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Monocyclopentadienyl and mono(2-methoxyethylcyclopentadienyl) zirconium methyl complexes☆

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Dedicated to Professor Dr Karl-Heinz Thiele on the occasion of his 70th birthday

Abstract

The reactions of $(\eta^5\text{-Cp})ZrCl_3(DME)$ and $(\eta^5{:}\eta^1\text{-Cp}^\circ)ZrCl_3$ ($Cp^\circ = C_5H_4CH_2CH_2OMe$) with 1–2 equivalents of MeLi or MeMgI and THF yield the mono- and dimethyl zirconium complexes $(\eta^5\text{-Cp})ZrCl_{3-x}Me_x(THF)$ and $(\eta^5{:}\eta^1\text{-Cp}^\circ)ZrCl_{3-x}Me_x$ ($x = 1, 2$), respectively. Reaction with three equivalents of MeMgI affords $(\eta^5\text{-Cp})ZrMe_3(THF)$ and $(\eta^5{:}\eta^1\text{-Cp}^\circ)ZrMe_3$. The reaction with three equivalents of MeLi affords $(\eta^5\text{-Cp})_2ZrMe_2$ or $(\eta^5\text{-Cp}^\circ)_2ZrMe_2$ and $ZrMe_4$, as a result of disproportionation. The reaction of $(\eta^5{:}\eta^1\text{-Cp}^\circ)ZrMe_3$ with $B(C_6F_5)_3$ in THF affords the cationic zirconium complex $[(\eta^5{:}\eta^1\text{-Cp}^\circ)ZrMe_2(THF)][MeB(C_6F_5)_3]$. The chloride-bridged complex $[(\eta^5{:}\eta^1\text{-Cp}^\circ)Zr(\mu\text{-Cl})Me_2]_2$ was characterized by single-crystal X-ray crystallography. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Monocyclopentadienyl; Mono zirconium complexes; Dimethyl zirconium complexes

1. Introduction

Dicyclopentadienyl zirconium complexes are well known pre-catalysts for the Ziegler–Natta polymerisation of α-olefins. Cationic methyl derivatives are thought to be the active catalysts after activation of the metallocene with methylalumoxane and these species have therefore been thoroughly investigated [1].

Monocyclopentadienyl zirconium compounds were much less studied with respect to Ziegler–Natta activity, although the increased unsaturation of the metal centre may lead to higher reactivity [2]. Studies on methyl complexes have been confined to ring-substituted cyclopentadienyl zirconium precursors. Thus, all members of the series $(\eta^5\text{-}C_5Me_5)ZrCl_{3-x}Me_x$ ($x = 1$, 2, 3) were synthesized by Bercaw [3]. More recently, several trimethyl complexes of the type $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}R_2]ZrMe_3$ were prepared ($R = {}^t\text{Bu}$ [4], $SiMe_3$ [5], $SiMe_2CH_2PPr^i_2$ [6]). Cationic complexes, e.g. $[(\eta^5\text{-}C_5Me_5)ZrMe_2L_2]^+$, were first reported by Jordan [7]. Surprisingly, there is almost no information on methyl zirconium complexes bearing the parent cyclopentadienyl ligand. A recent publication by Negishi claims the synthesis of $(\eta^5\text{-Cp})ZrMe_3$, but without much detail [8].

We therefore set out to investigate the reaction of $(\eta^5\text{-Cp})ZrCl_3(DME)$ [9] with methylating agents. As the resulting methyl zirconium derivatives appeared to be thermally sensitive and have some stability only in ethereal solvents (vide infra), we also studied the stabilizing influence of an internal ether linkage attached to the cyclopentadienyl ring. Therefore, our recently reported zirconium complex $(\eta^5{:}\eta^1\text{-Cp}^\circ)ZrCl_3$ ($Cp^\circ = C_5H_4CH_2CH_2OMe$) [10] was also used as a starting compound. With these two precursors we were able to isolate and/or characterize all possible combinations of

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(η^5-Cp)$ZrCl_{3-x}Me_x$(THF) and (η^5:η^1-Cp°)$ZrCl_{3-x}Me_x$ ($x = 1, 2, 3$). In addition, the cationic derivative $[(\eta^5:\eta^1\text{-Cp°})ZrMe_2(THF)]^+$ could be generated and identified.

2. Results and discussion

In the first instance, a suspension of (η^5-Cp)$ZrCl_3$(DME) or (η^5:η^1-Cp°)$ZrCl_3$ in THF held at -20 and -30°C was treated with increasing amounts of a solution of either MeLi or MeMgI in diethyl ether. Samples were taken regularly, evaporated to dryness, and the residue was extracted into C_6D_6 or THF-d_8 and analyzed as quickly as possible by ^{1}H- and ^{13}C-NMR at room temperature (Tables 1 and 2). However, solutions measured in C_6D_6 did not reveal any detectable Cp compounds, and the NMR spectra had to be run in THF-d_8 in order to detect any methyl zirconium complexes. Apparently, the coordination of THF is essential for their stability, but even in this solvent all compounds of the type (η^5-Cp)$ZrCl_{3-x}Me_x$(THF) have a lifetime of only a few hours at room temperature. In contrast, methyl zirconium derivatives containing the Cp° ligand turned out to be much more stable in both C_6D_6 and THF-d_8.

2.1. Reaction of (η^5-Cp)$ZrCl_3$(DME) and (η^5:η^1-Cp°)$ZrCl_3$ with 1–2 equivalents of MeLi and MeMgI

The reaction of (η^5-Cp)$ZrCl_3$(DME) with one equivalent of MeLi or MeMgI yields a mixture of two air-sensitive compounds: (η^5-Cp)$ZrCl_2Me$(THF) (**1**) and (η^5-Cp)$ZrClMe_2$(THF) (**2**), leaving behind some of the starting compound (Scheme 1). Similarly, (η^5:η^1-Cp°)$ZrCl_3$ yields a mixture of (η^5:η^1-Cp°)$ZrCl_2Me$ (**3**) and (η^5:η^1-Cp°)$ZrClMe_2$ (**4**) (Scheme 2). Therefore, the monomethyl compounds **1** and **3** could not be isolated as pure compounds. In contrast, the use of exactly two equivalents of MeLi or MeMgI affords pure (η^5-Cp)$ZrClMe_2$(THF) (**2**) and (η^5:η^1-Cp°)$ZrClMe_2$ (**4**), respectively (Schemes 1 and 2). Apparently, the rate of formation of the dimethyl derivative is similar to that of the monomethyl derivative, whereas formation of a trimethyl compound (vide infra) is much slower. The solubility of the complexes increases considerably the more chlorides get substituted for by methyl groups.

The compounds were identified by their ^{1}H- and ^{13}C-NMR spectra (Tables 1 and 2); Cp:Me ratios were obtained by integration of the respective ^{1}H signals. Because of its short lifetime and low solubility, the signal for the Zr–Me group of **1** could not be observed in the ^{13}C-NMR spectrum. There are striking similarities between the NMR data of **1** and **3**, and between those of **2** and **4**, indicating close structural similarities. Thus, the data for the methyl groups of **2** in THF-d_8 (δ_H 0.00, δ_C 41.6 ppm) may be compared with those in **4** (δ_H 0.03, δ_C 41.4 ppm). For the Cp° complexes **3** and **4**, the low field ^{13}C shifts of the CH_2OCH_3 nuclei of the Cp° ligand are indicative of a firm intramolecular coordination of the ether side-arm to zirconium [10]. These low-field shifts decrease the more chlorides are substituted for by methyl groups, which is in accord with an increase of electron density on the zirconium centre and a weakening of the Zr–O bond. In view of the secure coordination of the ether side-arm in **3** and **4**, and the analogies of the NMR spectra with those of the Cp derivatives **1** and **2**, it was concluded that the latter exist as mono(THF) adducts in THF-d_8.

Compound **4** could be isolated in 43% yield and, in addition to the NMR spectra, could be fully characterized by microanalysis and X-ray structure determination (Fig. 1). Selected bond lengths and angles are given in Table 3. The structure of **4** is very similar to that of the starting compound (η^5:η^1-Cp°)$ZrCl_3$ [10a]. Both are composed of six-coordinate chloride-bridged dimers. The Zr–Cl bond lengths in the bridge of **4** are significantly longer than in (η^5:η^1-Cp°)$ZrCl_3$ (*trans*-Cp: 2.681(2) vs. 2.642(2) Å; *trans*-Me(Cl): 2.663(2) vs. 2.562(2) Å), illustrating the higher electron density at the zirconium centre in **4** compared with that in (η^5:η^1-Cp°)$ZrCl_3$. Consequently, the Zr–O bond length in **4** (2.394(7) Å) is also considerably longer than in (η^5:η^1-Cp°)$ZrCl_3$ (2.264(4) Å), whereas the Zr–C(Cp) bond lengths are similar. The two methyl groups are *cis*-positioned (<C–Zr–C 92.9(4)°). The Zr–C bond lengths

Table 1
^{1}H- and ^{13}C-NMR data of the CpZr complexes

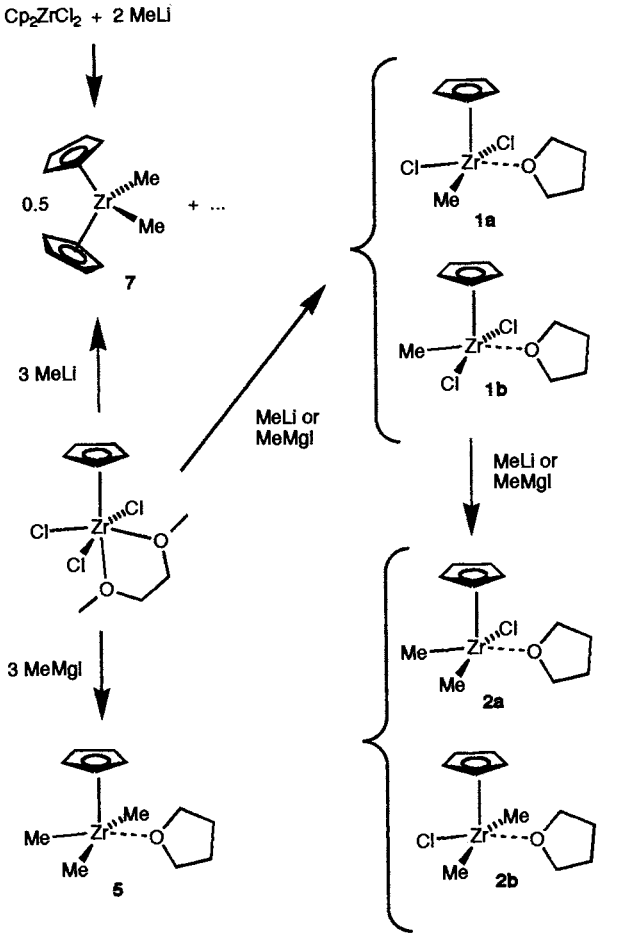
Compound	Solvent	C_5H_5	$ZrCH_3$	C_5H_5	$ZrCH_3$
$CpZrCl_3(THF)_2$	CD_2Cl_2	6.6 (5H)		120.3	
$CpZrCl_2Me$(THF) (**1**)	THF-d_8	6.35 (5H)	0.16 (3H)	116.7	n.o. [a]
$CpZrClMe_2$(THF) (**2**)	THF-d_8	6.25 (5H)	0.00 (6H)	114.2	41.6
$CpZrMe_3$(THF) (**5**)	THF-d_8	6.05 (5H)	−0.34 (9H)	111.3	37.8
Cp_2ZrMe_2 (**7**)	C_6D_6	5.71 (10H)	−0.13 (6H)	110.3	30.0
	THF-d_8	6.09 (10H)	−0.43 (6H)		

[a] n.o., not observed.

Table 2
^{1}H- and ^{13}C-NMR data of the Cp°Zr complexes [a]

Compound	Solvent	C_5H_4	CH_2	CH_2O	OCH_3	$ZrCH_3$	C_5H_4	CH_2	CH_2O	OCH	$ZrCH_3$
Cp°$ZrCl_3$	C_6D_6	6.42 (2H), 6.47 (2H)	1.91 (2H)	3.25 (2H)	3.01 (3H)		117.4, 121.7	26.5	81.4	63.5	
Cp°$ZrCl_2$Me (**3**)	C_6D_6	6.00 (2H), 6.19 (2H)	1.91 (2H)	3.08 (2H)	3.05 (3H)	0.90 (3H)	114.8, 115.8	27.2	79.1	61.5	58.3
Cp°$ZrClMe_2$ (**4**)	C_6D_6	5.82 (2H), 6.09 (2H)	1.89 (2H)	2.88 (2H)	3.02 (3H)	0.60 (6H)	110.9, 114.3	27.5	78.0	60.6	44.2(118)
	THF-d_8	6.24 (2H), 6.26 (2H)	2.73 (2H)	3.84 (2H)	3.50 (3H)	0.03 (6H)	113.7, 114.1	28.7	78.4	60.9	41.4
THF-d_8	(−80°C)	6.13 (4H)	2.69 (2H)	3.63 (2H)	3.34 (3H)	−0.34 (6H)	113.7, 116.1	29.2	76.9	60.4	36.2
Cp°$ZrMe_3$ (**6**)	C_6D_6	5.83 (2H), 6.09 (2H)	2.03 (2H)	2.96 (2H)	2.91 (3H)	0.43 (9H)	108.2, 112.6	27.8	78.2	59.9	40.2
	THF-d_8	6.09 (4H)	2.70 (2H)	3.79 (2H)	3.47 (3H)	−0.17 (9H)	110.2, 112.2	29.3	78.1	60.1	37.8
$Cp^{\circ}_2ZrMe_2$ (**8**)	C_6D_6	5.51 (4H), 5.77 (4H)	2.66 (4H)	3.35 (4H)	3.10 (6H)	−0.15 (6H)	108.1, 111.6	30.8	73.7	58.3	30.5
	THF-d_8	5.84 (4H), 5.97 (4H)	2.68 (4H)	3.50 (4H)	3.28 (6H)	−0.50 (6H)	108.9, 112.4	29.8	74.3	58.5	31.3
$[Cp^{\circ}ZrMe_2(THF)]^+[MeB(C_6F_5)_3]^-$ [b] (**13**)	THF-d_8	6.32 (4H), 6.48 (4H)	2.80 (2H)	3.60 (2H)	4.11 (3H)	0.04 (6H)	115.0, 117.5	27.3	82.6	62.5	42.1(115)

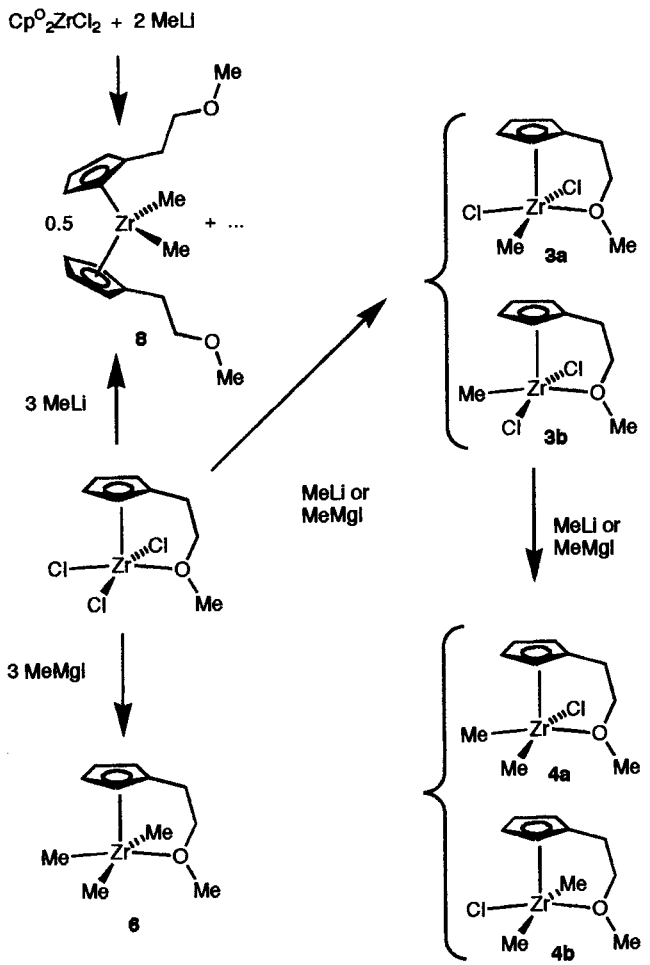
[a] $^{1}J_{CH}$ in parentheses; n.o., not observed.
[b] $[MeB(C_6F_5)_3]^-$: $\delta_H = 0.51$ (Me); $\delta_C = 10.4$ (br), 137.1 (d, $J_{CF} = 245$), 138.1 (d, $J_{CF} = 241$), 149.2 (d, $J_{CF} = 239$).



Scheme 1. All reactions in THF, −30°C to r.t.; MeLi or MeMgI added as ether solutions.

(2.261(11) and 2.298(9) Å) are unexceptional and may be compared with those in $(\eta^5\text{-Cp})_2ZrMe_2$ (2.273(5) and 2.280(5) Å) [11].

As for dimeric $(\eta^5{:}\eta^1\text{-Cp}^\circ)ZrCl_3$ the chloride bridges in **4** (and **1**–**3**) will be very weak, and in solution the compound is largely monomeric. It was noted that there are two possible structural isomers for the monomer depending on the relative positions of the chloride and methyl ligands; one has C_s symmetry (**1b**–**4b**), the other has no element of symmetry (**1a**–**4a**). The NMR spectra of **1**–**4** appear to be consistent with symmetric structures. Thus, the presence of only one signal for the two methyl groups in **4** suggests that these groups are *trans*-positioned, which however is in conflict with the solid state structure of **4**. It is therefore concluded that **4**, and **1**–**3** also, are highly dynamic in solution with rapid site exchange of chloride and methyl groups. The NMR spectrum of **4** in THF-d_8 at −80°C shows a gradual shift of the Zr–Me signal (Table 2), however, without decoalescence. The dynamical process obviously has a low barrier of activation. Several mechanisms are possible. One involves decomplexation of the ether side-chain in the Cp° derivatives (or THF in the Cp derivatives). Although this would yield a highly unsaturated 12e tetrahedral intermediate, stable monomeric compounds of the type $(\eta^5\text{-}C_5R_5)ZrCl_3$ are known [12]. Another mechanism involves a Berry type pseudorotation with trigonal bipyramidal intermediates. Finally, and in view of the dimeric solid state structure of **4**, intermolecular exchange can also not be excluded.



Scheme 2. All reactions in THF, −30°C to r.t.; MeLi or MeMgI added as ether solutions.

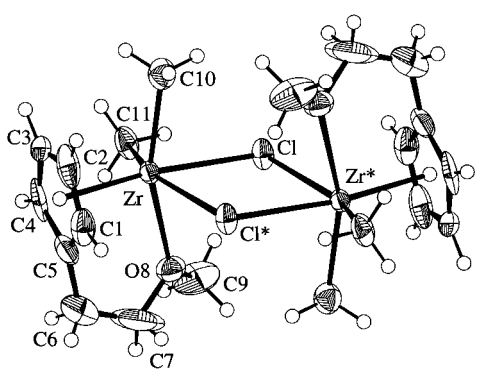
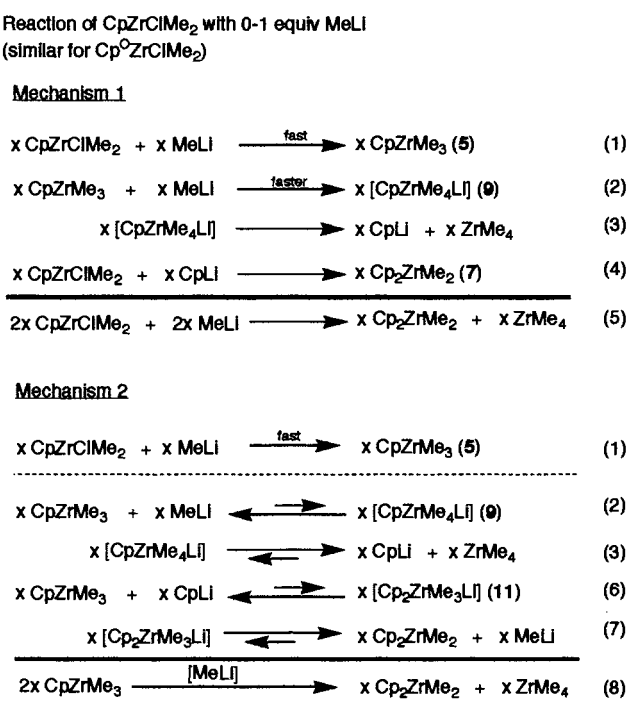


Fig. 1. Molecular structure of **4**.

Table 3
Selected bond distances (Å) and bond angles (°) for [(η^5:η^1-Cp°)Zr(μ-Cl)Me_2]$_2$ (**4**)

Bond distances			
Zr–C(10)	2.261(11)	O(8)–C(7)	1.41(2)
Zr–C(11)	2.298(9)	O(8)–C(9)	1.431(13)
Zr–Cl (*trans*-C(11))	2.663(2)	C(5)–C(6)	1.45(2)
Zr–Cl*(*trans*-Cp)	2.681(2)	C(6)–C(7)	1.36(2)
Zr–O(8)	2.394(7)		
Bond angles			
Cl–Zr–Cl*	73.10(8)	O(8)–Zr–C(11)	83.2(3)
Cl–Zr–O(8)	80.4(2)	C(10)–Zr–C(11)	92.9(4)
Cl–Zr–C(10)	94.4(3)	Zr–Cl–Zr*	106.90(8)
Cl–Zr–C(11)	150.9(3)	Zr–O(8)–C(7)	117.2(9)
Cl*–Zr–O(8)	78.2(2)	Zr–O(8)–C(9)	126.6(7)
Cl*–Zr–C(10)	81.8(3)	C(5)–C(6)–C(7)	116.7(11)
Cl*–Zr–C(11)	80.1(2)	O(8)–C(7)–C(6)	117.4(13)
O(8)–Zr–C(10)	160.0(3)	C(7)–O(8)–C(9)	112.3(11)



Scheme 3.

2.2. Reaction of (η^5-Cp)$ZrCl_3$(DME) and (η^5:η^1-Cp°)$ZrCl_3$ with 2–3 equivalents of MeMgI

The reaction of (η^5-Cp)$ZrCl_3$(DME) and (η^5:η^1-Cp°)$ZrCl_3$ with 2–3 equivalents of MeMgI yields the highly air sensitive complexes (η^5-Cp)$ZrMe_3$(THF) (**5**) and (η^5:η^1-Cp°)$ZrMe_3$ (**6**), respectively (Schemes 1 and 2). Again, the Cp derivative **5** slowly decomposes at room temperature, whereas the Cp° derivative **6** could be isolated in 58% yield. The isolated trimethyl complex **6** appears to be much more air sensitive than the mono- and dimethyl precursors **3** and **4**, probably because the former lacks a stabilizing chloride bridge in the solid state.

Although the coordination of THF in **5** will be weaker than in **1** and **2**, it is again essential for its (limited) stability at room temperature. The related complexes (η^5-$C_5H_4SiMe_2R$)ZrR_3(OEt_2) (R = Ph, C_6F_5) decompose when the coordinated ether is removed under high vacuum [13]. It was noticed that despite the formation of methane during the decomposition of **5** (or **1** and **2**), we have no indication that it was attended by the formation of methylene or methylidine derivatives [14].

Although a 2:1 pattern of methyl signals may be expected for **5** and **6**, only one resonance was observed for all three methyl groups, again suggesting rapid site exchange of these ligands around zirconium. Our NMR data for **5** (THF-d_8; Zr–Me: δ_H −0.34; δ_C 37.8 ppm) are somewhat different from those of Negishi (C_6D_6/THF; Zr–Me: δ_H −0.50; δ_C 32.9 ppm), and we think that the latter may have been misinterpreted [8]. This is corroborated by the fact that in our hands **5** cannot be synthesized by the reaction of (η^5-Cp)$ZrCl_3$(DME) with three equivalents of MeLi, as has been claimed by Negishi (vide infra). The ^{13}C chemical shifts for the methyl groups of **5** and **6** may be compared with that in [η^5-C_5H_3-1,3-(^{t}Bu)$_2$]$ZrMe_3$ (δ 45.6 ppm in C_6D_6) [4], [η^5-C_5H_3-1,3-($SiMe_3$)$_2$]$ZrMe_3$ (δ 45.2 ppm in CD_2Cl_2) [5] and [η^5-C_5H_3-1,3-($SiMe_2CH_2PPr^i_2$)$_2$]$ZrMe_3$ (δ 42.7 ppm in C_7D_8) [6].

2.3. Reaction of (η^5-Cp)$ZrCl_3$(DME) and (η^5:η^1-Cp°)$ZrCl_3$ with 2–3 equivalents of MeLi

Remarkably, the reaction of (η^5-Cp)$ZrCl_3$(DME) and (η^5:η^1-Cp°)$ZrCl_3$ with 2–3 equivalents of MeLi, instead of MeMgI, takes a completely different course (one may also start with the dimethyl complexes **2** and **4** and react them with MeLi). While using MeLi we never observed the formation of the trimethyl derivatives **5** or **6**. Instead, the only product to be detected was the metallocene derivative (η^5-Cp)$_2ZrMe_2$ (**7**) or (η^5-Cp°)$_2ZrMe_2$ (**8**) respectively (Schemes 1 and 2), obviously a result of a disproportionation reaction. The identity of the metallocenes was confirmed by an independent synthesis from (η^5-Cp)$_2ZrCl_2$ and (η^5-Cp°)$_2ZrCl_2$ with two equivalents of MeLi.

Two mechanisms can be put forward to explain the formation of these products (Scheme 3). After formation of the dimethyl complexes **2** and **4**, the reaction of more MeLi must lead to the formation of the trimethyl complexes **5** and **6** (Eq. (1) in Scheme 3). The crucial point now is that the trimethyl complexes quickly react with additional MeLi resulting in a fast equilibrium with CpLi (or Cp°Li) and $ZrMe_4$ through the intermediacy of the ate complexes [(η^5-Cp)$ZrMe_4$][$Li(THF)_n$] (**9**) or [(η^5-Cp°)$ZrMe_4$][$Li(THF)_n$] (**10**) (Eqs. (2) and (3)). In the first mechanism, CpLi (or Cp°Li) subsequently reacts with unreacted dimethyl complexes **2** or

4 forming **7** or **8** (Eq. (4)). In the second mechanism CpLi (or Cp°Li) reacts with remaining trimethyl complex **5** or **6** resulting in another fast equilibrium yielding MeLi and **7** or **8**, with the intermediacy of the ate complex $[(\eta^5\text{-Cp})_2ZrMe_3][Li(THF)_n]$ (**11**) or $[(\eta^5\text{-Cp°})_2ZrMe_3][Li(THF)_n]$ (**12**) (Eqs. (6) and (7)). According to the latter mechanism, only catalytic amounts of MeLi are needed to decompose the trimethyl complexes **5** and **6**.

In either mechanism the formation of **7** and **8** should be attended by the equimolar formation of $ZrMe_4$. This compound could not be observed directly; however, it is known that it is stable only up to ca. −15°C and than decomposes with blackening [15]. This blackening of our ether solutions at and above −15°C was indeed observed by us when using 2–3 equivalents of MeLi. This observation suggests that $ZrMe_4$ may indeed have been formed below −15°C, i.e. probably while conducting the reaction at ca. −30°C and moreover that its formation is not a result of disproportionation of **5** or **6** upon raising the temperature.

The second mechanism, as depicted in Scheme 3, is more likely. Thus, equilibria between $(\eta^5\text{-Cp})_2ZrR_2$ and RLi forming $(\eta^5\text{-Cp})ZrR_3$ and CpLi, such as proposed in Eqs. (2) and (3) of Scheme 3, have already been demonstrated [8]. There are no reports on stable zirconate complexes such as **9**/**10** and **11**/**12**, but such species have been suggested as intermediates [8,16]. Moreover, a stable trihydride complex $[(\eta^5\text{-}C_5Me_5)_2ZrH_3]Li$, reminiscent of **11**/**12**, is known [17]. Fryzuk observed that $[P_2Cp]ZrMe_3$ ($[P_2Cp] = \{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2PPr^i_2)_2\}$) decomposes in the presence of catalytic amounts of MeLi [6], suggesting the intermediacy of zirconate complexes similar to **9** and **10**. The disproportionation of $(\eta^5\text{-Cp})[CPh(NSiMe_3)_2]ZrMe_2$ to $(\eta^5\text{-Cp})_2ZrMe_2$ and $(Zr[CPh(NSiMe_3)_2]_2Me_2)$ by catalytic amounts of MeLi might proceed similarly [18].

2.4. Cationic complexes

The reaction of $(\eta^5{:}\eta^1\text{-Cp°})ZrMe_3$ (**6**) with $B(C_6F_5)_3$ affords the cationic complex $[(\eta^5{:}\eta^1\text{-Cp°})ZrMe_2(THF)][MeB(C_6F_5)_3]$ (**13**) (Scheme 4). Its structure is probably similar to that of $[(\eta^5\text{-}C_5Me_5)ZrMe_2(THF)_2][BPh_4]$ published by Jordan [7]. The ^{13}C signals of the CH_2OMe moiety of the Cp° ligand shift downfield compared with those of the starting compound **6**, indicating a stronger Zr–O bond. Interestingly, complex **13** is fluctional with respect to site-exchange of the methyl groups, since only one signal was observed, whereas two signals may have been expected. The ^{13}C resonance of the methyl group (δ 42.1 ppm with $J_{CH} = 115$ Hz) in **13** is close to the value of Jordan's complex (δ 50.5 ppm with $J_{CH} = 117$ Hz).

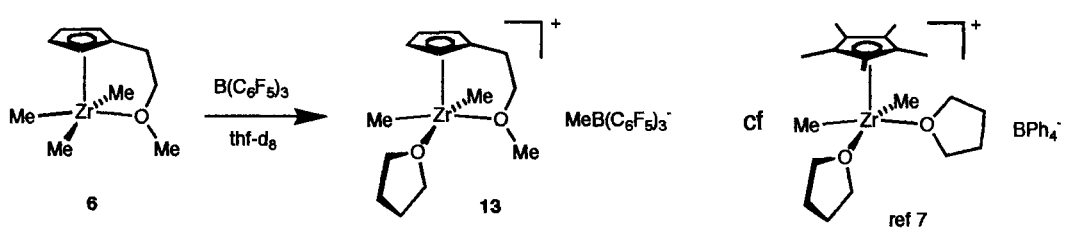
Upon activation with MAO, the complex $(\eta^5{:}\eta^1\text{-Cp°})ZrCl_3$ is a poor catalyst for the polymerisation of ethene [10a]. Complexes like **13** are reminiscent of the catalytically active species. The strong coordination of the side-chain in the cation **13** may explain the low activity, as it probably saturates the zirconium centre too much preventing facile docking of olefins. Another explanation may be the aggregation of these open monoCp systems.

3. Conclusions

We could demonstrate for the first time the existence of all members of the series $(\eta^5\text{-Cp})ZrCl_{3-x}Me_x(THF)$ [$x = 1$ (**1**), 2 (**2**), 3 (**5**)]. All compounds have a lifetime of only a few hours in ethereal solvents. Decomposition is attended by formation of methane (ethane was not detected), but we have no evidence for, nor can we exclude the formation of zirconium methylene or methylidine species.

In contrast to the Cp derivatives, the analogous Cp° derivatives $(\eta^5\text{-Cp°})ZrCl_{3-x}Me_x$ [$x = 1$ (**3**), 2 (**4**), 3 (**6**)] are all thermally stable solids at room temperature. This demonstrates the powerful stabilizing effect of the internal ether side-chain in these compounds.

The trimethyl compounds **5** and **6** can only be synthesized by using the Grignard reagent, the reaction with MeLi results in disproportionation with formation of the metallocene complexes **7** and **8**. This disproportionation (Scheme 3) seems to be limited to those cyclopentadienyl zirconium derivatives that have not more than one ring substituent. This is concluded from the fact that the trimethyl zirconium compounds $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]ZrMe_3$ [5] and $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}$



Scheme 4.

$(SiMe_2CH_2PPr^i_2)_2]ZrMe_3$ [6] can indeed be synthesized by using the lithium methylating reagent. It seems possible that equilibria of these compounds with excess MeLi, affording Cp′Li and $ZrMe_4$ (cf. Eqs. (2) and (3) in Scheme 3), do occur, but that steric hindrance prevents the formation of the zirconate complexes Cp'_2ZrMe_3Li that would lead to the formation of the metallocenes (cf. Eq. (6) in Scheme 3).

4. Experimental

All manipulations were conducted in Schlenk glassware 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 ^{1}H-NMR spectra were referenced to the residual ^{1}H signals of the deuterated solvents employed. The starting compounds (η^5-Cp)$ZrCl_3$(DME) [9a], (η^5:η^1-Cp°)$ZrCl_3$ [10a], and (η^5-Cp°)$_2ZrCl_2$ [19] were synthesized according to literature procedures.

4.1. Reactions of (η^5-Cp)$ZrCl_3$(DME), (η^5:η^1-Cp°)$ZrCl_3$, (η^5-Cp)$_2ZrCl_2$ and (η^5-Cp°)$_2ZrCl_2$ with MeLi or MeMgI (NMR experiments)

In a typical procedure, a suspension of (η^5:η^1-Cp°)$ZrCl_3$ (0.16 g, 0.5 mmol) in THF (30 ml) was kept between −20 and −30°C. Addition of 0.5 mmol of MeLi (0.32 ml of a 1.55 M solution in diethyl ether) resulted in the formation of a clear yellow solution. A sample (5 ml) was removed and evaporated to dryness. The residue was extracted with C_6D_6 or THF-d_8 and analyzed by ^{1}H- and ^{13}C-NMR at room temperature (r.t.). Then, another equivalent of MeLi (corrected for sample loss) was added and analyzed by the same procedure. The reactions with (η^5-Cp)$ZrCl_3$(DME), (η^5-Cp)$_2ZrCl_2$ and (η^5-Cp°)$_2ZrCl_2$ or with MeMgI (as an 1–2 M solution in diethyl ether) were investigated similarly.

4.2. Preparation of (η^5:η^1-Cp°)$ZrClMe_2$ (4)

To a cooled solution (−80°C) of (η^5:η^1-Cp°)$ZrCl_3$ (0.8 g, 2.5 mmol) in diethyl ether (50 ml) was added 3 ml of a 1.71 M solution of MeLi (5.13 mmol) in diethyl ether. The solution was stirred for 15 min and then allowed to warm to r.t. The solvent was removed in vacuo. The residue was extracted with toluene (20 ml), filtered, after which 20 ml of pentane was added. At 0°C colourless crystals of (η^5:η^1-Cp°)$ZrClMe_2$ precipitated (0.3 g, 1.1 mmol, 43%). Anal. Calc. for $C_{10}H_{17}ClOZr$ ($M = 279.91$): C, 42.91; H, 6.13. Found: C, 42.5; H, 6.1%.

4.3. X-ray structure determination of [(η^5:η^1-Cp°)Zr(μ-Cl)Me_2]$_2$

Formula $C_{20}H_{34}Cl_2O_2Zr_2$, $M = 559.82$, $0.25 \times 0.10 \times 0.10$ mm, $a = 10.685(2)$, $b = 7.732(3)$, $c = 14.901(6)$ Å, $\beta = 108.52(3)°$, $V = 1167.3(7)$ Å^3, $\rho_{calc} = 1.593$ g cm^{-3}, $\mu = 11.33$ cm^{-1}, empirical absorption correction via ψ scan data ($0.765 \leq T \leq 0.895$), $Z = 2$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 2144 reflections collected ($\pm h$, $-k$, $-l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 2057 independent ($R_{int} = 0.082$) and 1175 observed reflections [$I \geq 2\sigma(I)$], 121 refined parameters, $R = 0.056$, $wR^2 = 0.123$, max. residual electron density 0.79 (−0.97) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Data set was collected with an Enraf–Nonius CAD4 diffraktometer, using a sealed tube generator FR590. Programs used: data collection Express, data reduction MOLEN, structure solution SHELXS-86, structure refinement SHELXL-97, graphics DIAMOND.

4.4. Preparation of (η^5:η^1-Cp°)$ZrMe_3$ (6)

To a cooled (−80°C) suspension of (η^5:η^1-Cp°)$ZrCl_3$ (0.64 g, 2.0 mmol) in 50 ml of THF was added 3.5 ml of a 1.72 M solution of MeMgI in diethyl ether (5.8 mmol). The mixture was stirred for 10 min at −80°C, and than stirred another 30 min at ambient temperature. Solvents were removed in vacuo and the white residue was extracted with pentane (2 × 50 ml). Removing the pentane in vacuo afforded a yellowish solid of spectroscopically pure (η^5:η^1-Cp°)$ZrMe_3$ (0.3 g, 1.2 mmol, 58%). The obtained compound was found to be too reactive to do a microanalysis.

4.5. Reaction of 6 with $B(C_6F_5)_3$; formation of [(η^5:η^1-Cp°$ZrMe_2$(THF)][$MeB(C_6F_5)_3$] (13) (NMR experiment)

Approximately 0.15 g of (η^5:η^1-Cp°)$ZrMe_3$ were solved in THF-d_8 and transferred into an NMR tube. Then one equivalent of $B(C_6F_5)_3$ was added and the solution analyzed by ^{1}H- and ^{13}C-NMR.

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