biguously identified with high-resolution spectra and mass analysis and their formation pathways by double-resonance and MS/MS techniques.[26]

The nitriles were synthesized and fully characterized using established procedures, purified by preparative gas chromatography, and carefully degassed by multiple freeze–pump–thaw cycles immediately before the experiments. The label content was determined with NMR and mass spectrometry techniques.

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Registry No. 23, 617-80-1; Ti^+, 14067-04-0; V^+, 14782-33-3; Cr^+, 14067-03-9; Mn^+, 14127-69-6; Fe^+, 14067-02-8; Co^+, 16610-75-6; Ni^+, 14903-34-5; Cu^+, 17493-86-6; Zn^+, 15176-26-8.

Chalcogenametallacyclohexadienes by Thermally Induced Migratory Ring Enlargement of Furyl- and Thienylzirconocene Complexes

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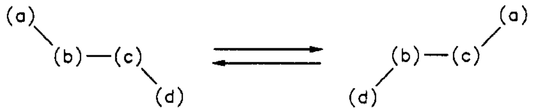
Zirconocene dichloride reacts with 2 molar equiv of (2-furyl)lithium to give bis(2-furyl)zirconocene (**1a**). The (σ-furyl)zirconocene complexes Cp_2ZrR(2-furyl) (R = CH_3, Ph, $SiMe_3$) were similarly prepared by treatment of the respective $Cp_2Zr(R)Cl$ complexes with (2-furyl)lithium. $Cp_2Zr(SiMe_3)$(2-thienyl) was obtained from the reaction of $Cp_2Zr(SiMe_3)Cl$ with (2-thienyl)lithium. The Cp_2ZrR(2-furyl) complexes with R = 2-furyl, methyl, or phenyl all undergo an intramolecular high-temperature (≥180 °C) σ,σ-exchange reaction to give the oxazirconacyclohexadienes $Cp_2\overline{ZrOCH{=}CHCH{=}C}(R)$ (**2a–c**). The **1a** → **2a** rearrangement follows first-order kinetics in the temperature range 140–180 °C and is characterized by the activation parameters $\Delta H^{\ddagger} = 30.9 \pm 2.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9 \pm 5$ cal mol^{-1} K^{-1}. The complexes $Cp_2Zr(SiMe_3)$(2-furyl) (**1d**) and $Cp_2Zr(SiMe_3)$(2-thienyl) (**1e**) undergo the analogous dyotropic rearrangements much faster. The **1d** → **2d** isomerization is fast at 0 °C and already takes place during the formation of **1d** from $Cp_2Zr(SiMe_3)Cl$ and (2-furyl)lithium. The activation parameters of the **1e** → **2e** ring enlargement reaction of the (2-thienyl)metallocene system are $\Delta H^{\ddagger} = 20.4 \pm 2.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -12 \pm 5$ cal mol^{-1} K^{-1}. The oxa- and thiazirconacyclohexadienes $Cp_2\overline{Zr{-}X{-}CH{=}CHCH{=}C}(SiMe_3)$ (X = O, **2d**; X = S, **2e**) were characterized by X-ray diffraction. Complex **2d** crystallizes in space group $P\bar{1}$ with cell parameters $a = 9.783$ (1) Å, $b = 11.514$ (1) Å, $c = 15.806$ (1) Å, $\alpha = 96.27$ (1)°, $\beta = 101.64$ (1)°, $\gamma = 98.89$ (1)°, $Z = 4$, $R = 0.037$, and $R_w = 0.053$. Complex **2e** crystallizes in space group Cc with cell parameters $a = 13.988$ (4) Å, $b = 30.774$ (2) Å, $c = 9.788$ (4) Å, $\beta = 122.93$ (1)°, $Z = 8$, $R = 0.034$, and $R_w = 0.035$. Both chalcogenazirconacyclohexadienes are monomeric in the solid state and exhibit nonplanar metallacyclic conformations with the metal–chalcogen vectors rotated significantly relative to the planes of the endocyclic conjugated diene moieties.

Introduction

Dyotropic rearrangements[1] are thermally induced concerted rearrangement processes in which the two groups a and d exchange their positions relative to a pivotal system of groups or atoms (b, c). Most known examples of compounds undergoing such coupled σ,σ-exchange have very electropositive main-group (Si)[2] or transition metals (Zr, Hf) and at the same time electronegative elements (O, S) involved.[3-6] For a variety of examples stepwise (i.e. nonconcerted) reaction mechanisms have been proposed or proven.[5-9]



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In the reported examples the target atom of the σ-ligand migration is always sp^3-hybridized carbon. It would be interesting to study coupled σ,σ-migration reactions where a carbon target in the central unit is connected to only three adjacent neighbors. The incorporation of a trigonally planar sp^2-hybridized carbon atom would create an interesting situation with regard to the transition-state structure of the rearrangement process. If the reorganization of bonds occurred only in the σ-plane, transition-state structures could develop which exhibit quite unusual coordination geometries at carbon. Investigating such coupled σ,σ-exchange rearrangement reactions involving π-bonded carbon centers in the bridge might, therefore, provide a stimulating addition to the ongoing actual discussion about the importance of "unnatural" coordination geometries of carbon in organic and organometallic systems.[10] We describe here several furyl- and thienylzirconocene complexes that undergo thermally induced σ,σ-exchange reactions which may formally meet with the requirements for an involvement of four-coordinate carbon in the plane of σ-bonds at some stage during the rearrangement process.[11]

Results and Discussion

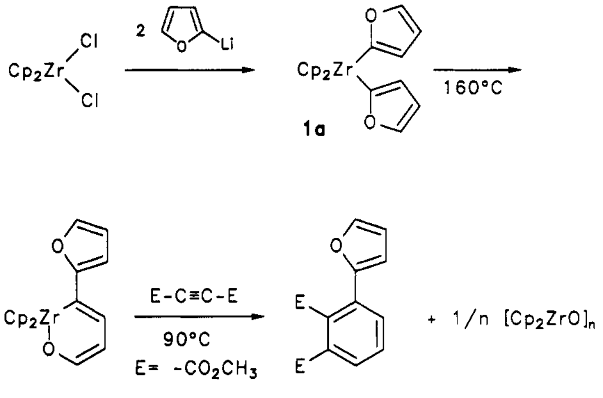
Preparation and Rearrangement of the Furyl- and Thienylzirconocene Complexes. There is a small number of transition-metal σ-2-furyl complexes known in the literature such as (2-furyl)$Mn(CO)_5$, (2-furyl)$(CH_3)_2(PPh_3)Au$, (cod)(2-furyl)PtCl, and (cod)(2-furyl)$_2$Pt.[12] (2-Thienyl)metal complexes are more abundant in the literature because of their relevance as model compounds for desulfurization processes.[13-16] Typical examples include (2-thienyl)$Mn(CO)_5$, the paramagnetic complexes Cp_2Nb(2-thienyl)$_2$ and Cp_2NbCl(2-thienyl), and also Cp_2Ti(2-thienyl)$_2$. The last compound was obtained in good yield from the reaction of (2-thienyl)lithium with titanocene dichloride.[15]

Table I. Activation Parameters of Dyotropic Rearrangements and Related σ,σ-Exchange Processes

compd	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu	ref
Cp_2Zr(2-furyl)$_2$ (**1a**)	30.9 ± 2	-9 ± 5	*a*
Cp_2Zr(2-thienyl)$SiMe_3$ (**1e**)	20.4 ± 2	-12 ± 5	*a*
$(CH_3)_3Si(OCC_{12}H_8)Si(CD_3)_3$	30.0 ± 0.6	-8.8 ± 0.8	2
$(CH_3)_3Si(OCPh_2)$allyl	31.9 ± 0.6^b	-7.7 ± 0.8^b	2
$Cp_2ZrPh[CH(Ph)SiMe_3]$	20.3 ± 1.5	-19 ± 3	6
$Cp_2ZrCl(CH_2OCH_2Ph)$	28.9 ± 1.5^b	+5.6 ± 4.2^b	7
$Cp_2ZrCl(CH_2O)ZrCp_2Cl$	7.0 ± 1.0^c		3
$Cp_2ZrPh(CH_2O)ZrCp_2Ph$	10.0 ± 0.5^d		3

^{a} This work. ^{b} Radical rearrangement pathway likely. ^{c} $\Delta G^\ddagger$ at 140 K. ^{d} $\Delta G^\ddagger$ at 190 K.

We have prepared bis(2-furyl)zirconocene (**1a**) by reacting 2 molar equiv of (2-furyl)lithium with zirconocene dichloride. The formation of the zirconium-substituted hetaryl system requires stirring for several hours at ambient temperature. The reaction proceeds considerably slower than, for example, the metathetical exchange between Cp_2ZrCl_2 and phenyllithium to give diphenylzirconocene (**5**).[17] Bis(2-furyl)zirconocene was obtained in 74% yield as a solid (mp 206 °C). Complex **1a** exhibits a ^1H NMR Cp signal in benzene-d_6 solution at δ 6.11. The σ-furyl ^1H NMR resonances are at δ 7.39 (dd, 5-H), 6.14 (dd, 4-H), and 6.31 (dd, 3-H) with coupling constants ^3J = 3.1 (3-H/4-H), 1.5 Hz (4-H/5-H) and ^4J = 0.4 Hz (3-H/5-H). The ^{13}C NMR signals (in $CDCl_3$ solution, J_{CH} in parentheses) of the symmetry-equivalent zirconium-bound 2-furyl ligands have been observed at δ 206.8 (C2), 123.2 (169 Hz, C3), 107.7 (172 Hz, C4), and 143.9 (195 Hz, C5).



1a **2a** **3**

In contrast to diphenylzirconocene (**5**), which decomposes at temperatures >70 °C by means of (aryne)zirconocene formation,[18] bis(2-furyl)zirconocene (**1a**) can be heated to much higher temperatures without suffering noticeable decomposition. There has been no indication of a thermally induced formation of (hetaryne)metallocene type complexes.[19] At rather high temperature (180 °C,

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6 h in toluene solution, sealed tube) bis(2-furyl)zirconocene (**1a**) rearranged to give 1,1-bis(cyclopentadienyl)-1-zircona-2-oxa-6-(2′-furyl)cyclohexa-3,5-diene (**2a**).

The C6-bound furyl substituent of **2a** exhibits ^{1}H NMR signals at δ 7.16 (5′-H), 6.30 (4′-H), and 6.04 (3′-H) (^3J = 3.2 (3′-H/4′-H), 1.9 Hz (4′-H/5′-H); ^4J = 0.8 Hz (3′-H/5′-H)) and ^{13}C NMR signals at δ 164.6 (C2′), 139.3 (C5′), 110.2 (C4′), and 99.8 (C3′). The three-spin ^{1}H NMR system of the metallacyclic six-membered-ring groups appears at δ 7.11 (5-H), 5.35 (4-H), and 6.90 (3-H) with coupling constants ^3J = 6.6 (4-H/5-H) and 5.3 Hz (3-H/4-H) (^4J (3-H/5-H) not observed). The ^{13}C NMR signals of the six-membered metallacyclic framework are at δ 178.2 (C6), 127.4 (C5), 109.3 (C4), and 151.7 (C3). This assignment was based on a ^{1}H/^{13}C shift correlation experiment. For assignment of some of the ^{13}C NMR resonances of the oxazirconacyclohexadiene it was helpful to have orientating qualitative ^{13}C shift increments for a Cp_2Zr "substituent" at a $X—C^1H=C^2H—Y$ olefinic system available. ($\delta^1 = 123.3 + I_{X1} + I_{Y2}$ and $\delta^2 = 123.3 + I_{Y1} + I_{X2}$, with $I_1 \approx 67$ and $I_2 \approx -8$ for the Cp_2Zr unit. These increment values were based on the observed chemical shifts of the α- and β-C(sp^2) centers in $Cp_2Zr(Cl)—C(CH_3)=CHCH_3$.[20])

The kinetics of the thermally induced **1a** → **2a** rearrangement in toluene/tetrahydrofuran (2:1) solution were determined at five temperatures between 140 and 180 °C. In this temperature range the furyl migration/ring enlargement reaction can be described by first-order kinetics. From the Arrhenius plot the activation parameters were determined as ΔH^{*} = 30.9 ± 2.0 kcal/mol and ΔS^{*} = −9 ± 5 eu. A comparison with activation energies and entropies of a variety of other examples of coupled σ,σ-exchange reactions is given in Table I.[2,3,6,7]

The oxametallacyclohexadiene **2a** reacts with $H_3CO_2C—C\equiv C—CO_2CH_3$ at 90 °C over 4 h to give dimethyl 3-(2′-furyl)phthalate (**3**) plus an insoluble precipitate of oligomeric zirconocene oxide. This transformation can formally be described as a sequence of Diels–Alder/retro-Diels–Alder reactions. However, a more detailed discussion of this interesting C_4H_3 unit transfer from furan (via α-metalation, transmetalation, and rearrangement) must await additional experimental investigation.[21]

After a preliminary communication of our work on the **1a** → **2a** rearrangement had appeared in the literature,[22] our findings were discussed by Jemmis et al. as a part of a theoretical study dealing with the migratory aptitudes of organic groups in σ,σ-exchange reactions.[23] As a result of an extended Hückel calculation of the (furyl)metallocene/oxametallacyclohexadiene system it was assumed that "if the compounds with Me and Ph were used in the reaction..., the formation of zirconacycles should according to this analysis, be facile". Actually, the activation barrier for methyl migration from zirconium to the furyl sp^2 carbon was calculated as 7 kcal/mol (i.e. to be by ca. 30% *lower* than the EHMO-*calculated* **1a** → **2a** activation barrier): according to this reported calculation[23] there should be no activation barrier for the corresponding phenyl migration. To test these predictions experimentally, we have prepared methyl(2-furyl)zirconocene (**1b**) and phenyl(2-furyl)zirconocene (**1c**) and briefly looked at their behavior upon thermolysis.

Table II. ^{1}H NMR Data for the Oxa- and Thiazirconacyclohexadiene Moieties[a]

compd	Cp	3-H	4-H	5-H	$^3J^b$	^4J
2a	5.93	6.90	5.35	7.11	5.3; 6.6	*c*
2b	5.81	7.10	5.26	6.87	4.9; 5.9	0.6^d
2c	5.94	6.91	5.46	6.80	5.3; 6.5	*c*
2d	5.90	6.80	5.41	7.34	5.3; 6.1	*c*
2e	5.80	7.73	6.56	7.22	6.1; 9.6	*c*

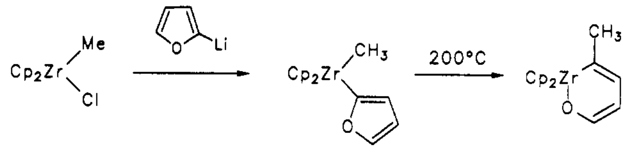
[a] In C_6D_6; chemical shifts in ppm relative to TMS, δ scale, with *J* values in Hz. [b] 3-H/4-H; 4-H/5-H. [c] Not observed. [d] 5-H/CH$_3$; ^5J(4-H/CH$_3$) = 0.4 Hz.

Table III. ^{13}C NMR Data for the Oxazirconacyclohexadienes 2a,d and the Thiacyclohexadiene 2e[a]

compd	Cp	C-3	C-4	C-5	C-6
2a	111.3	151.7	109.3	127.4	178.2
2d	111.6	153.1	112.0	142.2	207.1
2e	110.0	145.7	111.9	131.6	223.9

[a] In C_6D_6; chemical shifts in ppm relative to TMS, δ scale.

For this purpose we have reacted $Cp_2Zr(Cl)CH_3$ (**4**) with 1 molar equiv of (2-furyl)lithium in ether. After workup at room temperature, methyl(2-furyl)zirconocene (**1b**) was isolated in ca. 80% yield as a solid, admixed with about 5% of dimethylzirconocene and 13% of bis(2-furyl)zirconocene. The mixture was not further separated but subjected to the thermolysis studies as such. It turned out that methyl(2-furyl)zirconocene (**1b**) underwent an even slower migratory rearrangement as compared to bis(2-furyl)zirconocene (**1a**). Since the latter was present as a minor component in the reaction mixture, it served as an internal standard for the qualitative assessment of relative thermal stabilities of the two compounds. It actually required a temperature as high as 200 °C (sealed tube, toluene solution) to induce the rearrangement of **1b**. At this temperature, the overall reaction was not very clean, producing a mixture of organometallic compounds, among which 1,1-bis(cyclopentadienyl)-1-zircona-2-oxa-6-methylcyclohexa-3,5-diene (**2b**) was tentatively identified by its very characteristic ^{1}H NMR pattern of the ring-C_4H_3 moiety (see Table II).



4 **1b** **2b**

It is well-known that (η^2-benzyne)zirconocene (**6**), generated from diphenylzirconocene by thermolysis, reacts with aromatic hydrocarbons to give C–H activated products.[17,18,24] We used this reaction pattern of the reactive

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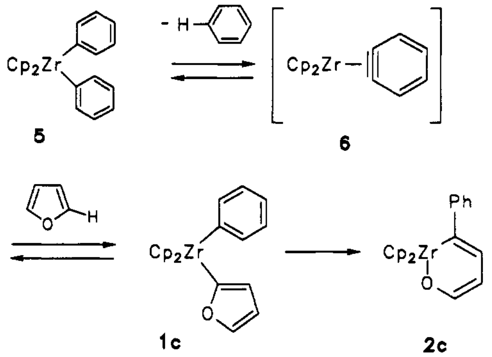
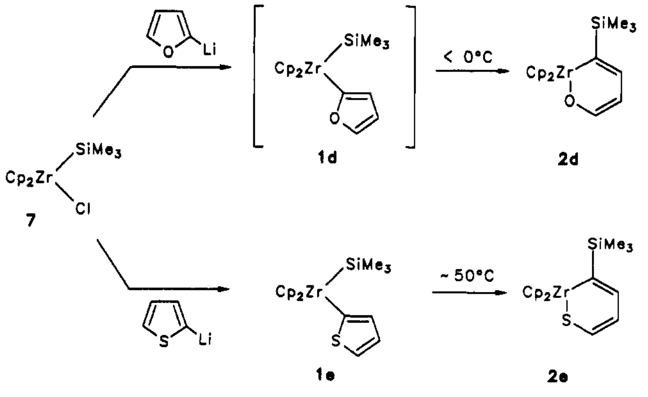


intermediate **6** to prepare phenyl(2-furyl)zirconocene. Complex **1c** was obtained admixed with a small amount of as yet unidentified minor byproducts upon thermolysis of diphenylzirconocene (**5**) at 90 °C in toluene solution in the presence of a ca. 10-fold excess of furan.

Complex **1c** is stable toward subsequent rearrangement under these reaction conditions. The thermolysis studies at higher temperatures were at first complicated by the rapid reversibility of the $\mathbf{5} \rightleftharpoons \mathbf{6} \rightleftharpoons \mathbf{1c}$ reaction sequence in arene solvent. This unfavorable alternative decomposition pathway of **1c** became sufficiently suppressed by carrying out the thermolyses at elevated temperature in furan solution (sealed tube). At 190 °C phenyl(2-furyl)zirconocene rearranges to give a complex mixture of products, among which the metallacycle **2c** was identified by ^{1}H NMR spectroscopy (see Table II). It should be noted that some of the 2′-furyl-substituted metallacycle **2a** was found in the reaction mixture, which indicates that bis(2-furyl)zirconocene is formed under the rather forcing reaction conditions from phenyl(2-furyl)zirconocene probably by a σ-metathesis type exchange reaction.

The EHMO study cited above[23] apparently did not adequately predict the reactivity trend as was now qualitatively observed for the σ,σ-exchange rearrangements of bis(2-furyl)zirconocene, methyl(2-furyl)zirconocene, and phenyl(2-furyl)zirconocene. Methyl as well as phenyl migration from zirconium to sp^2-hybridized carbon seems to proceed even more slowly than the 2-furyl shift. This is probably not caused by steric effects but may be the consequence of the specific electronic properties of this particular rearrangement type. This is supported by the much higher reaction rates of the coupled σ,σ-exchange rearrangement process starting from (2-furyl)- and (2-thienyl)(trimethylsilyl)zirconocene (**1d**,**e**).



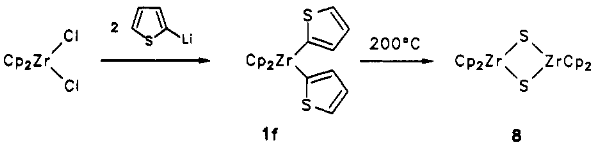
We have reacted $Cp_2Zr(Cl)SiMe_3$ (**7**)[25] with (2-furyl)lithium in the temperature range of −78 °C to room temperature. After the usual workup, a solid material was recovered in 63% yield which was not the expected (2-furyl)(trimethylsilyl)zirconocene (**1d**) but rather its dyotropic rearrangement product, 1,1-bis(cyclopentadienyl)-1-zircona-2-oxa-6-(trimethylsilyl)cyclohexa-3,5-diene (**2d**) (characterized by NMR spectroscopy—see Tables II and III—and by X-ray diffraction). Apparently, the σ,σ-exchange reaction of **1d**, proceeding by trimethylsilyl migration from zirconium to carbon, is several orders of magnitude faster than the corresponding σ-furyl shift.

The situation is slightly different when (trimethylsilyl)zirconocene chloride (**7**) is reacted with (2-thienyl)lithium. The reaction mixture was kept at 0 °C for 1 h to go to completion. After subsequent workup consequently carried out at 0 °C, the thermolabile primary product (2-thienyl)(trimethylsilyl)zirconocene (**1e**) could be isolated ca. 95% pure in about 90% yield. The compound was characterized by ^{1}H and ^{13}C NMR spectroscopy (see Table IV).

Complex **1e** is very thermolabile. In benzene-d_6 solution at ambient temperature it rearranges to 1,1-bis(cyclopentadienyl)-1-zircona-2-thia-6-(trimethylsilyl)cyclohexa-3,5-diene (**2e**) with a half-life of ca. 18 h. Complex **2e** was prepared on a preparative scale by keeping the crude reaction mixture for some time at 50 °C. The thiametallacyclohexadiene was isolated in >40% yield and characterized by spectroscopy (see Tables II and III) and by X-ray diffraction (see below).

In the temperature range between 30 and 70 °C the $\mathbf{1e} \rightarrow \mathbf{2e}$ rearrangement follows first-order kinetics. From the Arrhenius plot an activation enthalpy of $\Delta H^{\ddagger} = 20.4 \pm 2.0$ kcal mol^{-1} and an activation entropy of $\Delta S^{\ddagger} = -12 \pm 5$ eu were derived. A comparison with the analogous rearrangement of the bis(2-furyl)zirconocene system (**1a**) revealed that the trimethylsilyl migration reaction starting from **1e** proceeded about 10^4 times faster at 70 °C.

Bis(2-thienyl)zirconocene (**1f**), prepared from Cp_2ZrCl_2 by the reaction with 2 molar equiv of (2-thienyl)lithium, did not exhibit an increased tendency for the σ,σ-exchange rearrangement. Complex **1f** was shown to be stable for some time at temperatures below 160 °C. In the temperature range 185–205 °C it decomposed to give $[Cp_2ZrS]_2$ (**8**)[26] as the major organometallic product (ca. 80% yield isolated). Probably, the thiazirconacyclohexadiene rearrangement product, if at all formed, is not stable under these drastic reaction conditions but decomposes to give the zirconocene sulfide dimer. We have as yet not obtained any information about the organic products formed in this stoichiometric high-temperature organometallic desulfurization reaction.[13]



Molecular Structures of the Chalcogenametallacyclohexadienes 2d and 2e. Crystallization of 1,1-bis(cyclopentadienyl)-1-zircona-2-oxa-6-(trimethylsilyl)cyclohexa-3,5-diene (**2d**) from diethyl ether gave crystals suitable for a structure determination by X-ray diffraction. Complex **2d** is monomeric in the solid state. There are two independent molecules in the asymmetric unit; one of these shows a rotational disordering of the $-SiMe_3$ group. Bond distances and angles are given as averaged values. Complex **2d** contains a zirconium center that is pseudotetra-

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Table IV. Selected ^{1}H (^{13}C) NMR Data for (2-Furyl)- and (2-Thienyl)metal Complexes[a]

compd	Cp	C-2	(HC-3)	(HC-4)	(HC-5)	$^3J^b$	$^4J^c$
$Cp_2Zr(2\text{-furyl})$ (**1a**)	6.11		6.31	6.14	7.39	3.1; 1.5	0.4
	(110.5)	(206.8)	(123.1)	(107.7)	(143.9)[d]		
$Cp_2Zr(2\text{-furyl})CH_3$ (**1b**)	6.28		6.41	6.21	7.52	3.1; 1.6	0.4
	(110.4)	(204.4)	(123.5)	(107.6)	(144.1)[d]		
$Cp_2Zr(2\text{-furyl})Ph$ (**1c**)	5.93		6.52	6.30	7.52	3.2; 1.6	0.4
	(110.4)	(207.7)	(125.1)	(108.4)	(144.1)		
$Cp_2Zr(2\text{-thienyl})SiMe_3$ (**1e**)	5.97		*e*	*e*	7.35	4.5; *d*	0.6
$Cp_2Zr(2\text{-thienyl})_2$ (**1f**)	6.03		6.99	7.01	7.45	4.2; 3.2	1.1
	(111.8)	(179.1)	(137.1)	(130.8)	(126.6)		
$Cp_2Ti(2\text{-thienyl})_2$[f]	5.98		6.64	6.91	7.33	4.6; 3.3	0.8
	(115.1)	(189.8)	(133.7)	(128.9)	(125.8)		
(2-thienyl)Li[f]	(–)	(174.0)	(137.4)	(130.8)	(127.7)[g]		

[a] In C_6D_6, unless otherwise stated; chemical shifts in ppm relative to TMS, δ scale. [b] 3-H/4-H; 4-H/5-H. [c] 3-H/5-H, all coupling constants in Hz. [d] In $CDCl_3$. [e] Not observed. [f] See refs 15 and 16. [g] In thf-d_8.

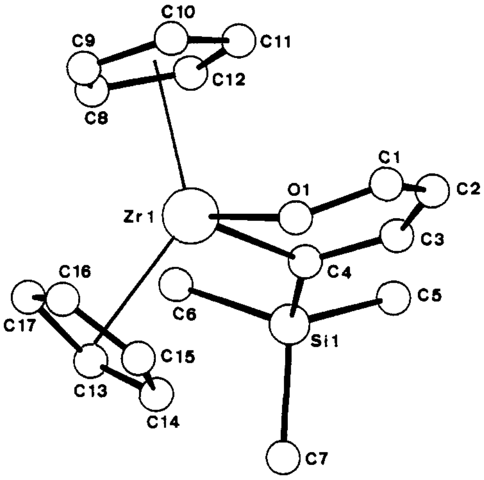

Figure 1. View of the molecular structure of **2d** in the crystal state with (nonsystematic) atom numbering scheme.

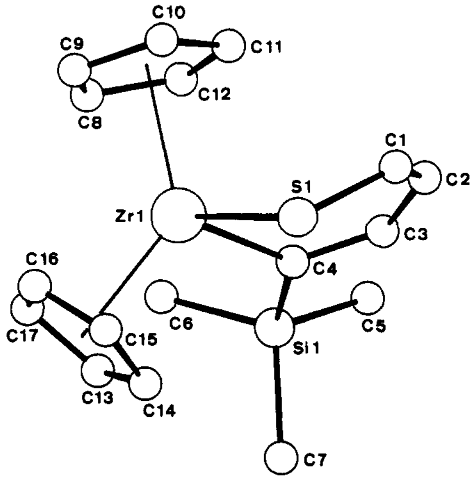

Figure 2. Molecular geometry of the thiazirconacyclohexadiene **2e** with (nonsystematic) atom numbering scheme.

Table V. Experimental X-ray Diffraction Data for 2d[a] and 2e[b]

	2d	2e
mol formula	$C_{17}H_{22}OSiZr$	$C_{17}H_{22}SSiZr$
mol wt	361.7	377.7
cryst color	yellow-brown	yellow-brown
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	*Cc*
a, Å	9.783 (1)	13.988 (4)
b, Å	11.514 (1)	30.774 (2)
c, Å	15.806 (1)	9.788 (4)
α, deg	96.27 (1)	90
β, deg	101.64 (1)	122.93 (1)
γ, deg	98.89 (1)	90
V, Å^3	1704.6	3536.4
Z	4	8
D_{calcd}, g cm^{-3}	1.41	1.42
μ, cm^{-1}	6.97	7.81
Mo Kα radiation, λ, Å	0.71069	0.71069
F(000), e	744	1552
diffractometer	Enraf-Nonius CAD4	
scan mode	ω–2θ	ω–2θ
$[(\sin\theta)/\lambda]_{max}$, Å^{-1}	0.65	0.65
T, °C	20	20
no. of measd rflns (±*h*,±*k*,+*l*)	8043	8333
no. of indep rflns	7759	7097
no. of obsd rflns ($I > 2\sigma(I)$)	6633	6121
no. of refined params	358	362
R	0.037	0.034
R_w ($w = 1/\sigma^2(F_o)$)	0.053	0.035
error of fit	2.80	1.54
resid electron dens, e Å^{-3}	0.60	0.59
structure soln	heavy-atom method	heavy-atom method

[a] H atom positions were calculated and kept fixed in the final refinement stage except on the disordered $-SiMe_3$ group; disordering 50:50. [b] H atom positions were calculated and kept fixed in the final refinement stage. Absolute configuration *K* = –0.03.

hedrally coordinated to two η^5-cyclopentadienyl ligands, a σ-bonded oxygen (O1), and a σ-bonded C(sp^2) center (C4). The Cp(centroid)–Zr–Cp(centroid) angle is 131°; the O1–Zr1–C4 angle is 89.0 (3)°. Both are within the typical range as observed for many 16-electron d^0-configurated zirconocene compounds.[27]

The characteristic feature of the structure of **2d** is the presence of a nonplanar oxazirconacyclohexadiene ring system, the conjugated diene portion of which (C1–C4) is planar and shows an alternating CC double-bond, single-bond, double-bond sequence (1.323 (6) Å (C1–C2), 1.449 (5) Å (C2–C3), 1.36 (1) Å (C3-C4)). These values do not deviate much from typical bond distances found in many organic conjugated diene systems (see e.g.: 1,3-butadiene, 1.330 Å (C1–C2), 1.455 Å (C2–C3); the C=C double-bond length in cyclohexa-1,3-diene is 1.332 Å).[28] The metal atom and O1 are oriented at opposite faces outside of the C1–C4 plane. While Zr is arranged at a distance of 0.55 Å "below" the diene carbon atom plane, O is located 0.22 Å "above" it. The Zr1–O1–C1 angle is very near to sp^2-hybridized oxygen at 122.1 (6)°, whereas the endocyclic

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Table VI. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for 2d with Standard Deviations in Parentheses[a]

atom	x	y	z	U_{eq}
Zr1	0.9010 (1)	0.8105 (1)	0.8191 (1)	0.037 (1)
Zr2	0.5664 (1)	0.7050 (1)	0.1593 (1)	0.037 (1)
Si1	1.0622 (1)	0.7305 (1)	0.6297 (1)	0.054 (1)
Si2	0.5338 (1)	0.7490 (1)	0.3911 (1)	0.076 (1)
O1	0.9296 (3)	0.9892 (2)	0.8480 (2)	0.053 (2)
O2	0.3917 (2)	0.5972 (2)	0.0840 (2)	0.050 (1)
C1	0.8957 (4)	1.0576 (3)	0.7863 (3)	0.057 (2)
C2	0.9087 (4)	1.0358 (3)	0.7049 (3)	0.056 (2)
C3	0.9617 (4)	0.9372 (3)	0.6662 (2)	0.051 (2)
C4	0.9819 (3)	0.8343 (3)	0.6964 (2)	0.042 (2)
C5	1.0373 (5)	0.7598 (5)	0.5142 (3)	0.083 (4)
C6	0.9798 (5)	0.5726 (4)	0.6258 (3)	0.082 (4)
C7	1.2552 (5)	0.7448 (5)	0.6731 (3)	0.081 (4)
C8	0.6946 (4)	0.6412 (4)	0.7713 (4)	0.077 (3)
C9	0.6679 (4)	0.7069 (5)	0.8408 (3)	0.074 (3)
C10	0.6430 (4)	0.8139 (4)	0.8191 (3)	0.071 (3)
C11	0.6535 (4)	0.8185 (4)	0.7343 (3)	0.069 (3)
C12	0.6860 (4)	0.7109 (5)	0.7023 (3)	0.081 (3)
C13	1.0904 (6)	0.6897 (5)	0.8635 (3)	0.080 (4)
C14	1.1555 (4)	0.8051 (5)	0.8891 (3)	0.073 (3)
C15	1.1049 (6)	0.8514 (4)	0.9517 (3)	0.079 (3)
C16	1.0032 (5)	0.7739 (6)	0.9692 (3)	0.084 (4)
C17	0.9895 (5)	0.6662 (4)	0.9146 (4)	0.096 (4)
C21	0.2598 (4)	0.6127 (3)	0.0878 (3)	0.053 (2)
C22	0.2210 (3)	0.6523 (3)	0.1598 (3)	0.053 (2)
C23	0.3107 (4)	0.6876 (3)	0.2467 (3)	0.051 (2)
C24	0.4560 (4)	0.7109 (3)	0.2718 (2)	0.046 (2)
C28	0.6865 (5)	0.9167 (3)	0.1704 (3)	0.073 (3)
C29	0.6649 (5)	0.8682 (4)	0.0835 (3)	0.074 (3)
C30	0.5201 (5)	0.8452 (4)	0.0477 (3)	0.071 (3)
C31	0.4500 (4)	0.8780 (3)	0.1113 (3)	0.062 (3)
C32	0.5527 (5)	0.9230 (3)	0.1882 (3)	0.067 (3)
C33	0.7715 (5)	0.6391 (5)	0.2541 (3)	0.081 (3)
C34	0.6669 (4)	0.5354 (4)	0.2218 (3)	0.065 (3)
C35	0.6563 (5)	0.5123 (3)	0.1349 (3)	0.068 (3)
C36	0.7459 (5)	0.5963 (4)	0.1096 (3)	0.074 (3)
C37	0.8193 (4)	0.6741 (4)	0.1811 (4)	0.079 (4)
C25a	0.397 (1)	0.765 (1)	0.4556 (7)	0.083 (3)
C25b	0.402 (1)	0.834 (1)	0.4465 (7)	0.089 (3)
C26a	0.678 (1)	0.8672 (9)	0.4230 (7)	0.062 (3)
C26b	0.701 (1)	0.888 (1)	0.4059 (8)	0.074 (3)
C27a	0.618 (1)	0.6044 (9)	0.4312 (7)	0.070 (3)
C27b	0.573 (1)	0.629 (1)	0.4440 (8)	0.096 (4)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{a}_i\cdot\bar{a}_j$.

Table VII. Comparison of Selected Structural Features of Complexes 2d and 2e[a]

	2d	2e
Zr1–O1/S1	2.021 (2)	2.503 (1)
Zr1–C4	2.263 (3)	2.266 (7)
O1/S1–C1	1.343 (5)	1.737 (6)
C1–C2	1.323 (6)	1.330 (7)
C2–C3	1.449 (5)	1.453 (8)
C3–C4	1.36 (1)	1.352 (8)
O1/S1–Zr1–C4	89.0 (3)	91.0 (1)
C1–O1/S1–Zr1	122.1 (6)	100.1 (3)
O1/S1–C1–C2	124.8 (3)	128.7 (5)
C3–C2–C1	127.3 (4)	130.6 (5)
C4–C3–C2	129.2 (3)	130.7 (6)
C3–C4–Si1	116.7 (3)	114.1 (7)
C3–C4–Zr1	113.8 (4)	118.0 (3)
Si1–C4–Zr1	129.5 (2)	127.6 (5)

[a] Distances (in Å) and angles (in deg) are averaged over the two independent molecules.

Table VIII. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for 2e with Standard Deviations in Parentheses[a]

atom	x	y	z	U_{eq}
Zr1	0.2626 (1)	0.4103 (1)	0.2867 (1)	0.040 (1)
Zr2	0.2874 (1)	0.0910 (1)	0.8643 (1)	0.044 (1)
S1	0.0521 (1)	0.4213 (1)	0.1033 (1)	0.060 (1)
S2	0.1626 (1)	0.0347 (1)	0.8753 (1)	0.054 (1)
Si1	0.3365 (1)	0.3261 (1)	0.6021 (2)	0.068 (1)
Si2	0.2621 (1)	0.1983 (1)	1.0179 (2)	0.066 (1)
C1	0.0079 (4)	0.3681 (2)	0.0432 (6)	0.068 (4)
C2	0.0488 (4)	0.3319 (2)	0.1298 (6)	0.068 (5)
C3	0.1439 (4)	0.3251 (1)	0.2962 (6)	0.062 (4)
C4	0.2354 (4)	0.3499 (1)	0.3947 (5)	0.050 (4)
C5	0.3193 (9)	0.2669 (2)	0.6021 (8)	0.16 (1)
C6	0.4866 (6)	0.3337 (3)	0.6720 (8)	0.136 (8)
C7	0.3113 (5)	0.3477 (2)	0.7562 (6)	0.088 (6)
C8	0.4239 (4)	0.3887 (1)	0.2616 (5)	0.056 (4)
C9	0.3638 (4)	0.4205 (1)	0.1426 (6)	0.059 (4)
C10	0.2584 (4)	0.4032 (2)	0.0266 (5)	0.062 (4)
C11	0.2537 (4)	0.3606 (2)	0.0734 (6)	0.064 (5)
C12	0.3567 (4)	0.3520 (1)	0.2178 (6)	0.060 (5)
C13	0.3543 (7)	0.4435 (2)	0.5647 (6)	0.099 (7)
C14	0.2487 (8)	0.4585 (4)	0.482 (1)	0.16 (1)
C15	0.2361 (9)	0.4847 (3)	0.364 (2)	0.19 (1)
C16	0.333 (1)	0.4857 (2)	0.3771 (9)	0.14 (1)
C17	0.4086 (5)	0.4604 (2)	0.4990 (9)	0.087 (6)
C21	0.2059 (4)	0.0395 (1)	1.0780 (5)	0.056 (4)
C22	0.2334 (4)	0.0752 (1)	1.1687 (5)	0.058 (4)
C23	0.2413 (3)	0.1201 (1)	1.1307 (5)	0.050 (3)
C24	0.2562 (3)	0.1372 (1)	1.0155 (4)	0.043 (3)
C25	0.2853 (6)	0.2214 (2)	1.2086 (7)	0.107 (8)
C26	0.3853 (5)	0.2167 (2)	1.0079 (7)	0.101 (6)
C27	0.1303 (5)	0.2239 (2)	0.8483 (8)	0.104 (6)
C28	0.4928 (4)	0.0976 (3)	0.9659 (9)	0.096 (6)
C29	0.4619 (5)	0.0553 (3)	0.9094 (8)	0.099 (7)
C30	0.4406 (5)	0.0342 (2)	1.0135 (9)	0.095 (7)
C31	0.4563 (4)	0.0626 (2)	1.1309 (6)	0.083 (5)
C32	0.4890 (4)	0.1020 (2)	1.1053 (7)	0.083 (5)
C33	0.2061 (5)	0.1486 (1)	0.6469 (5)	0.070 (5)
C34	0.1140 (4)	0.1246 (2)	0.6193 (5)	0.066 (4)
C35	0.1238 (6)	0.0833 (2)	0.5719 (6)	0.081 (5)
C36	0.2212 (7)	0.0813 (2)	0.5713 (7)	0.090 (7)
C37	0.2719 (5)	0.1208 (2)	0.6155 (6)	0.084 (5)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{a}_i\cdot\bar{a}_j$.

bond angles of the ring carbon atoms C1–C3 are all slightly larger at 124.8 (3), 127.3 (4), and 129.2 (3)°. In contrast, the C3–C4–Zr angle (113.8 (4)°) is reduced by 6° from the expected C(sp^2) value.

The zirconium–C4 bond is 2.263 (3) Å. This is within a typical range expected for a Zr–C(sp^2) σ-linkage (the Zr–(σ-vinyl) bond lengths of suitable reference molecules are about 2.25–2.27 Å[29]). There is no significant π-interaction between the organic conjugated diene system and the zirconium center in **2d**. A carbon to metal π-bonding component normal to the σ-framework would reveal itself in a markedly shortened Zr–C$_\alpha$ bonding distance. This effect has previously been observed in complexes such as, e.g., Cp$_2$ZrPh(CHPPh$_3$) (2.157 (4) Å),[24a] Cp$_2$Zr(μ-Cl)[μ-η^1:η^2-C(SiMe$_3$)=CPh]AlMe$_2$ (2.186 (3) Å), and Cp$_2$Zr(μ-C≡C-Ph)[μ-η^1:η^2-C(CH$_3$)=CPh]AlMe$_2$ (2.163 (3) Å).[30]

The Zr–O bond in **2d** is, at 2.021 (2) Å, close to a typical unperturbed Zr–OR linkage (e.g. Zr–O(Ar) = 2.074 Å, mean value).[31] We conclude that the product **2d**, derived from the thermal rearrangement of in situ generated Cp$_2$Zr(SiMe$_3$)(2-furyl) (**1d**), can be described as an ordinary oxametallacyclohexadiene, having the expected nonplanar structure which is not significantly planarized or coordinatively stabilized by oxygen to zirconium back-bonding or sp^2-carbon to zirconium delocalization.

The molecular structures of **2d** and **2e** in the crystal state are very similar. Complex **2e** also contains two inde-

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pendent molecules in the asymmetric unit. The Cp(centroid)-Zr-Cp(centroid) angles of both systems are identical (131°). The σ-ligand angle of the thiazirconacyclohexadiene complex is 91.0 (1)°. The conjugated diene portion and the orientation of the bulky trimethylsilyl substituent are almost alike for both metallacycles (see Table VII). The Zr-C(sp^2) bond length in **2e** averages to 2.266 (7) Å (d(Zr-C4)). The Zr-S distance is, at 2.503 (1) Å, close to the Zr-S(Ar) average (2.542 Å).[32] In contrast to the case for **2d**, the angle at the chalcogen atom is only 100.1 (3)° in **2e**. The presence of an almost unhybridized sulfur atom in the ring leads to a much larger deviation from planarity of the $SZrC_4$ skeleton. The zirconium atom is located outside the plane going through C1 to C4 of the conjugated diene system by 0.70 Å. The sulfur atom is oriented at the opposite face of this plane at a distance of 0.45 Å.

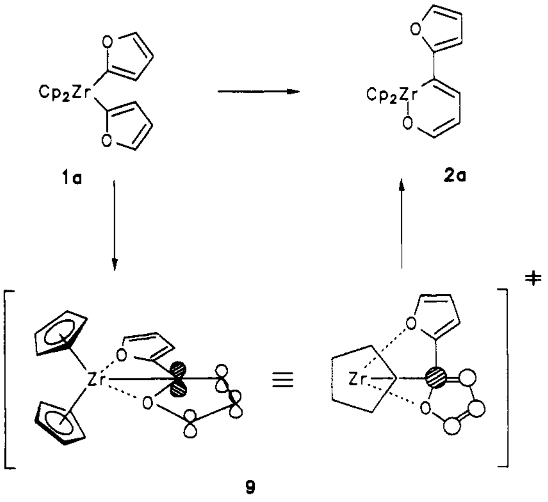
Conclusions

The furyl- and thienylzirconocene ring enlargement reactions described in this account represent some novel examples of thermally induced σ,σ-exchange reactions. The thermodynamically strong zirconium-carbon bond of a (σ-furyl)- (or (σ-thienyl)-) zirconocene moiety here serves as the pivot of the coupled σ,σ-migration reaction. At present the experimental observations are far from being sufficient to decide for or against a concerted reaction mechanism.[33] However, we have made a few key observations that may allow for a tentative interpretation of the essential features of this unusual rearrangement. The negative activation entropies observed for the **1a** to **2a** ($\Delta S^{\ddagger} = -9 \pm 5$ eu) and **1e** to **2e** ($\Delta S^{\ddagger} = -12 \pm 5$ eu) rearrangements point to an ordered transition state of this reorganization process. The observed $\Delta S^{\ddagger}$ values would be in accord with a dyotropic rearrangement process, although an alternative stepwise mechanism involving a caged radical pair would be hard to distinguish by the entropic argument alone (see Table I).[2,5]

Dyotropic rearrangements are likely to be "stepwise concerted" processes. Our observed $\Delta H^{\ddagger}$ values suggest that there is probably no significant furyl-*O* to zirconium or thienyl-*S* to zirconium interaction in the ground-state structures of complexes **1a** and **1e**, respectively.[3,4,7,8] However, the markedly faster reaction rates of the furylzirconocenes as compared to those of the thienylzirconocenes in otherwise comparable pairs of educts is an indication that building up the favorable chalcogen to transition-metal linkage in the course of the rearrangement process is a dominant factor for decreasing the activation barrier of the rearrangement process. This is a typical general feature of a dyotropic exchange reaction.[2,3]

Another noteworthy feature of the thermally induced furyl- and thienylzirconocene ring enlargement reactions is the observed sequence of σ-ligand migratory aptitudes. At similar half-lives e.g. $Cp_2Zr(\sigma\text{-furyl})_2$ and $Cp_2Zr(SiMe_3)(\sigma\text{-furyl})$ rearrange at temperatures differing by about 200 °C. If these rearrangement reactions of (σ-furyl)- and (σ-thienyl)metallocenes proceed concertedly, then an interesting question arises as to what the geometry of their transition states might look like. Due to the electronic features of the bent metallocene unit[27a] the σ,σ-exchange process directly involving the Cp_2Zr-C(sp^2) moiety is confined to take place in the CpZrCp bisecting plane. This means that all changes on the σ-bond level and all migratory movements of groups and substituents probably are taking place in the main plane of the bent metallocene unit. At some stage of the $Cp_2Zr(\sigma\text{-furyl})_2$ migratory rearrangement there must probably be some furyl oxygen to zirconium contact, thereby automatically inducing a coplanar arrangement of the σ-furyl framework with the reaction plane (see Scheme I). This would lead to the curious situation that migration of the other σ-furyl group from metal to carbon could potentially proceed through a transition-state geometry involving a planar tetracoordinate geometry at the α-carbon center.

Scheme I



Planar tetracoordinate carbon is characterized by having an electron-deficient σ-system (six electrons making four bonds) and an electron pair in a p orbital normal to the σ-plane.[11] Therefore, σ-donors (e.g. σ-bonded metal centers) would tend to stabilize this "unnatural" bonding form of carbon. In addition, π-acceptor substituents are required to remove electron density from an occupied nonbonding p orbital.[34] The very few examples of complexes exhibiting planar tetracoordinate carbon which were characterized by X-ray diffraction all possess two σ-donating metal substituents and have the p orbital being part of an extended π-system.[30,35] The transition state of the **1a** → **2a** rearrangement could possibly profit from both stabilizing effects: the early transition metal serving as a σ-donor and the furan π-system helping to delocalize p-electron density at the alleged planar tetracoordinate carbon center within the Zr-C pivot of the dyotropic rearrangement system.

One might speculate that the observed pronounced rearrangement-rate-enhancing effect of the trimethylsilyl

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migrating group would fit into this picture. Attaching a second metal center (i.e. a σ-donor) could further stabilize the electron-deficient σ-system at the central carbon center and thus lead to a reduced activation barrier of the overall rearrangement process. Whether sufficient additional stabilization can be achieved in related systems by introducing stronger σ-donating (e.g. aluminum-based) metal substituents that may eventually lead to novel stable and isolable examples of compounds exhibiting planar tetracoordinate carbon[30] is under active investigation in our laboratory.

Experimental Section

All reactions were carried out in an inert atmosphere using Schlenk type glassware (argon) or a glovebox (argon or nitrogen). Solvents were dried (potassium/benzophenone, lithium aluminum hydride, or P_4O_{10}) and distilled under argon prior to use. The following spectrometers were used: Bruker WP 200 SY NMR spectrometer (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz), some ^{13}C NMR data are given with ^1J(C,H) coupling constants in parentheses; Nicolet 5DXC FT IR spectrometer; Varian MAT CH7 and Finnigan 8200 MAT (exact mass) mass spectrometers. (2-Furyl)lithium, (2-thienyl)lithium, $Cp_2Zr(CH_3)Cl$, and Cp_2ZrPh_2 were prepared according to literature procedures.[17,36]

Bis(2-furyl)zirconocene (1a). A 26-mL portion of a 1.4 M solution of (2-furyl)lithium in ether was added dropwise over 1 h to a suspension of 5.34 g (18.3 mmol) of zirconocene dichloride in 100 mL of ether at −78 °C. The reaction mixture was warmed to room temperature with stirring over 18 h. Solvent was then removed in vacuo. The solid residue was stirred with 200 mL of chloroform for 30 min and then filtered from the remaining solid. The filtrate was stripped in vacuo to give 4.8 g (74%) of complex **1a**, mp 206 °C. ^{1}H NMR (benzene-d_6): δ 6.11 (s, 10 H, Cp); 2-furyl δ 7.39 (dd, 2 H, 5-H), 6.31 (dd, 2 H, 3-H), 6.14 (dd, 2 H, 4-H); coupling constants (Hz) ^3J = 3.1 (3-H/4-H), 1.5 (4-H/5-H), ^4J = 0.4 (3-H/5-H). ^{13}C NMR ($CDCl_3$): δ 110.5 (174 Hz, Cp); 2-furyl δ 107.7 (172 Hz, C-4), 123.1 (169 Hz, C-3), 143.9 (195 Hz, C-5), 206.8 (C-2). IR (KBr): ν 3101, 1436, 1017, 804 (Cp), 2964, 1394, 1262, 1099, 750 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2Zr$ (M_r 355.5): C, 60.81; H, 4.54. Found: C, 61.13; H, 4.79.

1,1-Bis(η-cyclopentadienyl)-1-zircona-2-oxa-6-(2′-furyl)cyclohexa-3,5-diene (2a). A laboratory autoclave fitted with a glass inlet was charged with a solution of bis(2-furyl)zirconocene (7.85 g, 22.1 mmol) in 100 mL of toluene. The solution was thermolyzed at 185 °C for 6 h. The dark red mixture was cooled and then filtered. Solvent was removed from the clear filtrate in vacuo to give a red oil. Stirring for 7 days with 70 mL of hexane yielded the product as a solid in 6.8 g (87%) yield, mp 69 °C. ^{1}H NMR (benzene-d_6): δ 5.93 (s, 10 H, Cp); 2-furyl δ 7.16 (dd, 1 H, 5′-H), 6.30 (dd, 1 H, 4′-H), 6.04 (dd, 1 H, 3′-H); coupling constants (Hz) ^3J = 3.2 (3′-H/4′-H), 1.9 (4′-H/5′-H), ^4J = 0.8 (3′-H/5′-H); metallacycle, see Table II. ^{13}C NMR (benzene-d_6): δ 111.3 (Cp); 2-furyl δ 164.6 (C-2′), 139.3 (C-5′), 110.2 (C-4′), 99.8 (C-3′); metallacycle, see Table III. IR (KBr): ν 3100, 1436, 1012, 807 cm^{-1} (Cp). UV (CH_2Cl_2): λ_{max} 229 (log ϵ = 4.3), 255 (log ϵ = 4.2), 350 nm (log ϵ = 3.9). MS (EI): m/e 354 (M$^+$). Anal. Calcd for $C_{18}H_{16}O_2Zr$ (M_r 355.5): C, 60.81; H, 4.54. Found: C, 60.34; H, 4.83.

Determination of the Activation Parameters of the 1a → 2a Rearrangement in the Temperature Range between 140 and 180 °C. Ca. 0.15 M solutions of **1a** in a toluene-d_8/tetrahydrofuran-d_8 (2:1) solvent mixture were used for the kinetic measurements. Samples were flame-sealed in 5-mm NMR tubes and then thermolyzed in a thermostated silicon oil bath (±0.1 °C temperature constant). After suitable reaction times the samples were removed from the hot oil bath and the rearrangement stopped by immersing the tube in an ice/water bath. The product analysis was carried out by ^{1}H NMR spectroscopy by integrating the bis(2-furyl)zirconocene Cp singlet at δ 6.10 against the Cp singlet at δ 5.81 of added $[Cp_2Zr(2\text{-furyl})]_2O$ standard. In addition, the **1a** + **2a** Cp intensity was monitored (using the same standard) to ensure that no product was lost during the thermolysis due to some unregistered side reaction. In the 140–180 °C temperature range the **1a** → **2a** rearrangement followed a first-order rate law. From the corresponding ln A/A_0 vs t plots the following rate constants (with estimated standard deviations in parentheses) were obtained: $k = [4.74\ (16)] \times 10^{-6}\ s^{-1}$ (140.0 °C); $[1.11\ (2)] \times 10^{-5}\ s^{-1}$ (150.0 °C); $[3.94\ (22)] \times 10^{-5}\ s^{-1}$ (160.0 °C); $[5.86\ (37)] \times 10^{-5}\ s^{-1}$ (170.0 °C); $[1.45\ (2)] \times 10^{-4}\ s^{-1}$ (180.0 °C). With these values the Arrhenius plot (ln k vs T^{-1}) produced the activation parameters of $\Delta H^* = 30.9$ ● 2.0 kcal mol^{-1} and $\Delta S^* = -9$ ● 5 cal mol^{-1} K^{-1}.

Reaction of 2a with Dimethyl Acetylenedicarboxylate. (a) NMR Experiment. To a solution of 30 mg (0.08 mmol) of **2a** in 0.5 mL of benzene-d_6 was added 10 μL (ca. 0.08 mmol) of $H_3CO_2CC{\equiv}CCO_2CH_3$. The mixture was transferred and sealed in a NMR tube and then kept at 90 °C for 4 h. The ^{1}H NMR spectrum of the resulting mixture revealed a small amount of residual starting material along with the typical resonances of the products **3** (see below) and cyclotrimeric zirconocene oxide ($[Cp_2ZrO]_3$: δ 6.21, s, Cp).

(b) Reaction on a Preparative Scale. The metallacycle **2a** (1.43 g, 4.02 mmol) was dissolved in toluene (30 mL). Dimethyl acetylenedicarboxylate (0.5 mL, 4.1 mmol) was added and the mixture then heated for 18 h at 105 °C. Solvent was removed in vacuo at ambient temperature. The residue was chromatographed (silica gel, 2:1 ethyl acetate/n-hexane) to give 0.74 g (70%) of **3** as a colorless oil. ^{1}H NMR (benzene-d_6): 2-furyl δ 7.06 (dd, 1 H, 5′-H), 6.66 (dd, 1 H, 3′-H), 6.10 (dd, 1 H, 4′-H); coupling constants (Hz) ^3J = 1.8 (4′-H/5′-H), 3.5 (3′-H/4′-H), ^4J = 0.7 (3′-H/5′-H); arene δ 7.71 (dd, 1 H, ^3J = 7.8, ^4J = 1.2), 7.62 (dd, 1 H, ^3J = 8.0, ^4J = 1.2), 6.88 (t, 1 H, ^3J = 8.0); $COOCH_3$ δ 3.72 (s, 3 H), 3.38 (s, 3 H). ^{13}C NMR (benzene-d_6): δ 51.5, 52.0, 109.2, 112.1, 129.19, 129.24, 130.9, 132.9, 142.5, 143.2, 151.1, 165.7, 169.1 (one signal hidden under solvent). IR (film): ν 1730 cm^{-1} (C═O). MS (EI): m/e 260.0685 (calcd and found, M$^+$).

(2-Furyl)methylzirconocene (1b). Methylzirconocene chloride (4; 1.03 g, 3.79 mmol) was dissolved in 50 mL of ether and the solution cooled to −78 °C. A 3.9-mL portion of a 1.16 M solution of (2-furyl)lithium (4.55 mmol) in ether was added dropwise. The reaction mixture was warmed to ambient temperature over 12 h with stirring. Solvent was then removed in vacuo and the residue extracted with 50 mL of chloroform. Filtration and removal of the solvent from the filtrate in vacuo gave 1.15 g (corresponding to an about quantitative yield) of a brownish solid (mp 128 °C) containing 82% of **1b**, 5% of bis(2-furyl)zirconocene, and 13% of dimethylzirconocene. The mixture was not further purified. The NMR signals of the major product **1b** are as follows. ^{1}H NMR ($CDCl_3$): δ 6.28 (s, 10 H, Cp), −0.15 (s, 3 H, CH_3); 2-furyl, see Table IV. ^{13}C NMR ($CDCl_3$): δ 110.4 (Cp), 34.7 (CH_3); 2-furyl, see Table IV. IR (KBr): ν 3097, 1441, 1015, 802 cm^{-1} (Cp). Anal. Calcd for $C_{15}H_{16}OZr$ (M_r 303.5): C, 59.36; H, 5.31. Found (for the 82:5:13 mixture of products): C, 57.36; H, 5.41.

Thermolysis of (2-Furyl)methylzirconocene (1b). A 0.27-g (0.9-mmol) sample of **1b** was dissolved in 10 mL of toluene and the solution sealed in a glass ampule. The solution was kept for 4 h at 200 °C (using a steel autoclave). The sealed tube was cooled and opened. The reaction mixture was filtered and the filtrate stripped in vacuo. The residue was washed with pentane (10 mL) and dried to give 0.1 g (37%) of a mixture of products, among which the dyotropic rearrangement product **2b** was tentatively assigned by ^{1}H NMR spectroscopy (see Table II).

(2-Furyl)phenylzirconocene (1c). Furan (5 mL, 64.4 mmol) was added to a solution of 6.05 g (16.1 mmol) of diphenylzirconocene in 80 mL of toluene. The mixture was stirred for 14 h at 90 °C. A red solution resulted, which was concentrated in vacuo to a volume of ca. 20 mL. The product **1c** precipitated and was collected by filtration, washed with 30 mL of hexane, and dried in vacuo to give 3.0 g (51%) of (2-furyl)phenylzirconocene (mp 146 °C). Addition of 50 mL of hexane to the mother liquor gave an additional 1.9 g (32%) of less pure **1c**. ^{1}H NMR (benzene-d_6): δ 6.92–7.07 (m, 5 H, Ph); Cp and 2-furyl, see Table IV. ^{13}C NMR (benzene-d_6): δ 184.8, 134.5, 127.2, 125.1; Cp and 2-furyl, see Table IV. IR (KBr): ν 3107, 1441, 1016, 805 cm^{-1} (Cp).

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Thermolysis of (2-Furyl)phenylzirconocene (1c). (a) In Benzene-d_6. A 10% solution of **1c** in 0.5 mL of benzene-d_6 was sealed in a 5-mm NMR tube and then thermolyzed in a laboratory autoclave. The progress of the reaction was monitored at various times and temperatures. Some reaction was taking place at temperatures above 120 °C and followed for a total of 6 h reaction time up to a limiting temperature of 155 °C. Initially, the formation of (deuterated) diphenylzirconocene was revealed by the appearance of a Cp signal at δ 5.82. Eventually, decomposition with formation of almost quantitative amounts of furan and benzene took place.

(b) In Furan Solution. A sample of 0.32 g (0.88 mmol) of **1c** was dissolved in 10 mL of furan and then heated in a sealed glass ampule inside a laboratory autoclave for 5 h at 190 °C. Some solid was allowed to precipitate; a sample was taken from the clear supernatant liquid and its solvent stripped in vacuo. The ^{1}H NMR spectrum of the residue in benzene-d_6 revealed that a mixture of organometallic compounds had been formed, among which **2a** was positively identified and **2c** was tentatively assigned from its very characteristic ^{1}H NMR appearance (see Table II).

1,1-Bis(η-cyclopentadienyl)-1-zircona-2-oxa-6-(trimethylsilyl)cyclohexa-3,5-diene (2d). A 1.6-mL portion of an ethereal solution of (2-furyl)lithium (1.9 mmol) was added dropwise to a solution of 0.6 g (1.8 mmol) of (trimethylsilyl)zirconocene chloride (**7**) in 20 mL of ether at −78 °C. The reaction mixture was warmed to room temperature over 12 h with stirring. Then, the solvent was removed in vacuo. The residue was extracted with 20 mL of toluene. The toluene solution was stripped and the solid washed with 15 mL of pentane to give 0.4 g (63%) of **2d**. Recrystallization from diethyl ether gave single crystals (mp 116 °C) suitable for the X-ray crystal structure analysis. ^{1}H NMR (benzene-d_6): δ 0.22 (s, 9 H, SiMe$_3$); Cp and metallacycle, see Table II. ^{13}C NMR (benzene-d_6): δ 1.99 (SiMe$_3$); Cp and metallacycle, see Table III. IR (KBr): ν 3108, 1439, 1016, 799 (Cp), 2961, 1569, 1465 cm^{-1}. UV (CH$_2$Cl$_2$): λ_{max} 229 (log ε = 4.0), 322 nm (log ε = 3.3). Exact mass: *m/e* calcd for $C_{17}H_{22}OSiZr(M^+)$ 361.7, found 360.047. For details of the X-ray crystal structure analysis of **2d** see Table V.

Bis(2-thienyl)zirconocene (1f). A suspension of 7.20 g (24.6 mmol) of zirconocene dichloride in 50 mL of ether was cooled to −78 °C. Then, 44.8 mL of a 1.1 M solution of (2-thienyl)lithium in ether (49.3 mmol) was added dropwise over 45 min with stirring. The reaction mixture was warmed to room temperature over 12 h. Solvent was then removed in vacuo and the remaining residue extracted with 100 mL of chloroform. Filtration and removal of the solvent from the filtrate gave 4.8 g (50%) of crude **1f** as a fine powder. Recrystallization from 50 mL of toluene at −78 °C gave crystalline **1f**: yield 3.6 g (38%); mp 185 °C. ^{1}H/^{13}C NMR: see Table IV. IR (KBr): ν 3085, 1442, 1014, 806 cm^{-1} (Cp). Anal. Calcd for $C_{18}H_{16}S_2Zr$ (M_r 387.7): C, 55.77; H, 4.16. Found: C, 55.63; H, 4.05.

Thermolysis of Bis(2-thienyl)zirconocene (1f). (a) NMR Experiment. A sample of **1f**, dissolved in benzene-d_6, was sealed in a 5-mm NMR tube and then thermolyzed at 185 °C in a laboratory autoclave containing toluene for pressure equalization. ^{1}H NMR analysis after 5 h revealed the formation of some zirconocene sulfide dimer (δ 6.26, s, Cp) and thiophene. After 18 h at 185 °C about 50% of the starting material **1f** was decomposed.

(b) A sample of 0.55 g (1.4 mmol) of bis(2-thienyl)zirconocene was dissolved in 10 mL of toluene and the solution sealed in a glass ampule. The reaction mixture was then thermolyzed at 205 °C inside a laboratory steel autoclave for 11 h, using toluene as a means of heat transfer and pressure equalization. After it was cooled to room temperature, the mixture was filtered and the filtrate stripped in vacuo. The resulting residue was washed with 20 mL of pentane to give 0.3 g (80%) of 1,3-bis(η-cyclopentadienyl)-1,3-dizirconadithietane (**8**) identified by ^{1}H/^{13}C NMR and MS comparison with an authentic sample (^{1}H NMR (benzene-d_6) δ 6.26 (s, Cp); ^{13}C NMR (benzene-d_6) δ 114.0 (Cp); MS (EI) *m/e* 504 (M$^+$)).

Methyl(2-thienyl)zirconocene. A 3.0-mL portion of a 1.1 M solution of (2-thienyl)lithium in ether was added dropwise to 0.56 g (2.1 mmol) of methylzirconocene chloride in 50 mL of ether at −78 °C. The solution was warmed to room temperature over 12 h. Solvent was removed in vacuo and the residue extracted with 30 mL of chloroform. After filtration and stripping of the solvent in vacuo a red oily residue resulted, which was washed with 30 mL of pentane and then dried in vacuo to give 0.6 g (90%) of a solid (mp 121 °C) containing methyl(2-thienyl)zirconocene (86%), bis(2-thienyl)zirconocene (11%), and dimethylzirconocene (3%). The mixture was not further separated. Methyl(2-thienyl)zirconocene (in the mixture) gave the following data. ^{1}H NMR (benzene-d_6): δ 5.86 (s, 10 H, Cp); 2-thienyl δ 7.52 (dd, 1 H, 5-H), 7.13 (dd, 1 H, 4-H), 7.05 (dd, 1 H, 3-H); coupling constants (Hz) ^3J = 4.5 (4-H/5-H), 3.2 (3-H/4-H), ^4J = 0.6 (3-H/5-H); δ 0.20 (s, 3 H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ 111.0 (Cp), 35.5 (CH$_3$), 176.7, 136.5, 130.4, 126.7 (2-thienyl). IR (KBr): ν 3089, 1439, 1015, 805 cm^{-1} (Cp). Anal. Calcd for $C_{15}H_{16}SZr$ (M_r 319.6): C, 56.38; H, 5.05. Found (for the 86:11:3 mixture of products): C, 54.68; H, 4.83.

Thermolysis of Methyl(2-thienyl)zirconocene. A sample of $Cp_2Zr(CH_3)(C_4H_3S)$ (ca. 10% in benzene-d_6) was thermolyzed in a sealed NMR tube as described above for **1f**. After 4 h at 160 °C extensive decomposition was monitored by ^{1}H NMR spectroscopy, yielding a mixture of $[Cp_2ZrS]_2$ and bis(2-thienyl)zirconocene (1.4:1 ratio) in addition to some thiophene and methane.

(2-Thienyl)(trimethylsilyl)zirconocene (1e). A solution of 0.90 g (2.73 mmol) of (trimethylsilyl)zirconocene chloride in 20 mL of ether was cooled to −78 °C. Then, a precooled (−78 °C) solution containing 3.27 mmol of (2-thienyl)lithium in 20 mL of ether was added dropwise with stirring. The reaction mixture was then warmed to −40 °C over 2 h. It was then stirred for another 1 h at 0 °C. Solvent was removed in vacuo at 0 °C. The residue was taken into toluene at 0 °C and the solution filtered cold. The solvent was removed at 0 °C in vacuo to give complex **1e** as a red solid (0.95 g, 92%) containing a small quantity of toluene. The thermolabile product was not further purified and characterized spectroscopically. ^{1}H NMR (toluene-d_8, −30 °C): δ 0.12 (s, 9 H, SiMe$_3$); for the remaining signals, see Table IV. ^{13}C NMR (toluene-d_8, −30 °C): δ 5.7 (SiMe$_3$); for Cp and 2-thienyl resonances, see Table IV.

Determination of the Activation Parameters of the 1e → 2e Rearrangement. The kinetics of the **1e** → **2e** rearrangement were determined similarly as described above for the **1a** → **2a** isomerization. The concentration decrease of the starting material **1e** was monitored by ^{1}H NMR spectroscopy in toluene-d_8 at −30 °C. The thermolyses were carried out at five temperatures between 30 and 70 °C using a thermostated 1:1 H$_2$O/ethylene glycol bath (±0.1 °C). The following rate constants (with esd's) were obtained: $k = [4.6\ (5)] \times 10^{-5}\ s^{-1}$ (30.0 °C); $[8.3\ (6)] \times 10^{-5}\ s^{-1}$ (40.0 °C); $[2.94\ (5)] \times 10^{-4}\ s^{-1}$ (50.0 °C); $[8.62\ (9)] \times 10^{-4}\ s^{-1}$ (60.0 °C); $[2.33\ (3)] \times 10^{-3}\ s^{-1}$ (70.0 °C). With these *k* values the Arrhenius plot gave activation parameters of $\Delta H^\ddagger = 20.4 \pm 2.0$ kcal mol^{-1} and $\Delta S^\ddagger = -12 \pm 5$ cal mol^{-1} K^{-1}.

1,1-Bis(η-cyclopentadienyl)-1-zircona-2-thia-6-(trimethylsilyl)cyclohexa-3,5-diene (2e). (Trimethylsilyl)zirconocene chloride (0.34 g, 1.03 mmol) was dissolved in 10 mL of ether and the solution cooled to −78 °C. A solution (1.1 mL, 1.2 mmol) of (2-thienyl)lithium in ether was added dropwise. Then, the reaction mixture was warmed to room temperature over 12 h. Solvent was removed in vacuo and the residue extracted with 20 mL of toluene. The filtered toluene solution was then heated for 3 h at 50 °C. The toluene solvent was removed in vacuo and the residue recrystallized from 15 mL of ether. Complex **2e** was obtained as a yellowish fine powder (yield 0.17 g, 44%). From the mother liquor a small amount of crystalline **2e** was obtained (mp 170 °C) which was suitable for the X-ray crystal structure determination. ^{1}H NMR (benzene-d_6): δ 0.15 (s, 9 H, SiMe$_3$); Cp and metallacycle, see Table II. ^{13}C NMR (benzene-d_6): δ 2.3 (SiMe$_3$); Cp and metallacycle, see Table III. IR (KBr): ν 3096, 1436, 1017, 803 cm^{-1} (Cp). Exact mass: *m/e* calcd and found for $C_{17}H_{22}SSiZr$ 377.7. For details of the X-ray crystal structure analysis, see Table V.

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Registry No. **1a**, 123384-33-8; **1b**, 139167-68-3; **1c**, 139167-69-4; **1e**, 139167-70-7; **1f**, 139167-71-8; **2a**, 123384-34-9; **2b**, 139167-72-9;

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2c, 139167-73-0; **2d**, 139167-74-1; **2e**, 139167-75-2; **3**, 123418-15-5; **4**, 1291-45-8; **5**, 51177-89-0; **7**, 76772-61-7; **8**, 92097-09-1; $H_3CO_2CC{\equiv}CCO_2CH_3$, 762-42-5; zirconocene dichloride, 1291-32-3; (2-furyl)lithium, 2786-02-9; (2-thienyl)lithium, 2786-07-4; methyl(2-thienyl)zirconocene, 139167-76-3; dimethylzirconocene, 12636-72-5.

Supplementary Material Available: Details of the X-ray crystal structure analyses of **2d** and **2e**, including listings of atomic fractional coordinates, thermal parameters, and bond distances and angles (16 pages); listings of observed and calculated structure factors (46 pages). Ordering information is given on any current masthead page.

Alkali-Induced Decomposition of (2-Hydroxyethyl)aquocobaloxime: Resolution of a Long-Standing Mechanistic Dilemma

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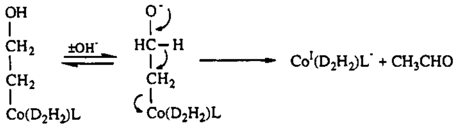
The kinetics of the alkali-induced decomposition of (2-hydroxyethyl)aquocobaloxime ($HOCH_2CH_2Co(D_2H_2)OH_2$) to form acetaldehyde have been studied in H_2O and in ${}^2H_2O$, as well as the kinetics of the alkali-induced decomposition of $HOC^2H_2C^2H_2Co(D_2H_2)OH_2$ in H_2O. The results are consistent with a simple kinetic scheme in which both the aquo and hydroxo complexes are reactive, with the latter being about 20-fold more labile. The kinetics of the base-catalyzed exchange of the acetaldehyde methyl protons with solvent deuterons in phosphate-buffered ${}^2H_2O$ and those of the exchange of perdeuterioacetaldehyde methyl deuterons with solvent protons in phosphate-buffered H_2O were also measured. Under all conditions, these exchange processes were faster than the alkali-induced decomposition of the relevant (2-hydroxyethyl)cobaloxime at the same basicity. In order to distinguish between a proposed mechanism in which acetaldehyde enolate is formed by elimination from a cis enolate intermediate and a mechanism in which acetaldehyde is directly formed by a 1,2-hydride shift, it was necessary to determine the isotopic composition of the acetaldehyde methyl group prior to its base-catalyzed exchange with solvent, when $HOCH_2CH_2Co(D_2H_2)OH_2$ was decomposed in ${}^2H_2O$ and when $HOC^2H_2C^2H_2Co(D_2H_2)OH_2$ was decomposed in H_2O. This was accomplished by sampling reaction mixtures at various times, quenching the reaction, and converting the acetaldehyde to its oxime for mass spectral analysis. The results show that at very short reaction times there is very little or no solvent hydrogen isotope in the acetaldehyde methyl group but that solvent hydrogen isotope accumulates in the acetaldehyde methyl group with increasing time due to base-catalyzed exchange. Since enol acetaldehyde ketonization in aqueous base occurs by rapid protonation of the β-carbon of the enolate anion by solvent, these observations eliminate all mechanisms for the alkali-induced decomposition of (2-hydroxyethyl)cobaloximes in which enol acetaldehyde is the immediate product. It is therefore concluded that the reaction occurs by the 1,2-hydride shift mechanism.

Introduction

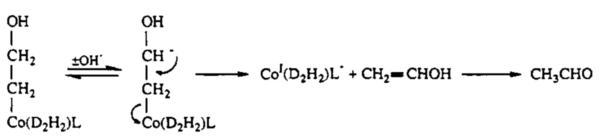
The alkali-induced decomposition of (2-hydroxyethyl)cobaloximes,[1] to yield acetaldehyde and cob(I)aloxime (eq 1) was originally described by Schrauzer and Windgassen[2] over 20 years ago. In that work and in later publications,[3,4]

$$HOCH_2CH_2Co(D_2H_2)L \xrightarrow{OH^-} Co^I(D_2H_2)L^- + CH_3CHO \qquad (1)$$

Schrauzer and co-workers proposed a 1,2-hydride shift mechanism (eq 2) for this reaction. The alternative base-catalyzed β-elimination mechanism (eq 3) was ruled out on the basis of the observation that (2-alkoxyethyl)(pyridine)cobaloximes were stable in aqueous base.[2-4] Subsequent observations by others,[5,6] however, showed that (2-alkoxyethyl)cobaloximes, $ROCH_2CH_2Co(D_2H_2)L$, are, indeed, unstable in aqueous base, albeit significantly less so than (2-hydroxyethyl)cobaloximes.[7] However, the alkali-induced decomposition of $ROCH_2CH_2Co(D_2H_2)L$ evidently occurs by a completely different mechanism. Thus, β-elimination products (i.e., alkyl vinyl ethers) are *not* obtained. Instead, the observed products are ethylene and the alcohol derived from the alkoxide group, ROH.[5,6] In a careful mechanistic study,[6] ethylene was found to be formed from a series of five $ROCH_2CH_2Co(D_2H_2)OH_2$'s via a mechanism in which hydroxide ion attack on an equatorial quaternary carbon leads to formation of an altered cob(III)aloxime product in which one of the Schiff base linkages has become hydrated.[9] No alkyl vinyl ethers could be detected during decomposition of any of the



$$HOCH_2CH_2Co(D_2H_2)L \overset{\pm OH^-}{\rightleftharpoons} {}^-OCH(H)CH_2Co(D_2H_2)L \longrightarrow Co^I(D_2H_2)L^- + CH_3CHO \qquad (2)$$



$$HOCH_2CH_2Co(D_2H_2)L \overset{\pm OH^-}{\rightleftharpoons} HO\overset{-}{C}HCH_2Co(D_2H_2)L \longrightarrow Co^I(D_2H_2)L^- + CH_2{=}CHOH \longrightarrow CH_3CHO \qquad (3)$$

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[1] Abbreviations: $RCo(D_2H_2)L$ = (alkyl)(ligand)cobaloxime = (alkyl)(ligand)bis(dimethylglyoximato)cobalt(III).

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[3] Schrauzer, G. N.; Sibert, J. W. *J. Am. Chem. Soc.* **1970,** *92,* 1022.

[4] Schrauzer, G. N.; Weber, J. H.; Beckham, T. M. *J. Am. Chem. Soc.* **1970,** *92,* 7078.

[5] Mock, W. L.; Bieniarz, C. *Organometallics* **1984,** *3,* 1279.

[6] Brown, K. L.; Szeverenyi, Z. *Inorg. Chim. Acta* **1986,** *119,* 149.

[7] Strongly donating axial ligands, L, such as pyridine, decrease the alkali-induced reactivity of $ROCH_2CH_2Co(D_2H_2)OH_2$'s[5] as well as that of $HOCH_2CH_2Co(D_2H_2)OH_2$.[8]

[8] Mock, W. L.; Bieniarz, C. *Organometallics* **1985,** *4,* 1917.

[9] For $ROCH_2CH_2Co(D_2H_2)OH_2$'s with good alkoxide leaving groups (R = C_6H_5 or CF_3CH_2) ethylene formation was quantitative. For complexes with poorer leaving groups (R = CH_3, CH_3CH_2, $(CH_3)_2CH$) hydroxide ion attack leads to less than stoichiometric yields of ethylene due to formation of a base-stable (alkoxyethyl)cobaloxime analogue, in which one of the Schiff base linkages is hydrated (vide infra).

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