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Formation and Rearrangement of (Siloxymethyl)zirconocene Chloride Complexes

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The zirconocene η^2-formaldehyde dimer **6** reacts with trialkylchlorosilanes R_3SiCl (R = ethyl, methyl, isopropyl) to yield the (η^2-(trialkylsiloxy)methyl)zirconocene chloride complexes $Cp_2\overline{Zr(Cl)CH_2O}SiR_3$ (**7a–c**). These complexes exhibit internal O-coordination; they belong to a metallaoxirane structural type. Thermolysis of **7b,c** at 110 °C leads to equilibration with the isomers **8b,c** and **9b,c**. Complexes **8** are the acyclic $Cp_2Zr(Cl)CH_2OSiR_3$ isomers of **7**, whereas dyotropic rearrangement has resulted in the formation of the $Cp_2Zr(Cl)OCH_2SiR_3$ products **9**. The kinetics of the thermally induced rearrangement of **7b** ($R = CH_3$) is described by a **8b** ⇌ **7b** → **9b** kinetic scheme. At 110 °C the K(**8b** ⇌ **7b**) equilibrium constant is 0.35. The Gibbs activation energy of the **7b** → **8b** isomerization at 110 °C is $\Delta G^{\ddagger}_{isom}(383\ K) = 30.9 \pm 0.5$ kcal mol^{-1}. The activation barrier of the **7b** → **9b** transformation is in the expected range of a concerted dyotropic rearrangement process at $\Delta G^{\ddagger}_{dyo}(383\ K) = 31.5 \pm 0.5$ kcal mol^{-1}. Treatment of **6** with triphenylchlorosilane has resulted in the direct formation of the acyclic addition product $Cp_2Zr(Cl)CH_2OSiPh_3$ (**8d**). Our study underlines the important participation of metallaoxirane type structures in dyotropic rearrangement systems.

Dimetallic metallaoxirane compounds of the general type **1** have been employed in a variety of attempts aimed at using well-defined molecular complexes for modeling reactions of methylene units at (metal oxide) surfaces. Several important single steps of the Fischer–Tropsch reaction sequence are mimicked by such molecular systems, including CH_2-group transfer and oligomerization.[1] Of special interest is the ability of the systems **1** to exhibit intramolecular methylene migration (i.e. **1** ⇌ **1′**), a reaction that may be looked at as a simple molecular analog of methylene mobility on a metal oxide surface.[2]

1 **1'**

Table 1. Gibbs Activation Energies of Dyotropic Rearrangements and Related Coupled σ-Exchange Reactions

compd	$\Delta G^{\ddagger}$ (kcal mol^{-1})	*T* (K)	ref
$(CH_3)_3Si(OCC_{12}H_8)Si(CD_3)_3$	26.3 ± 2	426	7
$(CH_3)_3Si(OCPh_2)allyl$	28.4 ± 2	450	8
$Cp_2ZrCl(CH_2O)ZrCp_2Cl$	7.0 ± 1.0	140	5
$Cp_2ZrPh(CH_2O)ZrCp_2Ph$	10.0 ± 0.5	190	5
$Cp_2Zr(Cl)CH_2OSi(CH_3)_3$	31.5 ± 0.5	383	*a*
$Cp_2Zr(Cl)CH_2OCH_2Ph$	26.8 ± 1.5	363	9

[a] This work.

There is evidence that the **1** ⇌ **1′** transformation represents an important contribution in molecular systems undergoing *dyotropic rearrangements*. Reetz has pointed out that the intermediate involvement of high-energy silaoxirane structures (**3**) may take place in the dyotropic rearrangement of the (silyl)siloxymethanes **2**.[3] Typically activation energies ~30 kcal mol^{-1} are observed for the concerted intramolecular silyl group exchange reaction at such systems (see Table 1 for selected examples) and a qualitative reaction profile as depicted in Figure 1is involved. Floriani has shown that the corresponding zirconium complexes **4** exhibit metallaoxirane ground state structures.[4] We have shown that their dyotropic rearrangement consequently is taking place much faster due to the thermodynamic stabilization of the metallaoxirane structure relative to the acyclic isomer **5** ($\Delta G^{\ddagger} \approx 7$–15 kcal mol^{-1}; see Table 1 and Figure 1).[2,5]

The qualitative reaction profiles as depicted in Figure 1 bear an interesting consequence for the "dyotropic" positional metal exchange in the hypothetical mixed transition-metal/main-group-metal systems $[Zr]{-}CR_2{-}O[Si] \rightleftharpoons [Si]{-}CR_2{-}O{-}[Zr]$. Only the zirconium section of such systems can energetically profit from the metallaoxirane formation, whereas three-membered-ring closure at the "silicon end" should only lead to a high-lying intermediate structure with a fleeting existence. Consequently,

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(2) Reviews: Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Erker, G. *Angew. Chem.* **1989**, *101*, 411; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397.

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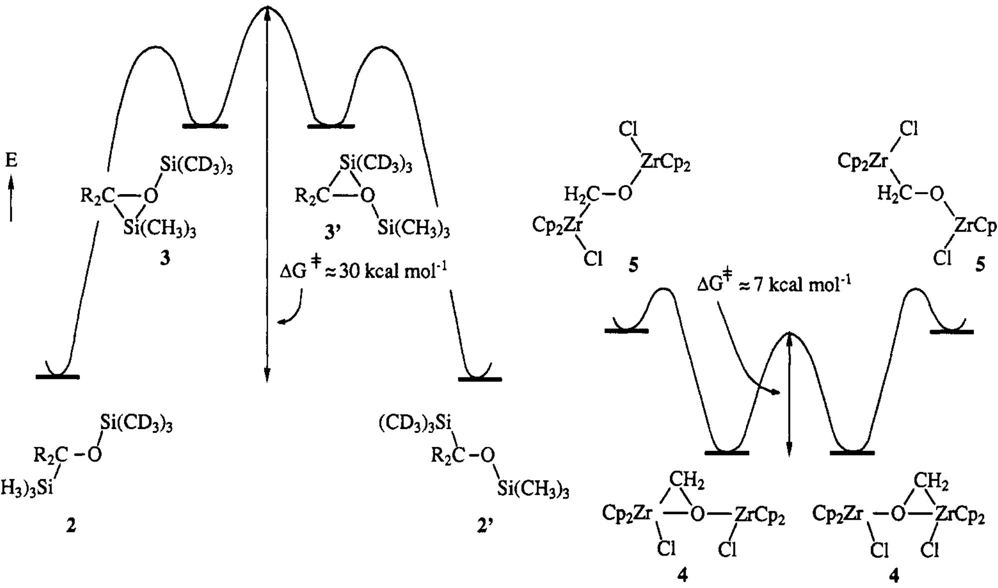
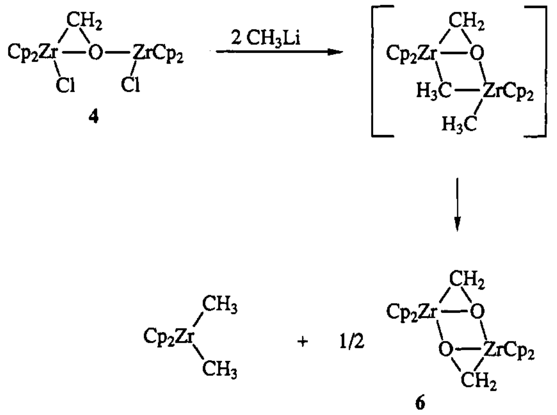


Figure 1. Typical qualitative reaction profiles of dyotropic rearrangements of M–CR$_2$–O–M′ systems (M = M′ = SiR$_3$ or Zr(X)Cp$_2$).

the high energy barrier associated with this section of the energy profile of a typical dyotropic rearrangement reaction must be overcome for the mixed [Zr][Si](μ-CR$_2$–O) system. Therefore, for such a rearrangement an activation barrier of ~30 kcal mol^{-1} (or higher) is expected for the concerted intramolecular metal exchange of such substrates. To our knowledge this consequence of the proposed general reaction profile of the dyotropic rearrangement has never been checked experimentally, since there was no straightforward synthetic entry to such zirconium- and silicon-containing materials. We have now developed a preparative route to [Zr][Si](μ-CH$_2$O) complexes[6] and qualitatively investigated their thermochemical behavior.

Results and Discussion

The dimeric zirconocene η^2-formaldehyde complex **6** has served as the starting material for our synthesis of the ((silyloxy)methyl)zirconocene chlorides **7a–d**. The metallaoxirane dimer **6** was prepared by treatment of (Cp$_2$ZrCl)$_2$(μ-CH$_2$O) (**4**) with 2 molar equiv of methyllithium, as previously described.[1a] The metathetical exchange product (Cp$_2$ZrMe)$_2$(μ-CH$_2$O) is probably formed initially in this reaction and then rapidly decomposes under the applied conditions to yield [Cp$_2$Zr(CH$_2$O)]$_2$ (**6**) and dimethylzirconocene.



Complex **6** was treated with triethylchlorosilane. A suspension of the metallaoxirane dimer **6** in tetrahydrofuran was charged with 2 molar equiv of ClSi(C$_2$H$_5$)$_3$ and stirred at 50 °C. A clear solution was obtained after 2 h from which ((triethylsiloxy)methyl)zirconocene chloride (**7a**) was isolated in near 80% yield. Complex **7a** has retained the metallaoxirane structure of the [ZrCH$_2$O] moiety. It shows a ^{1}H NMR singlet at δ 2.81 corresponding to the Zr-bound methylene group in the typical range of zirconaoxirane chemical shifts. The three-membered-ring structure is clearly deduced from the ^{13}C NMR features of the ZrCH$_2$O group: the methylene carbon center gives rise to a resonance signal at δ 67.0 (in benzene-d_6) with a $^1J_{CH}$ coupling constant of 150 Hz. We have shown previously that zirconaoxiranes exhibit some resemblance to cyclopropanes or oxiranes in featuring characteristically high values of the methylene $^1J_{CH}$ coupling constant (typically close to 150 Hz) that distinctly distinguishes them from their acyclic isomers (typical examples are given in Table 2 and below).

The reaction between **6** and triethylchlorosilane requires zirconium–oxygen bond breaking at some initial stage. This is achieved by thermal activation (see above) but can also be induced photochemically. Irradiation of **6** (suspension in tetrahydrofuran) with UV/vis light >300 nm in the presence of the triethylchlorosilane scavenger (1:2 molar ratio) at 0 °C rapidly led to the formation of **7a**.[12] The chlorosilane addition product **7a** was prepared photochemically from **6** and isolated in ca. 60% yield.

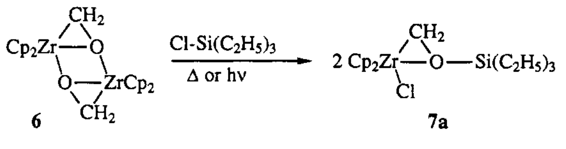


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Table 2. Comparison of Selected CH_2O NMR Data for Acyclic and Metallaoxirane Type $[M^1](\mu$-formaldehyde)$[M^2]$ Complexes and Related Compounds[a]

	acyclic isomer			metallaoxirane			
compd	^1H (δ)	^{13}C (CH_2O) (δ)	$^1J_{CH}$ (Hz)	^1H (δ)	^{13}C (CH_2O) (δ)	$^1J_{CH}$ (Hz)	ref
$[Cp_2Zr(CH_2O)]_2$ (**6**)	*b*			2.42^{c}	64.0^{c}	153	1a
$(Cp_2ZrCl)_2(CH_2O)$ (**4**)	*b*			2.72^{d}	72.4^{d}	153	4, 5
$Cp_2Zr(Cl)CH_2OCH_2Ph$	*b*			2.48	64.9	*g*	9
$Cp_2Ti(Cl)CH_2OCH_3$	3.55	102.4	140	*b*			10
$Cp_2Zr(Cl)CH_2OCH_3$	*b*			2.59	71.5^{h}	150	11
$Cp_2Zr(Cl)CH_2OSiEt_3$ (**7a**)	*g*			2.81	67.0	150	*f*
$Cp_2Zr(Cl)CH_2OSiMe_3$ (**8b/7b**)	3.20	50.4	132	2.74	66.2	151	*f*
$Cp_2Zr(Cl)CH_2OSi(iPr)_3$ (**8c/7c**)	3.24	50.8^{e}	134	3.01	68.5	150	*f*
$Cp_2Zr(Cl)CH_2OSiPh_3$ (**8d**)	3.26^{e}	51.4^{e}	134	*b*			*f*

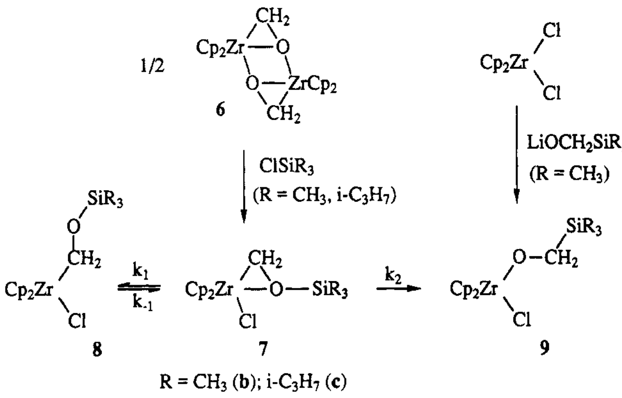
[a] Chemical shifts are relative to TMS; in benzene-d_6 if not otherwise noted. [b] Isomer not observed. [c] In $CDCl_3$. [d] In $CHFCl_2/CDCl_3$ (3:1). [e] In THF-d_8. [f] This work. [g] Not reported. [h] In toluene-d_8.

The addition of trimethylchlorosilane to the metallaoxirane moiety of **6** was achieved similarly. Photolysis of the zirconocene η^2-formaldehyde dimer with $ClSi(CH_3)_3$ in tetrahydrofuran at room temperature rapidly led to the formation of **7b**. Thermolysis of a $[Cp_2Zr(CH_2O)]_2/ClSi(CH_3)_3$ mixture in tetrahydrofuran (60 °C, 90 min) was equally effective to produce the metallaoxirane addition product **7b** (isolated in 76% yield). Complex **7b** was dissolved in benzene and thermolyzed at 110 °C for 10 h. During this time two new isomeric products were formed (**8b** and **9b**). Under these reaction conditions a mixture is obtained that contains the three isomers[13] in the ratio **7b**:**8b**:**9b** $\approx$ 10:4:5. Compound **9b** shows three singlets in the ^1H NMR spectrum at δ 5.96 (Cp_2Zr), 3.78 (OCH_2), and 0.07 ($SiMe_3$). It has been identified as the final dyotropic rearrangement product $Cp_2Zr(Cl)OCH_2SiMe_3$ by independent synthesis (stoichiometric reaction of $LiOCH_2SiMe_3$ with Cp_2ZrCl_2). As expected, the $^1J_{CH}$ coupling constant of the CH_2 group in **9b** (δ 72.6) is much reduced at $^1J_{CH}$ = 129 Hz as compared to its precursor **7b**.

The other reaction product (**8b**) shows $^1H/^{13}C$ NMR signals at δ 5.76/114.0 (Cp_2Zr), 3.20/50.4 (CH_2), and 0.08/1.7 ($SiMe_3$). In comparison with **7b** the methylene $^1J_{CH}$ coupling constant of **8b** is much reduced at 132 Hz. Consequently, we have assigned to this product (**8b**) the structure of the acyclic isomer of **7b** (see Table 2 for a comparison of typical NMR data). Compound **8b** is simply formed by a thermally induced cleavage of the zirconium–oxygen bond of the metallacyclic starting material **7b**, probably followed by a rapid conformational relaxation resulting in an η^1(O) outside arrangement (as depicted in Scheme 1) that is typical for systems of this overall structural type.[13,14]

We have followed the time-dependent change of the relative concentrations of the isomeric complexes **7b**, **8b**, and **9b** at 110 °C. This has revealed that the relative amount of **8b** formed at this temperature goes through a maximum. The time-dependent **7b**:**8b**:**9b** ratio is satisfactorily described by a kinetic scheme (**9b** $\leftarrow$ **7b** $\rightleftharpoons$ **8b**) which involves a thermally induced equilibration of the unrearranged isomers (**7b** $\rightleftharpoons$ **8b**) being in competition with the **7b** $\rightarrow$ **9b** dyotropic rearrangement reaction (see Scheme 1 for a definition of corresponding rate constants). In this scheme the actual metal migration reaction (**7b** $\rightarrow$ **9b**: $k_2 = 8.9 \times 10^{-6}$ s^{-1}; $\Delta G^{\ddagger}_{dyo}(383\ K) = 31.5 \pm 0.5$ kcal mol^{-1}) is rate determining. However, this kinetic analysis has revealed that the competing **7b** $\rightleftharpoons$ **8b** isomerization reaction is only slightly faster ($k_1 = 2.0 \times 10^{-5}$ s^{-1}; $k_{-1} = 5.7 \times 10^{-5}$ s^{-1} at 383 K). Under these conditions the Gibbs activation energy of the **7b** $\rightarrow$ **8b** isomerization is $\Delta G^{\ddagger}_{isom}(383\ K) = 30.9 \pm 0.5$ kcal mol^{-1}. The **7b** $\rightleftharpoons$ **8b** equilibrium at 383 K is $K_{isom} = 0.35$.

Scheme 1



The zirconocene η^2-formaldehyde dimer **6** reacts with triisopropylchlorosilane cleanly at 50 °C to give ((triisopropylsiloxy)methyl)zirconocene chloride (**7c**; 95% isolated yield). Its thermolysis proceeds very similarly to that for **7b**. After ca. 5 h at 110 °C one obtains a mixture containing the metallaoxirane starting material (**7c**), its acyclic isomer **8c**, and the rearrangement product **9c** in an approximate ratio of 7:2:10 (for typical NMR data see Table 2).

The reaction of **6** with triphenylchlorosilane takes a slightly different course. A single reaction product is obtained whose overall composition corresponds to a 1:1

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(12) For related insertion reactions of π-reagents with the zirconaoxirane unit see: Erker, G.; Aulbach, M.; Mena, M.; Pfaff, R.; Sosna, F. *Chem. Scr.* **1989**, *29*, 451. Erker, G.; Mena, M.; Werner, S.; Krüger, C. *J. Organomet. Chem.* **1990**, *390*, 323. Erker, G.; Mena, M.; Hoffmann, U.; Menjón, B.; Petersen, J. L. *Organometallics* **1991**, *10*, 291. Erker, G.; Mena, M.; Krüger, C.; Noe, R. *Organometallics* **1991**, *10*, 1201. Erker, G.; Mena, M.; Krüger, C.; Noe, R. *J. Organomet. Chem.* **1991**, *402*, 67. See also: Erker, G.; Noe, R.; Krüger, C.; Werner, S. *Organometallics* **1992**, *11*, 4174.

(13) For a general discussion about the η^1-/η^2-ligand isomerization at the group 4 metallocene framework see: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. Hofmann, R.; Staufert, P.; Shore, N. E. *Chem. Ber.* **1982**, *115*, 2153. Tatsumi, K.; Nakamura, A.; Hofmann, P.; Staufert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440. Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. See also: Erker, G.; Rosenfeldt, F. *Angew. Chem.* **1978**, *90*, 640; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605. Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1980**, *188*, C1.

(14) A reviewer has suggested that the complexes **8** could alternatively be (η^2-CH_2OSiR_3)Zr(Cl)Cp_2 isomers having the oxygen atoms in the "outside" position. This cannot rigorously be excluded. However, we regard this interpretation of our experimental data as being less likely in view of the spectroscopic features of complexes **8** (see Table 2) and the high lability of the related "O-outside" vs "O-inside" zirconocene η^2-acyl species.[13] It should be noted that $Cp_2Ti(Cl)CH_2OCH_3$ exhibits a stable η^1-type structure (characterized by X-ray diffraction) just as is proposed here for the isomers **8**.[10]

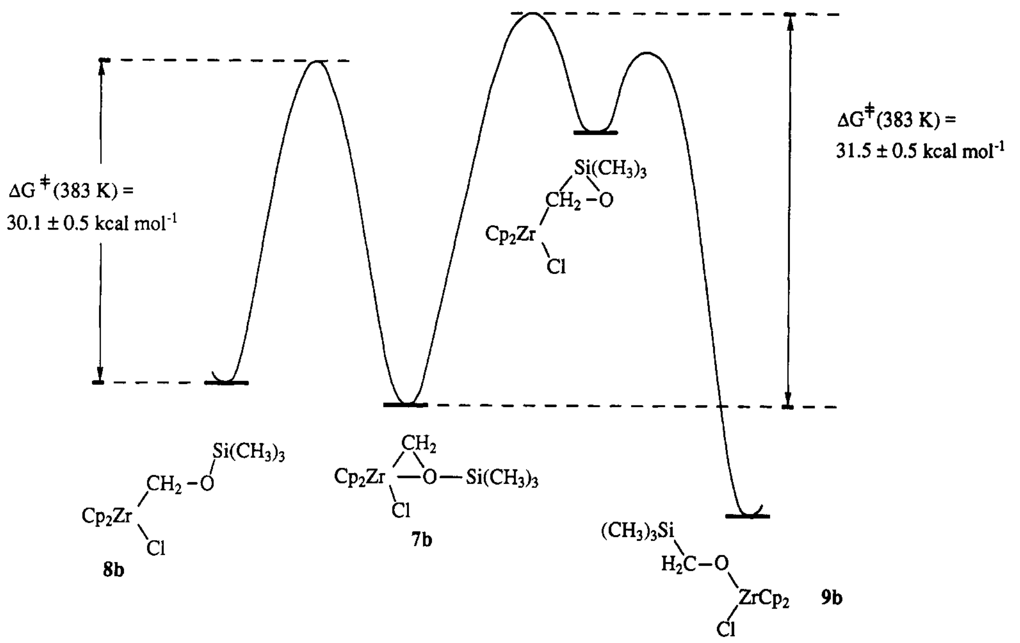
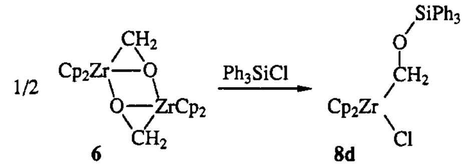


Figure 2. Qualitative reaction profile of the system of 8 ⇌ 7 → 9 rearrangements (R = CH_3).

addition product between the $Cp_2Zr(CH_2O)$ building block with the Ph_3SiCl reagent. However, in this case the three-membered-ring structure is apparently not retained. The substance obtained exhibits a ^{13}C NMR methylene carbon resonance at δ 51.4 (in tetrahydrofuran-d_8) with $^1J_{CH}$ = 134 Hz. In view of these very characteristic spectroscopic data (see Table 2 for a comparison) we assign to this product the structure of the acyclic ((triphenylsiloxy)-methyl)zirconocene halide complex **8d**. It seems that in this case the metallaoxirane isomer is markedly disfavored thermodynamically. The **8d** ⇌ **7d** equilibrium lies strongly on the side of the acyclic isomer **8d**. Thermolysis of **8d** at 110 °C did not lead to the formation of new products. Heating **8d** to higher temperatures eventually resulted in unspecific decomposition.



6 **8d**

In this study we have, of course, not proven the concerted nature of the observed rearrangement of the equilibrium system of isomers 8 ⇌ 7 to yield the zirconocene alkoxide complexes **9**. We have not carried out a number of possible experiments to exclude the stepwise mechanistic alternatives, thus narrowing the mechanistic picture toward the limiting situation of a concerted pathway.[15] Nevertheless, it is very likely that the (8 ⇌ 7) to **9** reorganization is indeed a dyotropic rearrangement. We note that an activation barrier was found as was expected for a concerted coupled exchange of the Zr/Si metal substituents at the central pivotal $-CH_2O-$ group from an extrapolation of the Si/Si- and Zr/Zr-containing systems (see above and Figure 1). Several features of the new "mixed" Zr/Si-containing rearrangement systems seem noteworthy. It is surprising that on the side of the starting materials both the three-membered metallacyclic and the open acyclic isomers (**7**, **8**) of the [Si]OCH_2[Zr] systems are found. To our knowledge this is the first time that both isomers have experimentally been shown to coexist in a dyotropic rearrangement system. For some alkyl substituents at silicon, the isomers 7 and 8 are rather close in energy. This behavior is in contrast to that of the previously described related [Zr]OCH_2[Zr] systems **4**[2,4-6] where the metallaoxirane is by far the favored structure and the acyclic isomer has not been observed experimentally. We assume that this difference in thermodynamic behavior is probably due to some destabilization of the metallaoxirane type structure in the Zr/Si-containing systems. It seems that R_3Si groups disfavor three-coordination at the adjacent (oxonium) oxygen center. This becomes very pronounced upon Ph_3Si substitution; in this case the three-membered-ring structure appears to have become so high in energy that only the acyclic isomer (**8d**) is observed under equilibrium conditions. Kinetically the 8 ⇌ 7 isomerization has a rather high barrier (as shown for the **8b,c**/**7b,c** rearrangements). This observation emphasizes the fact that a strong zirconium–oxygen bond has to be broken. Energetic compensation thus seems to require a considerable lengthening of the Zr–O linkage; it probably originates mainly from the energy difference between the silicon to three-coordinate vs two-coordinate oxygen bonding situations.

Conclusion

Our study has provided further evidence for the involvement of three-membered metallacyclic ring structures along the reaction path of dyotropic rearrangements.[2,3] The qualitative energy profile of the **8b** ⇌ **7b** → **9b** example (Figure 2) shows that the acyclic [Zr]CH_2O[Si] system **8b** first has to overcome a substantial energy barrier to undergo ring closure, forming the metallaoxirane type structure **7b**, which can then, by the coupled intramolecular σ,σ-exchange reaction, directly yield the rearrangement product **9b**. The involvement of the three-membered cyclic intermediate seems to be mechanistically important. However, it appears that the height of the overall barrier is mainly determined by the quality of the migratory aptitude of the remaining substituent at the three-

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(15) For a critical discussion of criteria for concertedness see: Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117. See also: Baldwin, J. E.; Fleming, R. H. *Fortschr. Chem. Forsch.* **1970**, *15*, 281.

coordinate oxygen.[16] A group 4 metallocene derived substituent can use an ideally located low-lying acceptor orbital[13] for interaction with the pivotal CH_2 unit and thus be able to achieve the dyotropic rearrangement situation very easily (**4** → **5**; see Figure 1). Migrating silicon requires a substantial thermal activation to cross the dyotropic rearrangement barrier (**7** → **9**). The activation barrier for the analogous migration of ordinary alkyl groups would probably be even higher. Buchwald has shown that in this case other stepwise mechanistic alternatives (Wittig rearrangement) are favored over the concerted dyotropic rearrangement reaction.[9]

Experimental Section

All reactions were carried out under an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents for the NMR experiments) were dried and distilled under argon prior to use. For a description of further general conditions and a listing of spectrometers used, see ref 16b. The zirconocene η^2-formaldehyde dimer **6** was prepared as previously described.[1a]

((Triethylsiloxy)methyl)zirconocene Chloride (7a). (a) Freshly distilled triethylchlorosilane (246 mg, 1.63 mmol) was added to a suspension of 390 mg (0.78 mmol) of the zirconocene η^2-formaldehyde dimer **6** in 20 mL of tetrahydrofuran. The mixture was stirred for 2 h at 50 °C. The resulting clear yellow solution was concentrated in vacuo to a volume of 4 mL and kept overnight at 5 °C. The resulting precipitate was recovered by filtration to yield 240 mg (78%) of **7a**, mp 113 °C (DSC). Anal. Calcd for $C_{17}H_{27}OSiClZr$ (402.2): C, 50.77; H, 6.77. Found: C, 49.45; H, 6.46. ^1H NMR (benzene-d_6): δ 5.71 (s, 10H, Cp), 2.81 (s, 2H, OCH_2), 0.95 (q, 6H, $SiCH_2$), 0.77 (t, 9H, $SiCH_2CH_3$). ^{13}C NMR (benzene-d_6): δ 109.7 ($^1J_{CH}$ = 172 Hz, Cp), 67.0 (150 Hz, OCH_2), 7.0 (125 Hz, CH_3), 5.5 (127 Hz, $SiCH_2$). ^{29}Si NMR (benzene-d_6, 71.5 MHz): δ 35.4. IR (KBr): $\tilde{\nu}$ = 3086, 2956, 2926, 2908, 2871, 1457, 1444, 1411, 1262, 1116, 1019, 918, 801, 746, 735, 728 cm^{-1}.

(b) A suspension of 500 mg (0.99 mmol) of **6** in 10 mL of tetrahydrofuran was charged with 300 mg (1.98 mmol) of triethylchlorosilane and then photolyzed (Philips HPK 125-W lamp, Pyrex filter) at 0 °C with stirring. The mixture was then filtered from a small amount of precipitate. The clear filtrate was concentrated in vacuo to a volume of 5 mL. Crystallization at −30 °C gave 470 mg (59%) of **7a**.

((Trimethylsiloxy)methyl)zirconocene Chloride (7b). (a) Zirconocene η^2-formaldehyde dimer **6** (1.0 g, 1.98 mmol) was suspended in 50 mL of tetrahydrofuran. Trimethylchlorosilane (0.48 g, 4.38 mmol) was added and the mixture stirred for 90 min at 60 °C. The clear yellow reaction mixture was concentrated until some product began to precipitate. The turbid solution was then kept for 2 days at −18 °C. The solid was recovered by filtration to give 890 mg of **7b**. Concentration of the mother liquor and crystallization at −18 °C gave an additional 190 mg of **7b** (76% total yield), mp 121 °C (DSC). Anal. Calcd for $C_{14}H_{21}OSiClZr$ (360.1): C, 46,70; H, 5.88. Found: C, 45.96; H, 5.76. ^1H NMR (benzene-d_6): δ 5.69 (s, 10H, Cp), 2.74 (s, 2H, OCH_2), 0.21 (s, 9H, $SiCH_3$). ^{13}C NMR (benzene-d_6): δ 109.6 ($^1J_{CH}$ = 172 Hz, Cp), 66.2 (151 Hz, OCH_2), 0.6 (120 Hz, $SiCH_3$). ^{29}Si NMR (benzene-d_6): δ 34.1. IR (KBr): $\tilde{\nu}$ 3087, 2966, 2955, 2923, 1443, 1263, 1249, 1017, 928, 845 cm^{-1}.

(b) A suspension of **6** (500 mg, 0.99 mmol) in 20 mL of tetrahydrofuran containing 216 mg (1.99 mmol) of trimethylchlorosilane was irradiated for 55 min at 22 °C (HPK 125-W lamp, Pyrex filter). Concentrating to a volume of 5 mL and cooling to −30 °C (3 days) gave 450 mg (64%) of **7a**.

Table 3. Observed and Calculated Time-Dependent Relative Concentrations during the 7b, 8b, 9b Isomerization at 383 K

	7b (%)		**8b** (%)		**9b** (%)	
t (s)	obsd	calcd	obsd	calcd	obsd	calcd
7 200	83.5	84.3	10.7	11.7	5.8	4.0
14 400	73.0	74.3	16.2	16.8	10.8	8.9
21 540	65.9	77.0	18.8	19.5	15.3	13.5
28 740	60.8	62.9	19.9	20.0	19.3	17.1
36 240	56.7	59.1	20.1	20.3	23.2	20.6
44 640	53.0	54.4	19.7	20.8	27.3	24.8
51 960	50.3	51.3	19.1	20.4	30.6	28.3
62 340	46.8	46.7	18.1	18.9	35.1	34.4
73 920	43.3	42.6	16.9	18.4	39.8	39.0
90 600	38.9	38.4	15.2	15.9	45.9	45.7
103 680	35.8	34.8	14.0	15.5	50.2	49.7
152 520	26.2	23.9	10.3	10.6	63.5	65.5

Thermolysis of 7b. A sample of **7b** (20 mg, 50 μmol) was dissolved in 600 μL of benzene-d_6 and sealed in a 5-mm NMR tube. The solution was thermolyzed for 10 h at 110 °C with use of a thermostat. The formation of the isomeric rearrangement products was monitored by NMR spectroscopy. The products **7b**, **8b**, and **9b** were present in the solution in a ratio of 10:4:5. ^1H NMR (benzene-d_6): **8b**, δ 5.76 (s, 10H, Cp), 3.20 (s, 2H, OCH_2), 0.08 (s, 9H, $SiCH_3$); **9b**, δ 5.96 (s, 10H, Cp), 3.78 (s, 2H, OCH_2), 0.07 (s, 9H, $SiCH_3$). ^{13}C NMR (benzene-d_6, 75 MHz): **8b**, δ 114.0 ($^1J_{CH}$ = 173 Hz, Cp), 50.4 (132 Hz, OCH_2), 1.7 (117 Hz, $SiCH_3$); **9b**, δ 113.3 ($^1J_{CH}$ = 173 Hz, Cp), 72.6 (129 Hz, OCH_2), −3.1 (118 Hz, $SiCH_3$). The rate constants of the **8b** ⇌ **7b** → **9b** isomerization were determined at 110 °C. A sealed 5-mm NMR tube containing a solution of **7b** in benzene-d_6 was thermolyzed for variable times with use of a thermostat at 110 °C (±0.1 °C). The sample was cooled in ice and then analyzed by ^1H NMR spectroscopy (integration of the methylene resonances of **7b, 8b**, and **9b** at δ 2.74, 3.20, and 3.78, respectively). The intensity of the C_6D_5H solvent resonance at δ 7.15 served as an internal standard. The time-dependent concentration change of the three isomers was simulated for a variety of possible kinetic schemes using standard computational procedures. Table 3 gives a listing of observed and calculated relative concentrations of **7b, 8b**, and **9b** using the kinetic scheme shown in Scheme 1 (i.e. **8b** ⇌ **7b** → **9b**). This gave the rate constants k_1(**7b** → **8b**) = 2.0×10^{-5} s^{-1}; k_{-1}(**8b** → **7b**) = 5.7×10^{-5} s^{-1}, and k_2 (**7b** → **9b**) = 8.9×10^{-6} s^{-1}. The corresponding Gibbs activation energies were calculated as $\Delta G^{\ddagger}$(383 K)[**8b** → **7b**] = 30.1 ± 0.5 kcal mol^{-1}, $\Delta G^{\ddagger}$(383 K)[**7b** → **8b**] = 30.9 ± 0.5 kcal mol^{-1}, and $\Delta G^{\ddagger}$(383 K)[**7b** → **9b**] = 31.5 ± 0.5 kcal mol^{-1}.

Independent Synthesis of 9b. The thermolysis product **9b** was independently synthesized by treatment of Cp_2ZrCl_2 with $LiOCH_2Si(CH_3)_3$. To a solution of 1.20 mL (1.00 g, 9.59 mmol) of $HOCH_2Si(CH_3)_3$ in 25 mL of ether was added 5.71 mL (9.59 mmol) of a 1.68 M ethereal methyllithium solution at 0 °C over 30 min. The clear solution was stirred at room temperature until the gas evolution had completely ceased (ca. 2 h). Solvent was then removed in vacuo to yield the $LiOCH_2Si(CH_3)_3$ reagent as a white solid (1.0 g, 95%). A solution of 300 mg (2.7 mmol) of this reagent in 10 mL of tetrahydrofuran was added dropwise over 1 h to a solution of 790 mg (2.7 mmol) of zirconocene dichloride in 20 mL of tetrahydrofuran. The solution was stirred for 10 min and then the solvent removed in vacuo. The residue was extracted twice with pentane (20 mL each). The combined pentane extracts were concentrated in vacuo to a volume of ca. 5 mL. The product was then crystallized at −18 °C to give 750 mg (77%) of **9b** (white needles), mp 81 °C (DSC). Anal. Calcd for $C_{14}H_{21}OSiClZr$ (360.1): C, 46.70; H, 5.88. Found: C, 46.90; H, 5.93. ^1H/^{13}C NMR: see above. IR (KBr): $\tilde{\nu}$ 3100, 2961, 1440, 1420, 1262, 1101, 1019, 857, 807, 757, 696, 673 cm^{-1}.

((Triisopropylsiloxy)methyl)zirconocene Chloride (7c). Triisopropylchlorosilane (308 mg, 1.59 mmol) was dissolved in

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(16) For other recent examples of related "dyotropic" rearrangement systems see: (a) Martin, J. G.; Ring, M. A.; O'Neal, H. E. *Organometallics* **1986**, *5*, 1228. Ward, A. S.; Mintz, E. A.; Kramer, M. P. *Organometallics* **1988**, *7*, 8. Curtis, C. J.; Haltiwanger, R. C. *Organometallics* **1991**, *10*, 3220. Bakhtiar, R.; Holznagel, C. M.; Jacobsen, D. B. *Organometallics* **1993**, *12*, 880. (b) Erker, G.; Petrenz, R. *J. Chem. Soc., Chem. Commun.* **1989**, 345. Erker, G.; Petrenz, R.; Krüger, C.; Lutz, F.; Weiss, A.; Werner, S. *Organometallics* **1992**, *11*, 1646.

3 mL of tetrahydrofuran and added to a suspension of 400 mg (0.80 mmol) of **6** in 20 mL of tetrahydrofuran. The reaction mixture was stirred for 2 h at 50 °C and then for 14 h at ambient temperature. Solvent was removed in vacuo from the clear yellow solution to give 670 mg (95%) of **7c**, mp 138 °C (DSC). Anal. Calcd for $C_{20}H_{33}OSiClZr$ (444.2): C, 54.07; H, 7.49. Found: C, 53.44; H, 7.56. ^{1}H NMR (benzene-d_6): δ 5.76 (s, 10H, Cp), 3.01 (s, 2H, OCH_2), 1.33 (sept, 3H, isopropyl CH), 1.09 (d, 18H, isopropyl CH_3). ^{13}C NMR (benzene-d_6): δ 109.8 ($^1J_{CH}$ = 173 Hz, Cp), 68.5 (150 Hz, OCH_2), 18.3 (126 Hz, SiCH), 13.3 (CH_3). ^{29}Si NMR (benzene-d_6): δ 29.4. IR (KBr): $\tilde{\nu}$ 3075, 2962, 2943, 1463, 1260, 1018, 901, 810, 723, 670, 642 cm^{-1}.

Thermolysis of 7c. A 5-mm NMR tube was charged with a solution of **7c** (20 mg, 45 μmol) in benzene-d_6 (600 μL) and then sealed. Thermolysis at 110 °C (4.5 h) gave a 7:2:10 mixture of the isomers **7c**, **8c**, and **9c**. The rearrangement products **8c** and **9c** were characterized only by NMR spectroscopy from the product mixture. A similar thermolysis of **7c** in tetrahydrofuran-d_8 gave a sample that had a higher content of **8c**. ^{1}H NMR (benzene-d_6): **8c**, δ 5.84 (s, 10H, Cp), 3.24 (s, 2H, OCH_2), 1.45–0.98 (m of the Si(isopropyl)$_3$ signals of all three isomers, overlapping); **9c**, δ 5.99 (s, 10H, Cp), 4.12 (s, 2H, OCH_2). ^{13}C NMR (benzene-d_6): **8c**, δ 112.1 ($^1J_{CH}$ = 173 Hz, Cp), 50.0 (134 Hz, OCH_2), 18.3 (isopropyl CH), 13.5 (isopropyl CH_3); **9c**, δ 113.3 ($^1J_{CH}$ = 173 Hz, Cp), 67.8 (130 Hz, OCH_2), 19.0 (126 Hz, $SiCHCH_3$), 10.6 (118 Hz, SiCH). ^{1}H NMR of **8c** in THF-d_8: δ 6.19 (s, 10H, Cp), 3.19 (s, 2H, OCH_2), 1.45 (sept, 3H), 1.06 (d, 18H, isopropyl). ^{13}C NMR of **8c** in THF-d_8: δ 112.8 ($^1J_{CH}$ = 172 Hz, Cp), 50.8 (134 Hz, OCH_2), 18.6 (126 Hz, $SiCHCH_3$), 14.1 (117 Hz, SiCH).

((Triphenylsiloxy)methyl)zirconocene Chloride (8d). A suspension of 300 mg (0.60 mmol) of **6** in 20 mL of tetrahydrofuran containing 350 mg (1.19 mmol) of triphenylchlorosilane was thermolyzed for 75 min at 70 °C and then for 3 h at 50 °C. The solution was concentrated in vacuo to a volume of 8 mL. Crystallization at −18 °C gave 435 mg (67%) of **8d**, mp 144 °C dec (DSC). Anal. Calcd for $C_{29}H_{27}OSiClZr$ (546.3): C, 63.76; H, 4.98. Found: C, 63.34; H, 5.00. ^{1}H NMR (THF-d_8): δ 7.6 (m, 6H, Ph, *m* hydrogens), 7.41, 7.33 (m, 9H, Ph, *o,p* hydrogens), 6.11 (s, 10H, Cp), 3.26 (s, 2H, OCH_2). ^{13}C NMR (THF-d_8): δ 138.2 (ipso C, Ph), 135.9 ($^1J_{CH}$ = 155 Hz), 130.2 (159 Hz), 128.4 (159 Hz, Ph), 113.1 (172 Hz, Cp), 51.4 (134 Hz, OCH_2). IR (KBr): $\tilde{\nu}$ 3068, 2965, 1587, 1483, 1427, 1262, 1114, 1097, 1021, 815, 705 cm^{-1}.

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