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Menthyl-Substituted Group 4 Metallocene Dihalides

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Menthyl-substituted group 4 metallocene dihalides of type Cp'_2MX_2 ($Cp' = \eta^5$-menthyl-C_5H_4) have been known so far for M = Ti, Zr, and X = Cl (**1-Ti**, **1-Zr**). A gap in knowledge is closed now by the expansion to hafnium (**1-Hf**) and the preparation of complexes with X = F (**4-Ti**, **4-Zr**, **4-Hf**). In a first catalytic application **1-Ti** is used in the enantioselective Buchwald hydrosilylation of imines and compared to (*S*,*S*)-(ebthi)TiF_2. Also the variation of the ligand to (η^5-8-phenylmenthyl-C_5H_4) is realized with a zirconocene dichloride (**3-Zr**). The reduction of **1-Ti** afforded compound **2**, a dimeric titanium(III) complex, $[Cp'_2Ti(\mu\text{-}Cl)_2TiCp'_2]$. Such a species is assumed to be an intermediate in the ring-opening reaction of epoxides with titanocene dichlorides as precatalysts.

Introduction

Many different substitution patterns at the cyclopentadienyl ligand are known, but only a few of them are suitable for applications in enantioselective catalysis.[1] For example Buchwald et al. introduced a reliable system to convert prochiral imines to the corresponding chiral amines with very good enantioselectivities and yields.[2] The precatalyst for this reaction was the complex (*S*,*S*)-(ebthi)TiF_2, with ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl), forming *in situ* the Ti(III)-monohydride, which is able to insert an imine into the Ti−H bond. The consecutive reaction with $PhSiH_3$ leads to the hydrosilylated amine and after workup to the free chiral amine. On the other hand the ebthi ligand bears an obstacle: it is well documented that the enantiomerically pure alkyne complexes (*S*,*S*)- and (*R*,*R*)-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$) form in solution racemic mixtures of the alkyne complexes.[3] This is due to racemization of the free metallocene fragments “(*S*,*S*)-(ebthi)Ti” and “(*R*,*R*)-(ebthi)Ti” by a reversible change in the complexation mode of one cyclopentadienyl moiety.

Recently, it was published that chiral metallocene dichlorides Cp'_2MCl_2 (**1-M**, $Cp' = \eta^5$-menthyl-C_5H_4, M = Ti, Zr), which possess menthyl-substituted Cp ligands and were first synthesized by Kagan et al., are useful precatalysts for the reductive epoxide opening,[4] and no complex racemization has been observed yet. This fact offers the possibility of performing enantioselective reactions with these enantiomerically pure complexes.

In this work, we report on several new aspects in the chemistry of menthyl-substituted group 4 metallocene dihalides. We were able to expand the knowledge of the well-known menthyl-substituted titanocene and zirconocene dichlorides to the corresponding difluorides and also including modifications at the menthyl group itself. The difluoride compounds (η^5-menthyl-C_5H_4)$_2MF_2$ (**4-M**, M = Ti, Zr, Hf) are important and were prepared using trimethyltin fluoride as fluorinating agent.[5a] Metallocene difluorides often show a better reactivity compared to the dichlorides, and in many cases this could be explained by the “fluoride effect”, which suggests that fluoride is a better leaving group than the other halides.[2,5b] This work will also show the accessibility of these new complexes in the Buchwald hydrosilylation of imines.

Furthermore, we succeeded in the synthesis of the unknown hafnocene congener (η^5-menthyl-C_5H_4)$_2HfCl_2$ (**1-Hf**), which was characterized by X-ray diffraction analysis. Another approach was the synthesis of (η^5-8-phenylmenthyl-C_5H_4)$_2ZrCl_2$ (**3-Zr**) because the phenyl substituent offers the possibility of a π-stacking effect that could positively influence catalytic reactions compared to the complexes (η^5-menthyl-C_5H_4)$_2MCl_2$. Additionally, it was found that reduction of **1-Ti**, which has the oxidation state IV, leads to the dinuclear Ti(III) complex **2**. This could be seen as proof of existence of the catalytically active species in the reductive epoxide opening reaction, which was postulated as a Ti(III) monochloride.[4c,e]

Results and Discussion

For the first experiments the compounds **1-Ti** and **1-Zr** were provided by Gansäuer et al.[4a] Later these complexes were prepared by a modified method. This altered synthesis of the

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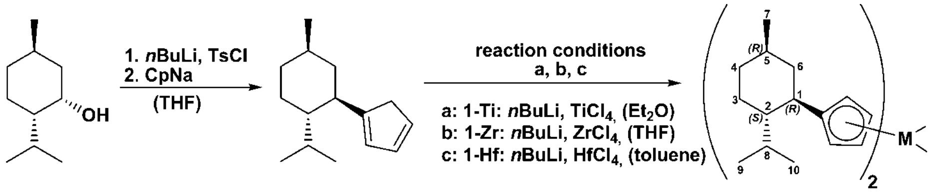
10.1021/om800605x CCC: $40.75

Scheme 1. Formation of the Ligand and Resulting Compound 1-M (M = Ti, Zr, Hf)



1-M

menthylcyclopentadiene substitutes THF for pyridine as solvent and utilizes *p*-toluenesulfonyl chloride instead of methanesulfonyl chloride, in analogy to an approach described by Marks et al.[6] Using these modifications a similar yield of the free ligand was obtained as described before. The synthesis of the individual Cp complexes required different solvents in each case to successfully afford the desired complexes **1-M** (Scheme 1). The hafnium compound (**1-Hf**) is isomorphous to **1-Ti** and **1-Zr**; they crystallize from different solvents in the tetragonal space group $P4_2$.

The new complex **1-Hf** (Figure 1) shows a high similarity to its zirconium congener **1-Zr**. This is obvious from the bond distances and angles of both compounds (see Table 1). The M1−Cp and M1−Cl1 distances are marginally shorter at 2.180 Å (**1-Hf**) vs 2.202 Å (**1-Zr**) and 2.422(1) Å (**1-Hf**) vs 2.450 Å (**1-Zr**), respectively. The coordination geometry at the hafnium center is distorted tetrahedral.

Synthesis of Titanocene(III) Monochloride 2. The aim of the formation of the dinuclear Ti(III) complex $[(\eta^5\text{-menthyl-}C_5H_4)_2TiCl]_2$ (**2**) was to corroborate the existence of an expected Ti(III) intermediate in the catalytic epoxide opening, which is initiated by a reduction step via zinc or manganese. Cyclic voltammetry studies and density functional calculations showed an equilibrium in solution between three Ti(III) species; two of them are dimeric and one is monomeric (Scheme 2).[4c,e]

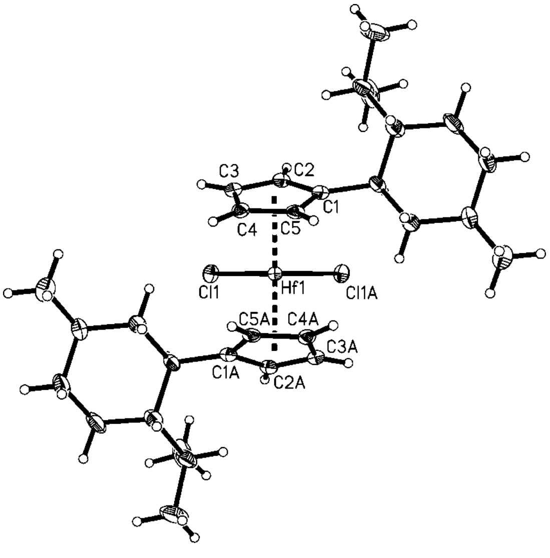
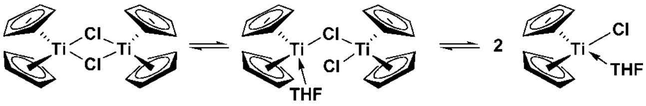


Figure 1. Molecular structure of compound **1-Hf**. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Hf1−Cp 2.180, Hf1−Cl1 2.422(1), Cp−Hf1−CpA 131.9, Cl1−Hf1−Cl1A 95.29(5); Cp typifies the centroid of the C1−C5 cyclopentadienyl ring atoms; CpA (C1A−C5A) and Cl1A are generated by symmetry operation: −*x*+1, −*y*, *z*.

Table 1. Comparison of Bond Distances and Angles of $(\eta^5\text{-menthyl-}C_5H_4)_2MCl_2$, M = Ti (1-Ti),[4b] M = Zr (1-Zr),[4a] M = Hf (1-Hf)

	1-Ti	1-Zr	1-Hf
M1−Cp/Å	2.070	2.202	2.180
M1−Cl1/Å	2.367(1)	2.450	2.422(1)
Cp−M1−CpA/deg	132.9	131.9	131.9
Cl1−M1−Cl1A/deg	93.20(6)	96.61	95.29(5)

Scheme 2. Equilibrium in Solution between Dimeric and Monomeric Ti(III) Species



The molecular structure of **2** represents the structural motif of the Ti(III) monochloride in the solid state, which is a dimer with two bridging chlorine atoms. This can be seen as a practical evidence for the dimer (Scheme 2, left) in accordance with these DFT calculations. The monomeric *meso*-(ebthi)Ti^{III}(THF)Cl[7] could be regarded as a proof for the right side of the equilibrium. Here, the dimerization is excluded because of sterical hindrance of the *meso*-(ebthi) ligand. To stabilize the complex, one solvent molecule (THF) is coordinated to the titanium center in this case. The mechanistic studies suggest the solvent coordination for the monomer (Scheme 2, right) as well.[4e] In contrast to this observation in the reduction of *rac*-(ebthi)$TiCl_2$ a dinuclear complex [*rac*-(ebthi)Ti^{III}Cl]$_2$ was formed.[8a]

The preparation of **2** was done in a different way than the *in situ* generation of the Ti(III) species by zinc or manganese in the epoxide opening.[4c] **1-Ti** was reduced with magnesium in THF to yield the blue-green complex **2**. Similar monochloride species were obtained also as byproducts occurring during the formation of titanocene bis(trimethylsilyl)acetylene complexes.[8a] Ti(III) compounds are not detectable by NMR spectroscopy because of their paramagnetic properties, but luckily we could

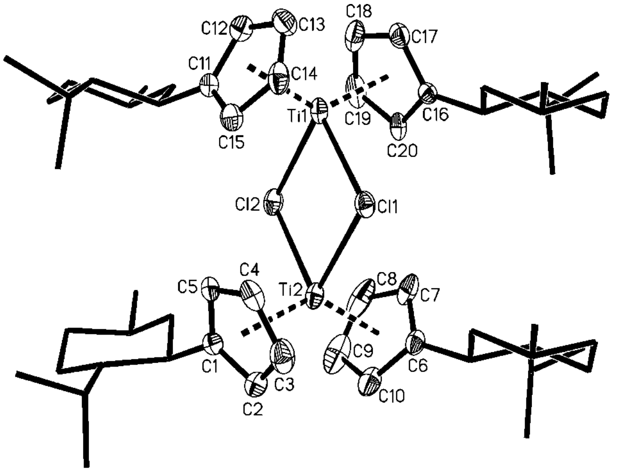
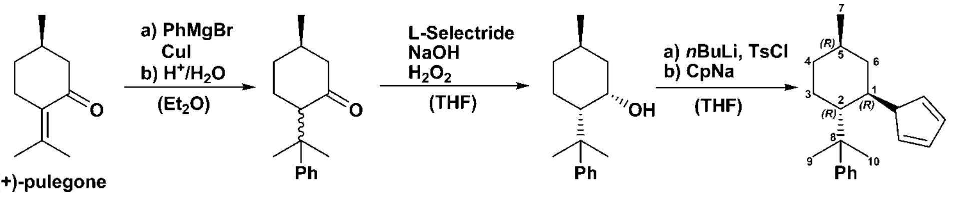
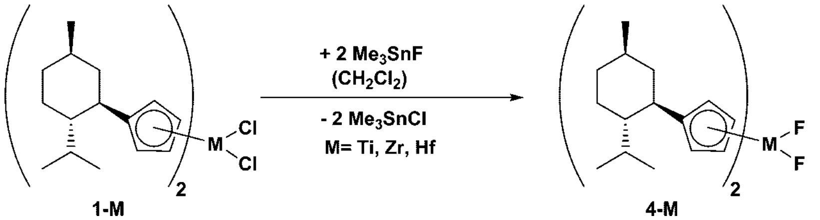


Figure 2. Molecular structure of compound **2**. The thermal ellipsoids correspond to 30% probability. Hydrogens are omitted for clarity. The menthyl substituents are represented by sticks. Selected bond lengths [Å] and angles [deg]: Ti1−Cl1 2.549(2), Ti2−Cl2 2.574(2), Ti2−Cl1 2.537(2), Ti1−Cl2 2.548(2), Ti1−Cl1−Ti2 104.33(5), Ti1−Cl2−Ti2 103.30(5), Cl1−Ti1−Cl2 76.29(4), Cl1−Ti2−Cl2 76.04(4).

Scheme 3. Preparation of the Free Ligand 8-phenylmenthyl-C_5H_5



Scheme 4. Synthesis of 4-M Starting from 1-M



obtain single crystals suitable for X-ray analysis to confirm the molecular structure of this complex (Figure 2). Similar dinuclear structural motifs are known for other ligands, too,[8] e.g., in complexes such as $[Cp_2TiCl]_2$,[8e] $[(CH_3\text{-}C_5H_4)_2TiCl]_2$,[8e] or [*rac*-(ebthi)TiCl]$_2$.[8a] The coordination geometry at each titanium can be best described as a distorted tetrahedron. Both titanium atoms are bridged by the two chlorine atoms, and the core unit Ti1, Cl1, Cl2, and Ti2 is almost planar, which was also found for the above-mentioned complexes.

Preparation of (η^5-8-phenylmenthyl-C_5H_4)$_2$ZrCl$_2$ (3-Zr). (η^5-8-phenylmenthyl-C_5H_4)$_2$TiCl$_2$ (**3-Ti**) was first synthesized by Vollhardt et al.[9a] and was used later on for the enantioselective ring opening of *meso*-epoxides together with **2-Ti**.[9b] The preparation of the compounds **3-M** starts with (+)-pulegone, which is a natural product. The four-step reaction sequence to obtain the substituted cyclopentadiene is shown in Scheme 3. The reaction of the cyclopentadiene with *n*BuLi and $ZrCl_4$ in THF yields the zirconocene dichloride **3-Zr** (Figure 3). In metallocene complexes like **3-M** three sides of the molecule are shielded by the two 8-phenylmenthyl-C_5H_4 ligands; only the side where the two chlorides are located is accessible for a reaction with substrates by replacement of either one or two chlorides.

The structure of **3-Zr** was confirmed by X-ray crystallography and shows similarity in bond distances and angles compared to **3-Ti**.

The arrangement of the phenyl ring above the Cp ring in **3-Zr** gives rise to the expectation of a π-stacking interaction. However, the term π-stacking is not well defined at all as discussed by C. Janiak.[10] The described possible interaction modes between cyclic aromatic systems offer a good basis for this consideration. In our case the two rings are not ideally parallel displaced (17.8°), but the value for the angle between the ring normal of the Cp ring and the vector of the ring centroids (7.6°) is small. In addition the distance between the centroids of the two aromatic rings is 3.464 Å. Therefore, in **3-Zr** a slipped π-stacking interaction could be assumed. Furthermore, the ^{13}C NMR spectrum shows six independent signals for the phenyl ring resulting from a hindered rotation. The discussed $\pi-\pi$ interaction should positively influence catalytic reactions because in contrast to the 8-phenylmenthyl-C_5H_4 ligand the rotation at the "simple" menthyl-C_5H_4 ligand should be less hindered by a lower rotation barrier, which causes a more or less undefined catalyst pocket.

Conversion of the Dichlorides to the Difluorides. Metallocene difluoride compounds have shown a different reactivity pattern compared to the dichloride complexes. For example it

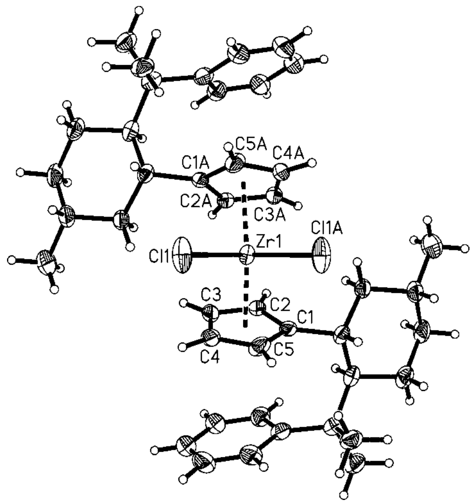


Figure 3. Molecular structure of compound **3-Zr**. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Zr1−Cp 2.206, Zr1−Cl1 2.448(2), Cp−Zr1−CpA 131.0, Cl1−Zr1−Cl1A 96.65(11); Cp typifies the centroid of the C1−C5 cyclopentadienyl ring atoms; CpA (C1A−C5A) and Cl1A are generated by symmetry operation: $-x+1$, $-y+1$, z.

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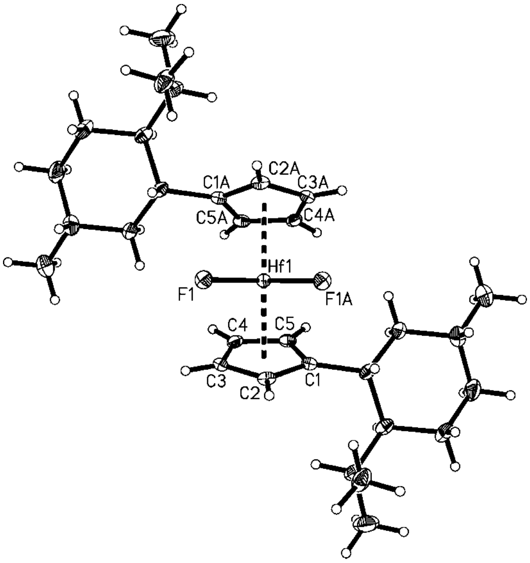


Figure 4. Molecular structure of compound **4-Hf**. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Hf1−Cp 2.188, Hf1−F1 1.955(2), Cp−Hf1−CpA 132.0, F1−Hf1−F1A 96.2(1); Cp typifies the centroid of the C1−C5 cyclopentadienyl ring atoms; CpA (C1A−C5A) and F1A are generated by symmetry operation: −*x*+1, −*y*, *z*..

is possible to form dihydrides starting from the difluorides by reacting them with *i*Bu_2AlH, but in such reactions the dichlorides do not show any reactivity.[5a] This so-called "fluoride effect" plays an important role in activitation and deactivation processes in olefin polymerizations.[5b] Another application of difluorides was presented by Buchwald et al. They used (*S*,*S*)-(ebthi)TiF_2 to hydrosilylate prochiral imines to chiral amines in high enantioselectivities.[2] First, our approach was to synthesize the so far unknown chiral titanocene, zirconocene, and hafnocene difluorides with menthyl-substituted Cp ligands. The general reaction pathway for their preparation is shown in Scheme 4.

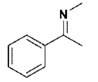
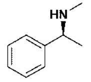
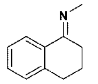
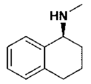
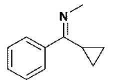
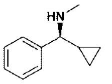
The compounds **4-Ti**, **4-Zr**, and **4-Hf** are isomorphous and crystallize from different solvents in the tetragonal space group $P4_2$. The molecular structure of **4-Hf** is shown as an example in Figure 4. The coordination geometry at the metal centers is distorted tetrahedral. The M1−Cp bond distances (**4-Ti**: 2.063 Å, **4-Zr**: 2.208 Å, **4-Hf**: 2.188 Å) and Cp−M1−CpA bond angles (**4-Ti**: 132.7°, **4-Zr**: 131.2°, **4-Hf**: 132.0°) are in the expected range as found in the dichloride congeners (see Tables 1 and 2).

Table 2. Comparison of Bond Distances and Angles of (η^5-menthyl-C_5H_4)$_2MF_2$, M = Ti (4-Ti), M = Zr (4-Zr), M = Hf (4-Hf)

	4-Ti	4-Zr	4-Hf
M1−Cp/Å	2.063	2.208	2.188
M1−F1/Å	1.863(2)	1.9645(9)	1.955(2)
Cp−M1−CpA/deg	132.7	131.2	132.0
F1−M1−F1A/deg	95.6(1)	97.59(6)	96.2(1)

Example for Catalytic Applications. To figure out the catalytic activity of the new complexes in enantioselective reactions, we chose the already mentioned Buchwald hydrosilylation of imines as a model reaction because it is well studied and optimized.

Table 3. Comparison of Catalysts in the Buchwald Hydrosilylation with Selected Imines

Entry	Imine	(*S*)-Amine	(*S*,*S*)-(ebthi)TiF_2 yield [%]	ee [%][a]	4-Ti yield [%]	ee [%][a]
1			94	98	92	7
2			80	96	81	27
3			91	97	89	21

[a] Determinded by GC analysis of the corresponding trifluoroacetamides on a Chiraldex column.

The results of our investigation are shown in Table 3, together with those of the reproduced reaction with (*S*,*S*)-(ebthi)TiF_2 as the precatalyst. Our system clearly displayes a dependence on the substituents of the imines. With sterically more demanding moieties at the imine, better results were achieved (see Table 3, entry 2). However, overall our system could not reach the very good enantioselectivities of the (*S*,*S*)-(ebthi)TiF_2 system. This could be explained by the sterical demand of the ebthi ligand, possessing a planar chirality that arises from the ethylene

Table 4. Crystallographic Data

	1-Hf	2	3-Zr	4-Ti	4-Zr	4-Hf
cryst syst	tetragonal	triclinic	orthorhombic	tetragonal	tetragonal	tetragonal
space group	$P4_2$	$P1$	$P2_12_12$	$P4_2$	$P4_2$	$P4_2$
a [Å]	15.337(1)	11.0360(5)	13.362(3)	15.356(2)	15.502(2)	15.4892(5)
b [Å]	15.337(1)	11.7476(6)	25.112(5)	15.356(2)	15.502(2)	15.4892(5)
c [Å]	6.4757(4)	11.8519(7)	6.516(1)	5.7986(6)	5.858(1)	5.8657(2)
α [deg]	90	83.696(5)	90	90	90	90
β [deg]	90	67.575(4)	90	90	90	90
γ [deg]	90	83.281(4)	90	90	90	90
V [Å^3]	1523.3(2)	1407.1(1)	2186.3(8)	1367.3(2)	1407.6(4)	1407.26(2)
Z	2	1	2	2	2	2
density [g·cm^{-3}]	1.430	1.157	1.095	1.196	1.264	1.471
μ(Mo Kα) [mm^{-1}]	3.615	0.414	0.397	0.342	0.419	3.734
T [K]	200(2)	293(2)	200(2)	200(2)	200(2)	200(2)
no. of rflns (measd)	21 446	20 186	28 519	6717	27 083	20 030
no. of rflns (indep)	2975 (R_{int} = 0.0496)	10 583 (R_{int} = 0.0502)	4052 (R_{int} = 0.0602)	2488 (R_{int} = 0.0859)	3599 (R_{int} = 0.0294)	2689 (R_{int} = 0.0309)
no. of rflns (obsd)	2000	5713	3288	1484	2925	1921
no. of params	150	573	204	150	150	150
GOF on F^2	0.829	0.709	0.928	0.790	0.902	0.982
R_1 ($I > 2\sigma(I)$)	0.0145	0.0389	0.0341	0.0518	0.0179	0.0129
wR_2 (all data)	0.0254	0.0562	0.0720	0.0644	0.0411	0.0276
Flack param	−0.007(7)	0.00(3)	−0.03(5)	0.08(4)	0.00(3)	0.003(10)

bridging unit, which inhibits the rotation of the indenyl rings coordinated to the metal atom. Therefore a defined catalytic pocket is formed. The (η^5-menthyl-C_5H_4)$_2$TiF_2 has no restricted rotation of the substituted Cp rings, leading to a more flexible and therefore less defined pocket. This difference could be the reason for the different enantioselectivities obtained with the two catalyst systems. Following these results **4-Ti** could be changed by additionally modifying the Cp ring or the menthyl substituent. We chose the second approach and tried to synthesize starting from the pure dichloride **3-Ti** the corresponding difluoride (η^5-8-phenylmenthyl-C_5H_4)$_2$TiF_2 (**5-Ti**), but unfortunately, we could not obtain pure samples of this complex. Nevertheless, we used these samples as precatalyst for the hydrosilylation. The suggested positive influence of the phenyl ring at the menthyl substituent could be seen by the slightly better ee values for (*E*)-*N*-(1-phenylethylidene)methanamine (**4-Ti**: 7%; **5-Ti**: 22%) and *N*-(3,4-dihydronaphthalen-1(2*H*)-ylidene)methanamine (**4-Ti**: 27%; **5-Ti**: 37%). This increase of the ee values suggests that with sterically more hindered imines, good enantioselectivities may be obtained.

Conclusion

The bis(η^5-menthyl-C_5H_4) metallocene dichlorides of the group 4 transition metals (**1-M**) are easily accessible by reaction of the metal tetrachlorides with the *in situ* lithiated ligand. We present the synthesis of the hitherto unknown (η^5-menthyl-C_5H_4)$_2$HfCl_2 (**1-Hf**). All these compounds can be converted with trimethyltin fluoride to their difluoride analogues (**4-M**). A comparison between **1-Zr** and **1-Hf** or **4-Zr** and **4-Hf** indicates only fractional differences between zirconium and hafnium, which highlights the similarity of these metals. Variation at the ligand system led to the synthesis of the new complex **3-Zr**, with the 8-phenylmenthyl-C_5H_4 ligand. First catalytic studies with **4-Ti** and **5-Ti** used in the Buchwald hydrosilylation give poor results, but two observations should be pointed out. First, **4-Ti** shows a strong dependence in its enantioselectivity on more sterically demanding substituents at the imine. Second, the positive influence of the phenyl rings at the menthyl substituents could be seen by the slightly better ee values in the comparison of **4-Ti** and **5-Ti**.

Experimental Section

General Procedures. All operations were carried out under argon with standard Schlenk techniques. Prior to use nonhalogenated solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvents (CD_2Cl_2, $CDCl_3$) were dried over molecular sieves, distilled, and stored under argon. (*S,S*)-(ebthi)TiF_2 was purchased from MCAT (Metallocene Catalysts & Life Science Technologies, Konstanz, Germany) and used without further purification. The following spectrometers were used. Mass spectra: AMD 402. NMR spectra: Bruker AV 300/AV 400. Chemical shifts (^{1}H, ^{13}C) are given relative to SiMe_4 and are referenced to signals of the used solvent: CD_2Cl_2 (δ_H 5.32, δ_C 53.8), $CDCl_3$ (δ_H 7.27, δ_C 77.0). The spectra were assigned with the help of DEPT and shift correlation experiments. Melting points: sealed capillary, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of 1-Hf. {(1*R*,2*S*,5*R*)-5-methyl-2-[prop-2-yl]-cyclohex-1-yl}cyclopentadiene (2.466 g, 12.1 mmol) was dissolved in 10 mL of toluene. Afterward *n*BuLi (8.2 mL, 13.1 mmol, 1.6 M in *n*-hexane) was added at 0−5 °C. This solution was added under stirring to a white suspension of HfCl_4 (1.942 g, 6.1 mmol) in 20 mL of toluene at 0 °C. The reaction mixture was warmed slowly to room temperature and was additionally stirred for 16 h at room temperature. To quench the reaction, H_2O (1.1 mL, 61.1 mmol) was added. The solution was filtered from the formed white precipate. All volatiles of the filtrate were removed under vacuum. Extraction with toluene and concentration yielded the product (0.685 g, 1.044 mmol, 17%) as fine colorless crystals, mp 250 °C under Ar. Anal. Calcd for $C_{30}H_{46}HfCl_2$: C, 54.92; H, 7.12. Found: C, 53.62; H, 7.06. NMR (298 K, $CDCl_3$): ^{1}H (300 MHz) δ 0.77−1.88 (m, 36H, menthyl), 2.66 (q, 2H, menthyl), 6.0 (m, 4H, Cp), 6.24 (d, 2H, Cp), 6.47 (d, 2H, Cp); ^{13}C (75 MHz) δ 15.5, 21.6, 22.8, 24.6, 27.3, 32.6, 35.2, 41.1, 41.4, 50.8 (menthyl), 104.6, 112.5, 114.3, 118.6, 139.9 (Cp). MS (70 ev, *m/z*): 656 $[M]^+$; 620 $[M - Cl]^+$; 453 $[M - \text{Cp ligand}]^+$; 204 $[\text{Cp ligand}]^+$.

Preparation of 2. (η^5-menthyl-C_5H_4)$_2$TiCl_2 (**1-Ti**) (0.323 g, 0.62 mmol) and finely cut magnesium wire (0.009 g, 0.375 mmol) were stirred at 60 °C in 15 mL of THF for 5 days. Within this time the color of the solution changed from red to purple. After 5 days the solvent was removed under vacuum and the obtained residue was extracted three times with *n*-hexane at 40 °C. The filtrate was concentrated under vacuum. Leaving the solution at −30 °C yielded the product as blue-green crystals (0.120 g, 0.122 mmol, 39%), mp 178−179 °C (dec) under Ar. Anal. Calcd for $C_{60}H_{92}Ti_2Cl_2$: C, 73.53; H, 9.46. Found: C, 72.99; H, 9.25. MS (70 ev, *m/z*): 480 $[(\eta^5\text{-menthyl-}C_5H_4)_2TiCl]^+$.

Preparation of 3-Zr. {(1*R*,2*R*,5*R*)-5-Methyl-2-[2-phenyl-propyl]cyclohex-1-yl}cyclopentadiene (6.420 g, 22.9 mmol) was dissolved in 20 mL of THF. Afterward *n*BuLi (15.02 mL, 24.0 mmol, 1.6 M in *n*-hexane) was added at 0−5 °C. This solution was added under stirring to a suspension of ZrCl_4 (2.667 g, 11.4 mmol) in 20 mL of THF at 0 °C. The reaction mixture was allowed to warm slowly to room temperature and was stirred for 16 h at room temperature. To quench the reaction, H_2O (4.1 mL, 227.8 mmol) was added. The volatiles were removed under vacuum, and the crude product was extracted with *n*-hexane. The filtrate was concentrated under vacuum to dryness, and recrystallization in benzene yielded the product (1.998 g, 2.771 mmol, 24%) as colorless crystals, mp 211 °C (dec) under Ar. Anal. Calcd for $C_{42}H_{54}ZrCl_2$: C, 69.96; H, 7.55. Found: C, 68.96; H, 7.76. NMR (298 K, $CDCl_3$): ^{1}H (300 MHz) δ 0.87−1.87 (m, 34H, menthyl), 2.63 (t, 2H, menthyl), 5.58 (dd, 2H, Cp), 5.98 (m, 2H, Cp), 6.08 (dd, 2H, Cp), 6.16 (dd, 2H, Cp), 6.96−7.12 (m, 10H, phenyl); ^{13}C (75 MHz) δ 22.5, 24.9, 28.2, 29.1, 32.6, 35.6, 40.8, 41.1, 44.8, 54.1 (menthyl), 105.9, 116.4, 117.9, 118.1 (Cp), 124.6, 125.4, 126.1, 127.7, 127.9 (phenyl), 139.5 (ipso C at Cp), 151.6 (ipso C at phenyl). MS (70 ev, *m/z*): 720 $[M]^+$, 682 $[M - Cl]^+$.

Preparation of 4-Ti. (η^5-menthyl-C_5H_4)$_2$TiCl_2 (**1-Ti**) (0.304 g, 0.579 mmol) and trimethyltin fluoride (0.275 g, 1.504 mmol) were dissolved in 15 mL of CH_2Cl_2. The solution was stirred 2 h at room temperature. The reaction mixture was filtrated at room temperature to remove the formed trimethyltin chloride. A second filtration at −78 °C gave 0.113 g (0.229 mmol, 75%) of the product as fine, yellow crystals, which were dried under vacuum, mp 261 °C (dec) under Ar. Anal. Calcd for $C_{30}H_{46}TiF_2$: C, 73.15; H, 9.41. Found: C,72.42; H, 9.642. NMR (298 K, CD_2Cl_2): ^{1}H (300 MHz) δ 0.72−1.93 (m, 36H, menthyl), 2.44 (m, 2H, menthyl), 6.23 (s, 2H, Cp), 6.28 (s, 2H, Cp), 6.29 (q, 2H, Cp), 6.40 (s, 2H, Cp); ^{13}C (75 MHz) δ 15.6, 21.7, 22.9, 25.0, 27.6, 33.0, 35.6, 40.5, 41.2, 50.4 (menthyl), 109.3, 116.2, 117.3, 120.6, 139.9 (Cp); ^{19}F (282 MHz) δ 70.1 (s, 2F). MS (70 eV, *m/z*): 492 $[M]^+$; 473 $[M - F]^+$.

Preparation of 4-Zr. (η^5-menthyl-C_5H_4)$_2$ZrCl_2 (**1-Zr**) (0.500 g, 0.879 mmol) and trimethyltin fluoride (0.418 g, 2.287 mmol) were dissolved in 15 mL of CH_2Cl_2. The solution was stirred 2 h at room temperature. The reaction mixture was filtrated at room temperature to remove the formed trimethyltin chloride. The volatiles were removed under vacuum to obtain the crude product. Recrystallization in toluene gave 0.115 g (0.214 mmol, 43%) of the product as colorless crystals, which were dried under vacuum, mp 242 °C under Ar. Anal. Calcd for $C_{30}H_{46}ZrF_2$: C, 67.24; H, 8.65. Found: C,67.13; H, 8.55. NMR (298 K, CD_2Cl_2): ^{1}H (300 MHz) δ 0.73−1.92 (m, 36H, menthyl), 2.45 (m, 2H, menthyl), 5.97 (q, 2H, Cp), 6.24 (m, 4H, Cp), 6.37 (q, 2H, Cp); ^{13}C (75 MHz) δ 15.7, 21.7, 22.9, 25.1, 27.6, 33.3, 35.6, 41.0, 41.4, 50.8 (menthyl), 108.3, 113.3, 114.6, 115.9,139.8 (Cp); ^{19}F (282 MHz) δ 20.5 (s, 2F). MS (70 ev, *m/z*): 534 $[M]^+$; 519 $[M - F]^+$.

Preparation of 4-Hf. (η^5-menthyl-$C_5H_4)_2HfCl_2$ (**1-Hf**) (0.328 g, 0.50 mmol) and trimethyltin fluoride (0.238 g, 1.30 mmol) were dissolved in 15 mL of CH_2Cl_2. The solution was stirred 2 h at 50 °C. The reaction mixture was filtrated at room temperature to remove the formed trimethyltin chloride. The volatiles were removed under vacuum to obtain the crude product. Recrystallization in *n*-hexane gave 0.130 g (0.209 mmol, 42%) of the product as colorless crystals, which were dried under vacuum, mp 246 °C under Ar. Anal. Calcd for $C_{30}H_{46}HfF_2$: C, 57.82; H, 7.44. Found: C, 57.67; H, 7.48. NMR (298 K, CD_2Cl_2): ^{1}H (300 MHz) δ 0.64−1.94 (m, 36H, menthyl), 2.45 (m, 2H), 5.90 (q, 2H, Cp), 6.16 (m, 4H, Cp), 6.29 (q, 2H, Cp); ^{13}C (75 MHz) δ 15.6, 21.7, 22.9, 25.0, 27.6, 33.2, 35.6, 40.9, 41.3, 50.9 (menthyl), 107.0, 111.8, 113.0, 115.1, 138.3 (Cp); ^{19}F (282 MHz) δ −22.4 (s, 2F). MS (70 ev, *m/z*): 622 $[M]^+$; 605 $[M - F]^+$.

General Procedure for Hydrosilylation of Imines (according to ref 2). A dry, resealable Schlenk vessel was charged under argon with Cp'_2TiF_2 (Cp'_2 = (*S*,*S*)-ebthi; **4-Ti** = (η^5-menthyl-$C_5H_4)_2$; 0.025 mmol) and 2 mL of dry THF. To this solution were added in this order $PhSiH_3$ (0.45 mL, 3.75 mmol), pyrrolidine (8 μL, 0.1 mmol), and methanol (4 μL, 0.1 mmol). The mixture was stirred at room temperature for 30−60 min, resulting in a color change from yellow to green. At this point, the imine[11] (2.5 mmol) was added. The reaction mixture was stirred at room temperature for 12 h; after this time period the consumption of the starting material was completed. The reaction mixture was worked up by dilution with Et_2O (20 mL) and stirring with 1 M HCl (10 mL) for 0.5 h. The aqueous layer was separated, alkalized with 3 M NaOH, and extracted three times with 20 mL of ether. The combined ether phases were dried over $MgSO_4$, and evaporation of the solvent yielded the (*S*)-(−)-*N*-methylamine.

Diffraction data were collected on a STOE IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97[12]) and refined by full-matrix least-squares techniques on F^2 (SHELXL-97[13]). XP (Bruker AXS) was used for graphical representations and for calculation of Cp−M1 bond distances and the Cp−M1−CpA bond angles. For compound **3-Zr** PLATON/SQUEEZE[14] was used to remove the disordered solvent. For **1-Hf**, **2**, **4-Ti**, and **4-Hf** a numerical absorption correction was applied.

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Supporting Information Available: Crystallographic data in cif file format, including bond lengths and angles of compounds **1-Hf**, **2**, **3-Zr**, **4-Ti**, **4-Zr**, and **4-Hf**. This material is available free of charge via the Internet at http://pubs.acs.org.

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