

Novel chiral Lewis acids based on a new asymmetric cyclopentadienyl ligand

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Abstract

The chiral N-functionalized cyclopentadiene ligand Cp^EH ($\text{Cp}^E = \text{C}_5\text{H}_4\text{CH}(\text{Ph})\text{CH}(\text{Me})\text{NMe}_2$) was used for the preparation of a series of (transition) metal complexes. Metallation of Cp^EH is accomplished by reaction with ${}^n\text{BuLi}$, K or TIOEt . Reaction of Cp^ELi with Me_3SiCl and AlCl_3 yields Cp^ESiMe_3 and Cp^EAlCl_2 respectively. In the aluminium compound a bidentate coordination of the Cp unit and the nitrogen side-arm is observed. Reaction of Cp^ESiMe_3 with MCl_4 ($\text{M} = \text{Ti}, \text{Zr}$) affords Cp^EMCl_3 in moderate yield. In Cp^ETiCl_3 the nitrogen side-arm is only weakly coordinated, whereas in Cp^EZrCl_3 it is firmly coordinated to the metal centre. Moreover, Cp^EZrCl_3 behaves as a moderate Lewis acid, and hitherto catalyzes the Diels–Alder reaction between methacroleine and cyclopentadiene, albeit with no measurable enantiomeric excess.

Keywords: Lewis acid; Titanium; Zirconium; Cyclopentadienyl; Catalysis; Chirality transfer

1. Introduction

The application of chirally modified cyclopentadienyl (Cp) ligands in metal-mediated organic transformations emerged about 20 years ago with the preparation of menthyl-substituted titanocene and zirconocene derivatives by Cesarotti et al. [1]. In order to increase the asymmetric induction around the complexed metal during catalysis, further improvements were mainly based on modification of the steric bulk of the chiral substituents [2]. A new development is the introduction of a functional group onto the chiral Cp ring, which by intramolecular coordination creates a more rigidly coordinated chiral pocket around the metal. A few recent examples of such ligands are shown in Fig. 1.

Recently, we designed a novel chiral Cp ligand [(1*S*, 2*S*)-(2-dimethylamino-1-phenylpropyl)cyclopentadiene, (Cp^EH), **4** in Fig. 1] whose synthesis was based on natural ephedrine as a chiral building block [6]. The configuration of the chiral centres was secured by a crystal structure study of a ferrocene derivative [7]. We now report on the syntheses of some organometallic derivatives with this ligand and electropositive elements that may be used as chiral Lewis acids.

2. Results and discussion

2.1. Synthesis of precursor compounds

Metallation of Cp^EH can be accomplished by ${}^n\text{BuLi}$, K and TIOEt (Scheme 1). The ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra of these and all further Cp^E derivatives are listed in Tables 1 and 2 respectively.

No NMR data are available for the K compound, since it is insoluble in all common organic solvents, even in coordinating ones like THF or pyridine. Although the compound was prepared in THF, its elemen-

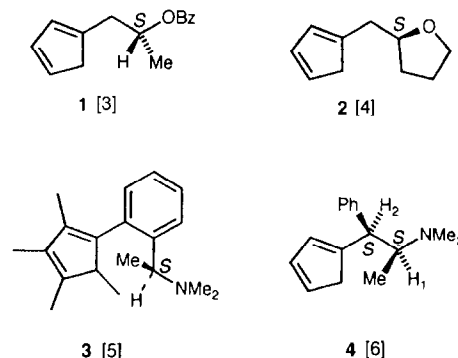
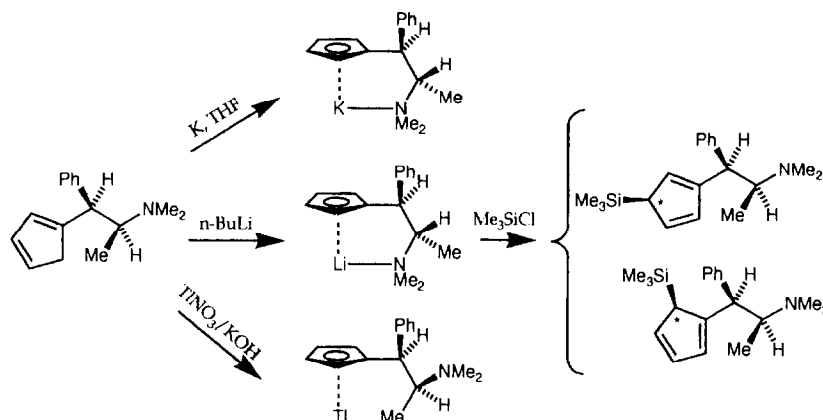


Fig. 1. Some recent examples of chiral, functionalized Cp ligands.

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Scheme 1.

tal analysis showed that it is free of THF. We think its structure consists of a chain-like Cp-bridged polymer, as in $\text{Cp}^*\text{K}(\text{OEt})_2$ [8a] or $\text{Cp}^*\text{K}(\text{py})_2$ [8b], in which the N-containing side-arms are intramolecularly coordinated. Although air-sensitive, Cp^*K may be stored for months in an inert atmosphere as a white powder without apparent decomposition. It reacts with methanol, giving back the starting material Cp^*H . Curiously, the analogous reaction with excess CD_3OD does not yield the expected monodeuterated $\text{Cp}^*\text{H}-d_1$, but instead the perdeuterated $\text{Cp}^*\text{H}-d_5$, as evidenced by the near-complete absence of characteristic Cp signals around 6 and 3 ppm in the ^1H NMR spectrum, as well as the appearance of C–D-coupled Cp signals in the ^{13}C NMR spectrum. Apparently, the potassium methoxide formed

upon methanolysis reversibly metallates the Cp ring and exchanges all hydrogens for deuteriums.

In contrast, reaction of Cp^*Li with CD_3OD yields monodeuterated $\text{Cp}^*\text{H}-d_1$. Air-sensitive Cp^*Li is soluble in both donor and non-donor solvents, including pentane. The ^1H and ^{13}C NMR spectra of Cp^*Li free of donor solvents in C_6D_6 show broad signals. The ^1H resonances around the N atom are shifted upfield from those of the free ligand, which seem to be caused by N–Li coordination. Its solubility in non-coordinated solvents, as well as the very broad NMR signals, suggest that Cp^*Li has a dynamic, oligomeric structure.

The thallium compound Cp^*Tl is air-stable for short periods of time. The NMR data suggest that the side-arm is *not* coordinated in solution (coordination should be

Table 1
 ^1H NMR data of the Cp^*E derivatives ^a

M	Solvent	CHCH_3 ^b	$\text{N}(\text{CH}_3)_2$ ^c	CHCH_3	CHPh ^b	Cp
H	CDCl_3	0.67 (6.3)	2.20	3.22 (m)	3.67 (10.4)	2.91, 6.08 (s), 6.19 (d, 5.2 Hz),
(two isomers)		0.68 (6.3)	2.22		3.71 (10.4)	6.24 (s), 6.33 (m), 6.51 (d, 5.2 Hz)
H · HCl	CD_3OD	1.16 (6.8)	2.83, 3.02	4.33 (m)	4.16 (11.3)	3.0, 6.45 (d, 5.1), 6.54 (d, 5.1)
(two isomers)		1.18 (6.8)	2.84, 3.02		4.18 (11.5)	6.62 (m), 6.80
Li ^d	C_6D_6	0.45	1.47	2.63	3.29	5.56, 5.91
Tl	CDCl_3	0.67 (6.5)	2.02	2.95 (dq)	3.49 (11.5)	5.95, 6.14
SiMe_3 ^c	CDCl_3	0.75	2.25	3.26	3.77	6.17, 6.22, 6.44, 6.59, 6.65
AlCl_2	CDCl_3	1.05 (6.4)	2.73, 2.74	3.63 (dq)	3.88 (11.1)	5.06, 5.83, 6.61 (2H)
	C_6D_6	0.23 (s,br)	1.86, 2.00	3.18 (dq)	3.38 (10.9)	4.90, 5.97, 6.81 (2H)
TiCl_3	CDCl_3	1.00 (6.3)	2.75	4.64 (dq)	4.23 (11.3)	6.51, 6.70, 7.17, 7.3?
	C_6D_6	0.87 (br)	2.21	4.24 (m)	3.57 (11.0)	5.98, 6.05, 6.73, 6.79
	$\text{CD}_2\text{Cl}_2, -80^\circ\text{C}$	0.94 (6.1)	2.60, 2.78	4.61 (dq)	4.32 (11.8)	6.47, 6.80, 7.12, 7.2?
$[\text{TiCl}_2(\text{HCl})](\mu\text{-O})_{0.5}$	CDCl_3	1.40	2.68, 2.86	4.63 (m)	5.30 (s, br)	6.33, 6.46, 6.72, 6.88
ZrCl_3	CDCl_3	0.97 (6.2)	2.72 (6H)	4.34 (dq)	4.10 (11.6)	6.41, 6.58, 6.79, 6.88
	C_6D_6	0.87 (6.4)	2.08, 2.21	4.05 (dq)	3.46 (11.5)	5.91, 6.02, 6.50, 6.57
$\text{ZrCl}_3(\text{crotonaldehyde})$	CDCl_3	0.88 (6.4)	2.49, 2.64	4.12 (dq)	3.92 (12.0)	6.38, 6.64, 6.77, 6.98?

^a Measured at 300.075 MHz at room temperature, unless stated otherwise; $^3J_{\text{HH}}$ couplings (Hz) in parentheses. Resonances of the phenyl group (m) found between 7.0 and 7.4 ppm. ^b Doublet. ^c Singlet. ^d All signals appear as broad singlets. ^e Mixture of at least four isomers (see text), only major signals are given; SiMe_3 at -0.17 and -0.01 ppm.

Table 2
¹³C NMR data of the Cp^EM derivatives^a

M	Solvent	CHCH ₃	N(CH ₃) ₂	CHPh	CHCH ₃	Ph(<i>p</i> -, <i>o</i> -, <i>m</i> -, <i>ipso</i> -C)	Cp
H	CDCl ₃	9.33	40.04	51.87	61.58	126.0	143.68
(two isomers)		9.42	40.18	52.74	61.87		40.87, 126.06, 131.03, 132.93, 151.18
H·HCl	CD ₃ OD	11.61	42.93, 43.34,	50.26	65.67	128.65	41.67, 126.35, 132.08, 133.91, 148.96
(two isomers)			43.89, 44.10	51.05	65.94		37.07, 130.96, 133.10, 134.91, 146.01
Li ^d	C ₆ D ₆	8.50	39.1	52.85	65.48	125.87	37.39, 131.43, 133.37, 137.49, 147.11
Ti ^d	CDCl ₃	10.34	38.79	51.28	62.23	125.60	101.5 (2×), 105.3 (2×), 122.0
SiMe ₃ ^b	CDCl ₃	9.08	40.02	50.38, 50.53	61.64	127.12?	145.66
				51.82, 52.00			107.28(4×?)
AlCl ₂	CDCl ₃	10.31	36.91, 45.35	50.75	65.64	125.70 ^d	40.0?, 125.68, 131.16, 144.22, 144.45
TiCl ₃	CDCl ₃	11.3	46.0 (br)	51.29	70.29	128.3	133.0, 125.80, 131.31, 147.42, 147.68
[TiCl ₂ (HCl)](μ-O) _{0.5} ^c	CDCl ₃	11.5	40.3, 42.9	47.1	64.1	128.2	109.2, 124.46 ^d , 127.29 ^d
	CDCl ₃	10.50	41.98, 47.41	49.97	69.39	127.85	120.33, 121.43, 125.07, 128? ^d , 138.43
ZrCl ₃	CDCl ₃						121.3 (vbr)

^a Measured at 75.462 MHz at room temperature. ^b Mixture of at least four isomers, not all signals were resolved; SiMe₃ at -1.96 and -2.15 ppm. ^c All signals broad. ^d May be interchanged.

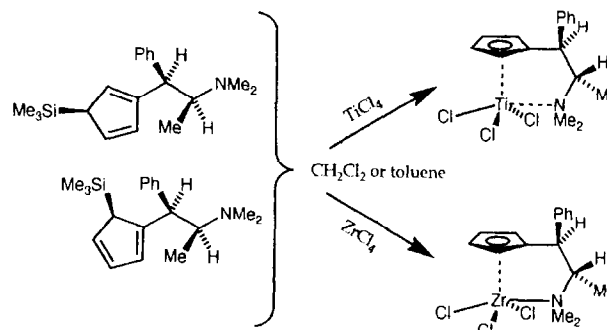
obvious by the appearance of diastereotopic signals of the NMe₂ group, *vide infra*).

The oily Me₃Si derivative consists of a complex mixture of (exchanging) isomers; four of them with equal abundance make up an estimated 90% of the mixture at room temperature. Two types of regiomers result by virtue of the two different olefinic C atoms in the Cp ring at which the side-arm is attached by preference. The aliphatic C atom of the Cp ring, at which the Me₃Si group preferentially binds, is chiral and, owing to the presence of a chiral substituent, gives rise to a further diastereomeric division. At room temperature most of the signals of the various isomers in the ¹H and ¹³C NMR spectra (partly) overlap, but the ¹³C resonances of CH(Ph) show a nice 1:1:1:1 pattern belonging to the four main isomers. The ²⁹Si NMR spectra in CD₂Cl₂ or THF-*d*₈ show only one signal at room temperature, at +6 or +3 ppm respectively, which splits into two or three barely separated signals at low temperature. The apparent dynamical behaviour is an obvious result of the mobility of the Me₃Si group along the Cp ring, that is typical of Si-substituted Cp compounds [9], and resembles that of the achiral *N,N*-dimethylaminoethyl-cyclopentadienyl analogue (Cp⁺) [10].

2.2. Synthesis of Lewis acid derivatives

In order to obtain chiral Lewis acid derivatives bearing the Cp^E ligand we first concentrated on the syntheses of mono-Cp derivatives of type Cp^EMCl₃ with M a Group 4 element. The reaction of Cp^ELi or Cp^EK with ZrCl₄ affords a compound with approximate stoichiometry Cp^E₂ZrCl₂. Its ¹H NMR spectrum, however, is rather confusing, and suggests a more complex structure than the expected classical metallocene one. Apparently, Jutzi encountered similar problems in isolating a Cp⁺₂MCl₂ compound [11].

The reaction of Cp^ESiMe₃ with TiCl₄ or ZrCl₄ in CH₂Cl₂ (toluene) but not in THF affords the complexes Cp^EMCl₃ in moderate yield (Scheme 2). The yellow titanium compound is extremely air-sensitive, even more than its unsubstituted analogue CpTiCl₃. The ¹H and



Scheme 2.

^{13}C NMR spectra of Cp^ETiCl_3 in CDCl_3 or C_6D_6 show only one broad signal for the NMe_2 group, but at low temperature in CD_2Cl_2 this signal splits into two resonances. This indicates a fluxional coordination of the amine side-arm. For the achiral analogue Cp^+TiCl_3 a rigid intramolecular coordination of the NMe_2 group is anticipated on the basis of ^1H chemical shift differences and an X-ray structure [12], but it is possible that this compound is also fluxional in solution. It is known that the parent CpTiCl_3 has a low affinity for O- and N-donating ligands [13], and therefore the Lewis acidity of this type of compound seems to be very low.

Exposure to moisture yields a product that was identified by its ^1H and ^{13}C NMR spectra as $[\text{Cp}^E\text{TiCl}_2(\text{HCl})_2(\mu\text{-O})]$ (Scheme 3). The diastereoscopic splitting of the NMe_2 signals is very diagnostic of the formation of an ammonium salt. Further hydrolysis yields the ammonium salt of the free ligand $\text{Cp}^E\text{H}\cdot\text{HCl}$. An analogous decomposition pathway was observed for Cp^+TiCl_3 [12].

The colourless zirconium analogue Cp^EZrCl_3 is only slightly less air-sensitive than its titanium congener. The ^1H and ^{13}C NMR spectra show two sharp signals for the NMe_2 group, indicating that in this case a solid, donating N–Zr bond exists. Although we were not able to obtain crystals suitable for X-ray diffraction work, the structure of Cp^EZrCl_3 probably resembles that of a four-legged piano stool, like that of $[\text{Cp}^+\text{ZrCl}_2(\mu\text{-Cl})_2]$ [14]. Fig. 2 gives an impression of its presumed structure, as calculated by molecular modelling methods. The calculated torsion angle $\text{H}_1\text{-C-C-H}_2$ of 176° is in accord with the observed $^3J(\text{H}_1, \text{H}_2)$ coupling of 11.6 Hz.

Additionally, Cp^EAlCl_2 could be synthesized by a straightforward reaction of Cp^ELi and AlCl_3 . The air-sensitive colourless complex shows two sharp signals in the NMR spectrum for the NMe_2 group, diagnostic of solid, intramolecular N–Al coordination. However, it seems likely that the Cp ring will not make full use of its η^5 -coordination potential, and Cp^EAlCl_2 is probably a coordinatively saturated pseudo-tetrahedron, just as the analogous compound Cp^+AlCl_2 reported by Jutzi and coworkers [15].

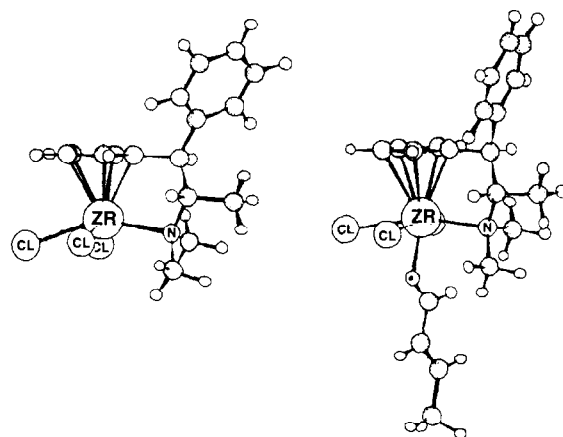
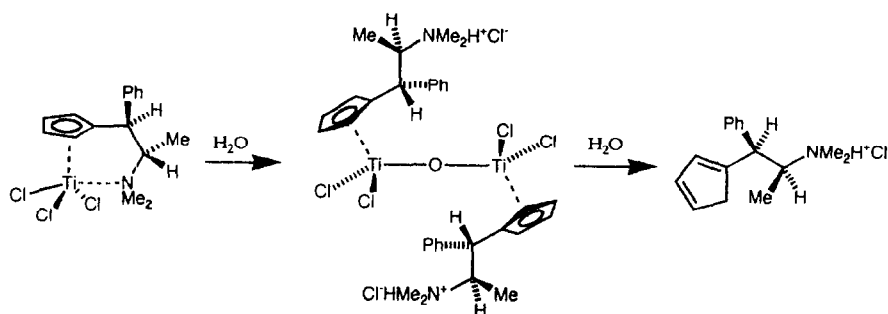


Fig. 2. Calculated structures of Cp^EZrCl_3 and its crotonaldehyde adduct.

2.3. Lewis acidity of Cp^EZrCl_3 and its catalytic potential

In 1982 Childs et al. [16] discovered that Lewis acidity may be estimated by measuring the difference in certain ^1H NMR shifts between 1:1 complexes of α,β -unsaturated carbonyls with Lewis acid and those of the free carbonyl. In 1990 Laszlo and Teston [17] gave a theoretical foundation for this phenomenon, and a number of (transition) metal compounds were ranked for their Lewis acidity [18]. The H_3 chemical shifts of crotonaldehyde have become the parameter of choice for these determinations.

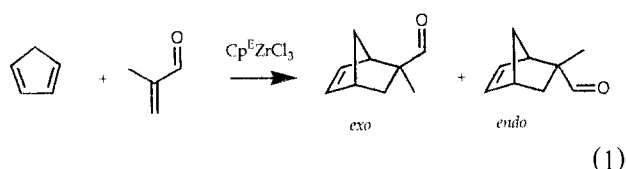
In order to determine the Lewis acidity of Cp^EZrCl_3 we treated it with increasing amounts of crotonaldehyde in CDCl_3 , and followed the events by ^1H NMR. All of the Cp^E signals show a gradual drift until equimolar amounts of the zirconium compound and crotonaldehyde are present. Further addition of the aldehyde had no influence on the ^1H resonances, and therefore the formation of a 1:1 adduct is anticipated. The H_3 resonance of crotonaldehyde in the adduct was shifted 0.53 ppm downfield. This makes Cp^EZrCl_3 a weak Lewis acid, comparable with $\text{CpFe}(\text{CO})_2^+$, Table 3. It is important to note that the ^1H and ^{13}C resonances of the



Scheme 3.

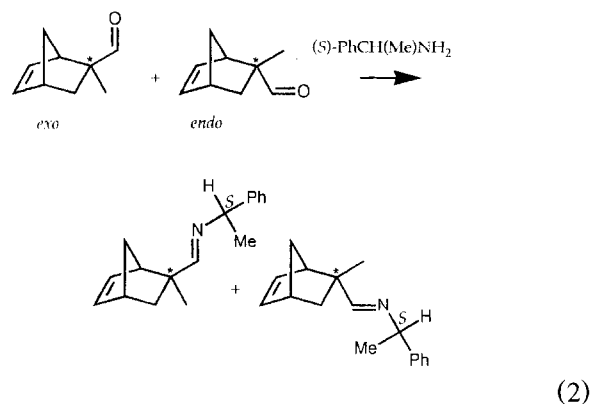
NMe₂ group still appear as two separate signals, indicating that this group is still coordinated in the new adduct. A similar situation apparently exists in the analogous compound Cp⁺ZrCl₃(THF), in which coordination of the THF molecule does not interfere with intramolecular coordination of the NMe₂ group [11]. Fig. 2 shows a calculated structure of the Cp^EZrCl₃–crotonaldehyde adduct. Support of the calculated structure is given by the observed coupling constant ³J(H₁, H₂) of 12.0 Hz.

Since it is known that Lewis acids can promote the Diels–Alder reaction between α,β-unsaturated carbonyls and dienes [19], Cp^EZrCl₃ was examined as a possible (enantioselective) catalyst. It was indeed found that Cp^EZrCl₃ catalyzes these reactions, e.g. that between methacrolein and cyclopentadiene, Eq. (1).



The *exo/endo* ratio of 86/14 resembles that of the same reaction catalyzed by CpZrCl₃(THF)₂ (89/11) [20].

The enantiomeric excess (ee) was determined by derivatizing the bicyclic aldehydes with (1*S*)-1-phenylethylamine, Eq. (2).



Unfortunately, no detectable ee was observed in this way for either the *exo* or the *endo* isomer.

Fig. 2 suggests that the stereogenic carbon centres of the Cp^E ligand cause an asymmetric distortion of the coordinated NMe₂ group in Cp^EZrCl₃, which should have an influence on the adjacent coordination site. In spite of this, there is no optical induction during the Diels–Alder reaction, and this might be due to the fact that the reactive centre of the methacrolein molecule (C=C double bond) is too distant from this side. Further development of such systems should therefore be aimed at increasing the chiral steric bulk on the functional group of the side-arm or focusing on catalytic

Table 3
Lewis acidity ^a

Lewis acid	Δδ(H ₂)	Δδ(H ₃)
BBr ₃	0.93	1.49
BCl ₃	0.85	1.35
SbCl ₅	0.78	1.32
EtAlCl ₂	0.77	1.25
AlCl ₃	0.76	1.23
BF ₃	0.74	1.17
TiCl ₄	0.60	1.03
W(CO) ₃ (NO)(PMe ₃) ⁺		0.93
Et ₂ AlCl	0.55	0.91
SnCl ₄	0.50	0.87
CpMo(CO) ₃ ⁺		0.70
Et ₃ Al	0.42	0.63
CpFe(CO) ₂ ⁺		0.54
Cp^EZrCl₃	0.33	0.53
W(CO) ₂ (NO)(PMe ₃) ₂ ⁺		0.28

^a Defined as δ[H_x(crotonaldehyde–Lewis acid adduct)] – δ[H_x(crotonaldehyde CDCl₃); x = 2 or 3. Data from Refs. [16,18].

processes that occur closer to the metal centre (e.g. ene and aldol type reactions). Further research in this direction will be reported in due course.

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 signals of the deuterated solvents employed. The combustion analyses were performed by Mrs. Jacob on a CHNS-932 LECO analyzer in our department.

3.1. Cp^EK

A solution of Cp^EH [6] (0.74 g, 3.2 mmol) in THF (30 ml) was charged with a piece of potassium metal (0.44 g, 11 mmol) and stirred at room temperature for 2 days, after which evolution of dihydrogen had ceased. Excess potassium was removed and the solution decanted, leaving a quantitative amount of Cp^EK as a very air-sensitive white solid. Anal. Found: C, 71.4; H, 7.4; N, 5.4. C₁₆H₂₀KN Calc.: C, 72.4; H, 7.6; N, 5.3%. The compound is virtually insoluble in all common organic solvents. Reaction with CD₃OD affords the ring perdeuterated derivative Cp^EH-*d*⁵ (identified by ¹H and ¹³C NMR).

3.2. Cp^ELi

To a solution of Cp^EH [6] (1.3 g, 5.7 mmol) in pentane (30 ml) was slowly added n-butyllithium (4 ml, 1.65 M in pentane). An exothermic reaction ensued, and

after stirring for 15 min at room temperature the clear solution was allowed to stand overnight at -80°C , precipitating $\text{Cp}^{\text{E}}\text{Li}$ as a very air-sensitive white solid (1.0 g, 75%) that was characterized by its ^1H and ^{13}C NMR spectra in C_6D_6 (Tables 1 and 2). Addition of CD_3OD to such a solution leads to the immediate formation of the monodeuterated $\text{Cp}^{\text{E}}\text{H-d}_1$ (NMR).

3.3. $\text{Cp}^{\text{E}}\text{Ti}$

A solution of KOH (0.30 g, 5.4 mmol) in water (15 ml) was degassed, after which TINO_3 (0.55 g, 2.1 mmol) and $\text{Cp}^{\text{E}}\text{H}$ (0.47 g, 2.1 mmol) were added at room temperature. The initially two-phased solution gradually became homogeneous with simultaneous deposition of a white solid within a few hours. The aqueous solution was then decanted and the remainder was washed a few times with ether and dried in vacuo. Yield 0.20 g (20%). Anal. Found: C, 42.2; H, 4.0; N, 3.6. $\text{C}_{16}\text{H}_{20}\text{NTi}$ Calc.: C, 42.6; H, 4.5; N, 3.1%.

3.4. $\text{Cp}^{\text{E}}\text{AlCl}_2$

To a solution of $\text{Cp}^{\text{E}}\text{H}$ (1.65 g, 7.3 mmol) in diethyl ether (30 ml) was added $^n\text{BuLi}$ (10.5 ml of a 0.78 M solution in hexane). The resulting suspension of $\text{Cp}^{\text{E}}\text{Li}$ was cooled to -50°C , whereupon AlCl_3 (1.00 g, 7.5 mmol) was added. A white suspension developed that was stirred overnight at room temperature. After solvents were evaporated, the residue was extracted with toluene. Concentrating and chilling of the toluene extracts afforded pure $\text{Cp}^{\text{E}}\text{AlCl}_2$ as white, air-sensitive needles (1.70 g, 75%). Anal. Found: C, 57.9; H, 5.7; N, 4.3%. $\text{C}_{16}\text{H}_{20}\text{AlCl}_2\text{N}$. Calc.: C, 59.3; H, 6.2; N, 4.3%.

3.5. $\text{Cp}^{\text{E}}\text{SiMe}_3$

To a solution of $\text{Cp}^{\text{E}}\text{H}$ (2.55 g, 11.7 mmol) in toluene (30 ml) was added $^n\text{BuLi}$ (15 ml of a 0.95 M solution in hexane) at room temperature. The resulting clear yellow solution was stirred for 15 min, upon which Me_3SiCl (20 ml of a 1.0 M solution in THF) was added. The resulting suspension was stirred for 3 h at room temperature and then evaporated to dryness. The residue was extracted several times with pentane. Filtration and removal of pentane in vacuo left an orange-brown oil (3.6 g, ca. 100%) that was used as such for further operations.

3.6. $\text{Cp}^{\text{E}}\text{TiCl}_3$

To a cooled (-50°C) solution of crude $\text{Cp}^{\text{E}}\text{SiMe}_3$ (0.9 g, ca. 3.0 mmol) in toluene (20 ml) was added TiCl_4 (0.4 ml, 3.7 mmol). A dark-coloured suspension was formed, which was stirred for 3 h at room temperature. This suspension was filtered hot, and then concen-

trated and chilled to afford a yellowish solid. This solid was washed several times with pentane, leaving $\text{Cp}^{\text{E}}\text{TiCl}_3$ as an extremely air-sensitive solid (0.40 g, 35%). Anal. Found: C, 50.4; H, 6.0; N, 4.1%. $\text{C}_{16}\text{H}_{20}\text{Cl}_3\text{NTi}$ Calc.: C, 50.5; H, 5.3; N, 3.7%.

Exposure to moisture affords $[\text{Cp}^{\text{E}}\text{TiCl}_2(\text{HCl})]_2-(\mu\text{-O})$ (identified by ^1H and ^{13}C NMR and by comparison of these data with those of $[\text{Cp}^{\text{E}}\text{TiCl}_2(\text{HCl})]_2(\mu\text{-O})$ [12]).

Further exposure to moisture or reaction of $\text{Cp}^{\text{E}}\text{TiCl}_3$ with CD_3OD affords $\text{Cp}^{\text{E}}\text{H}\cdot\text{HCl}$ (identified by NMR, see Tables 1 and 2).

3.7. $\text{Cp}^{\text{E}}\text{ZrCl}_3$

To a cooled (-80°C) suspension of ZrCl_4 (0.48 g, 2.1 mmol) in CH_2Cl_2 was added $\text{Cp}^{\text{E}}\text{SiMe}_3$ (0.45 g, ca. 1.5 mmol). The resulting suspension was stirred at room temperature overnight and subsequently filtered. Evaporation of solvent left 0.50 g of a yellowish substance, which after washing with pentane affords pure $\text{Cp}^{\text{E}}\text{ZrCl}_3$ as a white solid. Yield 0.33 g (0.78 mmol, ca. 50%). Anal. Found: C, 45.0; H, 4.9; N, 3.4. $\text{C}_{16}\text{H}_{20}\text{Cl}_3\text{NZr}$ Calc.: C, 45.3; H, 4.8; N, 3.3%.

3.8. Attempted synthesis of $\text{Cp}^{\text{E}}_2\text{ZrCl}_2$

To a solution of $\text{Cp}^{\text{E}}\text{H}$ (1.12 g, 4.9 mmol) in 30 ml of THF was added $^n\text{BuLi}$ (7.5 ml of a 0.78 M solution in hexane) and $\text{ZrCl}_4(\text{THF})_2$ (0.91 g, 2.4 mmol) a few minutes later. The almost clear solution was stirred overnight at room temperature, the solvents were removed in vacuo and the residue extracted with toluene. The toluene extracts were evaporated to dryness in vacuo, affording an orange oily residue. Washing with pentane eventually left a white solid (1.2 g). Anal. Found: C, 58.9; H, 6.3; N, 4.4; Cl, 11.4. $\text{C}_{32}\text{H}_{40}\text{Cl}_2\text{Zr}$. Calc.: C, 62.5; H, 6.5; N, 4.6; Cl, 11.6%. A flame test showed that the substance was free of residual lithium. The substance is perfectly soluble in CDCl_3 and CD_3OD , but the ^1H NMR spectra in these solvents show a very complicated pattern that could not be interpreted.

3.9. Catalytic formation of 2-formyl-2-methyl-bicyclo-[2.2.1]hept-5-ene

A solution of $\text{Cp}^{\text{E}}\text{ZrCl}_3$ (0.27 g, 0.64 mmol), methacrolein (1.0 ml, 12 mmol) and cyclopentadiene (2.0 ml, 24 mmol) in CH_2Cl_2 (20 ml) was stirred for 21 h at room temperature. The solution was quenched with a few drops of water, filtered and evaporated to dryness at room temperature, affording 1.52 g of an oily substance which, according to ^1H NMR, consisted of almost pure Diels–Alder product (11 mmol, ca. 90%). ^1H NMR (CDCl_3) *exo* isomer (86% by integration) 0.73

(d, 12.0 Hz, H₃), 0.98 (s, Me), 1.36 (s, H_{7,7'}), 2.22 (dd, 3.8 × 12.0 Hz, H₃), 2.80/2.87 (s, H_{1,4}), 6.08/6.27 (dd, 5.6 × 3.1 Hz, H_{5,6}), 9.67 (s, formyl); *endo* isomer (14%, not all signals were resolved and assigned), 1.27 (s, Me), 1.62 (m), 1.74 (dd, 12.1 × 2.3 Hz), 2.69 (s), 6.07 (m), 6.16 (dd, 5.5 × 3.1 Hz), 9.38 (s, formyl).

The crude reaction product was dissolved in THF (10 ml) and treated with (1*S*)-1-phenylethylamine (1.44 ml, 11.2 mol) overnight. Subsequent evaporation of solvent afforded an oil which, according to ¹H NMR, consisted of almost pure imine derivative. ¹H NMR (CDCl₃), two *exo* diastereomers with equal abundance: 0.82/0.84 (dd, 11.6 × 2.6 Hz, H₃), 1.00/1.01 (s, Me), 1.46/1.47 (d, 6.6 Hz, H₃CCH(Ph)N=), 2.39/2.40 (dd, 11.6 × 3.8 Hz, H₃), 2.66/2.69 (s, H₁), 2.83 (s, H₄), 4.32 (q, 6.6 Hz, MeCH(Ph)N=), 6.10/6.23 (m, H_{5,6}), 7.2–7.35 (m, Ph), 7.82 (s, N=C(H)-); most signals of the two *endo* diastereomers were hidden, except for the Me group at 1.34/1.36 ppm, showing less than 5% intensity difference, and the imine hydrogen at 7.58 ppm.

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