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Titanocenes and zirconocenes with (chiral) *O*-functionalized side chains on the Cp ring

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Abstract

A series of titanocene and zirconocene dichlorides was synthesized bearing ligands that contain a (chiral) ether group linked by an ethylene spacer group to the cyclopentadienyl ring. Surprisingly, the chiral zirconocenes $(\eta^5\text{-}C_5H_4CH_2CH_2OR)_2ZrCl_2$ with R = isobornyl and menthyl do not show Ziegler–Natta activity. This is probably caused by attack of the cocatalyst $(MeAlO)_n$ on the side chains, causing immobilization of the catalyst. Intramolecular coordination of the side chains is provoked by converting the dichlorides to the more Lewis-acidic mono and bis triflate complexes. The coordination of the ether chain depends on the size of the terminal group in the chain. In the achiral derivative $(\eta^5\text{-}C_5H_4CH_2CH_2OMe)_2Zr(O_3SCF_3)_2$ there is a rapid equilibrium between species with one and two intramolecularly-coordinated ether side chains. The monotriflate complex $(\eta^5\text{-}C_5H_4CH_2CH_2O$*iso*bornyl$)_2ZrCl(O_3SCF_3)$ decomposes rapidly, because ether coordination results in facile C–O bond cleavage and liberation of camphene. Accordingly, the bistriflate $(\eta^5\text{-}C_5H_4CH_2CH_2O$*iso*bornyl$)_2Zr(O_3SCF_3)_2$ could not be synthesized. The chiral triflate complexes $(\eta^5\text{-}C_5H_4CH_2CH_2OR)_2Zr(O_3SCF_3)_2$ with R = menthyl and fenchyl are active Diels–Alder catalysts, although no optical induction was observed, probably because the chiral ether handles are not sufficiently coordinated during catalysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Titanocene; Zirconocene; Dichlorides

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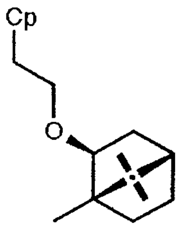
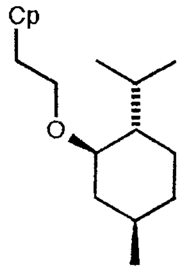
1. Introduction

Interest in transition metal complexes bearing cyclopentadienyl (Cp) systems with functionalized side chains has increased considerably in recent years [1]. The reasons for this attention are diverse. Firstly, one may wish to trap, or stabilize unstable metal cyclopentadienyl intermediates during organic transformations by (reversible) intramolecular coordination of the side chain to the metal center. Heterobimetallic complexes, synthesized with these bifunctional ligands, may have interesting catalytic properties [2]. Anchoring through the functional group of a metallocene unit onto a solid support is also feasible. Ammonium side chains have been used to enhance water solubility of the Cp complex [3]. But the main purpose of these ligands is to influence the electronic and steric properties of the metal center by a static intramolecular coordination of the side chain. In this context, chirally substituted ligands deserve special attention [4,5].

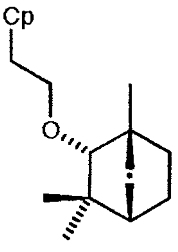
Recently we reported on the synthesis of novel bifunctional ligands having a Cp and a chiral alkoxy unit linked by an ethylene spacer group [6].



$Cp^{(iso)B(ornyl)}$



$Cp^{M(enthyl)}$



$Cp^{F(enchyl)}$

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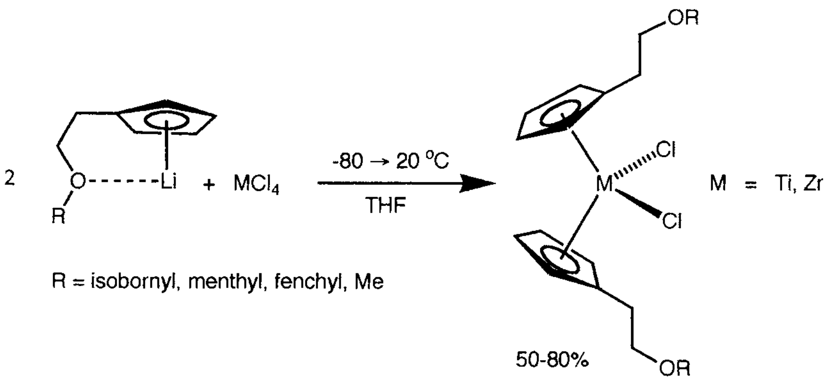

Scheme 1.

They were designed with the aim of preparing chiral Cp complexes in which the pendant ether group should function as a (reversible) coordinating group during asymmetric transformations and catalysis. In this paper we present the synthesis and characterization of the bent titanocene and zirconocene derivatives with these ligands. For comparison, we also include the achiral ligand $C_5Hz_4CH_2CH_2OMe$(CpO) in the investigations. Special emphasis is put on their application as catalysts for Ziegler–Natta olefin polymerization and for Diels–Alder reactions with α, β-unsaturated olefins.

2. Results and discussion

2.1. Syntheses of metallocenes

The titanocene and zirconocene dichlorides were prepared by conventional salt metathesis reactions, Scheme 1. The preparation of the achiral derivatives $Cp^O_2TiCl_2$ and $Cp^O_2ZrCl_2$ has been reported by Chinese workers [7]. However, we could improve the yield of the zirconium compound considerably by an adaptation of the work-up procedure. The syntheses of the chiral derivatives must be started at -80°C, since at room temperature yield is almost zero. This is probably due to ether cleavage of the side chain by the strong Lewis acids $TiCl_4$ or $ZrCl_4$ before formation of the Cp–metal bond [8]. In addition, the amount of Cp^XLi precursor employed should be in safe excess to the transition metal chloride (>2 eq), since any remaining metal chloride will attack the uncoordinated ether side chain, diminishing the overall yield.

The ^1H- and ^{13}C-NMR data of the dichloro complexes are listed in Tables 1 and 2, respectively. Since the chemical shifts around the oxygen atoms are not very different from those of the free ligands [6], it can be deduced that the ether handle is not coordinated. Although the metallocenes are unsaturated 16 electron species, intramolecular coordination is very unlikely. In the X-ray structures of $(\eta^5\text{-}Cp^O)_2TiCl_2$ [7](a), $(\eta_5\text{-}C_5H_4CH_2CH_2N^iPr_2)_2TiCl_2$ [1], $(\eta^5\text{-}C_5H_4CH_2C_4H_7O)_2TiCl_2$ [9] and $(\eta^5\text{-}C_5H_4CH(Me)CH_2OMe)_2MCl_2$ (M = Ti, Zr) [10], intramolecular coordination of the heteroatoms is also absent. However, Qian and Thiele showed that with appropriate ligand geometries, 18 electron metallocenes can be obtained, like in the cation $\{[\eta^5:\eta^5:\eta^1\text{-}C_5H_3N(CH_2C_5H_4)_2\text{-}2,6]ZrCl(H_2O)\}^+$ [11].

Due to the chiral terpene fragments in the Cp^B, Cp^M and Cp^F derivatives the NMR spectra are more complex than those of the achiral Cp^O derivatives. Thus, the CH_2O moiety shows a diastereotopic splitting of the hydrogen resonances in the ^1H-NMR, and because of that they show up as doublet of triplets (Table 1). The diastereotopicity of all five Cp carbons was cleanly resolved in the ^{13}C-NMR spectrum. In contrast, the Cp^O derivative has only three such signals (Table 2).

2.2. Ziegler–Natta polymerisation with $Cp^B_2ZrCl_2$ and $Cp^M_2ZrCl_2$

It has long been known that group 4 metallocenes are active catalysts for the Ziegler–Natta polymerization of α-olefins [12]. Rausch and Jutzi have shown that the activity of the catalyst can be influenced by the presence of heteroatoms on the Cp ring that are capable of intramolecular coordination [1,3,13]. For the Cp_2MCl_2/methylaluminoxane (MAO) systems, intramolecular coordination of the heteroatom side chain may affect the stability of metal–olefine π-coordination. It is also possible that coordination of the aluminium centers to these side chains changes the properties of the cocatalyst MAO.

We tested the chiral metallocenes $Cp^B_2ZrCl_2$ and $Cp^M_2ZrCl_2$ for Ziegler–Natta activity. We were surprised to find that in combination with methylalumoxane ($(MeAlO)_n$ or MAO), these complexes were fully inactive for the polymerization of ethylene. In contrast, Jutzi's complexes $(\eta^5\text{-}C_5H_4CH_2CH_2N^iPr_2)_2ZrCl_2$ are much more active, although less so than the parent

Table 1
^{1}H-NMR data[a]

Compound	C_5H_4	$CpCH_2$	CH_2O	OCH^b_X	Me(3x)[c]
$Cp^B_2TiCl_2$	6.37	2.86 (t, 6.2)	3.41/3.59 (dt, 9.1 × 6.2)	3.15	0.76, 0.81, 0.88
(in C_6D_6)	5.80 (2H), 6.18 (2H)	2.99 (br)	3.34/3.50 (br)	3.05	0.78, 0.95, 1.06
$Cp^B_2ZrCl_2$	6.26	2.80 (t, 6.1)	3.38/3.56 (dt, 9.1 × 6.1)	3.14	0.76, 0.81, 0.89
(in C_6D_6)	5.75 (2H), 6.07 (2H)	2.87 (t, 6.1)	3.29/3.45 (dt, 8.9 × 6.1)	3.05	0.79, 0.96, 1.08
$Cp^B_2ZrCl(O_3S\textit{p}tol)$[d]	6.40	2.68 (t, 5.9)	3.28/3.46 (dt, 9.1 × 5.9)	3.09	0.76, 0.78, 0.86
$Cp^B_2Zr(O_3S\textit{p}tol)^d_2$	6.35	2.55 (t. 5.9)	3.19/3.37 (dt, 9.1 × 6.0)	3.03	0.74 (2x), 0.82
$Cp^M_2TiCl_2$	6.38	2.91 (t, 6.1)	3.45/3.83 (dt, 9.1 × 6.1)	2.97	0.64, 0.82, 0.87
$Cp^M_2ZrCl_2$	6 27	2.85 (t, 6.3)	3.42/3.80 (dt, 9.0 × 6.3)	2.97	0.65, 0.83, 0.88
(in C_6D_6)	5.74 (2H), 6.06 (2H)	2.96 (t, 6.2)	3.30/3.70 (dt, 8.8 × 6.2)	2.89	0.79, 0.87, 0.93
$Cp^M_2ZrCl(OTf)$	6.40 (2H), 6.48 (2H)	2.83	3.39/3.77	2.96	0.64, 0.82, 0.88
$Cp^M_2Zr(OTf)_2$	6.50 (2H), 6.55 (2H)	2.81 (t, 5.9)	3.41/3.77 (dt, 9.0 × 5.9)	2.99	0.64, 0.83, 0.88
(in CD_2Cl_2)	6.63	2.80 (t, 6.0)	3.40/3.78 (dt, 9.1 × 6.0)	3.00	0.65, 0.84, 0.90
(in CD_2Cl_2, −80°C)	6.35 (m. vbr)	2.64 (br)	3.22/3.64 (vbr)	2.86 (br)	0.5 (br), 0.85 (2x, vbr)
$CP^F_2TiCl_2$	6.40	2.89 (t, 6.1)	3.52/3.66 (dt, 9.0 × 6.1)	2.82	0.78, 0.97, 1.00
$Cp^F_2ZrCl_2$	6.28	2.83 (t, 6.1)	3.49/3.62 (dt,8.9 × 6.1)	2.81	0.78, 0.96, 1.00
$Cp^F_2ZrCl(OTf)$	6.40 (2H), 6.49 (2H)	2.8	3.46/3.60	2.80	0.75, 0.96, 0.98
$Cp^F_2Zr(OTf)_2$	6.58 (2H), 6.63 (2H)	2.76	3.43/3.58 (dt, 9.1 × 6.0)	2.78	0.73, 0.94, 0.96
$Cp^O_2TiCl_2$	6.4	3.0 (t, 6)	3.6 (t, 6)	3.3	from [8]
$Cp^O_2ZrCl_2$	6.25 (2H), 6.29 (2H)	2.87 (t, 6.0)	3.54 (t, 6.0)	3.30	
$Cp^O_2ZrCl(OTf)$	6.41 (2H), 6.51 (2H)	2.86 (t, 6)	3.57 (t, 6.2)	3.31	
$Cp^O_2Zr(OTf)_2$	6.47 (2H), 6.56 (2H)	2.89 (t, 5.9)	3.93 (t, 5.9)	3.50	

[a] In $CDCl_3$, unless stated otherwise. Only selected data for the terpene fragments are given.

[b] $H_x = H_2$ (isobornyl and fenchyl), H_3 (menthyl).

[c] Doublets for Cp^M.

[d] *p*tol, 2.38 (s, CH_3), 7.23/7.70 (d, 7.9 Hz, aryl).

Cp_2ZrCl_2 [1]. For our complexes, it seems likely that the Lewis-acidic aluminium centers of MAO coordinate to the ether moieties and immobilize the catalyst. To test this idea we reacted $Cp^B_2MCl_2$ (M = Ti, Zr) with Et_2AlCl as a model compound for MAO. An insoluble material with composition $[C_5H_4CH_2CH_2OAl(Et)Cl]_2$-$MCl_2$ was isolated, obviously a product of O–C (terpene) bond scission. In previous studies we already found that coordination of strong Lewis acids may lead to ether cleavage in these ligands [8]. Although formation of insoluble material does not necessarily result in an inactive catalyst, it is possible that the formed alkoxy tentacles on the Cp-ring intramolecularly coordinate to the zirconium centre, blocking the polymerization of olefins.

2.3. Syntheses of metallocene triflates

Bosnich et al recently reported that the metallocene triflates $Cp_2Ti(OTf)_2$ and $Cp_2Zr(OTf)_2$ are excellent catalysts for both the Diels–Alder, Sakurai, and Mukaiyama reactions (OTf = triflate = O_3SCF_3) [14]. This is because the triflate anions dissociate easily, making the zirconium center much more Lewis-acidic. Very recently, Collins designed chiral derivatives producing up to 95% ee in Diels–Alder catalyzed reactions [15]. We therefore set out to synthesize the analogous triflate complexes of our zirconocene dichlorides. Then, it was hoped that especially the chiral ether handles of the Cp^B, Cp^M and Cp^F derivatives might be able to coordinate intramolecularly in these highly Lewis acidic systems, and influence the enantiomeric excess during a catalytic Diels–Alder reaction.

We first investigated the in situ reactions of $Cp^X_2ZrCl_2$ with AgOTf by NMR under anaerobic conditions (^{1}H and ^{13}C-NMR in Tables 1 and 2, respectively). Adding one equivalent of AgOTf to solutions of $Cp^O_2ZrCl_2$ in deuterated chloroform affords a mixture of $Cp^O_2ZrCl_2$, $Cp^O_2ZrCl(OTf)$ and $Cp^O_2Zr(OTf)_2$, so that the mixed compound $Cp^O_2ZrCl(OTf)$ cannot be isolated in a pure state by this method (Scheme 2). Because the parent compound $Cp_2ZrCl(OTf)$ is stable to disproportionation [16], our product mixture is obvious a result of competing rates between the reaction of the dichloride with AgOTf and of the mono(triflate) complex with AgOTf.

The reaction of the chiral metallocenes $Cp^M_2ZrCl_2$ and $Cp^F_2ZrCl_2$ proceeds more stepwise, and adding one equivalent of AgOTf affords almost pure $Cp^M_2ZrCl(OTf)$ and $Cp^F_2ZrCl(OTf)$, respectively. These complexes are stable for days in solution.

The reaction of $Cp^B_2ZrCl_2$ with one equivalent (or an excess) of AgOTf also yields the mono(triflate), but this complex is so unstable that it decomposes within several hours at room temperature generating camphene as well as insoluble material. Camphene is formed from a

Table 2
^{13}C-NMR data[a]

Compound	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C(Cp)
Cp$_2^B$TiCl$_2$	49.25	87.21	38.46	45.09	27.30	34.46	46.42	20.24*	20.30*	11.99	68.68	32.05	115.84, 115.91, 122.89, 123.11, 135.84
	(—)	(146)	(130)	(139)	(131)	(131)	(—)	(124)	(124)	(124)	(141)	(129)	(177) (177) (175) (175) (—)
Cp$_2^B$ZrCl$_2$	49.26	87.22	38.48	45.11	27.31	34.47	46.41	20.25*	20.28*	11.95	69.09	31.26	112.42, 112.57, 117.43, 117.63, 132.18
	(—)	(145)	(130)	(140)	(130)	(131)	(—)	(125)	(125)	(125)	(141)	(129)	(175) (175) (174) (174) (—)
Cp$_2^B$ZrCl(OTf)[b]		87.30									68.72	30.87	
Cp$_2^B$Zr(O$_3$S*p*tol)$_2^c$	49.11	87.02	38.30	44.93	27.20	34.31	46.30	20.16	20.21	11.87	68.82	30.26	113.83, 113.87, 118.25, 118.51, 132.48
	(—)	(147)	(130)	(140)	(132)	(130)	(—)	(124)	(124)	(125)	(141)	(125)	(175) (175) (173) (173) (—)
Cp$_2^M$TiCl$_2$	31.52	40.46	79.54	48.30	23.32	34.57	22.32	25.55	16.28	20.95	67.96	32.10	115.51, 116.04, 122.71, 122.94, 135.68
Cp$_2^M$ZrCl$_2$	31.55	40.51	79.56	48.32	23.37	34.60	22.33	25.56	16.27	20.95	68.32	31.33	112.34, 112.75, 117.12, 117.50, 131.94
Cp$_2^M$ZrCl(OTf)	31.53	40.44	79.67	48.29	23.34	34.56	22.29	25.59	16.23	20.92	68.00	31.02	114.1 (2x,vbr), 118.2 (2x, vbr), 134.67
Cp$_2^M$Zr(OTf)$_2$	31.54	40.36	79.94	48.20	23.31	34.49	22.24	25.64	16.18	20.91	67.67	30.32	115.09, 115.18, 119.88, 120.23, 133.77
In CD$_2$Cl$_2^d$	31.87	40.68	80.06	48.61	23.59	34.89	22.44	25.92	16.28	21.08	68.12	30.64	116.03 (2x), 120.12, 120.61, 135.92
In CD$_2$Cl$_2$, −80°C[e]	30.81	39.33	78.88	47.39	21.9*	33.74	21.89	24.61	15.08	21.9*	68.05	29.39	116.2 (2x), 120.4 (2x)
Cp$_2^F$TiCl$_2$	49.17	93.34	39.51	48.71	26.13	26.04	41.36	31.69	20.68	20.12	71.37	32.19	115.79, 115.84, 122.93, 123.06, 135.83
CpCp^{F}ZrCl$_2$	49.13	93.32	39.47	48.69	26.00*	26.11*	41.34	31.68	20.63	20.07	71.64	31.35	112.68, 115.63, 117.82, 117.91, 132.53
Cp$_2^F$ZrCl$_2$	49.10	93.26	39.44	48.67	26.09*,	25.97*	41.32	31.66	20.61	20.05	71.69	31.32	112.42 (2x), 117.39, 117.47, 132.03
Cp$_2^F$ZrCl(OTf)	49.04	93.39	39.35	48.57	25.97*,	25.87*	41.22	31.55	20.45	19.90	71.38	30.91	114.0 (2x,vbr), 118.5 (2x, vbr), 134.90
Cp$_2^F$Zr(OTf)$_2^f$	49.02	93.54	39.34	48.54	25.94*,	25.86*	41.18	31.48	20.41	19.84	71.18	30.21	115.94 (2x), 120.22, 120.31, 135.64
Cp$_2^O$TiCl$_2^g$	58.46										71.88	31.08	115.42, 122.98, 135.08
Cp$_2^O$ZrCl$_2$	58.40										72.19	30.22	112.42, 117.43, 131.48
Cp$_2^O$ZrCl(OTf)	58.99										72.58	29.7	114.34, 117.85, 134.29
Cp$_2^O$Zr(OTf)$_2^h$	62.8 (br)										79.1	28.2	115.3, 116.9, 135.9

[a] In CDCl$_3$(= 77.0 ppm) unless stated otherwise. $^1J(^{13}C-^{1}H)$ in parentheses.

[b] Incomplete dataset because of short lifetime.

[c] *p*tol at 21.18 (CH$_3$), 126.23, 129.32, 142.42 (aryl).

[d] O$_3$SCF$_3$ at 119.4 ppm ($^1J_{CF}$ = 320 Hz); $\delta(^{19}F)$ at −77.86 ppm.

[e] $\delta(^{19}F)$ at −78.4 ppm (br).

[f] O$_3$SCF$_3$ at 118.9 ppm ($^1J_{CF}$ = 318 Hz).

[g] From [8].

[h] See also Table 3.

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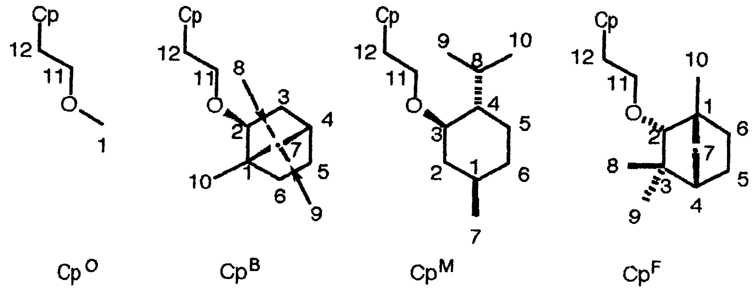
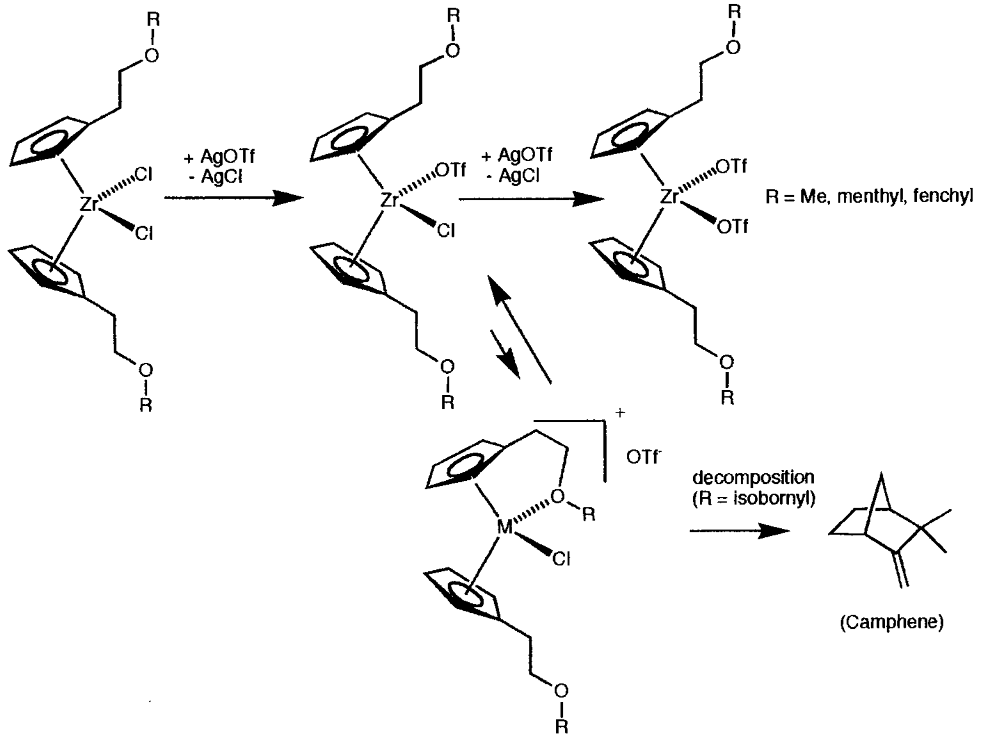




Scheme 2.

Wagner–Meerwein rearrangement of an isobornyl carbocation, and therefore is a result of a Lewis acid catalyzed ether cleavage (cf reaction of $Cp^{B}_{2}ZrCl_{2}$ with alkylaluminium compounds, vide supra). This means that the ether side handle in $Cp^{B}_{2}ZrCl(OTf)$ must have been coordinated to the zirconium center before C–O bond scission occurs [17]. It also means that in all other monotriflates the ether handle is (at least reversibly) coordinated. In the course of our investigations it was found that ether cleavage in the isobornyl ligands occurs much more facile than in the menthyl and fenchyl ligands, because of the formation of the rather stable norbornyl carbonium ion.

Adding two equivalents of AgOTf to solutions of $Cp^{X}_{2}ZrCl_{2}$ affords $Cp^{X}_{2}Zr(OTf)_{2}$ (X = O, M, F); $Cp^{B}_{2}Zr(OTf)_{2}$ could not be obtained. The Cp^{M} and Cp^{F} complexes slowly decompose within a few days so that they were only characterized spectroscopically (vide infra). Only $Cp^{O}_{2}Zr(OTf)_{2}$ could be isolated in a pure state.

The reaction of $Cp^{B}_{2}ZrCl_{2}$ with one equivalent of silver tosylate ($AgO_{3}S$*p*tol) affords a mixture of dichloride, mono(tosylate) and bis(tosylate). Adding 2 eq of silver salt affords the complex $Cp^{B}_{2}Zr(O_{3}S$*p*tol$)_{2}$. In contrast to the triflates, this complex is surprisingly stable and can be isolated without difficulty. This means that the isobornyl ether side chains are not at all coordinated, otherwise the complex would decompose via ether cleavage (vide supra). Obviously, the Zr–O bonds in the tosylate complex are stronger than in the triflate complexes. Therefore, the zirconium center is less Lewis acidic, and the tosylate groups show less tendency to dissociate, and the ether handles cannot coordinate intramolecularly.

2.4. *NMR investigations on the metallocene mono(triflates)*

For catalytic applications it is vital to know whether the ether side chains in our triflates are intramolecularly coordinated or not. From the vast amount of NMR data for the Cp^{O} ligand [7], it has been shown that intramolecular coordination of the ether handle causes significant down-field shifts of the hydrogens and carbons around the oxygen atom. Especially the ^{13}C chemical shifts of the $CH_{2}OCH_{3}$ moiety are very diagnostic. Non-coordinated ether handles have a ^{13}C resonance for the $CH_{2}O$ group at 73 and for the OCH_{3} group at 58 ppm. Upon coordination these data change to ca. 82 and 64 ppm, respectively. From these data, it can be concluded that in a compound like $Cp^{O}TiCl_{3}$, for which a crystal structure shows intramolecular coordination, the ether handle is mainly dissociated in solution [7,8].

For the mono(triflate) complexes $Cp^{X}_{2}ZrCl(OTf)$ (X = O, B, M, F) the ^{1}H and ^{13}C chemical shifts around the ether oxygen atom are not very different from those of $Cp^{X}_{2}ZrCl_{2}$, in which the ether moieties are certainly not coordinated (see Tables 1 and 2). However, from the rapid decomposition of $Cp^{B}_{2}ZrCl(OTf)$ (vide supra), it was concluded that for all mono(triflate) complexes

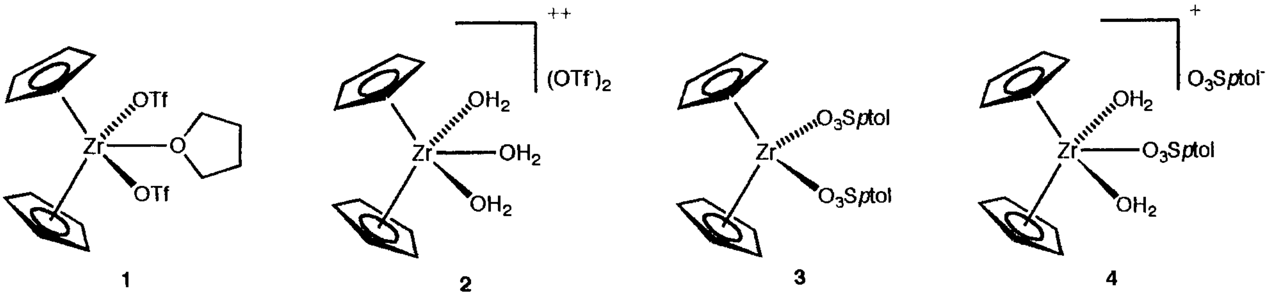


Fig. 1. Zirconocene triflate and tosylate complexes (from [18,20]).

at least a reversible coordination of one of the ether handles exists. However, according to the NMR data the equilibrium must lie far to the side of the uncoordinated conformation. The question arises whether the triflate fragment remains attached to the zirconium center upon coordination, affording a neutral 18 electron complex, or dissociates forming a cationic species. The compounds Cp_2ZrCl_2 and $Cp_2ZrCl(OTf)$ do not form stable adducts with, for instance, thf [16]. The bistriflate $Cp_2Zr(OTf)_2$ forms the neutral adduct $Cp_2Zr(OTf)_2(thf)$ with thf (Structure **1** in Fig. 1) ([18]a), and a cationic species $[Cp_2Zr(OH_2)_3][OTf]_2$ with water (Structure **2** in Fig. 1) ([18]b). In view of the large steric bulk of the chiral derivatives, it is concluded that reversible intramolecular coordination of one of the ether side chains in $Cp^X_2ZrCl(OTf)$ must be attended by dissociation of the triflate moiety (Scheme 2).

2.5. NMR investigations on the metallocene bis(triflates)

For $Cp^O_2Zr(OTf)_2$ the Cp^O ligand shows significant down-field shifts for both the ^{1}H and ^{13}C signals of the CH_2OCH_3 moiety, clearly indicative of internal ether coordination. However, most of the resonances are broad at room temperature, suggesting dynamic phenomena, and therefore low-temperature NMR measurements were conducted. In the ^{1}H-NMR spectra, the set of signals for the Cp^O ligand broadens upon cooling, and below −20°C gets very complicated due to partly overlapping signals, and these data are therefore not very diagnostic. The ^{13}C and ^{19}F-NMR measurements in CD_2Cl_2 show a better resolution of signals (Table 3). The ^{13}C resonances for the Cp^O ligand broaden upon cooling and almost vanish around −20°C. Only the ^{13}C resonance of the $CpCH_2$ moiety remains remarkably sharp throughout all temperatures. This is probably due to the fact that this group is located between the coordinating Cp and ether moieties and is rather insensitive to changes occurring around the zirconium center. Below −40°C two sets of Cp^O signals emerge. One minor set (**A**) of signals has relatively high-field ^{13}C resonances for the CH_2OCH_3 moiety (77 and 62 ppm), which are however still down-field from those of the free ligand (73 and 58 ppm); this set of signals disappears at −80°C. This may be either due to conversion of **A** to the second compound (**B**), or to decoalesence of the signals of **A**. Another, major set of signals (**B**) has ^{13}C resonances for the CH_2OCH_3 moiety (87 and 67 ppm) that are very down-field in comparison to those of the free ligand, and these signals persists down to −80°C. A single ^{19}F resonance at −77.91 ppm is observed at room temperature. Its value lies between that of $Cp_2Zr(OTf)_2$ (−77.5 ppm) [19] and of the free triflate ion (−78.5 ppm) [14,15]. The ^{19}F resonance splits into several signals below −40°C.

We propose the exchange mechanism as depicted in Scheme 3. Species **A** is the mono(ether) coordinated neutral isomer $(\eta^5{:}\eta^1\text{-}Cp^O)(\eta^5\text{-}Cp^O)Zr(OTf)_2$, whereas **B** is the salt-like bis(ether) coordinated isomer $[(\eta^5{:}\eta^1\text{-}Cp^O)_2Zr(OTf)][OTf]$. This will be elucidated. Based on the down-field shifts of the CH_2OCH_3 moieties in both species **A** and **B** at least one Cp^O-ligand must be *O*-coordinated. As the signals of isomer **B** are the furthest down-field it can be anticipated that in **B** both Cp^O ligands are *O*-coordinated. One triflate may be coordinated in the equatorial plane between the two ether handles. This yields a spiro-like salt, which is corroborated by the appearance of five ^{13}C signals for the Cp ring. The proposed structure for species **B** is very similar to that of $[Cp_2Zr(O_3S\textit{p}tol)(OH_2)_2][O_3S\textit{p}tol]$ (Structure **4** in Fig. 1), obtained by Thewalt upon hydrolysis of $Cp_2Zr(O_3S\textit{p}tol)_2$ (Structure **3** in Fig. 1) [20]. Collins observed similar 18 electron species of the type $\{[(S)\text{-}1,2\text{-ethylenebis}(\eta^5\text{-tetrahydroindenyl})]Zr(OTf)(L)_2\}\{OTf\}$ [15].

For species **A** there are two possibilities for the ether handle to coordinate, namely in the equatorial plane between the triflates or at the border position. The former description has a precedent, namely $Cp_2Zr(OTf)_2(thf)$ (Structure **1** in Fig. 1. For our system the strained geometry of the ether handle only allows for the second possibility. The proposed structure for species **A** contains one coordinated and one uncoordinated ether handle. This seems in conflict with the ^{13}C-NMR data, since only one set of signals is ob-

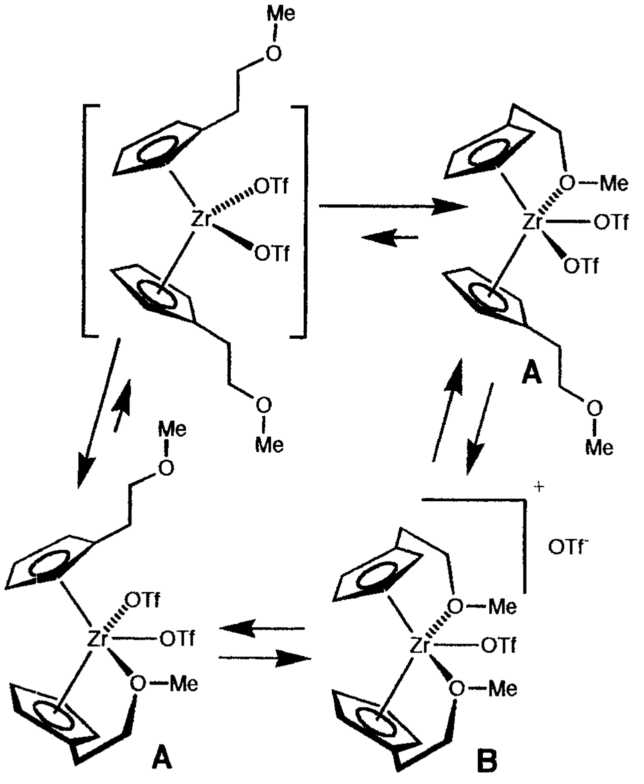
Table 3
Temperature dependent NMR data for $Cp^{O}_{2}Zr(OTf)^{a}_{2}$

T (°C)	^{13}C-NMR				^{19}F-NMR
	OCH_3	CH_2O	$CpCH_2$	C_5H_4	$O_3SCF^{b}_{3}$
+20	64.2(br)	81.2(vbr)	28.7	116.3(br)	−77.91(20)
0	64.4(vbr)	n.o.	28.5	115.6(vbr)	−78.05(25)
−20	n.o.	n.o.	28.3	n.o.	−78.17(40)
−40	(**A**) 61.6(br)	77.0(br)	28.1	118.3, 136.3	−78.31(55)
	(**B**) 67.6(br)	86.8(br)	28.1	108.1, 112.3, 113.6, 122.7, 144.8 (all br)	−78.08(sh)
−60	(**A**) 61.5	76.9	27.9	118.3, 136.3	−78.47(60)
	(**B**) 67.5	86.8	27.9	107.5, 112.3, 113.3, 122.3, 145.0	−78.17(15)
−80	(**A**) n.o.	n.o.	27.7?	n.o.	−78.05(30), −78.54(30), −78.75(br)
	(**B**) 67.4	86.6	27.7	106.8, 112.3, 113.0, 121.8, 145.2	−78.26(25)

n.o. = not observed.
[a] In CD_2Cl_2 [$\delta(^{13}C) = 53.8$ ppm].
[b] $\Delta\upsilon_{1/2}$ in Hz in parentheses.

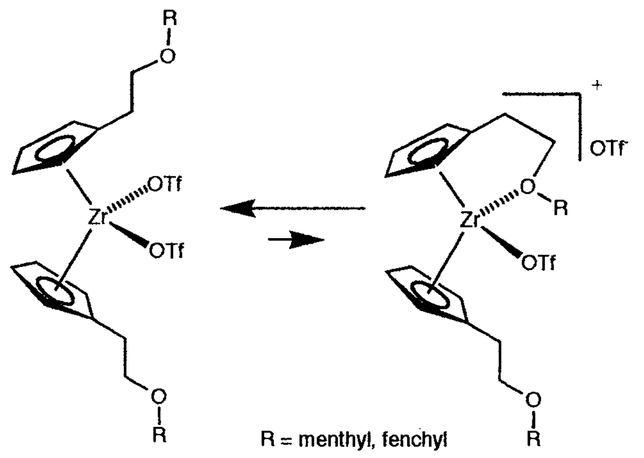
served. It is assumed that decoalescence for **A** starts below −80°C in the ^{13}C-NMR, but can just be observed by ^{19}F-NMR at −80°C (vide infra).

The ^{19}F-NMR data can be explained as follows. The sharp signal that grows in at −40°C (−78.08 ppm; at −60°C −78.17 ppm; at −80°C −78.26 ppm) corresponds to the zirconium-bound triflate in **B**. The other major signal at −40°C (78.31 ppm; at −60°C: −78.47 ppm) is the average signal of the free triflate of **B** and of bounded triflate in the fluxional species **A** [21]. At −80°C the latter signal starts to decoalesce, and splits into three signals: −78.05 and −78.54 ppm attributed to coordinated triflate in **A**, and −78.75 ppm attributed to free triflate.



Scheme 3.

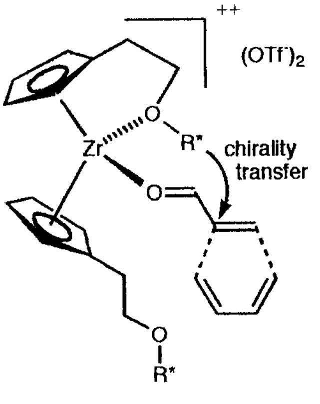
The NMR data of the chiral bis(triflate) complexes $Cp^{M}_{2}Zr(OTf)_2$ and $Cp^{F}_{2}Zr(OTf)_2$ are much less spectacular than those of $Cp^{O}_{2}Zr(OTf)_2$ The resonances of the ether side chain are not very different from those of the starting compound $Cp^{X}_{2}ZrCl_2$. Especially the ^{13}C resonances of C_{11}, C_2 for Cp^M and of C_3 for Cp^F (Table 2) are expected to show a down-field shift upon coordination [8]. The ^{19}F-NMR spectra of $Cp^{M}_{2}Zr(OTf)_2$ show a single resonance at −77.86 ppm at room temperature. This value is between that of $Cp_2Zr(OTf)_2$ (−77.5 ppm) [19] and free triflate (−78.4 ppm) [15]. Upon cooling to −80°C the ^{19}F resonance of $Cp^{M}_{2}Zr(OTf)_2$ broadens and shifts to −78.4 ppm. The ^{1}H- and ^{13}C-NMR spectra also show some broadening, although without much change of chemical shifts. These results can be interpreted as fast reversible coordination of one of the chiral ether side chains with replacement of triflate (Scheme 4). We have previously seen that reversible intramolecular coordination in the mono(triflates) complexes is very likely, based on the rapid decomposition of $Cp^{B}_{2}ZrCl(OTf)$. For the bis(triflate) complexes, in which the zirconium centers are still more Lewis-acidic, coordination is even more probable. However, it is possible that full deployment of ether coordination to the zirconium center, as for the methoxy ether, is hindered by the large steric bulk of the terpene fragments.



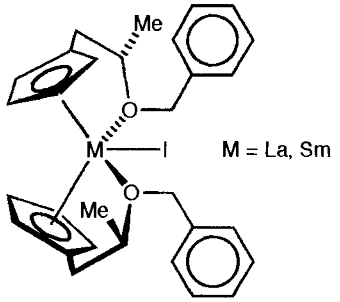
Scheme 4.

2.6. Diels–Alder reactions catalyzed by $Cp_2^MZr(OTf)_2$ and $Cp_2^FZr(OTf)_2$

As mentioned before, Collins obtained successful asymmetric inductions during Diels–Alder reactions catalyzed by chiral metallocene triflate complexes [15]. Transfer of chirality occurs through the presence of a chiral, linked bis(tetrahydroindenyl) ligand system. It occurred to us that intramolecular coordination of the chiral ether moieties in $Cp_2^MZr(OTf)_2$ and $Cp_2^FZr(OTf)_2$, might also have a chiral inductive effect on Diels–Alder reactions.



We therefore tested these systems on the reaction of methacrolein with cyclopentadiene. Not unexpectedly, our triflates are indeed efficient catalysts for this reaction (Table 4). However, no measurable enantiomeric excess was observed, not even at lower temperatures. The reason might be that the dienophile displaces the intramolecular coordination of the ether side chain, so that the chiral information gets out of range of the reaction center. It is possible that less sterically hindered chiral ether handles might be more effective. This is corroborated by recent results of Collin who observed moderate asymmetric inductions for the same Diels–Alder reaction described above, catalyzed by samarocene and lanthanocene derivatives [22]. Their ligand contains an ether handle with a smaller, benzyl endgroup and a stereogenic center in the spacer group between Cp and oxygen.

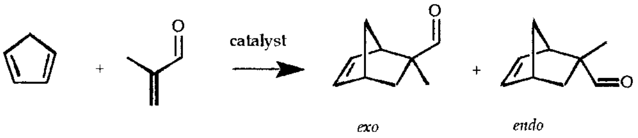


The smaller size of the ether chains obviously allows facile intramolecular coordination of the oxygen atom between the Cp_2M sandwich in these systems. It seems likely that under catalytic conditions at least one side arm remains coordinated in order to effect chirality transfer. Although modelling studies on our systems show that intramolecular coordination of at least one of the ether side arms seems possible despite the bulky Cp_2Zr core, steric strain is probably too large in our systems.

3. Experimental

All manipulations were carried out under an atmosphere of argon. Solvents were dried and degassed by conventional procedures prior to use. NMR spectra were obtained from a Varian Gemini 300 MHz spectrometer. The spectra were referenced to the residual ^1H and ^{13}C signals of the deuterated solvents employed. Mass spectra were obtained from an Intectra AMD 402 (El MS, 70 eV) mass spectrometer. The combustion analyses were performed on a CHNS-932 LECO analyzer in our department.

Table 4



Diels–Alder catalysis by $Cp_2^XZr(OTf)_2^a$

Catalyst	T (°C)	Yield (%)	Exo/endo
$Cp_2^MZr(OTf)_2$	r.t.	100	95/5
$Cp_2^MZr(OTf)_2$	−4	85	88/12
$Cp_2^MZr(OTf)_2$	−78	<5	
$Cp_2^FZr(OTf)_2$	−4	90	88/12
$Cp_2Zr(OTf)_2^b$	r.t.	100	85/15

r.t. is room temperature.

[a] Conditions: catalyst (2 mol%) prepared in situ in 10 ml of dichloromethane; methacrolein, 1.0 ml (12 mmol); cyclopentadiene, 2.0 ml (24 mmol), reaction time, 24 h.

[b] From [14](b).

3.1. $Cp_2^OTiCl_2$

This compound was prepared according to [7] (a). Calcd for $C_{16}H_{22}Cl_2O_2Ti$ (365.1): C, 52.5; H, 6.1; Cl, 19.4. Found: C, 52.2; H, 5.7; Cl, 19.1.

3.2. $Cp_2^BTiCl_2$

A solution of Cp^BLi in 60 ml of thf was generated from Cp^BH (7.4 g, 30.2 mmol) and 20.5 ml of a 1.67 M solution of *n*-buthyllithium at 0°C. The clear yellow solution was cooled to − 78°C, whereupon $TiCl_4$ (1.6 ml, 14.6 mmol) was added. The initially dark colored solution was stirred for 1 h and than slowly warmed to room temperature. After stirring overnight, the reddish-brown solution was evaporated to dryness, and extracted with toluene. The toluene extracts were filtered off from LiCl and evaporated to dryness. The residue was washed several times with pentane, leaving a brick-red solid (3.8 g). Combining and chilling of the pentane extracts afforded another crop (1.45 g): total yield: 5.25 g (59%). Anal. Calcd for $C_{34}H_{50}Cl_2O_2Ti$ (609.55): C, 67.0; H, 8.3. Found: C, 64.8; H, 8.0.

3.3. $Cp_2^MTiCl_2$

As for $Cp_2^BTiCl_2$. Yield: 50%. MS (EI; *m/z*): 438 ($[M\text{-menthyl-Cl}]^+$), 403 ($[M\text{-menthyl-2Cl}]^+$), 330 ($[M–Cp^M–Cl]^+$), 265 ($[M\text{-2menthyl-2Cl}]^+$), 227 ($[M–Cp^M\text{-menthyl}]^+$), 192 ($[M–Cp^M\text{-menthyl-Cl}]^+$), 139 ($[\text{menthyl}]^+$).

3.4. $Cp_2^FTiCl_2$

As for $Cp_2^BTiCl_2$. Yield: 65%. Anal. Calcd for $C_{34}H_{50}Cl_2O_2Ti$ (609.6): C, 66.9; H, 8.2; Cl, 11.7. Found: C, 66.9; H, 8.2; Cl, 11.9. MS (EI; *m/z*): 436 ($[M\text{-fenchyl-Cl}]^+$), 401 ($[M\text{-fenchyl-2Cl}]^+$), 363 ($[M–Cp^F]^+$), 328 ($[M–Cp^F–Cl]^+$), 265 ($[M\text{-2fenchyl-2Cl}]^+$), 137 ($[\text{fenchyl}]^+$)

3.5. $Cp_2^OZrCl_2$

To a solution of Cp^OLi in 50 ml of THF, prepared from Cp^OH (1.67 g, 13.5 mmol) and 9.6 ml 1.68 M *n*-BuLi in pentane, was added $ZrCl_4(THF)_2$ (1.70 g, 4.6 mmol). After stirring overnight at room temperature, solvents were removed in vacuo. The residue was extracted with 50 ml of CH_2Cl_2. After treating the extract with 5 ml of concentrated HCl, it was dried over Na_2SO_4, filtered, and concentrated to 10 ml. After addition of 20 ml of pentane and chilling 1.52 g (3.7 mmol, 81%) of a white microcrystalline powder were obtained. Anal. Calcd for $C_{16}H_{22}Cl_2O_2Zr$ (408.48): C, 47.0; H, 5.4. Found: C, 46.9; H, 5.5.

3.6. $Cp_2^BZrCl_2$

To a cooled solution (− 78°C) of Cp^BLi (6.1 g, 24.2 mmol) in 50 ml of thf was added solid $ZrCl_4$(thf)2 (4.5 g, 12.0 mmol). The resulting clear yellow solution was stirred for 1 h at − 78°C and than gradually warmed to room temperature. After stirring overnight, solvent was removed under vacuum and the residue extracted with toluene. The extracts were concentrated and, after addition of pentane cooled to − 30°C to afford a white precipitate (4.5 g). Concentration of the filtrate and precipitation with pentane yielded a second crop (1.0 g): total yield 5.5 g (70%). Anal. Calcd for $C_{34}H_{50}Cl_2O_2Zr$ (652.90): C, 62.5; H, 7.7. Found: C, 59.4; H, 7.7.

3.7. $Cp_2^MZrCl_2$

As for $Cp_2^BZrCl_2$. Yield: 65%. Anal. Calcd for $C_{34}H_{54}Cl_2O_2Zr$ (656.93): C, 62.2; H, 8.3; Cl, 10.8. Found: C, 63.4; H, 8.1; Cl, 10.2. MS (EI; *m/z):* 620 ($[M–Cl]^+$), 481 ($[M\text{-menthyl-Cl}]^+$), 407/409 ($[M–Cp^M]^+$), 268/270 ($[M–Cp^M\text{-mentyl}]^+$), 139 ($[\text{menthyl}]^+$).

3.8. $Cp_2^FZrCl_2$

As for $Cp_2^BZrCl_2$. Yield: 61%. Anal. Calcd for $C_{34}H_{50}Cl_2O_2Zr$ (653.0): C, 62.6; H, 7.7; Cl, 10.9. Found: C, 62.5; H, 7.3; Cl, 10.8. MS (EI; *m/z):* 479 ($[M\text{-fenchyl-Cl}]^+$), 405/407 ($[M–Cp^F]^+$), 268/270 ($[M–Cp^F\text{-fenchyl}]^+$), 137 ($[\text{fenchyl}]^+$).

3.9. Attempted polymerisation of ethylene with $Cp_2^BZrCl_2$ and $Cp_2^MZrCl_2$

A toluene solution of a few mg (ca. 3 μmol) of the metallocene and methylaluminoxane (10 ml of a 10% solution in toluene) was transferred to an autoclave. After 1 h at 70°C under 7 bar of ethylene, no polyethylene could be isolated.

3.10. Reaction of $Cp_2^BMCl_2$ (M = Ti, Zr) with Et_2AlCl

To a solution of $Cp_2^BMCl_2$ (ca. 0.2 g, 0.3 mmol) in 10 ml of toluene was added Et_2AlCl (ca. 1 ml of a 1 M solution in toluene). A solid (red for Ti; creme for Zr) was deposited over a period of several hours. For titanium, combustion analysis of this material gave: C, 42.2; H, 5.2%. $[C_5H_4CH_2CH_2OAl(Et)Cl]_2TiCl_2$ requires: C, 41.7; H, 5.1%. The solution was decanted and evaporated to dryness in vacuo at room temperature. NMR analysis shows that the main component was camphene, by comparison with an authentic sample.

3.11. $Cp_2^OZr(OTf)_2$

A solution of $Cp_2^OZrCl_2$ (0.28 g; 0.69 mmol) in 10 ml of toluene was treated with AgOTf (0.36 9; 1.40 mmol) at room temperature in the dark. The color of the suspension turned black-violet immediately. After stirring for 2 h the toluene was filtered and concentrated to 4 ml. Pentane (15 ml) was added and the resulting suspension was cooled to −78°C upon which a dark oil formed. Solid product was isolated by washing with 10 ml of Et_2O and drying in vacuo (0.31 g; 0.49 mmol; 70%). Anal. Calcd for $C_{18}H_{22}O_8F_6S_2Zr$ (635.69): C, 34.0; H, 3.5; S, 10.1. Found: C, 32.6; H, 3.5; S, 9.7.

3.12. $Cp_2^MZr(OTf)_2$ and $Cp_2^FZr(OTf)_2$

These compounds were prepared similarly, but were found to be unstable upon prolonged storage. They were characterized by NMR as soon as possible. $Cp_2^BZr(OTf)_2$ could not be prepared (see text).

3.13. $Cp_2^BZr(O_3Sptol)_2$

To a solution of $Cp_2^BZrCl_2$ (0.15 g, 0.23 mmol) in 20 ml of CH_2Cl_2 was added AgO_3S*p*tol (0.17 g, 0.61 mmol). The greyish solution was stirred overnight and filtered over Celite. Evaporation of solvents afforded an off-white solid (0.20 g, 95%). Anal. Calcd for $C_{48}H_{64}O_8S_2Zr$ (924.37): C, 62.4; H, 7.0; S, 6.9. Found: C, 61.8; H, 7.4; S, 7.0.

3.14. Diels–Alder reactions catalyzed by$Cp_2^XZr(OTf)_2$

Ca. 0.2 mmol of the catalyst was prepared in situ as described above. After filtering off the silver salts, the solution was tempered and methacrolein (1.0 ml (12 mmol) and cyclopentadiene 2.0 ml (24 mmol) were added by syringe, and the reaction mixture was stirred for 24 h. Workup and analyses of diastereomer and enantiomer ratios was accomplished as described in ([5] c).

Acknowledgements

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