Preparation of α-Zirconocenyl Thioethers. We have found that α-zirconocenyl thioethers are conveniently prepared by treatment of bis(cyclopentadienyl)zirconium dichloride with α-lithio thioethers which were prepared by the metalation of the corresponding thioethers with *n*-butyllithium in THF/hexane (eq 2). α-Zirconocenyl

$$RCH_2SR' \xrightarrow[\text{THF}]{n\text{-BuLi}} LiCH(SR')R \qquad (2)$$

thioethers **1**, **4**, and **5** were prepared in 45–80% yield by the very slow dropwise addition of a THF/hexane solution of the appropriate α-lithio thioether to a suspension of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in THF at −74 °C followed by warming to room temperature and proper workup (eq 3). The alkyl and aryl derivatives of **1** and **4** were readily prepared by the dropwise addition of an etheral solution of the appropriate Grignard reagent to an ether solution of compounds **1** or **4** at room temperature in the absence of light,

$$(\eta^5\text{-}C_5H_5)_2ZrCl_2 \xrightarrow[\text{THF, −74 °C}]{\text{LiCH(SR')R}} (\eta^5\text{-}C_5H_5)_2ZrCl[CH(SR')R]$$
$$\mathbf{1},\ R = Si(CH_3)_3,\ R' = CH_3$$
$$\mathbf{4},\ R = Si(CH_3)_3,\ R' = C_6H_5$$
$$\mathbf{5},\ R = C_6H_5,\ R' = C_6H_5 \qquad (3)$$

to give complexes **2** and **6**–**8** in 60–82% yield (eq 4).

$$(\eta^5\text{-}C_5H_5)_2ZrCl[CH(SR')R] \xrightarrow[\text{ether}]{R''MgX} (\eta^5\text{-}C_5H_5)_2ZrR''[CH(SR')R] \qquad (4)$$
$$\mathbf{2},\ R = Si(CH_3)_3,\ R' = CH_3,\ R'' = C_6H_5$$
$$\mathbf{6},\ R = Si(CH_3)_3,\ R' = CH_3,\ R'' = CH_3$$
$$\mathbf{7},\ R = Si(CH_3)_3,\ R' = CH_3,\ R'' = C_6H_5CH_2$$
$$\mathbf{8},\ R = Si(CH_3)_3,\ R' = C_6H_5,\ R'' = C_6H_5$$

Attempted alkylation of the chloro complexes **1** and **4** with lithium alkyls lead to much lower yield of the corresponding alkyl complexes. The bis(α-alkyl thio) complexes **9** and **10** were prepared in 41% and 65% yields, respectively, by the dropwise addition of 2 equiv of the appropriate α-lithio thioether to a THF suspension of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ at −74 °C followed by warming to room temperature and proper workup (eq 5).

$$(\eta^5\text{-}C_5H_5)_2ZrCl_2 \xrightarrow[\text{THF, −74 °C}]{\text{2LiCH(SR')R}} (\eta^5\text{-}C_5H_5)_2Zr[CH(SR')R]_2$$
$$\mathbf{9},\ R = H,\ R' = C_6H_5$$
$$\mathbf{10},\ R = C_6H_5,\ R' = C_6H_5 \qquad (5)$$

The 270-MHz ^1H NMR spectra of complexes **1**, **2**, **4**, **6**–**8**, and **10** all exhibit two cyclopentadienyl resonances in the range δ 5.4–5.9 at room temperature. Further study indicates that these simple spectra observed at room temperature are the high-temperature average spectra of two conformations in dynamic equilibrium on the NMR time scale. When spectra of these complexes are recorded at 270 MHz at −80 °C, two sets of the cyclopentadienyl resonances are exhibited. In complexes **1**, **2**, **4**, **8**, and **10** these two sets of cyclopentadienyl resonances were observed to be in approximately a 1:5 ratio as depicted for **4** in Figure 1. Irradiation at −80 °C of one of the resonances for the minor conformer of complex **4** causes one of the resonance of the major conformer to disappear, thus indicating that the major and minor conformers interconvert readily on the NMR time scale even at low temperatures. Complexes **6** and **7** exhibit two sets of two cyclopentadienyl resonances with an approximately 2:1 and 1:1 ratio, respectively, at 270 MHz and −80 °C. Complex **5** exhibits two sets of two cyclopentadienyl resonances in the ^1H NMR at 270 MHz, at room temperature in an approximately 1:7 ratio, analogous to the low-temperature ^1H NMR spectrum of complexes **1**, **2**, **4**, **8**, and **10**. In contrast to the above complex, **9** exhibits only one cyclopentadienyl resonance at 270 MHz at room temperature and at −80 °C. The other protons in these complexes give rise to the expected proton resonances at room temperature (see Experimental Section), with the appropriate changes observed in the low-temperature NMR spectrum.

The 67.5-MHz ambient-temperature proton-decoupled ^{13}C NMR spectra of complexes **1**, **2**, **4**, **6**–**8**, and **10** all exhibit two cyclopentadienyl resonances analogous to what was observed in the 270-MHz ^1H NMR of these complexes. The 67.5-MHz proton-decoupled ^{13}C NMR spectra of complex **5** was found to exhibit two sets of two resonances at ambient temperature due to the cyclopentadienyl carbons, analogous to its ^1H NMR spectrum. In contrast to the other α-zirconocenyl thioethers reported in this study, the proton-decoupled ^{13}C NMR spectrum of **9** exhibits only one cyclopentadienyl resonance at ambient temperature.

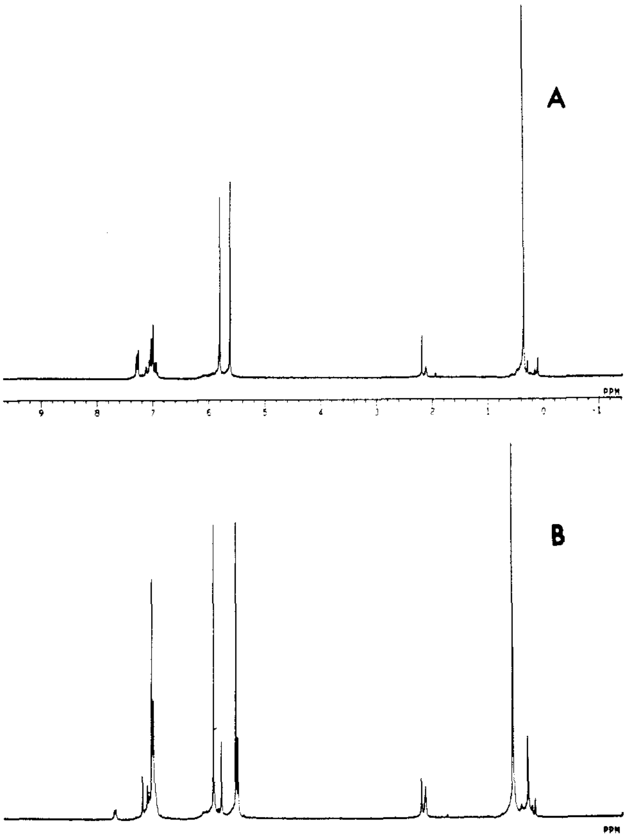
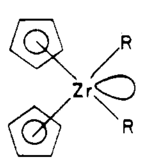


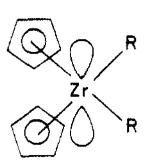
Figure 1. 270-MHz ^1H NMR of $(\eta^5\text{-}C_5H_5)_2ZrCl[CH(SC_6H_5)(Si(CH_3)_3)]$ in $C_6D_5CD_3$ at (A) 22 °C and (B) −80 °C.

In the room-temperature proton-coupled ^{13}C NMR spectrum of complexes 1, 2, 6, and 7 we have observed that the methyl carbon of the S–CH_3 group exhibits an unusually large three-bond coupling to the methine proton in the (methylthio)(trimethylsilyl)methyl ligand (ca. 10 Hz).[19] In contrast to this we have observed that the analogous three-bond coupling in $CH_3SCH_2Si(CH_3)_3$ is only 3.5 Hz. We have further investigated this point and found that at 67.5 MHz and −80 °C complexes 1, 6, and 7 exhibit two proton-decoupled resonances due to the SCH_3 group, and in the coupled spectrum each of the resonances due to the S–CH_3 groups exhibit a 10-Hz three-bond coupling with the methine proton. At 50 °C (high-temperature limiting spectra) the S–CH_3 group in complexes 1, 6, and 7 still exhibits a 10-Hz three-bond coupling constant with the methine carbon. This large three-bond coupling constant suggests that the methylthio group in these complexes is unable to rotate freely.

In the coordinatively unsaturated 16-electron complexes $(\eta^5\text{-}C_5H_5)_2ZrR_2$ a chemically significant empty orbital exists in the girdle plane. In principle this empty orbital can occupy either of two geometrically distinct positions as shown in 12 and 13.[9e,16,17]

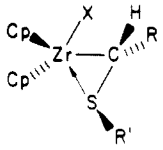


12

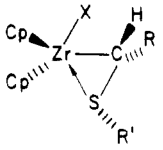


13

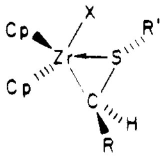
It has recently been reported that the (diphenylphosphino)methyl and (dimethylphosphino)methyl groups in $Cp_2Zr(X)CH_2PR_2$[11,12] serve as η^1 two-electron ligands. This result has been attributed to unfavorable steric interactions, whereas it has also been reported for a model compound $Cp_2Zr(Cl)CH_2PH_2$ that an extended Hückel MO calculation favors an η^2 structure.[11,16] In light of this the (methylthio)methyl and (phenylthio)methyl group in these α-zirconocenyl thioethers with their sterically less demanding methylthio and phenylthio groups would be expected to serve as an η^2 four-electron ligand, analogous to that reported in $Mo(CO)_2(\eta^2\text{-}CH_2SCH_3)$,[4] $Ni(PPh_3)(Cl)(\eta^2\text{-}CH_2SCH_3)$,[5] $Pd(PPh_3)_2(\eta^2\text{-}CH_2SCH_3)X$,[6] $Fe(PMe_3)_3(\eta^2\text{-}CH_2SCH_3)Cl$,[7] $[(CH_3)_2Ga(N_2C_3H_3)(OCH_2CH_2N(CH_3)_2)]Mo(CO)_2(\eta^2\text{-}CH_2SCH_3)$, $[(CH_3)_2Ga(N_2C_5H_7)(OCH_2CH_2N(CH_3)_2)]Mo(CO)_2(\eta^2\text{-}CH_2SCH_3)$[8] and the well-known η^2 acyl- and iminoacyl-zirconocene complexes $Cp_2Zr(X)COR$[9] and $Cp_2Zr(X)[C(NR)R']$,[10] respectively. The interaction of one of the lone pairs on the sulfur with the vacant orbital on zirconium in α-zirconocenyl thioethers[4-8,18] leads to four possible conformations: outside trans (**14a**), outside cis (**14b**), inside trans (**15a**), and inside cis (**15b**).



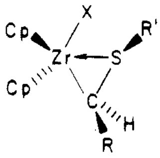
14a (outside trans)



14b (outside cis)



15a (inside trans)
R = SiMe, C_6H_5
R' = CH_3, C_6H_5



15b (inside cis)

Although there are four possible conformations for complexes 1, 2, and 4–8, on the basis of their low-temperature NMR spectra, only two appear to be present. There are three possible explanations for this. (1) One explanation is that these complexes exist in only the sulfur outside isomer 14 analogous to acylzirconium complexes and that the two conformations are due to a cis and trans distribution of the phenyl or methyl group on sulfur relative to the trimethylsilyl or phenyl group on the methine carbon in the three-membered ring. (2) Both the inside and outside conformations are accessible and inversion at sulfur is fast even at −80 °C, so that only two apparent conformations 14 and 15 are observed, with no stereochemical consequences of the pyramidal sulfur. (3) The phenyl or methyl group on sulfur and the trimethylsilyl or phenyl group on the methine carbon are locked into a trans configuration on the three-membered ring due to steric bulk, and we are seeing conformations 14a and 15a at low temperature giving rise to two sets of two cyclopentadienyl resonances. We favor the latter explanation for the following reasons. (1) To avoid steric crowding, one would expect the trimethylsilyl or phenyl group on the methine carbon to be trans to methyl or phenyl group on sulfur in the three-membered ring. (2) In complexes 1, 2, 6, and 7 we have observed the same large three-bond coupling constant between the carbon of the *S*-methyl

---

(16) Hofman, P.; Stauffert, P.; Schore, E. N. *Chem. Ber.* **1982**, *115*, 2153–2174.

(17) (a) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440–4451. (b) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

(18) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 364–414.

(19) Schwartz, J. A.; Perlin, A. S. *Can. J. Chem.* **1972**, *50*, 3667–3676.

group and the methine proton on the thioether ligand (vide supra) in both the high-temperature and the low-temperature limiting spectrum suggesting that either the CH_3–S–C–H dihedral angle is frozen at both high and low temperature or that the inversion at sulfur is fast on the NMR time scale even at −80 °C. We feel that the former situation is probably the case. However, either result is consistent with the idea of the two low-temperature species being the "inside" and "outside" conformers **14** and **15**, analogous to the iminoacyl–zirconocene complexes reported by Lappert et al.[10]

Thermal Stability. These new α-zirconocenyl thioethers show a remarkable range of thermal stability. All of the new complexes reported here with the exception of complex **10** were found to be indefinitely stable at room temperature under an inert atmosphere in the dark. Complex **10** slowly decomposes at room temperature to produce $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2$ (**11**) and stilbene (eq 6). To

$$\mathbf{10} \rightarrow (\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2 + C_6H_5CH{=}CHC_6H_5 \qquad (6)$$

date we have not been able to obtain complex **10** in analytically pure form due to contamination with complex **11**. Thermolysis of **10** at 70 °C for 24 h was found to produce **11** and stilbene in 95% and 90% yields, respectively (eq 6).[20] It has been briefly reported that thermolysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_2SC_6H_5)_2$ produces $(\eta^5\text{-}C_5H_5)_2Ti(SC_6H_5)_2$ and $(\eta^5\text{-}C_5H_5)_2TiSC_6H_5$.[21]

We have previously found that the chloro complex **1** has half-life in toluene at 100 °C of greater than 1 month and that 0.2 M solutions methyl and benzyl complexes **6** and **7** were found by NMR measurement not to be decomposed after 1 week in $C_6D_5CD_3$ at 82 °C.[1] In contrast to this the phenyl complex **2** was shown to undergo a unique thermal rearrangement to give **3** with a first-order rate constant of $8.14 \times 10^{-6}\ s^{-1}$ at 82 °C (eq 1).[1] Further studies are in progress to investigate the mechanisms behind this wide range of thermal reactivity.

Acknowledgment. We thank the National Science Foundation (Grant RII-8011453) and the West Virginia University Energy Research Center for generous support of this research. NMR spectra were recorded on an instrument supported by the National Science Foundation (Grant PRM 801143).

Registry No. **1**, 96445-76-0; **2**, 96445-77-1; **3**, 96445-78-2; **4**, 102493-94-7; **5**, 102493-95-8; **6**, 96445-79-3; **7**, 96445-80-6; **8**, 102493-96-9; **9**, 102493-97-0; **10**, 102493-98-1; $CH_3SCH_2Si(CH_3)_3$, 10428-57-6; $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, 1291-32-3; C_6H_5Br, 108-86-1; $C_6H_5SCH_2Si(CH_3)_3$, 17873-08-4; $C_6H_5CH_2SC_6H_5$, 831-91-4; CH_3Br, 74-83-9; $C_6H_5CH_2Cl$, 100-44-7; $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2$, 37206-34-1; *trans*-stilbene, 103-30-0; thioanisole, 100-68-5.

---

[20] Mintz, E. A.; Ward, A. S. *J. Organomet. Chem.*, in press.

[21] Taube, R.; Steinburn, D. *J. Organomet. Chem.* **1974**, *65*, C9–C12.