www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 584 (1999) 274–285

Journal of Organometallic Chemistry

Synthesis, conformation analysis and catalytic properties of chiral zirconium complexes containing etherfunctionalized Cp ligands

Adolphus A.H. van der Zeijden *, Chris Mattheis

Institut für Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg, Geusaer Straße, D-06217 Merseburg, Germany

Received 18 January 1999; received in revised form 19 February 1999

Abstract

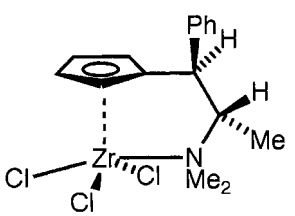
A novel series of chiral ligands was synthesized having a cyclopentadienyl (Cp) ring attached to an ether moiety. Four chiral monoCp zirconium derivatives contain these ligands in a bidentate Cp/O coordination mode. Complexes **4d**, **6d**, and **7d** bear an aryl group at the end of the ether chain. The racemic complexes **3d** and **4d** show moderate activity for the polymerisation of ethylene. Complexes **6d** and **7d** are enantiopure and were used as asymmetric Lewis acid catalysts for the hydrocyanation of benzaldehyde. The negligible enantiomeric excess thereby is due to decomplexation of the weakly coordinated aryl ether side-chains during catalysis.

Keywords: Zirconium; Cyclopentadienyl; Ethylene polymerisation; Hydrocyanation of benzaldehyde

1. Introduction

Monocyclopentadienyl (Cp) zirconium complexes can be used both as Lewis acid catalysts in organic synthesis [1], as well as Ziegler–Natta catalysts for the polymerisation of α-olefins [2]. Chiral modifications of the metal complex should allow the control of enantioselectivity and polyolefin-stereoregularity on these processes. However, the chiral modification of a Cp ligand is hampered by its high fluctionality, which makes it difficult to obtain a rigid chiral environment required for asymmetric transformations [3]. We [4] and others [5] are therefore investigating the use of functional groups attached to the Cp ring capable of intramolecular coordination, thus giving rise to a more rigid chelate. Following these guidelines we synthesised a chiral monoCp zirconium complex based on the natural compound ephedrine **1** [4b]:

(3)



1

However, the combination of an amino side-chain and an oxophilic element like zirconium makes **1** extremely hydrophilic, which limits its practical use as a Lewis acid catalyst. Nevertheless, **1** catalyses the Diels–Alder reaction, although with poor enantioselectivity. Obviously, transfer of chirality from the chiral side-chain through the relatively small NMe_2 group to the catalytic centre is ineffective in this arrangement.

We recently published the synthesis of an (achiral) complex **2** bearing an ether side-chain [4d]. This complex is much less water sensitive than **1**, and it is even possible to conduct Diels–Alder and hydrocyanation reactions under aerobic conditions.

* Corresponding author. Tel.: 49-3461-462105; fax: +49-3461-462002.

E-mail address: zeijden@chemie.uni-halle.de (A.A.H. van der Zeijden)

0022-328X/99/$ - see front matter
PII: S0022-328X(99)00164-3

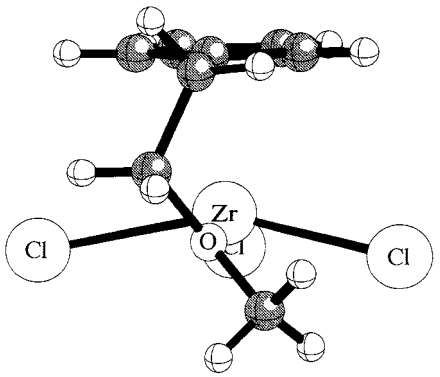
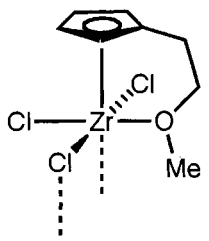


Fig. 1. Detail from the X-ray structure of **2** [4d].



2

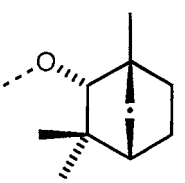
A closer look at the crystal structure of **2** reveals a puckered, and therefore chiral, arrangement of the side-chain (Fig. 1). In solution, the complex rapidly swings between the two enantiomeric extremes via a wind-screen-wiper-wise rotation around the Zr–O axis. Fixing the geometry in one of the extreme conformations would yield a genuine chiral complex. There are several options for doing this. First, introducing one or more substituents onto the Cp ring should favour one of the enantiomers more than the other, creating a more static chiral puckering of the side-chain. In the current work, this was accomplished by substituting two bulky Me_3Si groups in 2,4-position onto the Cp ring [6] (a 1-substituted indenyl ligand would have the same function) [7]. The substitution of two or more different substituents onto a coordinated Cp ring creates an additional stereogenic centre, and although the resulting metal complex will be chiral, it is still racemic.

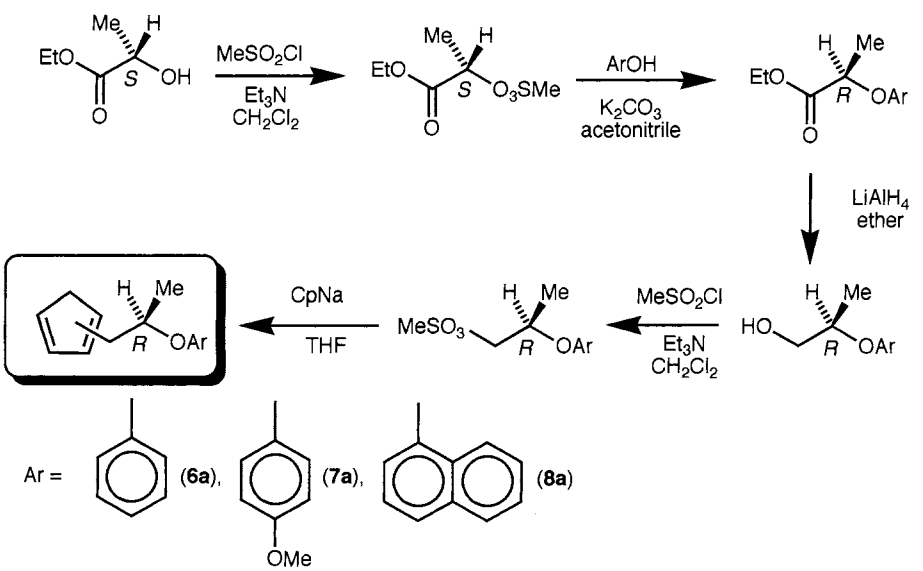
To obtain enantiomerically pure compounds, the ligand system either needs to be separated in enantiomers (which will be difficult) or needs a source of enantiopurity. In the present study this was accomplished either by introducing a chiral substituent ((1*R*)-fenchyl) on the terminal ether group [4c] or by a stereogenic carbon in the ethylene bridge. In the latter case the terminal methyl group was substituted for a larger aryl group in order to amplify the chirality more effectively into the metal coordination sphere.

2. Results and discussion

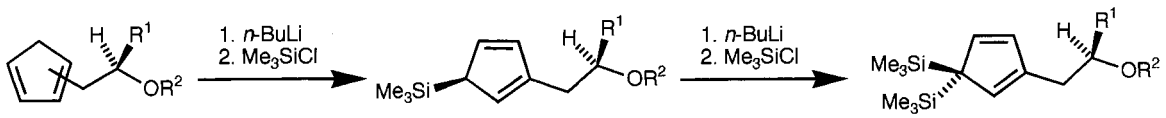
The bidentate cyclopentadiene ligand $C_5H_5CH_2$-CH_2OMe (**3a**) was synthesised by published methods [8]. The phenyl-substituted analogue $C_5H_5CH_2CH_2OPh$ (**4a**) was synthesised by a straightforward reaction between CpNa and $BrCH_2CH_2OPh$. The synthesis of the chiral ligand $C_5H_5CH_2CH_2OC_{10}H_{17}$ [**5a**; $C_{10}H_{17}$ = (1*R*)-fenchyl] has been published[1] recently by us [4c]. The syntheses of the enantiomerically pure aryl ligands (*R*)-$C_5H_5CH_2CH(Me)OAr$ [Ar=Ph (**6a**), C_6H_4-4-OMe (**7a**), α-naphthyl (**8a**)] were based on (*S*)-ethyl lactate as a starting material (Scheme 1). The conversion to the

[1]





Scheme 1.



nr R^1 R^2
3a H Me
4a H Ph
5a H fenchyl
6a Me Ph
7a Me C_6H_4-4-OMe
8a Me α-naphthyl

3b-8b **3c-8c**

Scheme 2.

Table 1
^{1}H-NMR data for the $SiMe_3$ derivatives of the Cp ligands[a]

Compound	Me	C(H)O	CH_2	C_5H_x ring	OR	$SiMe_3$
$C_5H_4(CH_2CH_2OMe)(SiMe_3)$ (**3b**)	–	3.52(t, 7.1)	2.68 (t, 7.1)	3.26, 6.13, 6.42, 6.46	3.33	−0.06
$C_5H_4(CH_2CH_2OPh)(SiMe_3)$ (**4b**)	–	4.13	2.93	3.34, 6.24, 6.48, 6.55	6.93 (3H), 7.27 (2H)	−0.02
$C_5H_4(CH_2CH_2Ofenchyl)(SiMe_3)$ (**5b**)	–	3.49/3.62 (m)	2.65 (m)	3.26, 6.12, 6.41, 6.49	[b]	−0.06
$C_5H_4(CH_2CH(Me)OPh)(SiMe_3)$ (**6b**)	1.34	4.57 (m)	2.70/2.91 (m)	3.31, 6.22, 6.47, 6.56	6.93 (3H), 7.28 (2H)	−0.02
$C_5H_4(CH_2CH(Me)OC_6H_4$-4-OMe) $(SiMe_3)$ (**7b**)	1.30	4.42 (m)	2.65/2.90 (m)	3.29, 6.21, 6.47, 6.54	3.74 (3H), 6.84 (4H)	−0.01
$C_5H_4(CH_2CH(Me)O$-α-naphthyl) $(SiMe_3)$ (**8b**)	1.45	4.78 (m)	2.82/3.03 (m)	3.30, 6.26, 6.46, 6.60	6.85 (1H), 7.4 (4H), 7.78 (1H), 8.34 (1H)	−0.05
$C_5H_3(CH_2CH_2OMe)(SiMe_3)_2$ (**3c**)	–	3.47 (t, 7.2)	2.70(t, 7.2)	6.13, 6.40, 6.54	3.33	−0.10 (18H)
$C_5H_3(CH_2CH_2OPh)(SiMe_3)_2$ (**4c**)	–	4.09(t, 7.1)	2.93(t, 7.1)	6.24, 6.45, 6.63	6.92 (3H), 7.27 (2H)	−0.06 (18H)
$C_5H_3(CH_2CH_2Ofenchyl)(SiMe_3)_2$ (**5c**)	–	3.46/3.57 (m)	2.66 (m)	6.12, 6.38, 6.56	b	−0.10 (18H)
$C_5H_3(CH_2CH(Me)OPh)(SiMe_3)_2$ (**6c**)	1.32(d, 6.0)	4.53 (m)	2.68/2.93 (m)	6.21, 6.44, 6.61	6.91 (3H), 7.27 (2H)	−0.06, −0.07
$C_5H_3(CH_2CH(Me)OC_6H_4$-4-OMe) $(SiMe_3)_2$ (**7c**)	1.28(d, 5.9)	4.40 (m)	2.65/2.90 (m)	6.20, 6.44, 6.61	3.74 (3H), 6.82 (4H)	−0.06, −0.07
$C_5H_3(CH_2CH(Me)O$-α-naphthyl) $(SiMe_3)_2$ (**8c**)	1.45(d, 6.1)	4.77 (m)	2.86/3.07 (m)	6.28, 6.45, 6.68	6.88 (1H), 7.4 (4H), 7.79 (1H), 8.34 (1H)	−0.05, −0.08

[a] In $CDCl_3$; all signals (broad) singlets, unless stated otherwise; coupling in Hz in parentheses; the signals for the mono(Me_3Si) derivatives were all slightly broadened.
[b] Characteristic fenchyl signals at 2.88 (OC*H*) and 0.89, 1.01, 1.07 (all s, Me).

mesylate ester and their S_N2-substitution by phenolates were developed by Burkard and Effenberger [9]. The chiral esters were reduced to the alcohols by $LiAlH_4$ in 83–90% yield. The alcohols were esterified by mesylchloride, and subsequent reaction with CpNa affords the chiral Cp ligands **6a**–**7a** in 54–60% yield after distillation (**8a** could not be distilled without decomposition due to its high boiling point).

The syntheses of the mono- and bis(trimethylsilyl)derivatives **3b**–**8b** and **3c**–**8c** were accomplished by consecutive reactions with *n*BuLi and Me_3SiCl (Scheme 2). Compounds **3b**–**8b** exist as a single isomer according to NMR, although the broadening of the signals indicates mobility of the Me_3Si group. The patterns of the ^{1}H- and ^{13}C-NMR signals (Tables 1 and 2) are consistent with an 2-alkyl-5-Me_3Si substituted Cp ring. Compounds **3c**–**8c** also exist as a single isomer. In this case, the NMR signals are in accord with a 2-alkyl-5,5-bis(Me_3Si) substituted Cp ring.

Deprotonation of **3c** and **4c** by *n*-BuLi and the stoichiometric reaction with $ZrCl_4$ in diethyl ether afford the monoCp zirconium complexes **3d** and **4d** (Scheme 3) in good yield. Due to the steric congestion of the Cp ligands there is no formation of metallocenes

by this method. From the analogous reaction with the fenchyl-substituted ligand **5c** we could not isolate a similar complex. It is possible that C–O bond cleavage of the bulky ether moiety by the Lewis acidic zirconium centre is a serious side-reaction here [4d].

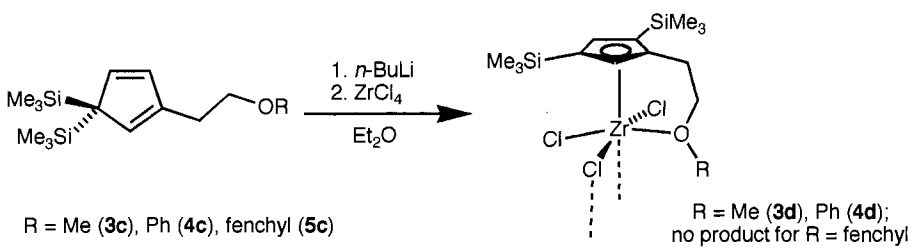
Due to the presence of two Me_3Si groups on the Cp ring, compounds **3d** and **4d** are much more soluble than **2**; they even show moderate solubility in pentane. They are hygroscopic colourless solids that were characterised by elementary analysis and by their ^{1}H- and ^{13}C-NMR spectra in $CDCl_3$ (Tables 3 and 4). As for **2**, compounds **3d** and **4d** (and **6d**, **7d** vide infra) are probably chloride-bridged dimers in the solid state, but monomeric in solution. The lack of a plane of symmetry in the molecules is indicated by the presence of an ABXY spin system in the ^{1}H-NMR spectrum for the ethylene moiety, and by the appearance of two signals for the Me_3Si groups in the ^{1}H- and ^{13}C-NMR spectrum. Therefore, the three substituents on the Cp ring are in an 1,3-bis(Me_3Si)-4-alkyl arrangement. Intramolecular coordination of the ether side-chain in **3d** is deduced from the low-field ^{13}C-shifts of the CH_2O-moiety (9 ppm) and of the OCH_3-moiety (5 ppm) with respect to those signals in the starting compounds **3a–c**. These coordination shifts are very similar to those of **2** [4d].

In **4d** there is an even larger similar low-field ^{13}C shift of the CH_2O-moiety of about 14 ppm. In addition, the phenyl group only shows low-field ^{13}C shifts for the *ortho* and *para* carbons of about 6 and 5 ppm, respec-

Table 2
^{13}C-NMR data for the $SiMe_3$ derivatives of the Cp ligands[a]

Compound	Me	C(H)O	CH_2	C_5H_x ring	OR	$SiMe_3$
$C_5H_4(CH_2CH_2OMe)(SiMe_3)$ (**3b**)	–	72.8	30.1	51.2, 128.4, 132.0, 133.8, 141.7	58.3	−2.19
$C_5H_4(CH_2CH_2OPh)(SiMe_3)$ (**4b**)	–	67.76	29.82	51.53, 128.92, 131.89, 134.11, 141.03	114.55, 120.53, 129.38, 158.92[d]	−2.05
$C_5H_4(CH_2CH_2Ofenchyl)(SiMe_3)$ (**5b**)	–	72.11	30.81	51.17, 128.3, 132.5, 133.6, 141.8	[b]	−2.05
$C_5H_4(CH_2CH(Me)OPh)(SiMe_3)$ (**6b**)	19.48	73.58	36.44	51.23, 129.69, 132.45, 134.02, 141.13	115.84, 120.45, 129.46, 157.99[d]	−2.18
$C_5H_4(CH_2CH(Me)OC_6H_4$-4-$OMe)(SiMe_3)$ (**7b**)	19.54	74.69	36.51	51.09, 129.41, 132.30, 133.74, 141.10	55.32, 114.43, 117.17, 151.80, 153.67	−2.15
$C_5H_4(CH_2CH(Me)O$-α-naphthyl)$(SiMe_3)$ (**8b**)	19.31	73.83	36.45	51.23, 129.72, 132.54, 133.98, 141	[c]	−2.27
$C_5H_3(CH_2CH_2OMe)(SiMe_3)_2$ (**3c**)	–	73.4	29.9	53.1, 131.8, 132.3, 136.5, 142.1	58.4	−1.0
$C_5H_3(CH_2CH_2OPh)(SiMe_3)_2$ (**4c**)	–	68.06	29.67	56.2, 131.99, 132.17, 136.72, 141.50	114.56, 120.48, 129.35, 158.93[d]	−0.81
$C_5H_3(CH_2CH_2Ofenchyl)(SiMe_3)_2$ (**5c**)		72.5	30.6	51.2, 131.5, 132.7, 136.2, 142.9	[b]	−1.0
$C_5H_3(CH_2CH(Me)OPh)(SiMe_3)_2$ (**6c**)	19.53	73.97	36.29	54.2, 132.54, 132.91, 136.68, 141.63	115.93, 120.47, 129.50, 158.08[d]	−0.87, −0.91
$C_5H_3(CH_2CH(Me)OC_6H_4$-4-$OMe)(SiMe_3)_2$ (**7c**)	19.49	74.99	36.25	55.4?, 132.32, 132.55, 136.33, 141.51	55.41, 114.42, 117.18, 151.79, 153.59	−0.88, −0.92
$C_5H_3(CH_2CH(Me)O$-α-naphthyl)$(SiMe_3)_2$ (**8c**)	19.38	74.27	36.30	56.2?, 132.71, 133.06, 136.70, 141.59	[c]	−0.87, −0.94

[a] In $CDCl_3$.
[b] Fenchyl signals at 20.0/20.7 ($C_{9/10}$), 25.9/26.1 ($C_{5/6}$), 31.7 (C_8), 39.4 (C_3), 41.4 (C_7), 48.7 (C_4), 49.1 (C_1), 93.1 (C_2).
[c] The naphthyl-group has signals between 105 and 155 ppm; due to the presence of impurities (see text) not all signals could be unambiguously assigned.
[d] *Ortho*, *para*, *meta*, *ipso* carbons, respectively.



Scheme 3.

Table 3
^{1}H-NMR data for the zirconium compounds[a]

Compound	$CH(CH_3)$	CH_2CH_xO	CH_2CH_xO	C_5H_2	OR	$SiMe_3$
$[C_5H_2(CH_2CH_2OMe\}(SiMe_3)_2]ZrCl_3$ (**3d**)	–	4.24 ('dt', 8.9×5) 4.44 ('q', 8.7)	3.04 (2H, 't', 6.4)	6.75 6.87	3.73 (s, 3H)	0.34 0.36
$[C_5H_2(CH_2CH_2OPh)(SiMe_3)_2]ZrCl_3$ (**4d**)	–	4.61 ('dt', 8.9×5) 4.88 ('dt', 5.4×8.8)	3.12 ('dt', 14.2×5.0) 3.23 (ddd, $14.2\times8.6\times6.2$)	6.82 7.03	7.1–7.3 (m, 5H)	0.34 0.42
$[C_5H_2(CH_2CH(Me)OPh)(SiMe_3)_2]ZrCl_3$ (**6d**)	1.29 (d, 6.2)	5.18 (m)	3.02 (dd, 14.1×8.6) 3.25 (dd, 14.1×5.1)	6.91 6.93	7.1–7.3 (m)	0.33 0.40
(minor isomer)	1.18 (d. 5.6)	5.32 (m)	3.10 (dd, 14×11.3)[b] 3.19 (dd, 14×4.3)[b]	6.81 7.07	7.1–7.3 (m)	0.33[b] 0.44
$[C_5H_2(CH_2CH(Me)OC_6H_4$-4-OMe$\}(SiMe_3)_2]ZrCl_3$ (**7d**)	1.28 (d, 6.2)	5.19 (m)	2.97 (dd, 13.9×8.2)	6.89	6.78 (2H), 7.20 (2H)	0.34
(major isomer)			3.25 (dd, 13.9×5.0)	6.91	3.76 (3H)	0.40
(minor isomer)	1.16 (d, 5.9)	5.35 (m)	3.06 (dd, 14×11.5)[b] 3.20 (dd, 14×3.9)[b]	6.8?[b] 7.07	6.8[b], 7.2[b] 3.74 (3H)	0.34[b] 0.44

[a] In $CDCl_3$; coupling in Hz in parentheses
[b] Poorly resolved.

Table 4
^{13}C-NMR data for the zirconium compounds[a]

Compound	Me	C(H)O	C_2	Cp ($2\times CH$, $3\times C$)	OR	$SiMe_3$
$[C_5H_2(CH_2CH_2OMe\}(SiMe_3)_2]ZrCl_3$ (**3d**)	–	82.40	27.48	129.70, 130.81, 133.90, 137.03, 142.87	64.18	0.01, 0.23
$[C_5H_2(CH_2CH_2OPh)(SiMe_3)_2]ZrCl_3$ (**4d**)	–	82.40	28.55	129.6, 131.46, 134.94, 137.31, 141.24	120.64, 125.66, 129.61, 159.27[c]	−0.08, 0.29
$[C_5H_2(CH_2CH(Me)OPh)(SiMe_3)_2]ZrCl_3$ (**6d**)	20.31	87.61	36.83	129.44, 133.48, 134.4, 137.87, 141.92	122.86, 125.49, 129.28, 155.61[c]	−0.19, 0.11
Idem, minor isomer[b]	20.25	87.6?	36.62	128.18, 131.74, 133.5?, 138.8, 141.4	123.22, 125.5?, 129.3?, 155.6?[c]	−0.27, 0.29
$[C_5H_2(CH_2CH(Me)OC_6H_4$-4-OMe$\}(SiMe_3)_2]ZrCl_3$ (**7d**)	20.38	90.36	36.58	129.48, 133.66 (2x?), 137.79, 141.76	55.48, 114.11, 124.90, 148.76, 157.49[d]	−0.09, 0.14
Idem, minor isomer[b]	20.22	89.88	36.40	128.12, 131.41, 133.7?, 138.92, 141.55	55.48, 114.05, 125.14, 148.8?, 157.5?[d]	−0.19, 0.32

[a] In $CDCl_3$.
[b] Incomplete data due to severe overlap with signals of the major isomer.
[c] *Ortho*, *para*, *meta*, *ipso* carbons, respectively.
[d] OMe, *Meta*, *ortho*, *ipso*, *para* carbons, respectively.

tively. In contrast, the ^{13}C chemical shifts of the *ipso* and *meta* carbons hardly change upon coordination (<0.5 ppm). This interesting phenomenon is obviously a result of mesomeric effects. As the ether group coordinates to the zirconium centre, electron density is withdrawn from the oxygen atom. Because of resonance this also results in a decrease of electron density in the *ortho* and *para* positions of the phenyl ring and consequently in a low-field shift for these carbons. Similar observations were made for instance for the $AlCl_3$ adduct of MeOPh: the methyl, *ortho* and *para* carbons of the phenyl ring show down-field shifts of 14, 7 and 7 ppm, respectively, in the ^{13}C-NMR spectrum upon complexation [10].

The conformation of the chelate rings in **3d** and **4d** can be deduced from the coupling patterns of the ethylene hydrogens in the ^{1}H-NMR spectra, that of **4d** being better resolved as that for **3d** (Fig. 2 and Table 3). As for **2**, there exist two conformations for the chelate rings in **3d** and **4d** (**A** and **B** in Fig. 2), but in contrast to **2** they are not equally likely. This is best seen by the $^3J_{HH}$ couplings: uniform values of about 6–7 Hz (cf. 6.3 Hz in **2**) would be expected when conformations **A** and **B** were equally abundant. Since both larger (8.6 Hz)

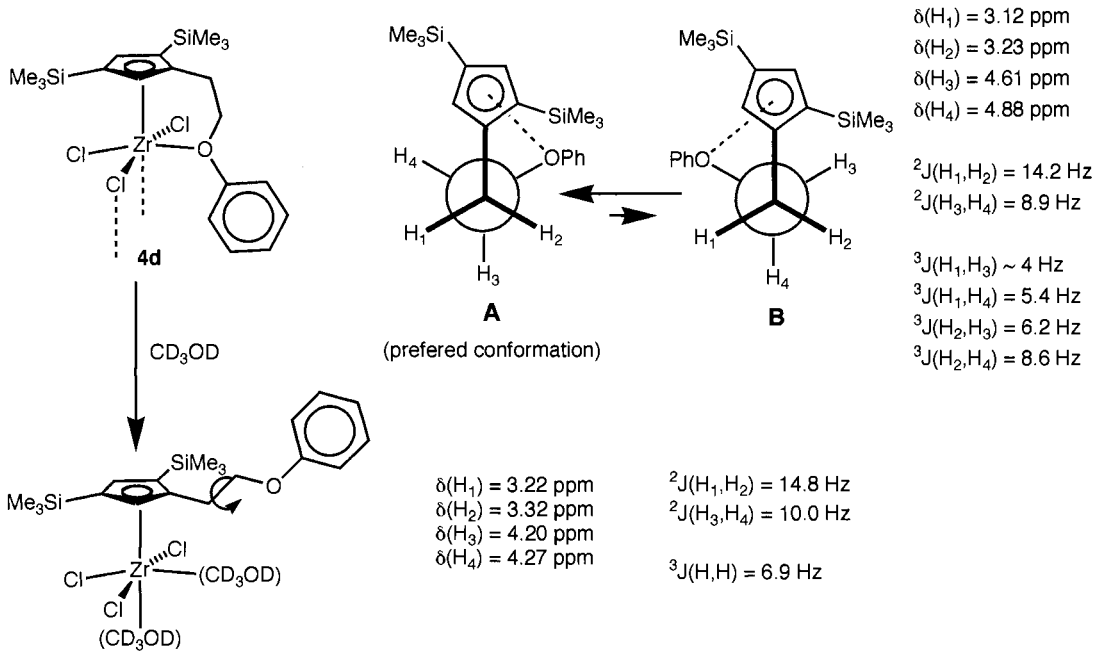


Fig. 2. Conformation analysis on **4d**.

and smaller (4 Hz) $^3J_{HH}$ couplings are observed, there is clearly a preference for one of the conformers. A closer inspection of the two conformers (Fig. 3) reveals that there is an unfavourable interference between the ethylene bridge and the adjacent Me_3Si group in conformation **B**, and therefore we believe that **4d** and also **3d** mainly reside in conformation **A**. This is corroborated by molecular modelling studies (PCMODEL), which predict a somewhat lower energy for conformation **A**.

When **4d** is dissolved in methanol, the coordination of the ether side chain is lost and a bis(methanol) solvate is formed (Fig. 2), reminiscent of **2**. The enhanced mobility of the side chain is nicely seen by the $^3J_{HH}$ couplings which now show a uniform value of 6.9 Hz, being consistent with a more or less free rotation around the C–C(O) bond.

The enantiomerically pure zirconium compounds **6d** and **7d** were prepared from **6c** and **7c** in a similar way as for **3d** and **4d** (Scheme 4). Reactions with the naphthyl derivative **8c** were unsuccessful. It is possible that the steric bulk of the naphthyl group prevents the formation of a stable monoCp zirconium compound.

Compounds **6d** and **7d** contain a stereogenic carbon in the chelate ring having *R* configuration. Because the triple substituted Cp ring presents a further stereogenic centre, there are two possible diastereomers. Apparently, the enantiopure carbon in the chelate ring exerts 46% diastereoselectivity on the coordination mode of the Cp rings, since the two diastereomers are present in a 73:27 ratio for both **6d** and **7d**. An explanation for this diastereoselectivity is hampered by the complexity of the mechanism of the transmetallation of the bidentate ligand, which is largely unknown. For the same reason one cannot be completely sure whether the observed diastereomer ratio reflects the difference in the thermodynamical stability of the two isomers, moreover since there appears to be no dynamic equilibrium between the two in solution.

There are four different conformations possible for the chelate rings in **6d** and **7d** (two for each diastereomer). However, conformations **A1** and **A2** in Fig. 4 can be ruled out since the methyl groups in the side chain are in a very unfavourable position. Therefore, these methyl groups will be *trans*-positioned to the Cp unit, and this is corroborated by the coupling patterns of the bridgehead hydrogens in the ^{1}H-NMR spectra (Fig. 4). Similar conformations are also found in Ca[(*S*)–$C_5H_4CH_2CH(R)OMe]_2$, with R = Me or Ph [5g]. The conformations of **6d** and **7d** are therefore

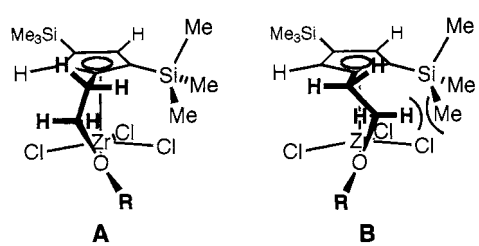
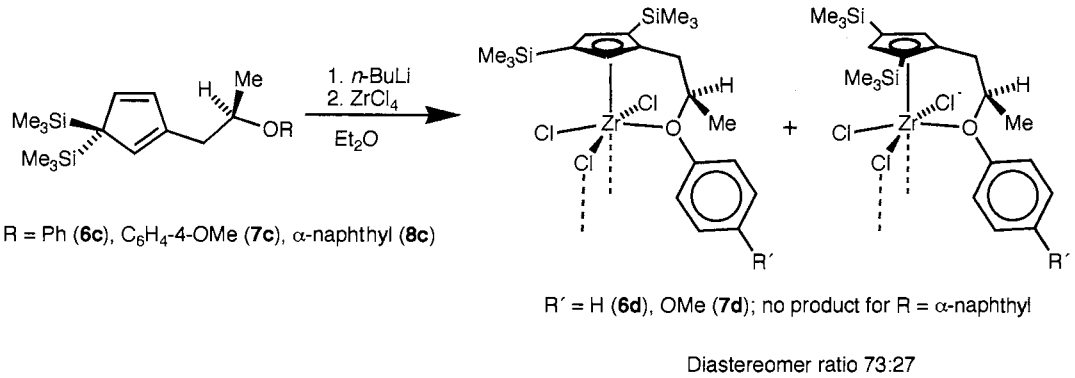


Fig. 3. Possible conformations of **3d** and **4d**, showing preference for conformation **A** over that of **B** on steric grounds.



Scheme 4.

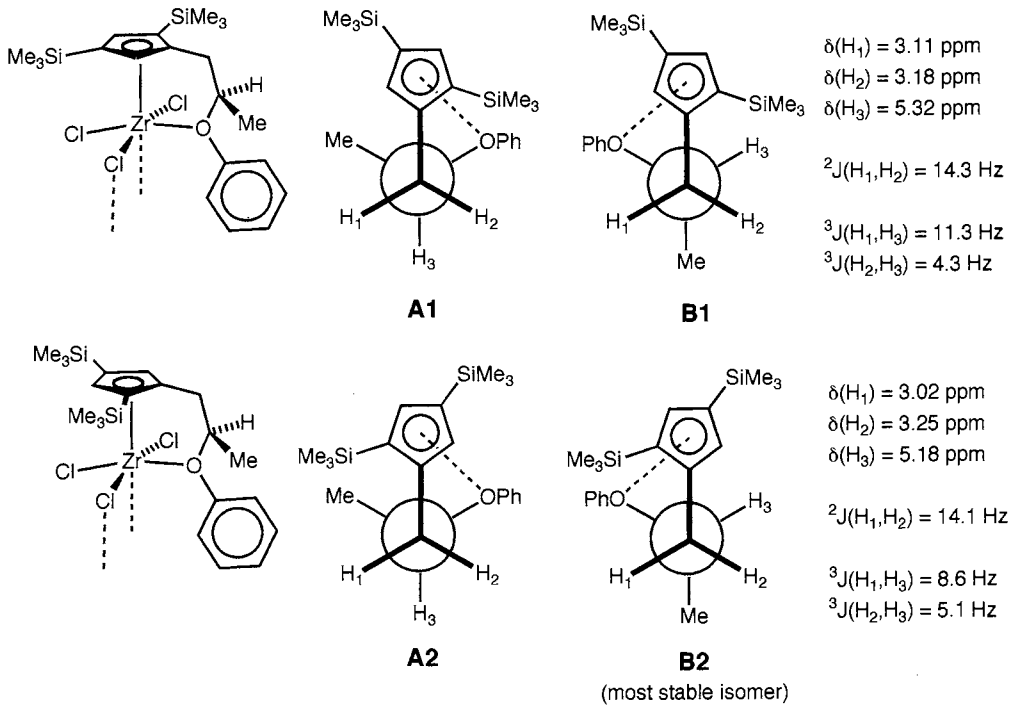


Fig. 4. Conformation analysis on **6d**.

ruled by the stereogenic carbon in the chelate ring and not by the position of the Me_3Si groups like in **3d** and **4d**. However, for the same reasons as in **3d** and **4d**, it is obvious that diastereomer **B2** is more stable than **B1** (Fig. 5), and it is assumed that **B2** is the prevalent isomer. It is noted that for both of the diastereomers of **6d** and **7d** the aryl group points in the same direction, and therefore it is expected that during a Lewis acid catalysed reaction, both diastereomers should exert the same asymmetric effect on the chiral products.

Compounds **3d** and **4d** were tested for their activity on the polymerisation of ethylene. The activity is ca 50–100 g polyethylene/mmol Zr/h/bar ethylene, which is rather moderate, compared to $CpZrCl_3$ (ca. 1000) or Cp_2ZrCl_2 ($>10\,000$) [2b]. Although **3d** and **4d** are much more soluble than **2**, the activity of **2** is the same [4d]. We believe that the strong coordination of the ether moiety in these compounds saturates the zirconium centre too much, for a significant Ziegler–Natta

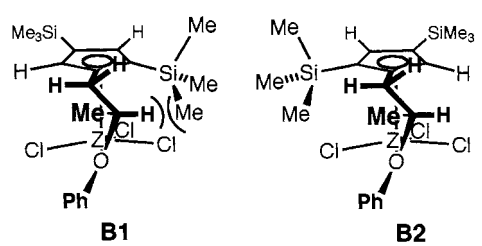
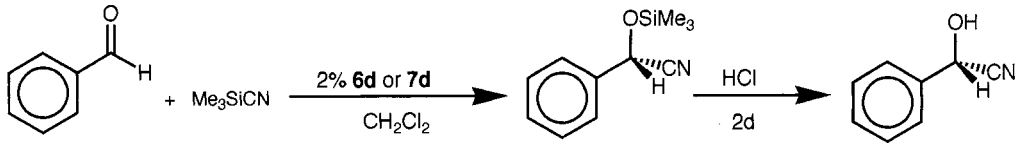
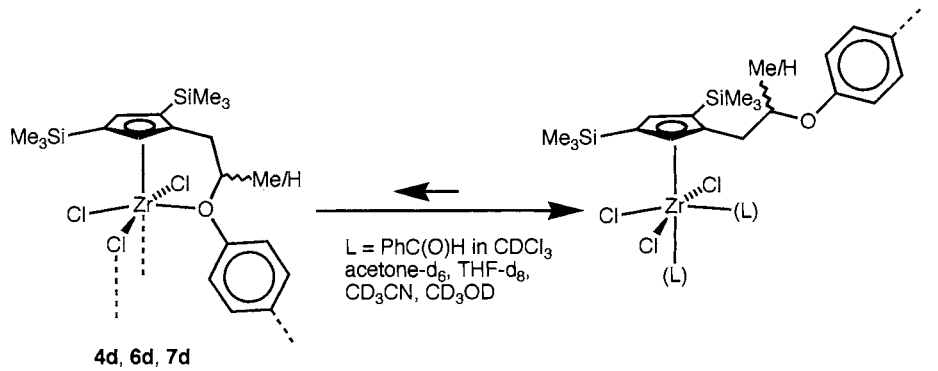


Fig. 5. Possible conformations of the two diastereomers of **6d**, showing preference for conformation **B2** over that of **B1**.



Scheme 5.



Scheme 6.

activity to develop. This is further corroborated by the fact that the sulphur-analogue of **2** shows significantly better activity (400), which can be attributed to the poorer coordination of the thioether to zirconium [11].

As **2** is known to be an active Lewis acid catalyst, we tested the analogous, chiral complexes **6d** and **7d** as a hydrocyanation catalyst (Scheme 5) [12].

Although both zirconium complexes catalyse the reaction between benzaldehyde and Me_3SiCN very well, the resulting alcohol that was obtained after hydrolysis, was not enantiomerically enriched. This result was somewhat surprising, since it might have been expected that the asymmetric position of the bulky aryl ether moiety should have some influence on the enantioselectivity. To explain this, we investigated the reaction of the model compound **4d** with benzaldehyde by ^{1}H- and ^{13}C-NMR. Adding 1–2 equivalents of benzaldehyde causes severe broadening of all signals for **4d**. Upon addition of five or more equivalents of benzaldehyde, the signals sharpen up again, but show large differences compared to the starting situation. Especially, those ^{13}C shifts that are characteristic for the coordination of the ether moiety have returned to the values which they had in the (noncoordinating) Me_3Si precursors, e.g. 72.1 ppm for CH_2O, 116.4 ppm for the *ortho*-phenyl carbon, and 122.0 ppm for the *para*-phenyl carbon. Apparently, under catalytic conditions, with a large excess of benzaldehyde, the ether moiety is not coordinated anymore and will bent away from the reaction centre. Transfer of chirality in this arrangement during catalysis is very unlikely.

Obviously, the aryl ether moieties in **4d**, **6d**, and **7d** are much less strongly coordinated than the alkyl ether groups in **2** and **3d**. As can be deduced from the ^{13}C chemical shift of the CH_2O moiety, in coordinating solvents like acetone-d_6 (68.7 ppm), thf-d_8 (69.8), CD_3CN (69.0) and CD_3OD (69.6) the aryl ether–zirconium bond in **4d** is also broken, whereas in the non-coordinating solvent C_6D_6 (80.9) it is not (Scheme 6). In contrast, the coordination of the alkyl ether side-chain in **3d** (and **2**) is only broken in methanol-d_4, but not in the other solvents [13]. This sensitivity towards a wide variety of functional groups of course precludes the use of the aryl ether complexes **6d** and **7d** as chiral Lewis acid catalysts.

3. Conclusions

Compounds **3d**, **4d**, **6d**, **7d** present a unique class of chiral mono(Cp) zirconium complexes having ether side-chains attached to the Cp ring. Despite the renowed oxophilicity of zirconium, the coordination of the aryl-substituted side-chains in **4d**, **6d**, and **7d** is very weak compared to that in the alkyl-substituted complexes **3d** and **2**. Actually, without being supported by the rigid coordination of the Cp ring, stable coordination of the aryl ether moieties in the former compounds does not seem possible. We are currently designing chiral Cp ligands having SPh and especially PPh_2 side-chains, since the electron-withdrawing effect of the aryl group should have less effect on the donor capability of these heavier donor elements.

4. Experimental

All manipulations were carried out under an atmosphere of argon using Schlenk glassware. Solvents were dried and degassed by conventional procedures prior to

use—^{1}H- and ^{13}C-NMR: Varian Gemini 300. The ^{1}H- and ^{13}C-NMR spectra were measured in $CDCl_3$ unless stated otherwise ($CHCl_3$: $\delta_H = 7.24$; $CDCl_3$: $\delta_C = 77.0$) The combustion analyses (C,H) were performed on a CHNS-932 LECO analyser in our department (consistently lower carbon contents for our zirconium complexes (1–2%) were attributed to the formation of zirconium carbides during analysis). (*R*)-EtOOC-CH(Me)OAr (Ar=Ph, C_6H_4-4-OMe, α-naphthyl) and $C_5H_5CH_2CH_2OMe$ (**3a**) were synthesised according to Refs. [9] and [8], respectively.

4.1. $C_5H_5CH_2CH_2OPh$ (**4a**)

To a solution of CpNa prepared from 3.35 g (146 mmol) of sodium and 13.5 ml (164 mmol) cyclopentadiene in 100 ml of THF, 24.5 g (120 mmol) of $PhOCH_2CH_2Br$ was added. After refluxing for 3 h, a few ml of water was added and the mixture was evaporated to dryness. The residue was extracted with pentane; the pentane extracts were concentrated in vacuo and the residue was distilled at 200–220°C at 4 mmHg affording 9.9 g (53 mmol, 44%) of $C_5H_5CH_2CH_2OPh$. The pale yellow oil was a 1: 1 mixture of two regioisomers. (^{1}H-NMR: $\delta = 2.95$ (m, 2H, $C_5H_5CH_2$), 3.05 (s, 2H, C_5H_5-aliphatic), 4.19 (m, 2H, CH_2O), 6.23, 6.38, 6.52, 6.59 (sbr, 3H, C_5H_5-olefinic), 7.0 (m, 3H, Ph), 7.35 (m, 2H, Ph). ^{13}C-NMR: $\delta = 29.79$, 30.39 ($C_5H_5CH_2$), 41.41, 43.75 (C_5H_5-aliphatic), 67.09, 67.52 (CH_2O), 127.74, 128.05, 131.28, 132.34, 133.88, 134.55, 142.99, 145.17 (C_5H_5-olefinic), 114.50 (*o*-Ph), 120.58 (*p*-Ph), 129.35 (*m*-Ph), 158.80 (*ipso*-Ph).

4.2. (R)–$HOCH_2CH(Me)Oaryl$ (aryl = Ph, C_6H_4-4-OMe, α-naphthyl)

4.2.1. (R)–$HOCH_2CH(Me)OPh$

To a solution of 12.92 g (66.6 mmol) of (*R*)-EtOOC-CH(Me)OPh in 100 ml of ether was carefully added small portions of $LiAlH_4$ (waterbath cooling and condensor). After 6 h of stirring and the addition of 6.9 g $LiAlH_4$ the reaction was complete. Water was added very carefully and than concentrated HCl. The aqueous layer was extracted with ether; the combined ether extracts were dried over Na_2SO_4 and than evaporated to dryness affording spectroscopically pure (*R*)–$HOCH_2CH(Me)OPh$ (8.60 g, 56.6 mmol, 85%) as a pale yellow oil. This material was used without further purification. ^{1}H-NMR: $\delta = 1.25$ (d, 6.1 Hz, 3H, CH_3), 3.72 (m, 2H, CH_2OH), 4.49 (m, 1H, CHOPh), 6.93 (m, 3H, Ph), 7.27 (m, 2H, Ph). ^{13}C-NMR: $\delta = 15.66$ (CH_3), 66.28 (CH_2OH), 74.69 (CHOPh), 116.19 (*o*-Ph), 121.30 (*p*-Ph), 129.67 (*m*-Ph), 157.8 (*ipso*-Ph). Other alcohols were prepared similarly.

4.2.2. (R)–$HOCH_2CH(Me)OC_6H_4$-4-OMe

Pale yellow oil: yield: 83%. ^{1}H-NMR: $\delta = 1.20$ (d, 6.2 Hz, 3H, CCH_3), 3.66 (m, 2H, CH_2OH), 3.74 (s, 3H, OCH_3), 4.33 (m, 1H, CHOaryl), 6.82 (m, 4H, aryl-H). ^{13}C-NMR: $\delta = 15.47$ (CH_3), 55.23 (OCH_3), 65.65 (CH_2OH), 75.67 (CHOaryl), 114.45, 117.55, 151.50, 154.02 (aryl-*C*).

4.2.3. (R)–$HOCH_2CH(Me)O$-α-naphthyl

Greyish oil: yield: 90%. ^{1}H-NMR: $\delta = 1.34$ (d, 6.2 Hz, 3H, CH_3), 3.85 (m, 2H, CH_2OH), 4.69 (m, 1H, CHOaryl), 6.88 (d, 7.5 Hz, 1H, naphthyl-*H*), 7.37 (m, 1H, naphthyl-*H*), 7.45 (m, 3H, naphthyl-*H*), 7.81 (m, 1H, naphthyl-*H*), 8.27 (m, 1H, naphthyl-*H*). ^{13}C-NMR: $\delta = 15.68$ (CH_3), 66.23 (CH_2OH), 75.13 (CHOaryl), 106.89 (naphthyl-C_2), 120.68 (naphthyl-C_4), 121.95 (naphthyl-C_8), 125.27 (naphthyl-C_7), 125.83 (naphthyl-C_3), 126.40 (naphthyl-C_6), 126.45 (naphthyl-C_9), 127.61 (naphthyl-C_5), 134.77 (naphthyl-C_{10}), 153.39 (naphthyl-C_1).

4.3. (R)–$MeSO_3CH_2CH(Me)Oaryl$ (aryl = Ph, C_6H_4-4-OMe, α-naphthyl)

4.3.1. (R)–$MeSO_3CH_2CH(Me)OPh$

A solution of 8.60 g (56.6 mmol) of (*R*)–$HOCH_2CH(Me)OPh$ and 10 ml (72 mmol) of Et_3N in 100 ml of CH_2Cl_2 was cooled to −40°C, upon which 4.8 ml (62 mmol) of $MeSO_2Cl$ was added. The colourless suspension that formed was stirred for 30 min at room temperature. Than, water was added resulting in the formation of two clear, layered solutions. The CH_2Cl_2 layer was washed with water several times, than separated and dried over Na_2SO_4. Filtration and removal of solvent gave an almost quantitative yield (12.82 g, 55.8 mmol, 99%) of (*R*)–$MeSO_3$-$CH_2CH(Me)OPh$ as a pale yellow-brown oil. This material was used without further purification. ^{1}H-NMR: $\delta = 1.34$ (d, 6.2 Hz, 3H, CH_3), 3.00 (s, 3H, O_3SCH_3), 4.31 (m, 2H, CH_2O), 4.64 (m, 1H, CHOPh), 6.89 (m, 3H, Ph), 7.27 (m, 2H, Ph). ^{13}C-NMR: $\delta = 16.03$ (CH_3), 37.54 (O_3SCH_3), 71.7 (CH_2O and CHOPh), 116.13 (*o*-Ph), 121.74 (*p*-Ph), 129.76 (*m*-Ph), 157.2 (*ipso*-Ph). Other mesylates were prepared similarly.

4.3.2. (R)–$MeSO_3CH_2CH(Me)OC_6H_4$-4-OMe

Pale yellow oil: yield: 100%. ^{1}H-NMR: $\delta = 1.28$ (d, 6.2 Hz, 3H, CCH_3), 2.99 (s, 3H, O_3SCH_3), 3.72 (s, 3H, OCH_3), 4.27 (m, 2H, CH_2O), 4.47 (m, 1H, CHOaryl), 6.82 (m, 4H, aryl-H). ^{13}C-NMR: $\delta = 15.97$ (CH_3), 37.37 (O_3SCH_3), 55.46 (OCH_3), 71.77 (CH_2O), 72.93 (CHOaryl), 114.71, 117.81, 151.08, 154.64 (aryl-*C*).

4.3.3. (R)–$MeSO_3CH_2CH(Me)O$-α-naphthyl

Pale orange oil: yield: 92%. ^{1}H-NMR: $\delta = 1.45$ (d, 6.2 Hz, 3H, CH_3), 2.95 (s, 3H, O_3SCH_3), 4.44 (m, 2H,

CH_2O), 4.86 (m, 1H, CHOaryl), 6.87 (d, 7.5 Hz, 1H, naphthyl-*H*), 7.37 (m, 1H, naphthyl-*H*), 7.46 (m, 3H, naphthyl-*H*), 7.80 (m, 1H, naphthyl-*H*), 8.25 (m, 1H, naphthyl-*H*). ^{13}C-NMR: $\delta = 16.19$ (CH_3), 37.62 (O_3SCH_3), 71.60/72.07 (CH_2O and CHOaryl), 106.90 (naphthyl-C_2), 121.20 (naphthyl-C_4), 121.93 (naphthyl-C_8), 125.47 (naphthyl-C_7), 125.72 (naphthyl-C_3), 126.27 (naphthyl-C_9), 126.54 (naphthyl-C_6), 127.58 (naphthyl-C_5), 134.75 (naphthyl-C_{10}), 152.79 (naphthyl-C_1).

4.4. (R)–$C_5H_5CH_2CH(Me)$Oaryl (aryl = Ph, C_6H_4-4-OMe, α-naphthyl)

4.4.1. (R)–$C_5H_5CH_2CH(Me)$OPh

To a precooled (−40°C) solution of CpLi in 150 ml THF obtained by reacting 6.0 ml (73 mmol) of CpH and 40.0 ml of 1.78 M solution of *n*BuLi in hexane (71.2 mmol), was added 12.82 g (56.6 mmol) (*R*)–$MeSO_3CH_2CH(Me)OPh$. Upon raising the temperature, a brick-red suspension formed that was stirred overnight at room temperature. After addition of a few ml of water, the volatiles were removed in vacuo. The residue was extracted with pentane and the pentane extracts were evaporated to dryness in vacuo. The residue was distilled at 200°C (3 mmHg) affording 6.10 g (30.5 mmol, 54%) of (*R*)-$C_5H_5CH_2CH(Me)OPh$ as a pale yellow oil. It exists as a 1:1 mixture of regioisomers. ^{1}H-NMR: $\delta = 1.29$ (m, 3H, CH_3), 2.6–2.9 (m, 2H, CH_2), 2.95 (s, 2H, C_5H_5-aliphatic), 4.54 (m, 1H, CHOPh), 6.11, 6.26, 6.41, 6.48 (sbr, 3H in total C_5H_5-olefinic), 6.90 (m, 3H, Ph), 7.26 (m, 2H, Ph). ^{13}C-NMR: $\delta = 19.56$, 19.58 (CH_3), 36.59, 37.38 (CH_2CO), 41.28, 44.02 (C_5H_5-aliphatic), 73.35, 73.66 (CHOPh), 128.65, 128.92, 131.50, 132.38, 133.81, 135.02, 143.10, 145.22 (C_5H_5-aliphatic), 115.94, 116.04 (*o*-Ph), 120.63, 120.66 (*p*-Ph), 129.51, 129.54 (*m*-Ph), 158.03, 158.07 (*ipso*-Ph). Other Cp ligands were prepared similarly.

4.4.2. (R)–$C_5H_5CH_2CH(Me)OC_6H_4$-4-OMe

Yellow oil: b.p. 240°C (3 mmHg). Yield: 60%. ^{1}H-NMR: $\delta = 1.28$ (m, 3H, CH_3), 2.5–2.9 (m, 2H, CH_2), 2.96 (s, 2H, C_5H_5-aliphatic), 3.76 (s, 3H, OCH_3), 4.43 (m, 1H, CHOaryl), 6.12, 6.27, 6.29, 6.43, 6.50 (sbr, 3H in total, C_5H_5-olefinic), 6.83 (sbr, 4H, aryl-*H*). ^{13}C-NMR: $\delta = 19.79$ (CCH_3), 36.74, 37.52 (CH_2CO), 41.39, 44.11 (C_5H_5-aliphatic), 55.66 (OCH_3), 74.63, 74.91 (CHOaryl), 128.56, 128.79, 131.43, 132.34, 133.77, 134.95, 143.13, 145.32 (C_5H_5-olefinic), 114.64, 117.37/117.52, 151.94, 153.90 (aryl-*C*).

4.4.3. (R)–$C_5H_5CH_2CH(Me)O$-α-naphthyl

Due to its high boiling point the brownish, viscous oil could not be purified. A crude yield of 85% was obtained, containing an estimated 75% of the wanted product. ^{1}H-NMR: $\delta = 1.45$ (m, 3H, CH_3), 2.7–3.1 (m, 4H, CH_2 and C_5H_5-aliphatic), 4.79 (m, 1H, CHOaryl), 6.19, 6.30, 6.34, 6.45, 6.57 (sbr, 3H in total, C_5H_5-olefinic), 6.85 (m, 1H, naphthyl-*H*), 7.35–7.55 (m, 4H, naphthyl-*H*), 7.80 (m, 1H, naphthyl-*H*), 8.31 (m, 1H, naphthyl-*H*). ^{13}C-NMR: $\delta = 19.60$ (CH_3), 36.68, 37.49 (CH_2CO), 41.38, 44.12 (C_5H_5-aliphatic), 73.56, 73.88 (CHOaryl), 128.72, 128.94, 131.52, 132.28, 133.79, 134.94, 142.94, 145.1 (C_5H_5-olefinic), 105.9 (naphthyl-C_2), 119.89 (naphthyl-C_4), 122.27/122.35 (naphthyl-C_8), 124.94 (naphthyl-C_7), 125.81 (naphthyl-C_3), 126.21 (naphthyl-C_6), 127.38 (naphthyl-C_5), 134.69/134.94 (naphthyl-C_{10}), 153.51 (naphthyl-C_1), signals for C_9 could not be assigned unambiguously.

4.5. $C_5H_4(CH_2CH_2OPh)(SiMe_3)$ (**4b**) and $C_5H_3(CH_2CH_2OPh)(SiMe_3)_2$ (**4c**)

A solution of 6.0 g (32 mmol) of **4a** in 30 ml of THF was cooled to −30°C and 19.5 ml of *n*BuLi in hexane (1.78 M, 34.7 mmol) was added. After stirring for 15 min at room temperature, the solution was cooled again to −30°C and 4.6 ml (36.4 mmol) of Me_3SiCl was added. A precipitate (LiCl) formed and after stirring for 2 h at room temperature a solution containing virtually pure **4b** had formed (NMR data in Tables 1 and 2). After cooling the previous solution to −30°C 23.5 ml of *n*BuLi in hexane (1.78 M, 41.8 mmol) was added. After stirring for 30 min at room temperature the mixture was cooled again to −30°C and 6.0 ml (47.4 mmol) of Me_3SiCl was added. After stirring for 2 h at room temperature a few drops of water were added, the mixture was filtered and the filtrate was evaporated to dryness affording 9.5 g (28.8 mmol, 90%) of spectroscopically pure **4c** (NMR data in Tables 1 and 2). The oily substance could not be distilled without decomposition and was therefore used without further purification. The other $SiMe_3$ derivatives $C_5H_{(5-x)}(CH_2CH_2OR)(SiMe_3)_x$ ($x = 1,2$; R = Me (**3b**,**c**), fenchyl (**5b**,**c**)) and (*R*)–$C_5H_{(5-x)}(CH_2CH(Me)OR)(SiMe_3)_x$ ($x = 1,2$; R = Ph (**6b**,**c**), C_6H_4OMe (**7b**,**c**), α-naphthyl (**8b**,**c**)) were prepared and handled similarly. Yields were essentially quantitative. The α-naphthyl derivatives were impure (see above). The ^{1}H- and ^{13}C-NMR data are given in Tables 1 and 2.

4.6. Synthesis of organozirconium compounds

4.6.1. [η^5:η^1-$C_5H_2(CH_2CH_2OPh)(SiMe_3)_2$]$ZrCl_3$: (**4d**)

To a solution of 1.70 g (5.2 mmol) of **4c** in 25 ml of diethyl ether was added 3.3 ml of *n*BuLi in hexane (1.73 M, 5.7 mmol) at room temperature. After stirring for 2 h a clear orange solution emerged. After cooling to −60°C 1.15 g (4.94 mmol) of freshly sublimed $ZrCl_4$ was added and the resulting colourless suspension was stirred overnight at room temperature. The mixture was

filtered and the filtrate evaporated to dryness. The residue was extracted with toluene, filtered and evaporated to dryness. After washing the residue with cold (-30°C) pentane 1.32 g (2.50 mmol, 51%) of analytically pure **4d** was obtained as a beige powder. $C_{19}H_{29}Cl_3OSi_2Zr$ (527.2): calc. C 43.3, H 5.6, Cl 20.2; found C 41.2, H 5.6, Cl 20.4. Other zirconium compounds were prepared similarly.

*4.6.2. [η^5:η^1-$C_5H_2(CH_2CH_2OMe)(SiMe_3)_2$]$ZrCl_3$: (**3d**)*

Yield: 88%: $C_{14}H_{27}Cl_3OSi_2Zr$ (464.5): calc. C 36.2, H 5.8; Found C 36.1, H 5.9.

*4.6.3. [η^5:η^1-(R)–$C_5H_2(CH_2CH(Me)OPh)(SiMe_3)_2$]-$ZrCl_3$: (**6d**)*

Yield: 48%: $C_{20}H_{31}Cl_3OSi_2Zr$ (541.2): calc. C 44.4, H 5.8, Cl 19.7; Found C 42.7, H 5.9, Cl 19.7.

*4.6.4. [η^5:η^1-(R)–$C_5H_2(CH_2CH(Me)OC_6H_4$-4-OMe)-$(SiMe_3)_2$]$ZrCl_3$: (**7d**)*

Yield: 37%: $C_{21}H_{33}Cl_3O_2Si_2Zr$ (571.2): calc. C 44.2, H 5.8, Cl 18.6; Found C 42.3, H 5.8, Cl 18.9.

Similar reactions with **5c** and **8c** were unsuccessful; no monoCp zirconium compound could be isolated.

4.7. Hydrocyanation reactions

A solution of ca. 0.10 g (0.2 mmol) of **6d** or **7d** in 15 ml of CH_2Cl_2 was thermostated at $+21$, -4, or -35°C. Than 1.0 ml (10 mmol) of benzaldehyde and 1.6 ml of Me_3SiCN (12 mmol) were added, and the reaction was stirred overnight (or 1 week at -35°C), after which the reaction was complete. Hydrochloric acid (1 N) was added and the mixture stirred for two days at room temperature. The CH_2Cl_2 layer was separated and filtered over a short column of silica, after which it was evaporated to dryness. The yield of PhCH(CN)OH was usually quantitative. The enantiomeric excess, as was determined by ^{1}H-NMR using $Eu(hfc)_3$ as a chiral shift reagent, was always <1%.

4.8. Polymerisation experiments

A mixture of a few mg (ca. 5–10 μmol) of **3d** or **4d** was dissolved in toluene and activated with a 30% solution of methylaluminoxane in toluene (Al/Zr: 3000–5000/1) This mixture was transfered to an autoclave and subjected to 10 bar of ethylene in heptane for 1 h at 40–50°C. The amount of polyethylene (PE) isolated correlates with a polymerisation activity of 110 g PE/mmol Zr/h/bar ethylene for **3d**, and 55 for **4d**.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft, the Alexander-von-Humboldt-Stiftung and the Bundesland Sachsen-Anhalt (HSP III program) is gratefully acknowledged. We thank Aventis Research & Technologies (formerly Hoechst) for performing the polymerisation experiments.

References

[1] (a) G. Erker, C. Sarter, S. Werner, C. Krüger, J. Organomet. Chem. 377 (1989) C55. (b) G. Erker, C. Sarter, M. Albrecht, S. Dehnicke, C. Krüger, E. Raabe, R. Schlund, R. Benn, A. Rufinska, R. Mynott, J. Organomet. Chem. 383 (1990) 89. (c) G. Erker, J. Organomet. Chem. 400 (1990) 185. (d) G. Erker, A.A.H. van der Zeijden, Angew. Chem. 102 (1990) 543. (e) G. Erker, J. Schamberger, A.A.H. van der Zeijden, S. Dehnicke, C. Krüger, R. Goddard, M. Nolte, J. Organomet. Chem. 459 (1993) 107 (f) F. Bökman, H. Bertagnolli, O. Schupp, G. Bringmann, J. Organomet. Chem. 474 (1994) 117.

[2] (a) J.C.W. Chien, B.-P. Wang, J. Polym. Sci. A Polym. Chem. 27 (1989) 1539. (b) ibid., 28 (1990) 15. (c) N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sironi, M. Moret, Organometallics, 9 (1990) 3098. (d) C. Pellecchia, A. Proto, P. Longo, A. Zambelli, Makromol. Chem. Rapid Commun. 12 (1991) 663. (e) C. Pellecchia, P. Longo, A. Proto, A. Zambelli, Makromol. Chem. Rapid Commun. 13 (1992) 265. (f) ibid., 277. (g) C. Pellecchia, A. Immirzi, A. Grassi, A. Zambelli, Organometallics 12 (1993) 4473. (h) P. Longo, A. Proto, L. Oliva, Macromol. Rapid Commun. 15 (1994) 151. (i) Q. Wang, R. Quyoum, D.J. Gillis, M.-J. Tudoret, D. Jeremic, B.K. Hunter, M.C. Baird, Organometallics 15 (1996) 693. (j) G. Jimenez Pindado, M. Thornton-Pett, M. Bouwkamp, A. Meetsma, B. Hessen, M. Bochmann Angew. Chem. 109 (1997) 2457. (k) R. Duchateau, S.J. Lancaster, M. Thornton-Pett, M. Bochmann, Organometallics 16 (1997) 4995. (l) S. Doherty, R.J. Errington, A.P. Jarvis, S. Collins, W. Clegg, M.R. J. Elsegood, Organometallics 17 (1998) 3408.

[3] R.L. Halterman, Chem. Rev. 92 (1992) 965.

[4] (a) A.A.H. van der Zeijden, Tetrahedron Asymm. 6 (1995) 913. (b) A.A.H. van der Zeijden, J. Organomet. Chem. 518 (1996) 147. (c) A.A.H. van der Zeijden, C. Mattheis, Synthesis (1996) 847. (d) A.A.H. van der Zeijden, C. Mattheis, R. Fröhlich, Organometallics 16 (1997) 2651. (e) A.A. H. van der Zeijden, C. Mattheis, J. Organomet. Chem. 555 (1998) 5.

[5] (a) Q. Huang, Y. Qian, Synthesis (1987) 910. (b) Q. Huang, Y. Qian, Y. Tang, Trans. Met. Chem. 14 (1989) 315. (c) B. Rieger, J. Organomet. Chem. 420 (1991) C17. (d) P. Van de Weghe, C. Bied, J. Collin, J. Marcalo, I. Santos, J. Organomet. Chem. 475 (1994) 121. (e) H. Adams; N.A. Bailey, M. Colley, P.A. Schofield. C. White, J. Chem. Soc. Dalton Trans. (1994) 1445. (f) Y. Kataoka, Y. Saito, K. Nagata, K. Kitamura, A. Shibahara, K. Tani, Chem. Lett. (1995) 833. (g) G.A. Molander, H. Schumann, E.C.E. Rosenthal, J. Demtschuk, Organometallics 15 (1996) 3817. (h) A.A. Trifonov, P. Van der Weghe, J. Collin, A. Domingos, I. Santos, J. Organomet. Chem. 527 (1997) 225. (i) B. Antelmann, U. Winterhalter, G. Huttner, B.C. Janssen, J. Vogelsang, J. Organomet. Chem. 545–546 (1997) 407. (j) B. Antelmann, G. Huttner, J. Vogelsang, O. Walter, U. Winterhalter, J. Organomet. Chem. 549 (1997) 139. (k) B. Antelmann, G. Huttner, U. Winterhalter, J. Organomet. Chem. 555 (1998) 119. (l) L. Schwink, P. Knochel, T. Eberle, J. Okuda, Organometallics 17 (1998) 7.

[6] M. Enders, R. Rudolph, H. Pritzkow, J. Organomet. Chem. 549 (1997) 251.

[7] (a) T. Kauffmann, K. Berghus, A. Rensing, Chem. Ber. 118 (1985) 3737. (b) ibid., 4507. (c) P. Foster, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem. 527 (1997) 71. (d) Y. Kataoka, Y.Saito, A.

Shibahara, K. Tani, Chem. Lett. (1997) 621. (e) Y. Kataoka, A. Shibahara, Y. Saito, T. Yamagata, K. Tani, Organometallics 17 (1998) 4338.
[8] W.S. Rees, K. Dippel, Org. Prep. Proc. Int. 24 (1992) 527.
[9] U. Burkard, F. Effenberger, Chem. Ber. 119 (1986) 1594.
[10] L.I. Belen'kii, V.S. Bogdanov, I.B. Karmanova, Izv. Akad. Nauk SSSR, Se Khim. (1979) 1735; Chem. Abstr. 91 (1979) 166018r.
[11] A.A.H. van der Zeijden, J. Jimenez, unpublished results.
[12] (a) M.T. Reetz, F. Kunisch, P. Heitmann, Tetrahedron Lett. 27 (1986) 4721. (b) K. Narasaka, T. Yamada, H. Minamikawa, Chem. Lett. (1987) 2073. (c) H. Minamikawa, S. Hayakawa, T. Yamada, N. Iwasawa, K. Narasaka, Bull. Chem. Soc. Jpn. 61 (1988) 4379.
[13] A.A.H. van der Zeijden, C. Mattheis, R. Fröhlich, F. Zippel, Inorg. Chem. 36 (1997) 4444.