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Reaction of ether and thioether functionalised 1-Alkenes with the cationic permethylzirconocene olefin polymerisation catalyst $[(\eta^5\text{-}C_5Me_5)_2ZrMe]^+$. Molecular structure of the insertion product $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2OEt]^+$ [1]

Erik A. Bijpost, Martin A. Zuideveld, Auke Meetsma, Jan H. Teuben *

Groningen Centre for Catalytic Olefin Polymerisation, Department of Chemistry, University of Groningen, Nijenborgh 4, Groningen, 9747 AG, Netherlands

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Abstract

Reaction of $[(\eta^5\text{-}C_5Me_5)_2ZrMe][MeB(C_6F_5)_3]$ (**1**) with (thio)ether functionalised alkenes: 3-ethoxy-1-propene and 3-(methylthio)-1-propene gives stable insertion products $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2XR][MeB(C_6F_5)_3]$ (**2**: X = O, R = Et; **3**: X = S, R = Me) in which the (thio)ether function is intramolecularly coordinated to zirconium. The molecular structure of **2** shows a regular 1-oxa-2-zirconacyclopentane in an envelope conformation. The metallacycles in **2** and **3** are stable toward further insertion of (functionalised) alkenes and cannot be activated for ethene polymerisation by pre-complexation of the (thio)ether function with strong Lewis acids ($AlCl_3$, $MgCl_2$, $B(C_6F_5)_3$ or $[Ph_3C]^+$). The strong alkylating co-catalyst Me_3Al regenerates complex **1** by exchange of the (thio)ether function for methyl and thus initiates polymerisation of ethene. © 1998 Elsevier Science S.A.

Keywords: Metallocene; Zirconium; Olefins; X-ray structure; Polymerisation; Catalysis

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1. Introduction

Neutral group 3 hydrides $[(\eta^5\text{-}C_5Me_5)_2LnH]_2$ and cationic group 4 alkyls $[(\eta^5\text{-}C_5Me_5)_2ZrR]^+$ are active catalysts for the polymerisation of ethene [1]. An important extension of the scope of catalytic potential of these compounds is the copolymerisation of 1-alkenes with functionalised monomers, since this may result in highly valuable polymers, e.g., with improved adhesive properties, higher affinity for dyes and better compatibility with other polar polymers.

Sometimes allylic hydrogen chain transfer [2] frustrates polymerisation of higher olefins. More important for olefins with polar functions is catalyst deactivation by C–X activation (X = heteroatom). It is also possible that insertion of the functionalised alkene leads to intra- or intermolecular coordination of the polar function to the metal centre to give stable intermediates that subsequently obstruct polymerisation.

Rapid splitting of C–X bonds (X = heteroatom) by early transition metal complexes to yield stable M–X bond containing species is well-established [2,3]. Our group has shown that organolanthanide hydrides $[(\eta^5\text{-}C_5Me_5)_2LnH]_2$ cleave 3-alkoxy-1-propenes to form alkoxides $[(\eta^5\text{-}C_5Me_5)_2LnOR]$ and propene [2]. With sulphur functionalised olefins, e.g., 3-(methylthio)-1-propene C–X activation was not observed but the alkene was neither oligomerised nor polymerised. Possibly, intramolecular coordination of the sulphur atom after insertion of the olefin into the Ln–H bond gives a stable five-membered metallacycle, unable to undergo further insertion.

Kesti et al. have reported that 1-alkenes containing a bulky polar functionality (*tert*-butyldimethylsilyloxy, di-isopropylamine) can be polymerised using $[(\eta^5\text{-}C_5Me_5)_2ZrMe]^+$ as a catalyst [4]. Interestingly, monomers with sterically less demanding polar substituents cannot be polymerised. Piers et al. have studied

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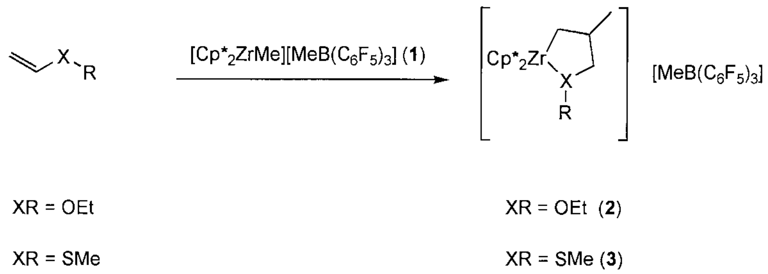
* Corresponding author. E-mail: teuben@chem.rug.nl.

[1] Dedicated to Professor Peter M. Maitlis on the occasion of his 65th birthday.



Scheme 1. Reaction of complex **1** with 3-functionalized-propenes.

catalytic cyclization of various functionalised dialkenes with scandocene compounds [5]. They report that cyclization of diallylether is not possible and suggest that a stable 1-oxa-2-scandacyclopentane has been formed. [2]

We decided to explore the potentially catalytic system formed by the cationic group 4 complex $[(\eta^5\text{-}C_5Me_5)_2ZrMe][MeB(C_6F_5)_3]$ (**1**) [6], (which is isoelectronic with $[(\eta^5\text{-}C_5Me_5)_2LnR]$) and (thio)ether functionalised terminal olefins to probe it for homo- and co-polymerisation properties and to study fundamental aspects of the interaction of the olefins with the metal centre.

2. Results and discussion

Reaction of $[(\eta^5\text{-}C_5Me_5)_2ZrMe][MeB(C_6F_5)_3]$ (**1**) with the functionalised 1-propenes, $CH_2=CHCH_2XR$ ($X=O$, $R=Et$; $X=S$, $R=Me$) was investigated in toluene with the reagents in 1:1 ratio at room temperature on preparative scale. Stable products $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)XR][MeB(C_6F_5)_3]$ were isolated. It turned out that one single alkene insertion into the Zr–Me bond had occurred, followed by intramolecular coordination of the heteroatom to zirconium to form 1-oxa(thia)-2-zirconacyclopentanes $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2OEt][MeB(C_6F_5)_3]$ (**2**) and $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2SMe][MeB(C_6F_5)_3]$ (**3**) (Scheme 1). Remarkably, neither C–X activation nor allylic C–H activation was observed, even when heating the reaction mixtures for prolonged times at 100°C.

The metallacycles are stable at $-20°C$ in diethylether and pentane under nitrogen for months. They slowly decompose in dichloromethane-d_2 (room temperature) with release of isobutylethylether (**2**) and isobutylmethylsulfide (**3**), respectively [7]. [3] Methanolysis of **2** and **3** shows (GC-MS), in addition to C_5Me_5H and C_6F_5H [4], the hydrolysed alkyl ligands as isobutylethylether (from **2**) and isobutylmethylsulfide (from **3**) as expected.

To determine the exact bonding of the inserted functionalised alkene in $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2OEt][MeB(C_6F_5)_3]$ (**2**), a single crystal X-ray diffraction study was undertaken. An *ORTEP* drawing of the molecule is depicted in Fig. 1. Selected bond lengths and bond angles are given in Table 1.

The C_5Me_5 ligands are η^5-coordinated to zirconium as normally is observed in bent sandwich metallocene compounds [8]. The Cp(centroid)–Zr–Cp(centroid) angle (137.5°) and Zr–C_{ring} distances (2.532(9) Å av) are close to those found in **1** (136.6° and 2.537 Å, respectively) [6]. The long Zr · · · Me(B) and Zr · · · F distances (5.114 Å or longer) indicate that there is no direct interaction between cation and anion. The Zr–C23 bond (2.297(12) Å) is longer than the corresponding Zr–C bond (2.223 Å) in **1** [6]. The strong stabilisation of the Zr centre by the co-ordinating oxygen atom causes the metal centre in **2** to be less electron deficient than in **1**, resulting in a longer Zr–C bond. The dative Zr–O bond (2.259(6) Å) is longer than the ionic Zr–O bond (2.008 Å) in the neutral compound $[(\eta^5\text{-}C_5Me_5)_2Zr(CH_2CH_2CH_2CH_2O)]$ [9], and also longer than the dative Zr–O bond (2.122 Å) in $[(\eta^5\text{-}C_5H_5)_2ZrMe(THF)][BPh_4]$ [10,11]. The atoms C21, C23, O and Zr are located in a plane. Atom C22 is bent away from that plane, giving the metallacycle a stable envelope conformation [12]. [5]

Complexes **2** and **3** are inactive toward ethene, propene, 1-hexene and 3-functionalised-1-propenes (excess of olefin, gases at 1 atm, CD_2Cl_2 or C_6D_5Br, 25–100°C). Neither oligomerisation nor polymerisation of the olefins was observed. This indicates that in experiments to (homo- or co-)polymerise 3-functiona-

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[2] Although formally not correct, we propose here to call the cyclic products, containing an alkyl fragment with an M–C bond and simultaneously intramolecularly coordinated through a dative M–X bond, metallacycles.

[3] Isobutylethylether (**2a**) and isobutylmethylsulfide (**3a**) have been formed by hydrogen abstraction from a methyl substituent of a cyclopentadienyl ligand by a Zr–C bond.

[4] C_5Me_5H and C_6F_5H are formed during hydrolysis of $[(\eta^5\text{-}C_5Me_5)_2ZrR]^+$ and $[MeB(C_6F_5)_3]^-$, respectively.

[5] The stability of analogous organic compounds has been well-documented.

lised-1-propenes using **1** as catalyst, the formation of a 1-oxa(thia)-2-zirconacyclopentane will be the main deactivation pathway. This has been confirmed under catalytic conditions in reactions between **1** and 3-(thio)ether functionalised 1-propenes (1:200 ratio, in benzene, bromobenzene or toluene, 25–100°C, 5 days). After quenching the reaction mixtures with methanol the only products found were, in addition to the catalyst residues C_5Me_5H and C_6F_5H [2], unreacted alkene and isobutylethylether (with **2**) and isobutylmethylsulfide (with **3**). The latter in about 0.5% of the initial amount of olefin used, i.e., as expected for only one insertion per metal centre and formation of metallacycle **2** (**3**).

A possibility to activate the dative Zr–X (X = O, S) bond in **2** and **3** is addition of a Lewis acid to compete with zirconium for the (thio)ether function of the inserted alkene and thus induce decomplexation. In this way, a free coordination site on the metal can be created, which should allow coordination and insertion of a 1-alkene into the Zr–C bond of **2** and **3** and thus start polymerisation. The problem is that the Zr(IV) centre is highly electrophilic, which results in a strong dative $Zr \leftarrow X$ bond and in addition also the chelate effect will stabilise this complexation. Therefore, it is reasonable to assume that cleavage of the Zr–X bond can only be accomplished by a strong Lewis acid, such as $MgCl_2$, $AlCl_3$, $B(C_6F_5)_3$ or Ph_3C^+.

To test this hypothesis, **2** (and **3**) was dissolved in dichloromethane-d_2, treated with one equivalent of the Lewis acid of choice and brought under ethene (1 atm, 25°C). The reactions were monitored by ^1H NMR spectroscopy at regular intervals for 24 h. For $B(C_6F_5)_3$ or $MgCl_2$, no ethene consumption was observed. $AlCl_3$ and the extremely strong Lewis acid Ph_3C^+ (added as $[Ph_3C][B(C_6F_5)_4]$) also did not give the expected activation. [6] For all four Lewis acid reactions the regular slow release of isobutylethylether and isobutylmethylsulfide from the zirconacyclopentanes (**2**, **3**) was observed [7].

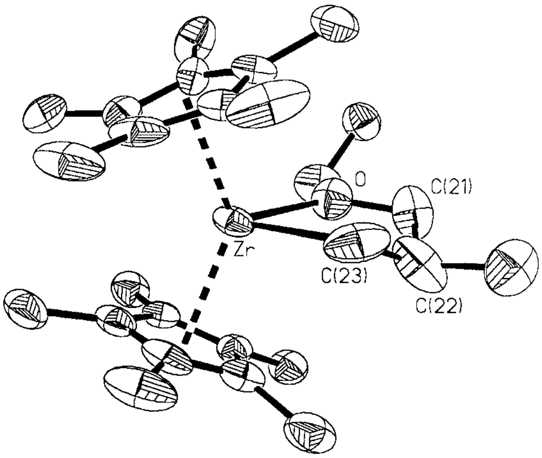

Fig. 1. Perspective *ORTEP* drawing of the molecular structure of complex **2** shown at the 50% probability level. Counter anion $[MeB(C_6F_5)_3]^-$,hydrogen atoms and non-coordinating diethylether have been omitted for clarity.

Table 1
Selected structure data for $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2OEt][MeB(C_6F_5)_3]$ (**2**)

Bonds (Å):			
Zr–O	2.259(6)	C(21)–C(22)	1.501(15)
Zr–C(22)	2.297(12)	C(22)–C(23)	1.510(17)
O–C(21)	1.430(11)	C(22)–C(26)	1.537(16)
O–C(24)	1.447(10)		
Angles (°)			
Zr–O–C(21)	119.9(5)	Zr–C(23)–C(22)	108.5(7)
O–C(21)–C(23)	108.8(8)	C(21)–C(22)–C(26)	110.6(9)
C(21)–C(22)–C(23)	113.5(10)	C(23)–C(22)–C(26)	113.1(9)
O–Zr–C(23)	73.5(3)	Zr–OC–(24)	124.3(5)

Successful activation of **2** and **3** appeared to be possible with Me_3Al. When treated with one equivalent of Me_3Al, ethene polymerisation started immediately. After quenching the reaction mixture with methanol, the soluble fraction contained exclusively isobutylethylether (**2**) or isobutylmethylsulfide (**3**). The insoluble fraction appeared to be polyethene (IR). The yields of isobutylethylether and isobutylmethylsulfide were determined and correspond with the amount of zirconacyclopentane **2** (**3**) started with. This strongly indicates that no functional groups have been incorporated in polyethene.

To find out about the nature of the catalyst activation, an experiment was performed with Me_3Al and **2** in a 1:1 ratio at room temperature in dichloromethane-d_2. After 3 h the characteristic resonances of notable amounts of $[(\eta^5\text{-}C_5Me_5)_2ZrMe]$ $[MeB(C_6F_5)_3]$ (**1**) and broadening of the functionalised alkyl resonances were observed in the ^1H NMR-spectrum. From this, it can be suggested that initiation takes place by transmetallation, i.e., the alkyl(thio)ether fragment is transferred from zirconium to aluminium, [7] yielding Me_2Al–alkyl(thio)ether and the classical cationic $[(\eta^5\text{-}C_5Me_5)_2ZrMe]^+$ complex, the well-known catalyst for the polymerisation of ethene. [2]

Intentional chain transfer of an alkyl ligand from zirconium to aluminium has been utilized by Shaunessy

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[6] Instead the Lewis acids reacted with the Me–B bond of the counter anion $[MeB(C_6F_5)_3]^-$. These reactions have not been investigated further and the identity of the products formed remains to be established. To avoid reaction of Lewis acids with $[MeB(C_6F_5)_3]^-$, a less reactive counter anion, $[B(C_6F_5)_4]^-$, was used. When $AlCl_3$ was added to a solution of $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2OEt][B(C_6F_5)_4]$ (made from $[(\eta^5\text{-}C_5Me_5)_2ZrMe][B(C_6F_5)_4]$ and 3-methoxy-1-propene) in dichloromethane-d_2 and the mixture was brought under ethene (1 atm, 25°C). No ethene was consumed, but also no reaction with the complex anion was observed.

[7] See for example [13].

and Waymouth for cycloalkylation of α,ω-dienes with Me_3Al with and $[(\eta^5\text{-}C_5Me_5)_2ZrMe]^+$ as catalyst [13].

2.1. Concluding remarks

This investigation has shown that oligomerisation and polymerisation of 3-oxygen- and 3-sulphur-functionalised-1-propenes by $[(\eta^5\text{-}C_5Me_5)_2ZrMe][MeB(C_6F_5)_3]$ (**1**) after a smooth initial insertion is prevented by the formation of stable zirconacyclopentanes. The systems appear to be insensitive to typical catalyst deactivation reactions such as C–X and allylic C–H activation. The insertion products $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2XR][MeB(C_6F_5)_3]$ (**2**: X = O, R = Et; **3**: X = S, R = Me) are incapable of effecting alkene polymerisation. Addition of $AlMe_3$ regenerates $[(\eta^5\text{-}C_5Me_5)_2ZrMe][MeB(C_6F_5)_3]$ (**1**) a known polymerisation catalyst. Destabilisation of the metallacyle, e.g., by using longer spacers between the olefinic and the (thio)ether function or by introducing more steric bulk on the (thio)ether part R of the alkene $CH_2=CHXR$ may lead to higher catalytic activity. This is under investigation at the moment.

3. Experimental

3.1. General considerations

All experiments were performed under nitrogen using standard Schlenk, glovebox (Braun MB200) and vacuum line techniques. Solvents and reagents like allymethylether and allymethylsulfide were distilled from Na–K alloy and stored under nitrogen. Dichloromethane-d_2 was stored under nitrogen over 3 Å molecular sieves. $[(\eta^5\text{-}C_5Me_5)_2ZrMe][MeB(C_6F_5)_3]$ was prepared according to a published procedure [14]. Polymerisation grade ethene and propene were supplied by DSM and used without further purification. 1-Hexene (Merck) was filtered over alumina, distilled from CaH_2 and degassed prior to use. NMR spectra were recorded on Varian Gemini 200 (^{19}F, 188 MHz), Varian VXR-300 (^1H, 300 MHz; ^{13}C, 75.4 Mhz) and Varian Unity 500 (^1H, 500 MHz) spectrometers at ambient temperatures. ^1H NMR spectra were assigned via COSY analysis. Chemical shifts for ^1H and ^{13}C NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. ^{19}F NMR shifts are referenced to external α,α,α-trifluorotoluene (−63.8 ppm). GC analyses were carried out on a Hewlett-Packard HP5890-A instrument equipped with a HP-1 30 m × 0.53 mm capillary column. GC-MS measurements were performed on a Ribermag R10-10C equipped with a CP Sil 5 CB 25 m × 0.32 mm capillary column. Elemental analyses were carried out at the Micro-Analytical Department of the University of Groningen. The determinations are the average of at least two

3.2. Synthesis of $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2OEt][MeB(C_6F_5)_3]$ (2)

$[(\eta^5\text{-}C_5Me_5)_2ZrMe][MeB(C_6F_5)_3]$ (**1**) (0.60 g, 0.66 mmol) was dissolved in 30 ml of toluene. 3-Ethoxy-1-propene μ100 (L, 0.83 mmol) was added at once, resulting in an orange oil. After 15 min, the volatiles were removed in vacuo. The orange residue was stripped three times with pentane. The orange solid was dissolved in 30 ml diethylether. The solution was filtered, concentrated and slowly cooled to −20°C to yield 0.49 g (0.50 mmol, 75%) of yellow crystals of **2**. The crystals contain non-coordinating diethylether, which was removed for spectroscopic and elemental analyses by powdering the solid followed by evacuation (< 0.05 mm Hg). ^1H NMR (CD_2Cl_2) δ 3.74 (m, $CH(CH_3)CH_2O$, 1 H), 3.48 (m, CH_3CH_2O, 2H), 3.11 (m, $CH(CH_3)CH_2O$, 1 H), 2.60 (m, $CH(CH_3)CH_2$, 1H), 2.38 (t, $J = 12.8$ Hz, $ZrCH_2CH(CH_3)$, 1 H), 2.03 (s, $C_5(CH_3)_5$, 15H), 1.97 (s, $C_5(CH_3)_5$, 15 H), 1.29 (t, $J = 7.0$ Hz, OCH_2CH_3, 3H), 0.93 (d, $J = 6.4$ Hz, $CH_2CH(CH_3)$, 3H), 0.47 (bs, BCH_3, 3H), 0.12 (bd, $J = 12.4$ Hz, $ZrCH_2CH(CH_3)$, 1H). ^{13}C NMR (CD_2Cl_2) δ 148.8 (d, $J_{CF} = 236$ Hz, C_6F_5), 137.9 (d, $J_{CF} = 241$ Hz, C_6F_5), 136.6 (d, $J_{CF} = 256$ Hz, C_6F_5), 126.0 (s, $C_5(CH_3)_5$), 125.6 (s, $C_5(CH_3)_5$), 83.3 (t, $J_{CH} = 151$ Hz, $CH(CH_3)CH_2O$), 70.1 (t, $J_{CH} = 146$ Hz, OCH_2CH_3), 34.7 (d, $J_{CH} = 115$ Hz, $CH_2CH(CH_3)CH_2$), 22.4 (q, $J_{CH} = 127$ Hz, OCH_2CH_3), 12.6 (q, $J_{CH} = 128$ Hz, $C_5(CH_3)_5$), 11.9 (bs, BCH_3), 11.2 (q, $J_{CH} = 127$ Hz, $CH_2CH(CH_3)CH_2$), 11.0 (q, $J_{CH} = 125$ Hz, $C_5(CH_3)_5$). The $ZrCH_2$ resonance was not assigned due to overlap with other signals in the region $\delta = 70-60$ ppm; for comparison see $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH_3(THF)]^+$, [Ref. [11]]. ^{19}F NMR (CD_2Cl_2) δ-134.94 (d, $J_{FF} = 20.3$ Hz, *o*-F), −167.23 (t, $J_{FF} = 20.3$ Hz, *p*-F), −169.81 (d, $J_{FF} = 18.0$ Hz, *m*-F). Anal. Found: C, 54.35; H, 4.82; Zr, 9.22. Calc. for $C_{45}H_{46}BF_{15}OZr$: C, 54.60; H, 4.68; Zr, 9.22.

3.3. Synthesis of $[(\eta^5\text{-}C_5Me_5)_2ZrCH_2CH(Me)CH_2SMe][MeB(C_6F_5)_3]$ (3)

$[(\eta^5\text{-}C_5Me_5)_2ZrMe][MeB(C_6F_5)_3]$ (**1**) (0.52 g, 0.58 mmol) was dissolved in 20 ml of toluene. 3-Methylthio-1-propene (66 μL, 0.60 mmol) was added at once, resulting in an orange oil. After 15 min, the volatiles were removed in vacuo. The orange residue was stripped with 3 × 10 ml pentane and washed with 2 × 10 ml pentane. The resulting solid was dried in vacuum (0.05 mm Hg) for 30 min to give an orange–yellow powder

(0.26 g, 0.25 mmol, 43%). ^{1}H NMR (CD_2Cl_2) δ 2.86 (m, CH_2S, 2H), 2.72 (m, CH(CH_3), 1H), 2.34 (t, $J = 6.4$ Hz, ZrCH_2CH, 1H), 2.29 (s, SCH_3, 3H), 2.03 (s, $C_5(CH_3)_5$, 15H), 1.98 (s, $C_5(CH_3)_5$, 15H), 0.98 (d, $J = 6.0$ Hz, $CH_2CH(CH_3)$, 3H), 0.47 (bs, BCH_3, 3H), -0.78 (dt, $J = 12.8$ Hz, $J = 2.8$ Hz, ZrCH_2CH, 1H). ^{13}C NMR (CD_2Cl_2) δ 148.6 (d, $J_{CF} = 222$ Hz, C_6F_5), 137.8 (d, $J_{CF} = 242$ Hz, C_6F_5), 136.7 (d, $J_{CF} = 258$ Hz, C_6F_5), 125.7 (s, $C_5(CH_3)_5$), 74.8 (Zr$C$$H_2$), 52.3 ($CH_2$S), 38.7 ($CH_3$S), 28.0 ($C$H($CH_3$)), 17.7 (CH($CH_3$), 12.0 ($C_5(CH_3)_5$), 10.6 (bs, B$CH_3$). ^{19}F NMR ($CD_2Cl_2$) δ-134.91 (d, $J_{FF} = 20.3$ Hz, *o*-F), -166.80 (t, $J_{FF} = 20.3$ Hz, *p*-F), -169.50 (t, $J_{FF} = 19.2$ Hz, *m*-F). Anal. Found: C, 52.58; H, 4.57. Calc. for $C_{44}H_{44}BF_{15}SZr$: C, 53.28; H, 4.47.

3.4. General procedure for attempts to polymerise functionalised 1-alkenes.

In a drybox [(η^5-C_5Me_5)$_2$ZrMe$_2$] (5.1 mg, 13 μmol) (Cp* = η^5-C_5Me_5) and $B(C_6F_5)_3$ (6.5 mg, 13 μmol) were placed in an ampoule and were dissolved in 0.4 ml of bromobenzene or toluene to give a yellow solution. The functionalised alkene (200 equivalents) was then added to the catalyst solution. The ampoule was sealed and placed in a thermostated bath at a fixed temperature (25–100°C). After 5 days, the reaction mixture was quenched with methanol and passed over a column of silica. The resulting mixture was analyzed with GC and GC-MS.

*3.5. General procedure for pre-complexation of **2** and **3** by Lewis acids under ethene atmosphere*

In a drybox 10 μmol of **2**(**3**) and 10 μmol of Lewis acid ($MgCl_2$, $AlCl_3$, $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, $AlMe_3$) were placed in an NMR tube equipped with a Young valve and dissolved in 0.4 ml CD_2Cl_2. The NMR tube was taken out of the drybox and attached to the high-vacuum line. The solution was cooled to -196°C. The tube was evacuated and brought under ethene (~ 1 atm). The mixture was then warmed to room temperature. The reaction was monitored by NMR spectroscopy. When no further reaction was observed, the mixture was quenched with methanol and passed over a column of silica. The soluble organic fraction was analyzed by GC-MS.

*3.6. Crystal data and structure determination of [(η^5-C_5Me_5)$_2$ZrCH$_2$CH(Me)CH$_2$OEt][MeB(C_6F_5)$_3$][$C_4H_{10}O$]$_{0.5}$ (**2**)*

$C_{45}H_{46}BF_{15}OZr[C_4H_{10}O]_{0.5}$, $M_r = 1026.93$, triclinic space group P1 with $a = 10.742(3)$, $b = 14.674(2)$, $c = 14.827(3)$ Å, $\alpha = 95.16(1)°$, $\beta = 102.20(1)°$, $\gamma = 96.42(1)°$, $V = 2254.5(8)$ Å^3, $Z = 2$, $D_x = 1.513$ g cm^{-3}, F(000) = 1050. Besides compound **2**, the crystal also contains non-coordinating diethylether molecules in a 1:2 ratio with the zirconium complex. Data were collected on an Enraf-Nonius CAD-4F diffractometer an on-line liquid nitrogen cooling system [15] at 130 K with Mo $K\bar{\alpha}$($\lambda = 0.71073$ Å). Unit cell parameters and orientation matrix were determined from a least-squares treatment of the SET4 [16] setting angles of 22 high order reflections. The unit cell was identified as triclinic, space group P$\bar{1}$. Reduced cell calculations did not indicate any higher metric lattice symmetry [17] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements [18–20].

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF* [21]. The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (*CRYLSQ*) [22] minimising the function $Q = \sum_h [w(|F_o| - k|F_c|)^2]$. A subsequent difference Fourier synthesis resulted in the location of most of the hydrogen atom positions, but also showed some density which could be correlated to *a*, over an inversion centre, disordered solvent molecule of diethylether. No discrete model could be fitted in this density. The *BYPASS* procedure [23] was used to take into account the electron density in the potential solvent area, which resulted in an electron count of 22.3 in a volume of 207 Å^3 in the unit cell. The hydrogen atoms were included in the refinement riding on their carrier atoms with their positions calculated by using sp^2 or sp^3 hybridisation at the C-atom as appropriate with a fixed C–H distance of 0.98 Å. Final refinement on F_o by full-matrix block-diagonal least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and one overall common thermal displacement factor for the hydrogen atoms converged at $R_F = 0.079$ ($wR = 0.088$); $W = D$ for 6023 reflections with $I > 2.5\,\sigma$(I) and 569 parameters. Unit weights were used throughout the refinement. The peaks in the final difference Fourier map calculations showed residual electron densities of no chemical significance. Neutral atom scattering factors [24] were used and anomalous dispersion factors [25] were included in F_c. All calculations were carried out on the HP9000/735 computer at the University of Groningen with the programme packages *Xtal* [26], *PLATON* [27] (calculation of geometric data) and a locally modified version of the programme *PLUTO* [8] (preparation of illustrations).

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Tables of crystal data, anisotropic thermal displacement parameters, atomic coordinates, bond lengths, bond angles and torsion angles have been deposited at the Cambridge Crystallographic Data Centre.

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