Aqua Complexes of [(2-Methoxyethyl)cyclopentadienyl]zirconium Trichloride

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The behavior of $[(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2OMe)ZrCl_2(\mu\text{-}Cl)]_2$ (**1**) toward a variety of solvents, and especially water, was investigated. The bidentate coordination of the $C_5H_4CH_2CH_2OMe$ ligand is retained in chloroform, dichloromethane, benzene, acetone, thf, and acetonitrile. No stable adducts of **1** with the last three solvents could be isolated. In methanol and water, coordination of the ether side chain is broken; however, removal of solvent retains this coordination and the stable mono adducts $(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2OMe)ZrCl_3(MeOH)$ and $(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2OMe)ZrCl_3(H_2O)$ were isolated. An X-ray structure of the thf solvate of the latter compound was determined: space group $P2_1/c$, $a = 11.612(1)$ Å, $b = 10.759(2)$ Å, $c = 14.291(2)$ Å, $\beta = 105.50(1)°$, $V = 1720.5(4)$ Å³, $Z = 4$, $R = 0.062$. The intramolecular coordination of the ether side chain is also broken in DMSO, but in this case it is not retained after removal of solvent. A cationic aqua complex $[(\eta^5\text{-}C_5H_4CH_2CH_2OMe)ZrCl_2(H_2O)(DMSO)_2]^+Cl^-$ crystallized from the solution: space group $P\bar{1}$, $a = 8.297(1)$ Å, $b = 10.097(1)$ Å, $c = 12.883(1)$ Å, $\alpha = 71.12(1)°$, $\beta = 86.60(1)°$, $\gamma = 87.45(1)°$, $V = 1019.0(2)$ Å³, $Z = 2$, $R = 0.049$. Compound **1** is a Diels−Alder catalyst even under moist conditions.

Introduction

Monocyclopentadienyl (Cp) zirconium trichlorides and their ring-substituted analogues have been used as Lewis acidic catalysts in organic synthesis.[1] However, an unwanted property of most Lewis acids is their sensitivity toward moisture. This may lead to hydrolytic decay and inactivition of catalytic properties. For instance, the complex $(\eta^5\text{-}C_5Me_5)ZrCl_3(H_2O)_2$ easily decays to polynuclear hydroxo and oxo complexes under mildly basic conditions.[2] On the other hand, aquo complexes of $(\eta^5\text{-}Cp)ZrCl_3$ may be isolated under certain conditions.[3] We are currently investigating the possibility of controlling and directing the high reactivity of the CpZrCl₃ fragment by using a chelating side chain on the Cp ring.[1e] We are therefore investigating the ligand $C_5H_4CH_2CH_2OMe$,[4] and especially chiral modifications thereof,[5] with the eventual goal of asymmetric catalysis.[6]

We recently reported a high-yield synthesis of the monocyclopentadienylzirconium complex $[(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2OMe)$-

$ZrCl_2(\mu\text{-}Cl)]_2$ (**1**).[7] This compound is a chloride-bridged dimer in the solid state but is essentially monomeric in solution (see Scheme 1). Therefore, coordination of an additional ligand (S) seems possible in a position *trans* to the Cp ring, affording $(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2OMe)ZrCl_3(S)$. During catalytic applications, such as a Diels−Alder reaction, this will also be the position of temporal coordination of substrate molecules like α,β-unsaturated olefins and aldehydes. However, it is also possible that certain substrates will displace the intramolecular coordination of the ether side chain affording bisadducts $(\eta^5\text{-}C_5H_4CH_2CH_2OMe)ZrCl_3(S)_2$. This is certainly unwanted when *chiral* ether handles are being used for asymmetric conversions. We therefore need to know the behavior of this type of bidentate Cp/ether ligand in the complex under various conditions. Accordingly, we first investigated the achiral complex **1** and the stability of the intramolecular ether handle toward a variety of coordinating solvents, especially water.

Results and Discussion

The ^1H and ^{13}C NMR spectra of **1** in various solvents or combinations thereof are listed in Tables 1 and 2. The chemical shifts of the $C_5H_4CH_2CH_2OMe$ ligand show a large spread. From the NMR data of other $C_5H_4CH_2CH_2OMe$ derivatives it is known that intramolecular coordination of the ether handle is expressed by significant downfield shifts of the hydrogens

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‡ X-ray structure determinations.

⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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Scheme 1
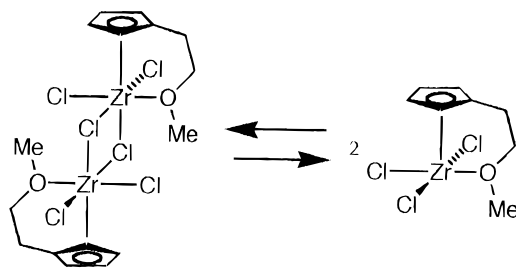
and carbons around the oxygen atom. However, due to anisotropic effects in several of these solvents, comparison of the ^1H NMR data should be treated with caution in this sense. On the other hand, the ^{13}C chemical shifts of the CH_2O (*ca.* 82 vs 73 ppm) and OCH_3 (*ca.* 64 vs 58 ppm) moieties are much more reliable tools to detect whether the ether side chain is coordinated or not.[7]

The solubility of **1** in the potentially coordinating solvents acetone, tetrahydrofuran (thf), and acetonitrile (MeCN) is rather poor. From the NMR data it is seen that in these solvents the intramolecular coordination of the ether handle is retained. Especially for acetone this is an important observation, since it is to be expected that during a Diels−Alder reaction, using α,β-unsaturated olefins, the intramolecular coordination of the ether side chain will also be retained. The NMR data in the aforementioned solvents neither indicate nor exclude the formation of a monosolvent adduct $(\eta^5:\eta^1-C_5H_4CH_2CH_2OMe)ZrCl_3$-(S). The ^1H NMR spectra of **1** in $CDCl_3$ containing a 10-fold excess of acetone or thf are hardly different from that of pure **1** (Table 1). The broadness of some or all of the CH_2OMe signals suggests some interaction with these solvents (Scheme 2). There may also be an interaction with residual water present (*vide infra*), although these hygroscopic solvents were dried as well as possible. All attempts to isolate acetone, thf, or acetonitrile adducts resulted in the isolation of the starting compound **1**.

The behavior of **1** stands in contrast with that of the parent $[\eta^5-CpZrCl_3]_n$. The polymeric structure of this complex is readily broken up by acetone, thf, and MeCN, affording the stable complexes $[(\eta^5-Cp)ZrCl_2(\mu-Cl)(acetone)]_2,$[8] $(\eta^5-Cp)ZrCl_3$-$(thf)_2$ (**2**),[1b] and $(\eta^5-Cp)ZrCl_3(MeCN)_2,$[9] respectively. Even more intriguing is the fact that stable thf adducts are known for complexes similar to **1**, but with nitrogen and sulfur atoms in the side chain instead of oxygen, i.e. $(\eta^5:\eta^1-C_5H_4CH_2CH_2$-$NMe_2)ZrCl_3(thf)$ (**3**)[10] and $(\eta^5:\eta^1-C_5Me_4CH_2CH_2SMe)ZrCl_3(thf)$ (**4**).[11]

We think that the resistance of **1** to thf coordination is related to the presence of an exceptionally strong Zr−O bond. The strength of this bond is attributed to a large π-electron donation from the oxygen atom. This apparently saturates the zirconium center to such an extent that any additional bonding *trans* to the Cp ring is substantially weakened. Curiously, **2** also contains a zirconium−ether bond *cis* to the Cp unit, and this arrangement obviously does not prevent the coordination of a second thf molecule. However, there is an important difference between **1** and **2**. The trigonal plane of the oxygen atom in **1** is coplanar with the Cp ring, whereas in **2** it is perpendicular to this ring.[12,13]

Donation of π electrons from the Cp ring in these complexes mainly involves the d_{xz} and d_{yz} orbitals of zirconium. Donation of π electrons from the p orbital of the oxygen atom in **1** involves the d_{xy} orbital of zirconium, whereas in **2** the respective p orbital donates to the d_{xz} orbital. This means that in **2** π electrons from oxygen and π electrons from the Cp ring *compete* for the same zirconium d orbital (see Figure 1). Therefore, **1** will be electronically more saturated than the $(\eta^5-Cp)ZrCl_3(thf)$ fragment and the latter will accept another thf molecule whereas **1** will not. In **3** and **4**, the nitrogen and sulfur heteroatoms do not have π electrons that can donate to zirconium, so they too are electonically much less saturated than **1**.

Adding water to the acetone, thf, or acetonitrile solution of **1** dramatically changes the NMR spectra (Tables 1 and 2). First, the solubility of **1** is markedly increased, but at the same time, the intramolecular coordination of the ether side arm is readily broken. This means that at least *two* water molecules coordinate to **1** affording the complex $(\eta^5-C_5H_4CH_2CH_2OMe)ZrCl_3(H_2O)_2$, similar to the known $(\eta^5-C_5Me_5)ZrCl_3(H_2O)_2.$[2c] Compound **1** may also be dissolved in *pure* D_2O. It is stable in water for several days, but after longer standing, insoluble material is deposited, obviously as a result of slow hydrolysis and formation of polynuclear hydroxides or oxides. Solvation of **1** may also lead to saltlike species such as $[(\eta^5-C_5H_4CH_2CH_2OMe)ZrCl_2$-$(H_2O)_3][Cl]$. This is corroborated by the fact that adding a few drops of water to a $CDCl_3$ solution of **1** results in almost complete disappearance of NMR signals (see Table 1) because the resulting saltlike complex apparently prefers to reside in the upper water phase. Aqueous solutions of **1** react very acidically, implying the formation of zirconium hydroxides. These hydroxides cluster between zirconium centers, and sequential loss of hydrogen chloride eventually leads to irreversible formation of polynuclear species.

When freshly made aqueous solutions of **1** or "wet" solutions of **1** in acetone, thf, or acetonitrile are evaporated to dryness a monoaqua adduct $(\eta^5:\eta^1-C_5H_4CH_2CH_2OMe)ZrCl_3(H_2O)$ (**5**) is formed. The intramolecular coordination of the ether side chain is restored thereby. Recrystallization from thf (or diethyl ether) affords the thf solvate **5**(thf) (*vide infra*). When these monoaqua adducts are dissolved again in $CDCl_3$, the ^1H NMR resonances are almost identical to those of parent **1**, water, and uncomplexed thf (Table 1). This suggests that a single water molecule is not very strongly coordinated to **1** in solution. On the other hand, in the solid state, the water coordination seems to be strenghtened through hydrogen bridging, as is evidenced by the solid-state structure of **5**(thf). The results of the X-ray diffraction analysis are shown in Figure 2. Crystal data are listed in Table 3, and selected bond lengths and angles are given in Table 4.

The molecule consists of a distorted octahedron in which a water molecule is coordinated *trans* to the Cp ring. Both of the hydrogen atoms of the coordinated water molecule could be located, and both were found to bridge to oxygen atoms of the thf molecules (see Table 4 for geometrical details). Four H bridges are located around a crystallographically-imposed inversion center, so that two molecules of **5** are actually held together in a thf-bridged dimer (Figure 3). The thermal ellipsoids of C(12) and C(13) are rather large, which suggests some flipping of the thf molecule around the C(11)−C(14) axis.

The coordinated water molecule seems to be involved in a third, intramolecular hydrogen bridge. It is found that one of the hydrogens of the adjacent methyl group points to the oxygen atom of the water molecule (Figure 4). Moreover, this hydrogen

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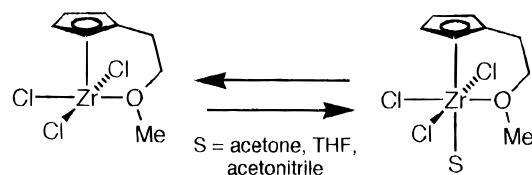
Table 1. ^{1}H NMR of **1** in Various Solvents[a]

solvent	C$_5$H$_4$	CpCH$_2$[b]	CH$_2$O[b]	OCH$_3$	H$_2$O[c]
CDCl$_3$	6.57, 6.75	2.92 (6.3)	4.33 (6.3)	3.75	
CDCl$_3$ +10 equiv of acetone	6.51, 6.73	2.90 (6.1)	4.30 (6.1)	3.73	
CDCl$_3$ +10 equiv of thf	6.51, 6.73	2.92 (6.0)	4.35 (6.0)	3.75?	
CDCl$_3$/H$_2$O	6.36, 6.46	2.86 (5.4)	3.67 (5.4)	3.30	5.0 (br)
CD$_2$Cl$_2$	6.56, 6.75	2.97 (6.3)	4.36 (6.3)	3.75	
C$_6$D$_6$	6.42, 6.47	1.91 (6.1)	3.25 (6.1)	3.01	
acetone-d_6	6.38, 6.53	2.95*	4.13*	3.61	
acetone-d_6/H$_2$O	6.40, 6.56	2.94 (6.2)	3.62 (6.2)	3.29	4.5 (br)
thf-d_8	6.34, 6.62	2.91 (6.2)	4.27*	3.65	
thf-d_8/H$_2$O	6.26, 6.44	3.00 (6.6)	3.6?	3.28	3.4 (br)
MeCN-d_3	6.40, 6.60	2.89 (6.2)	4.18*	3.60	
MeCN-d_3/H$_2$O	6.42, 6.55	2.96 (5.9)	3.68*	3.34	4.3 (vbr)
CDCl$_3$ +1 equiv of MeOH	6.50, 6.72	2.89*	4.28*	3.66, MeOH at 3.87	
CDCl$_3$ +2 equiv of MeOH	6.50, 6.66	2.90 (5.9)	4.21*	3.63	
CD$_3$OD	6.38, 6.50	3.04 (6.5)	3.71*	3.41	
CD$_3$OD (−60 °C)	6.32, 6.51	3.03 (6.6)	3.63 (6.6)	3.38	
CDCl$_3$ +10 equiv of DMSO	5.68, 5.93	2.59*	3.05 (6.2)	2.82	
DMSO-d_6	6.04, 6.30	2.72 (6.6)	3.44 (6.6)	3.19	
D$_2$O[d]	6.40, 6.51	2.92*	3.73*	3.36	
Monoaqua Complex[e]					
CDCl$_3$	6.55, 6.73	2.91 (6.3)	4.30 (6.3)	3.73	1.83/3.76 (thf), 6.5 (H$_2$O)
CDCl$_3$	6.53, 6.73	2.91*	4.30*	3.73	1.18/3.47 (Et$_2$O), 6.1 (H$_2$O)

[a] Chemical shifts are given in ppm. Values marked with an asterisk represent broadened signals. [b] $^3J_{HH}$ values in hertz are given in parentheses (triplet). [c] Prepared *in situ*. Except for CDCl$_3$ the chemical shifts depend somewhat on the amount of water added (±0.05 ppm). [d] Referenced against added thf (1H: 1.85/3.75). [e] Isolated from thf or Et$_2$O; see text.

**Table 2.** ^{13}C NMR of **1** in Various Solvents[a]

solvent	C$_5$H$_4$	C$_5$H$_4$[b]	CpCH$_2$	CH$_2$O	OCH$_3$
CDCl$_3$	118.1, 122.3	129.5	27.5	82.3	64.8
CD$_2$Cl$_2$	118.2, 121.5		27.7	83.4	64.8
C$_6$D$_6$	117.4, 121.7		26.5	81.4	63.5
acetone-d_6	117.9, 121.8	129.6	28.8	80.2*	63.0*
acetone-d_6/D$_2$O	118.9, 119.6		31.0	73.3	58.9
thf-d_8	117.3, 123.8		28.2	81.7	64.2
thf-d_8/D$_2$O	118.7, 119.5	130.3	31.5	74.7*	58.9*
MeCN-d_3	123.1 (2×)	130.5	28.1	82.6*	64.7*
MeCN-d_3/D$_2$O	119.6, 119.9	133.7*	30.7	73.2*	59.2*
CDCl$_3$ +1 equiv of MeOH[c]	117.6, 122.4	129.0	27.2	82.4	64.3
CDCl$_3$ +2 equiv of MeOH[d]	117.7, 122.1*	128.9*	27.4	81.8*	63.8*
CD$_3$OD	119.7, 120.5 (174, 173)	131.8	31.9* (130)	74.6* (141)	59.4* (140)
CDCl$_3$ +10 equiv of DMSO	117.6 (2×)	129.1	29.5	71.6	57.3
DMSO-d_6	118.2 (2×) (174)	129.7	30.3 (129)	72.4 (142)	57.9 (141)
D$_2$O[e]	114.2, 114.8	130.0	21.6	64.4	54.6

[a] Chemical shifts are given in ppm. Values marked with an asterisk represent broadened signals. $^1J_{CH}$ values in hertz are given in parentheses. [b] Due to low solubility, the quarternary Cp carbon was not always observed. [c] MeOH at 54.0 ppm. [d] MeOH at 52.1 ppm. [e] Referenced against added thf (^{13}C: 25.8/67.9 ppm).

Scheme 2

bond perfectly fits into the tetrahedral geometry around the oxygen atom. In addition, the C···O length of 2.97 Å is well within range of other C–H···O bridges (3.0–4.0 Å).[14] These bridges are usually not very strong (<10 kJ/mol), and they will not play any meaningful role in solution.

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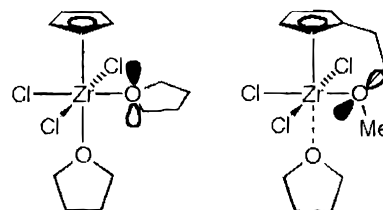
Figure 1. Zr–O bonding in (η^5-Cp)ZrCl$_3$(thf)$_2$ (left) and (η^5:η^1-C$_5$H$_4$-CH$_2$CH$_2$OMe)ZrCl$_3$(thf) (right) showing the favorable position of the *cis*-Cp positioned oxygen atom for donation of π-electons in the latter.
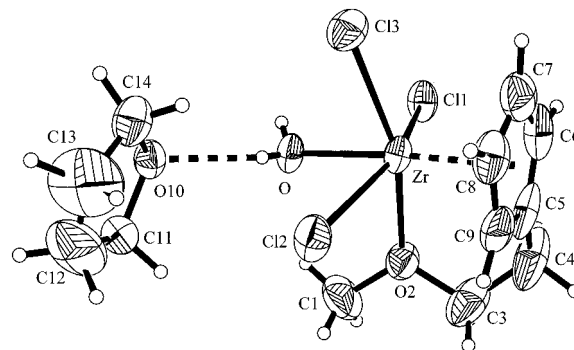
Figure 2. Molecular structure of [(η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_3$-(H$_2$O)](thf) (**5**(thf)).

The Zr–O(ether) distance of 2.345(4) Å in **5**(thf) is significantly longer than that in **1** (2.264(4) Å). It is also slightly longer than the Zr–O distance of the *cis*-Cp coordinated thf molecule in **2** (2.314 (3) Å),[1b] although the latter bond is in principle weaker because of its unfavorable geometry for π-donation (*vide supra*). All three terminal Zr–Cl bonds are also slightly longer than in **1**: Zr–Cl$_{trans-O}$ = 2.461(2) vs 2.455-(2) Å and Zr–Cl$_{cis-O}$ = 2.491(1)/2.489(2) vs 2.472(2) Å. The coordination of the water molecule apparently weakens all bonds in the equatorial plane. The geometry around O(2) is trigonal (sum of angles: 358.3°), indicating 4e σ,π-donation to the zirconium center. The trigonal plane of the chelating ether side chain is not exactly perpendicular to the Cp ring. Instead, it is rotated 17° around the Zr–O axis away from this situation, which however is much less than in **1** (43°). The geometry

**Table 3.** Crystallographic Data for **5**(thf) and **7**[Cl]

	5(thf)	**7**[Cl]
empirical formula	$C_{12}H_{21}Cl_3O_3Zr$	$C_{12}H_{25}Cl_3O_4S_2Zr$
cryst dimens, mm	$0.9 \times 0.5 \times 0.4$	$0.3 \times 0.3 \times 0.2$
mol wt	410.86	495.01
cryst system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	11.612(1)	8.297(1)
b, Å	10.759(2)	10.097(1)
c, Å	14.291(2)	12.883(1)
α, deg	90	71.12(1)
β, deg	105.50(1)	86.60(1)
γ, deg	90	87.45(1)
V, Å^3	1720.5(4)	1019.0(2)
Z	4	2
d_{calc}, g cm^{-3}	1.586	1.613
μ(Mo Kα), cm^{-1}	11.1	11.5
$F(000)$	832	504
T, K	223	223
λ, Å	0.710 73	0.710 73
R^a	0.062	0.049
$R_{w2}{}^b$	0.158	0.145

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_{w2} = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.
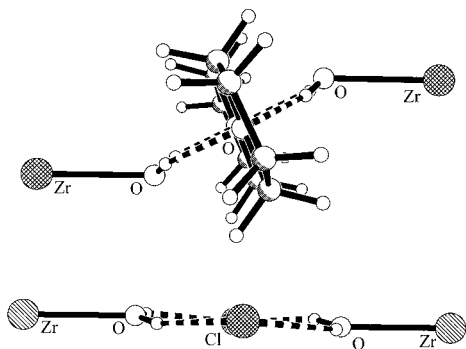
Figure 3. Core structures of the hydrogen-bonded dimers in **5**(thf) (top) and **7**[Cl] (bottom).

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $[(\eta^5:\eta^1-C_5H_4CH_2CH_2OMe)ZrCl_3(H_2O)](thf)$ (**5**(thf))

Zr−Cl(1)	2.491(1)	Zr−C(7)	2.552(6)
Zr−Cl(2)	2.489(2)	Zr−C(8)	2.508(6)
Zr−Cl(3)	2.461(2)	Zr−C(9)	2.463(6)
Zr−O	2.221(4)	O(2)−C(1)	1.429(7)
Zr−O(2)	2.345(4)	O(2)−C(3)	1.444(8)
Zr−C(5)	2.476(5)	C(3)−C(4)	1.429(11)
Zr−C(6)	2.515(6)	C(4)−C(5)	1.482(9)
Cl(1)−Zr−Cl(2)	150.29(5)	Cl(3)−Zr−O(2)	159.44(11)
Cl(1)−Zr−Cl(3)	92.49(5)	O−Zr−O(2)	78.48(14)
Cl(1)−Zr−O	76.15(11)	Zr−O(2)−C(1)	125.1(4)
Cl(1)−Zr−O(2)	81.67(11)	Zr−O(2)−C(3)	120.4(4)
Cl(2)−Zr−Cl(3)	93.87(6)	C(1)−O(2)−C(3)	112.8(5)
Cl(2)−Zr−O	76.24(11)	O(2)−C(3)−C(4)	111.4(6)
Cl(2)−Zr−O(2)	82.26(11)	C(3)−C(4)−C(5)	112.6(6)
Cl(3)−Zr−O	80.99(12)		
	Hydrogen Bridges		
O−H(1D)	0.78(6)	Zr−O−H(1D)	121(5)
O−H(1E)	0.70(6)	Zr−O−H(1E)	107(6)
O(10)···H(1E)	2.09(6)	H(1D)−O−H(1E)	110(7)
O(10)*···H(1D)	1.93(7)	O−H(1E)−O(10)	156(7)
O···O(10)	2.737(5)	O−H(1D)−O(10)*	170(7)
O···O(10)*	2.701(5)	O(10)···O···O(10)*	93.3(2)
		O···O(10)···O*	86.7(2)

around the oxygen atom of the water molecule is clearly tetrahedral, and therefore only 2e are σ-donated to the zirconium center, the other pair of electrons being used in a C−H···O bridge (*vide supra*). The Zr−O(water) distance of 2.221(4) Å is in line with other Zr−O(water) distances which usually fall
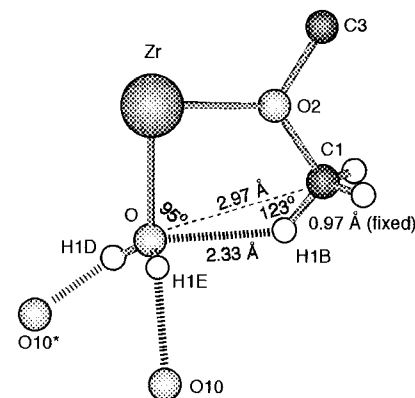
Figure 4. Detail of the crystal structure of $[(\eta^5:\eta^1-C_5H_4CH_2CH_2OMe)ZrCl_3(H_2O)](thf)$ showing intramolecular C−H···O hydrogen bridge.

Scheme 3
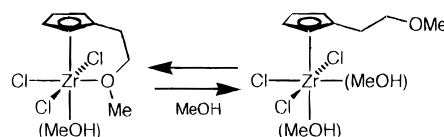
into the range of 2.20−2.29 Å.[15] The *trans*-Cp positioned water molecule in $[(\eta^5-Cp)ZrCl_3(H_2O)_2](15\text{-crown-}5)$ has a much longer Zr−O distance of 2.295(6) Å.[3b]

The NMR spectrum of **1** in CD$_3$OD shows broad ^{1}H and ^{13}C resonances for the CH$_2$OCH$_3$ moiety, which sharpen upon cooling (Tables 1 and 2). The chemical shifts are in accord with the ether handle being uncoordinated. However, titrations of CDCl$_3$ solutions of **1** with methanol (Tables 1 and 2) reveal that, at low concentrations of methanol, the ether handle is partially coordinated. We interpret this as an equilibrium between a mono- and a bis(methanol) adduct (Scheme 3).

After removal of the solvent *in vacuo* one molecule of methanol remains coordinated, and the complex $(\eta^5:\eta^1-C_5H_4-CH_2CH_2OMe)ZrCl_3(MeOH)$ (**6**) can be isolated.

Complex **1** readily dissolves in dimethyl sulfoxide (DMSO) (Tables 1 and 2). Titration of **1** with DMSO in CDCl$_3$ reveals that, with less than 2 equiv of DMSO, the intramolecular coordination of the ether side arm is completely lost. This indicates a high affinity of **1** for this solvent. In contrast to the case of all other solvents mentioned previously, the intramolecular coordination of the ether handle does not recover after removal of solvents. Instead, two molecules of DMSO remain coordinated to the zirconium center. Surprisingly, recrystallization under aerobic conditions yields a complex in which an additional water molecule is coordinated affording the salt $[(\eta^5-C_5H_4CH_2CH_2OMe)ZrCl_2(DMSO)_2(H_2O)][Cl]$ (**7**[Cl]).

Single crystals suitable for X-ray diffraction could be obtained, and the structure is shown in Figure 5. Crystal data are listed in Table 3, and selected bond lengths and angles are given in Table 5.

The cation **7** is a distorted octahedron. The six ligands are in an "all-*cis*" configuration: two DMSO ligands, two chloride atoms, and the Cp/water moieties complete the coordination around the zirconium center. The coordinated water molecule separates the third chloride atom from the zirconium center. Both hydrogen atoms of the coordinated water molecule could

(15) Fay. R. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Vol. 3, Chapter 32.4.4. For further reviews on the structure of water in metal hydrates, see: (a) Lutz, H. D. *Struct. Bonding* **1988**, *69*, 97. (b) Chiari, G.; Ferraris, G. *Acta Crystallogr.* **1982**, *B38*, 2331. (c) Hunt, J. P.; Friedman, H. L. *Prog. Inorg. Chem.* **1983**, *30*, 359.
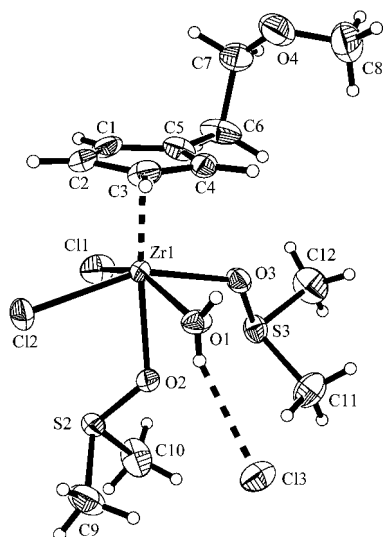
Figure 5. Molecular structure of [(η^5-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_2$(DMSO)$_2$-(H$_2$O)][Cl] (**7**[Cl]).

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for [(η^5-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_2$(H$_2$O)(DMSO)$_2$][Cl] (**7**[Cl])

Zr−Cl(1)	2.490(2)	S(2)−O(2)	1.543(4)
Zr−Cl(2)	2.510(2)	S(3)−O(3)	1.543(4)
Zr−O(1)	2.175(4)	S(2)−C(9)	1.775(7)
Zr−O(2)	2.189(4)	S(2)−C(10)	1.767(7)
Zr−O(3)	2.160(4)	S(3)−C(11)	1.777(7)
Zr−C(1)	2.524(6)	S(3)−C(12)	1.753(7)
Zr−C(2)	2.538(6)	O(4)−C(8)	1.411(10)
Zr−C(3)	2.511(7)	O(4)−C(7)	1.381(10)
Zr−C(4)	2.497(6)	C(6)−C(7)	1.531(10)
Zr−C(5)	2.540(6)	C(5)−C(6)	1.493(9)
Cl(1)−Zr−Cl(2)	92.11(6)	O(2)−S(2)−C(10)	103.4(3)
Cl(1)−Zr−O(1)	153.54(14)	C(9)−S(2)−C(10)	99.8(4)
Cl(1)−Zr−O(2)	80.76(12)	O(3)−S(3)−C(11)	105.2(3)
Cl(1)−Zr−O(3)	85.50(12)	O(3)−S(3)−C(12)	103.4(3)
Cl(2)−Zr−O(1)	90.03(13)	C(11)−S(3)−C(12)	100.0(4)
Cl(2)−Zr−O(2)	80.14(11)	Zr−O(2)−S(2)	128.1(2)
Cl(2)−Zr−O(3)	156.34(12)	Zr−O(3)−S(3)	126.7(2)
O(1)−Zr−O(2)	73.6(2)	C(7)−O(4)−C(8)	112.1(7)
O(1)−Zr−O(3)	82.1(2)	C(6)−C(7)−O(4)	114.5(6)
O(2)−Zr−O(3)	76.2(2)	C(5)−C(6)−C(7)	112.2(6)
O(2)−S(2)−C(9)	103.5(3)		

	Hydrogen Bridges		
O(1)−H(1A)	0.76(8)	Zr−O(1)−H(1A)	103(6)
O(1)−H(1B)	0.86(8)	Zr−O(1)−H(1B)	123(5)
Cl(3)···H(1A)	2.40(8)	H(1A)−O(1)−H(1B)	134(8)
Cl(3)*···H(1B)	2.15(8)	O(1)−H(1A)···Cl(3)	143(7)
Cl(3)···O(1)	3.035(5)	O(1)−H(1B)···Cl(3)*	161(6)
Cl(3)*···O(1)	2.981(5)	Cl(3)···O(1)···Cl(3)*	94.78(13)
		O(1)···Cl(3)···O(1)*	85.22(13)

be located, and they are essentially bonded to the oxygen and *not* to the chloride atom. Therefore, the complex really is a cation and not a neutral hydroxide with interstitial HCl molecules.

We only know of two other monocyclopentadienylzirconium singly charged cations, namely those in [(η^5-C$_5$Me$_5$)ZrMe$_2$(Me$_2$-PCH$_2$CH$_2$PMe$_2$)(thf)][BPh$_4$][16] and [(η^5-Cp)ZrCl$_2$(MeCN)$_3$]-[SbCl$_6$].[9] The latter exists as a mixture of three isomers in solution, whereas the former has its anionic methyl ligands in mutually *trans*-positions. These salts owe their existence to the presence of large "noncoordinating" anions, whereas the existence of our complex is attributed to the high solvation power of DMSO. For ZrCl$_4$, it is known that its solution in DMSO affords a complex containing eight or nine DMSO molecules.[15]

(16) Crowther, D. J.; Jordan, R. F.; Baenziger, N. C.; Verma, A. *Organometallics* **1990**, *9*, 2574.

Both hydrogens of the water molecule are involved in O−H···Cl bridges. Because these bridges are located around a crystallographically-imposed inversion center, two cations **7** actually form a chloride-bridged dimer (Figure 3). The water molecule is trigonal in contrast to that in **5**(thf), which is tetrahedral. The trigonal plane is virtually perpendicular to the Cp ring, which is also predicted on the basis of maximal π-donation (*vide supra*).[17] Not surprisingly, the Zr−O(water) bond length of 2.175(4) Å is very short. It is much shorter than for similar equatorially coordinated water molecules like those in [(η^5-Cp)ZrCl$_3$(H$_2$O)$_2$](15-crown-5) (2.264(5) Å)[3b] and [(η^5-C$_5$Me$_5$)ZrCl$_2$(H$_2$O)(μ-OH)]$_2$ (2.246(3) Å).[2c] Only in the highly charged complex [(η^5-Cp)Zr(μ-OH)(H$_2$O)$_3$]$_2^{4+}$ is a Zr−O(water) bond length of 2.164(3) Å found.[3a]

The Zr−Cl distances (2.490(2) and 2.510(2) Å) in **7** are comparable to those in **5**(thf). The Zr−O bond length of the *trans*-Cp positioned DMSO ligand (2.189(4) Å) is longer than for the *cis*-Cp positioned DMSO ligand (2.160(4) Å), but this is also seen in a number of other complexes of the type *cis-mer*- [η^5-CpZrCl$_3$(L)$_2$].[1b] The Zr−O=S angle of the DMSO ligand *trans* to Cp is slightly more widened (∠Zr−O(2)−S(2) = 128.1(2)°) than that of the DMSO ligand *cis* to Cp (∠Zr−O(3)−S(3) = 126.7(2)°). A similar situation exists for the Zr−O=C angles in (η^5-Cp)ZrCl$_3$(DMF)$_2$ (130.6(2) vs 128.4(2)°). The S=O bond lengths (both 1.543(4) Å) are slightly longer and the S−C bond lengths (average of 1.77 Å) are slightly shorter than those in the uncomplexed sulfoxide. This seems to be very common, since the analyses of Allen *et al.* report S=O and S−C bond lengths of 1.53(2) and 1.79(2) Å for complexed sulfoxides compared to 1.50(1) and 1.81(2) Å for uncomplexed ones.[18] The Zr−O=S plane of the DMSO ligand *trans* to Cp perfectly bisects the Cl(1)−Zr−Cl(2) angle as well as the C(9)−S(2)−C(10) angle. The other DMSO ligand is not so well-behaved, and the methyl groups are rotated 22° around the S=O axis.

It is noted that the ether side-arm in **7** is not involved in any bonding. This suggests that a similar complex can also be synthesized, from the parent [(η^5-Cp)ZrCl$_3$]$_n$, but we are not aware of such an analogue in the literature.

Another interesting aspect of this compound is why the ether handle is not coordinated in place of the water molecule. The reason might be that if the ether handle were coordinated, there would be no possibility for the chloride anion to stabilize its "nakedness" by OH···Cl bridges.

Diels−Alder Catalysis

In order to determine its Lewis acidity, we reacted **1** with crotonaldehyde.[19] No visible interaction could be observed by ^{1}H NMR, which is not surprising after the negative reaction with acetone. However, this does not rule out Lewis acidity, and we therefore tested **1** as a catalyst for the Diels−Alder reaction (Table 6).

Indeed, **1** effectively catalyzes the reaction between methacrolein and cyclopentadiene in dry dichloromethane (entry 1). On the basis of the preceding results, we also performed this reaction under moist conditions and did observe the same activity (entry 2). However, it is conceivable that it is not necessarily the zirconium center acting as the catalyst but also acidic hydrogens of water molecules complexed to **1**.[15] We

(17) Mohr, R.; Berke, H.; Erker, G. *Helv. Chim. Acta* **1993**, *76*, 1389.
(18) (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, S1. (b) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1989**, S1.
(19) (a) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801. (b) Laszlo, P.; Teston, M. *J. Am. Chem. Soc.* **1990**, *112*, 8750.

Table 6. Diels−Alder Catalysis by (Lewis) Acids[a]
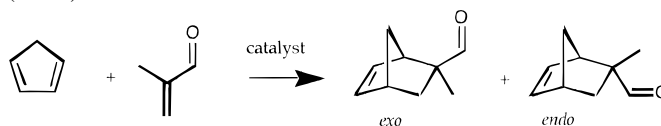
entry	catalyst	amt, μmol	solvent	amt of product, g (%)	*exo/endo*
1	**1**	310	dry CH$_2$Cl$_2$	1.7 (100)	87/13
2	**1**	190	wet CH$_2$Cl$_2$	1.7 (100)	91/9
3	HCl	b	dry CH$_2$Cl$_2$	1.5 (90)	85/15
4	1 mL of 1 N aq HCl		CH$_2$Cl$_2$	0.2 (10)	82/18
5	none		dry CH$_2$Cl$_2$	0	
6	none		wet CH$_2$Cl$_2$	0	
7	**1**	60	water (pH $\sim$ 2)	1.2 (70)	84/16
8	ZrCl$_4$	200	water (pH $\sim$ 1)	1.2 (70)	86/14
9	0.1 N HCl		water (pH = 1)	1.0 (60)	82/18
10	none		water (pH = 7)	0	

[a] Conditions: reaction time, 24 h; temperature, 21 °C; substrate, methacrolein, 1.0 mL (12 mmol); cyclopentadiene, 2.0 mL (24 mmol); 10 mL of solvent. [b] CH$_2$Cl$_2$ solution saturated with dry HCl gas.

found that a CH$_2$Cl$_2$ solution, saturated with dry HCl gas, promotes the reaction as well (entry 3). However, it must be stated that the proton activity of pure HCl will be much higher than that of bound aquo groups. We therefore think that, even in wet dichloromethane solutions, our Diels−Alder reactions are still mainly catalyzed by the zirconium center of **1**. This is corroborated by the results of Bosnich,[20] who reported similar Diels−Alder reactions in dichloromethane using [Cp$^*_2$Ti-(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$ as a catalyst. Despite the presence of coordinated water, catalysis must be through the titanium center, since it was found that trifluoroacetic acid is *not* a catalyst for these reactions.

Using *aqueous* HCl (entry 4), catalysis is much less efficient, probably because in this two-phase system HCl is mainly in the water phase, whereas our two reagents are diluted in the CH$_2$Cl$_2$ phase. In *pure* water, **1** is surprisingly active, but aqueous solutions of ZrCl$_4$ and HCl work just as well (entries 7−9), so that, in these cases, it is probably protons that react in water with the undiluted reagents.

Conclusions

Bidentate coordination of the bifunctional C$_5$H$_4$CH$_2$CH$_2$OMe ligand in [(η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_2$(μ-Cl)]$_2$ (**1**) is very strong. Because of the chelate effect in combination with an optimal position for π-donation of the ether oxygen, **1** resists Zr−O bond scission in coordinating solvents like acetone, thf, and acetonitrile. Only strongly polar solvents like water, methanol, and DMSO are capable of disrupting the coordination of the ether side chain. However, evaporating the water or methanol restores this coordination, and only for DMSO is the scission final. The behavior of **1** toward water is remarkably different in solution and in the solid state: excessive solvation with at least two coordinated water molecules is observed in solution, whereas only a monoaqua adduct can be isolated as a solid. Intramolecular coordination of the ether side chain reduces the Lewis acidity of the complexed zirconium center to such an extent that coordination of an additional ligand is weak. However, this is an ideal prerequisite for catalytic applications, and accordingly **1** catalyzes the Diels−Alder reaction in dichloromethane, even when water is present.

Experimental Section

When required, solvents were dried and/or distilled prior to use: CH$_2$-Cl$_2$ and CHCl$_3$ were distilled from CaH$_2$; acetone was distilled from CaCl$_2$ (stored over molecular sieves), and thf, from sodium wire;

(20) (a) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 5464. (b) Hollis, T. K.; Odenkirk, W.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Tetrahedron* **1993**, *49*, 5415.

methanol was stored over molecular sieves; acetonitrile was distilled from P$_2$O$_5$. NMR spectra were obtained from a Varian Gemini 300 MHz spectrometer. The ^{1}H NMR spectra were referenced to the residual ^{1}H signals of the deuterated solvents employed relative to SiMe$_4$. The ^{13}C NMR spectra were referenced to the solvent signals.

(η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_3$(H$_2$O) (5). Complex **1** (0.02 g, 0.03 mmol) was dissolved in 1 mL of water. After 10 min at room temperature, the water was removed in vacuo and the residue was kept under dynamic vacuum for a few hours, leaving an off-white solid in quantitative yield. Anal. Calcd for C$_8$H$_{13}$Cl$_3$O$_2$Zr (M_r = 338.77): C, 28.4; H, 3.9; Cl, 31.4. Found: C, 29.4; H, 4.3; Cl, 29.9.

[(η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_3$(H$_2$O)](thf) 5(thf). Complex **5** (0.11 g, 0.32 mmol) was transferred into a Soxhlet apparatus and extracted with 20 mL of dry thf. A crystalline product was isolated by cooling the mixture to 0 °C and removing the supernatant solution. The yield was 78% (0.12 g, 0.25 mmol). Anal. Calcd for C$_{12}$H$_{21}$-Cl$_3$O$_3$Zr (M_r = 410.88): C, 35.1; H, 5.1. Found: C, 34.9; H, 4.9.

A diethyl ether solvate was obtained the same way.

[(η^5-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_2$(DMSO)$_2$(H$_2$O)][Cl] (7[Cl]). Complex **1** (0.05 g, 0.08 mmol) was dissolved in 1 mL of DMSO in air. After 15 min at room temperature, the solvent was removed in vacuo. The residue (a yellow oil) was washed with 3 mL of Et$_2$O, affording a brown solid (0.05 g, 65%). Anal. Calcd for C$_{12}$H$_{23}$Cl$_3$O$_4$S$_2$Zr (M_r = 493.01): C, 29.2; H, 4.7; S, 13.0. Found: C, 29.0; H, 5.2; S, 14.1. Crystals were obtained by saturating a CH$_2$Cl$_2$ solution with (η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_3$ and DMSO and cooling this mixture to 0° C for a few weeks.

(η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_3$(MeOH) (6). Complex **1** (0.2−0.3 g) was dissolved in a few milliliters of methanol under an atmosphere of argon. After the mixture was stirred for 15 min at room temperature, the solvent was removed in vacuo. The residue was washed with diethyl ether, and drying in vacuo afforded an off-white solid. An adduct of composition (η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_3$-(MeOH) was isolated in virtually quantitative yield. Anal. Calcd for C$_9$H$_{15}$Cl$_3$O$_2$Zr (M_r = 352.80): C, 30.6; H, 4.3. Found: C, 30.4; H, 5.0.

Attempted Syntheses of (η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_3$(acetone), (η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$OMe)ZrCl$_3$(thf), and (η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$OMe)-ZrCl$_3$(MeCN). The procedure was the same as for the methanol reaction. The analogous experiments with acetone, thf, and acetonitrile gave back the starting compound **1**, as evidenced by NMR or elementary analysis.

Catalytic Formation of 2-Formyl-2-methylbicylo[2.2.1.]hept-5-ene. A suspension/solution of **1** in CH$_2$Cl$_2$ (10 mL) was cooled to −30 °C, and cyclopentadiene (2.0 mL, 24 mmol) and methacrolein (1.0 mL, 12 mmol) were added. The solution was brought to room temperature and stirred overnight. The reaction was quenched by adding a few drops of aqueous NH$_4$Cl. The mixture was filtered, and the filtrate was evaporated to dryness at room temperature, affording 1.7 g (100%) of an oily substance. NMR analysis showed that it consisted of virtually pure Diels−Alder product. The exo/endo ratio was determined by integration (see ref 1e for ^{1}H NMR data of products).

Other catalytic experiments were performed similarly (see Table 6). Reactions in water were two-phased; isolation of products was accomplished by pentane extraction.

X-ray Crystal Structure Analysis of 5(thf): Empirical absorption correction via φ scan data ($0.800 \leq C \leq 0.995$), Enraf-Nonius MACH3 diffractometer, $\lambda = 0.710\ 73$ Å, $\omega/2\theta$ scans, 3625 reflections collected ($\pm h, +k, +l$), $(\sin\theta)/\lambda = 0.62$ Å^{-1}, 3480 independent and 2604 observed reflections [$I \leq 2\sigma(I)$], 179 refined parameters, $R = 0.062$, $R_{w2} = 0.158$, hydrogens calculated and riding. Because of the large size of the crystal, absorption correction was not optimal, resulting in relatively large residual electron density around Zr (2.16 and -1.71 e Å^3) and Cl.

X-ray Crystal Structure Analysis of 7[Cl]: Empirical absorption correction via φ scan data ($0.953 \leq C \leq 0.999$), Enraf-Nonius MACH3 diffractometer, $\lambda = 0.710\ 73$ Å, $\omega/2\theta$ scans, 4376 reflections collected ($\pm h, -k, \pm l$), $(\sin\theta)/\lambda = 0.62$ Å^{-1}, 4129 independent and 2865 observed reflections [$I \leq 2\sigma(I)$], 210 refined parameters, $R = 0.049$, $R_{w2} = 0.145$, maximum residual electron density 1.13 (-0.82) e Å^3, hydrogens calculated and riding. Programs used: MolEN, SHELXS-86, SHELXL-93, XP.

Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **5**(thf) and **7**[Cl] are available on the Internet only. Access information is given on any current masthead page.