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Preliminary communication

THERMALLY INDUCED ELIMINATION OF STILBENE FROM $(\eta^5\text{-}C_5H_5)_2Zr[CH(SC_6H_5)C_6H_5]_2$

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Summary

The thermolysis of $(\eta^5\text{-}C_5H_5)_2Zr[CH(SC_6H_5)C_6H_5)]_2$ (**3**) in toluene solution follows clean first-order kinetics to give $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2$ and $C_6H_5CH{=}CHC_6H_5$ in high yield. Activation parameters $\Delta H^{\neq}$ 24.8(1.4) kcal mol^{-1} and $\Delta S^{\neq} - 4.56(0.39)$ eu for the decomposition of **3** were determined. A mechanism is proposed to account for the formation of $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2$ and stilbene from complex **3**.

Early transition metal alkyl complexes have been shown in recent years to exhibit a rich and varied chemistry. As a part of our investigation of the effect of α-heteroatom substitution on the reactivity of alkyl complexes of the early transition metals we have recently reported the novel thermally induced rearrangement of $(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)[CH(Si(CH_3)_3)SCH_3]$ (**1**) (eq. 1) [1].

$$\underset{(1)}{(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)[CH(Si(CH_3)_3)SCH_3]} \xrightarrow[C_6H_5CH_3,\ 22\ h]{82^\circ C} \underset{(2)}{(\eta^5\text{-}C_5H_5)_2Zr(SCH_3)[CH(Si(CH_3)_3)(C_6H_5)]} \quad (1)$$

We report here the preparation and novel thermal reactivity of bis(η^5-cyclopentadienyl)bis[(1-phenyl-1-thiophenyl)methyl]zirconium(IV), $(\eta^5\text{-}C_5H_5)_2Zr[CH(SC_6H_5)C_6H_5]_2$ (**3**) [2].

Complex **3** is conveniently prepared by the slow dropwise addition of two equivalents of $Li[CH(SC_6H_5)C_6H_5]$ to $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in THF followed by proper work-up [2].

$$(\eta^5\text{-}C_5H_5)_2ZrCl_2 + 2Li[CH(SC_6H_5)C_6H_5] \xrightarrow{THF} (\eta^5\text{-}C_5H_5)_2Zr[CH(SC_6H_5)C_6H_5]_2 \quad (2)$$

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Complex 3 once prepared has proven to be moderately stable and decomposes only slowly at room temperature in the dark under an inert atmosphere in line with the α-zirconocenylthioether 1 and in contrast to the α-zirconocenylether $(\eta^5\text{-}C_5H_5)_2ZrCl[C(C_6H_5)_2OCH_3]$ (4) which has been reported by Erker and Rosenfeldt to be unstable, with a half-life of 48 h at room temperature, decomposing to give $(\eta^5\text{-}C_5H_5)_2ZrCl(OCH_3)$ and $Ph_2C{=}CPh_2$ [3]. Erker and Rosenfeldt have also reported that at 100° C complex 4 undergoes a carbon—oxygen homolytic bond cleavage with anchimeric assistance by the $(\eta^5\text{-}C_5H_5)_2ZrCl$ unit to produce upon hydrolysis 1,1-diphenylethanol, and 2- and 4-methylbenzophenone [3]. Taube and Steinborn have reported that the thermolysis of $(\eta^5\text{-}C_5H_5)_2\ Ti(CH_2SC_6H_5)_2$ gives $(\eta^5\text{-}C_5H_5)_2\ Ti(SC_6H_5)$ and $(\eta^5\text{-}C_5H_5)_2\ Ti(SC_6H_5)_2$ [4].

In our work we have found that not only are α-zirconocenylthioethers more thermally stable than α-zirconocenylethers, but also that the heteroatom substitution opens up reaction pathways not available to other alkyl- and aryl-zirconocene and -titanocene complexes bearing simple hydrocarbon ligands [5].

Complex 3 upon thermolysis at 70° C for 24 h produces $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2$ (5) and stilbene in 95 and 90% isolated yield respectively, and a trace amount of benzylphenylsulfide [6]. Although the stilbene isolated from this is primarily *trans* the *cis/trans* ratio was found to vary from run to run, this variation in the stilbene *cis/trans* ratio observed in this reaction suggests that, the stilbene may be isomerized under the reaction conditions. It is of interest to note that no products analogous to those produced by the homolytic cleavage of 4 reported by Erker were observed from the thermolysis of 3 [3].

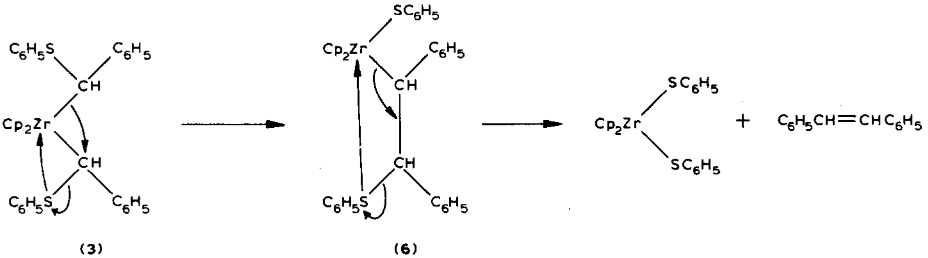
$$(\eta^5\text{-}C_5H_5)_2Zr[CH(SC_6H_5)(C_6H_5)]_2 \xrightarrow[C_5H_5CH_3,\ 24\ h]{70^\circ C} (\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2 + C_6H_5CH{=}CHC_6H_5 \qquad (3)$$

TABLE 1

SUMMARY OF THE RATE CONSTANTS FOR THE THERMALLY INDUCED DECOMPOSITION OF $(\eta^5\text{-}C_5H_5)_2\ Zr[CH(SC_6H_5)C_6H_5]_2$ AT 0.2 *M* IN TOLUENE

Temperature (°C)	K_{obsd} (s^{-1})
62.0	$4.86(0.34) \times 10^{-5}$
72.1	$1.87(0.14) \times 10^{-4}$
81.9	$3.62(0.09) \times 10^{-4}$

SCHEME 1



A tentative mechanism for this reaction is proposed in Scheme 1.

Complex **3** could initially undergo thermally induced intramolecular nucleophilic attack (migration) of one of the (1-phenyl-1-thiophenyl)methyl groups onto the methine carbon of the other 1-phenyl-1-thiophenylmethyl group with anchimeric activation of the thiophenyl group by the neighboring $(\eta^5\text{-}C_5H_5)_2Zr$, analogous to the rearrangement of complex **1** to **2**, to produce the β thioalkyl complex (**6**) [1,7]. Complex **6** could then undergo a β metal thiolate elimination analogous to the well established β hydride elimination to produce $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2$ and stilbene. The β thiolate elimination, as proposed for **6** has precedence in the elimination reaction of β-thio Grignard reagents [8] and the phosphine-induced β-aryloxy elimination of $Pt(PPh_3)_2Br(CH_2CH_2OC_6H_5)$ [9]. Very recently Yamamoto and coworkers have proposed a β-metal thiolate elimination to account for allyl—sulfur bond cleavage induced by rhodium hydride complexes [10].

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2 Complex **3** was prepared by the dropwise addition of $Li[CH(SC_6H_5)C_6H_5]$, prepared by treating 7.2 g (36 mmol) of $C_6H_5CH_2SC_6H_5$ in 50 ml of THF with 23 ml (36 mmol) of 1.55 *M* n-butyllithium in hexane at room temperature for 4 h, 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 stirred overnight. After removal of the solvent under vacuum, the reaction mixture was extracted with toluene, the toluene was removed under vacuum and the residue was washed with pentane to give 6.90 g (65% yield) of **3** as a yellow microcrystalline solid contaminated with a small amount of $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2$: m.p. 125—130°C (dec). ^1H NMR (60 MHz, C_6D_6) δ 4.20 (2H, s, CH), 5.40 (5H, s, Cp), 5.75 (5H, s, Cp), 6.8—7.7 (10H, m, Ar); ^{13}C $\{^1H\}$NMR (67.5 MHz, C_6D_6), δ 49.4 (CH), 109.8 (Cp), 110.2 (Cp), 123.0 (Ar), 125.6 (Ar), 125.7 (Ar), 127.2 (Ar), 128.4 (Ar), 129.0 (Ar), 141.0 (i-Ar), 151.2 (i-Ar). Anal. Found: C, 67.56; H, 5.45. $C_{36}H_{32}S_2Zr$ calcd.: C, 69.74; H, 5.20%.

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6 A 1.00 g (1.61 mmol) sample of **3** in 15 ml of toluene was heated to 70°C for 24 h in a sealed tube. The volatiles were removed under vacuum and the residue washed with two 50 ml portions of pentane to yield 0.67 g (94% yield) of $(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)_2$. ^1H NMR (60 MHz, C_6D_6) δ 6.97 (10H, s, Cp), 8.00—9.07 (10H, m, C_6H_5). Anal. Found: C, 60.06; H, 4.43. $C_{22}H_{20}S_2Zr$ calcd.: C, 60.09; H, 4.58%. Distillation of the volatiles follwed by recrystallization gave 0.23 g (90% yield) of *trans*-stilbene and a trace of benzylphenylsulfide identified by ^1H NMR and GC/MS.

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