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Chiral Fluorous Dialkoxy-Diamino Zirconium Complexes: Synthesis and Use in Stereospecific Polymerization of 1-Hexene

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Abstract: New catalysts for the isospecific polymerization of 1-hexene based on cationic zirconium complexes incorporating the tetradentate fluorous dialkoxy-diamino ligands $[OC(CF_3)_2CH_2N(Me)(CH_2)_2N(Me)CH_2C(CF_3)_2O]^{2-}$ $[(ON^2NO)^{2-}]$ and $[OC(CF_3)_2CH_2N(Me)(1R,2R\text{-}C_6H_{10})N(Me)CH_2C(CF_3)_2O]^{2-}$ $[(ON^{Cy}NO)^{2-}]$ have been developed. The chiral fluorous diamino-diol $[(ON^{Cy}NO)H_2$, **2**] was prepared by ring-opening of the fluorinated oxirane $(CF_3)_2\overline{COC}H_2$ with (*R*,*R*)-*N*,*N*′-dimethyl-1,2-cyclohexanediamine. Proligand **2** reacts cleanly with $[Zr(CH_2Ph)_4]$ and $[Ti(OiPr)_4]$ precursors to give the corresponding dialkoxy complexes $[Zr(CH_2Ph)_2(ON^{Cy}NO)]$ (**3**) and $[Ti(OiPr)_2(ON^{Cy}NO)]$ (**4**), respectively. An X-ray diffraction study revealed that **3** crystallizes as a 1:1 mixture of two diastereomers (Λ-**3** and Δ-**3**), both of which adopt a distorted octahedral structure with *trans*-O, *cis*-N, and *cis*-CH$_2$Ph ligands. The two diastereomers Λ-**3** and Δ-**3** adopt a C_2-symmetric structure in toluene solution, as established by NMR spectroscopy. Cationic complexes $[Zr(CH_2Ph)(ON^2NO)(THF)_n]^+$ ($n=0$, anion $=[B(C_6F_5)_4]^-$, **5**; $n=1$, anion $=[PhCH_2B(C_6F_5)_3]^-$, **6**) and $[Zr(CH_2Ph)(ON^{Cy}NO)(THF)]^+[PhCH_2B(C_6F_5)_3]^-$ (**7**) were generated from the neutral parent precursors $[Zr(CH_2Ph)_2(ON^2NO)]$ (**H**) and $[Zr(CH_2Ph)_2(ON^{Cy}NO)]$ (**3**), and their possible structures were determined on the basis of ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy and DFT methods. The neutral zirconium complexes **H** and **3** (Λ-**3**/Δ-**3** mixture), when activated with $B(C_6F_5)_3$ or $[Ph_3C]^+[B(C_6F_5)_4]^-$, catalyze the polymerization of 1-hexene with overall activities of up to 4500 kg PH mol Zr^{-1} h^{-1}, to yield isotactic-enriched (up to 74 % *mmmm*) polymers with low-to-moderate molecular weights ($M_w=4800$–47200) and monodisperse molecular-weight distributions ($M_w/M_n=1.17$–1.79).

Keywords: dioxygen ligands · fluorinated ligands · polymerization · tacticity · zirconium

Introduction

The replacement of ubiquitous cyclopentadienyl-type ligands in early transition-metal complexes has been widely investigated in recent years. Hard, electronegative, π-donor ligands such as aryl oxides/alkoxides are attractive because they form strong metal–oxygen bonds that are expected to stabilize the complexes of these electropositive metals.[1] Also, the great variety of these ligands, which can be conveniently obtained from alcohols, allows considerable stereoelectronic variations. Accordingly, Group 4 metal complexes of the type $[MX_2(OZ)_2]$ and $[MX_2(OZZO)]$, where OZ$^-$ and OZZO^{2-} are monoanionic and chelating dianionic ligands, respectively, still attract considerable attention. The stereoselectivity of such octahedral coordination complexes is of considerable interest, in particular, for the generation of chirality at the metal center.[2] Some of these complexes are also extremely performant α-olefin polymerization catalysts.[3] The most successful developments in terms of syn-

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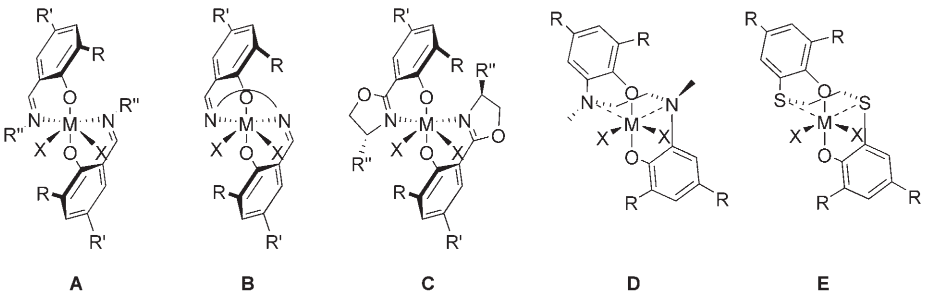
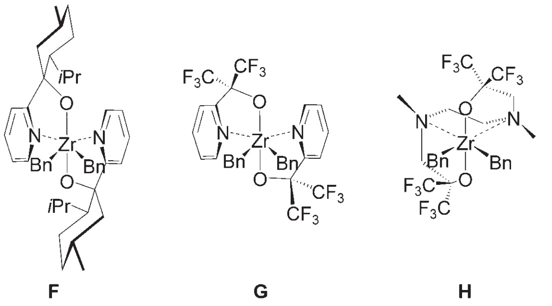
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It contains additional spectroscopic data for cationic complex **7**, details of DFT computations performed on cations **I** and **II**, and representative NMR spectra and GPC traces of poly(1-hexene)s.

thetic organometallic chemistry and catalysis have been achieved by using aryl oxide (phenolate) ligands (Scheme 1), with significant contributions from the groups of Fujita,[4] Coates,[5] Kol,[6] Okuda,[7] and many others.[8]



Scheme 1. Examples of aryl oxide based $[MX_2(OZ)_2]$ and $[MX_2(OZZO)]$ complexes.

Comparatively, Group 4 metal $[MX_2(OZ)_2]$- and $[MX_2(OZZO)]$-type complexes incorporating simple (amino-)alkoxide ligands have been studied much less (Scheme 2).[9,10] This is mainly due to the aggregation problems traditionally encountered with these relatively more basic ligands (relative to aryl oxides).[1] A valuable approach to overcoming this problem involves the introduction of electron-withdrawing CF_3 groups α to the alkoxide moiety; this generates increased intra- and intermolecular repulsions and a much less basic alkoxide oxygen atom, and in turn a much reduced bridging ability. Based on this principle, Jordan et al. have developed "fluorous" Group 4 complexes with two pyridine-alkoxide ligands (**G**).[11] We have also recently designed tetradentate $(ON^nNO)^{2-}$ ligands with an ethylene- ($n=2$) or propylenediamine ($n=3$) bridge flanked by two fluorinated tertiary alkoxides and prepared neutral Group 3, 4, and 13 metal complexes derived from these ligands (e.g. **H**).[12,13,14]



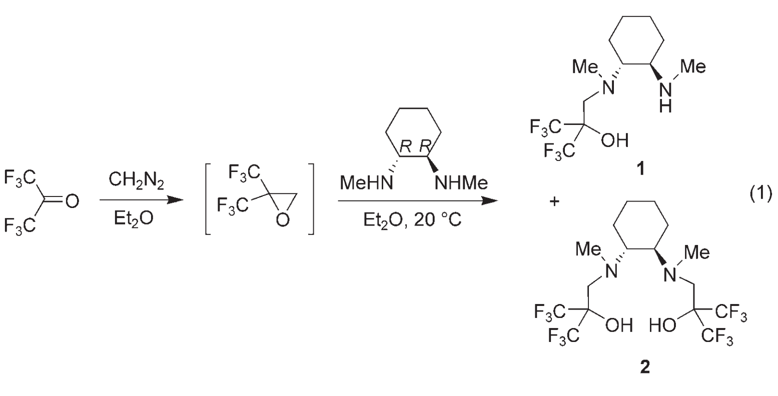
Scheme 2. Examples of (amino-)alkoxide-based $[MX_2(OZ)_2]$ and $[MX_2(OZZO)]$ complexes (Bn = benzyl).

Herein, we describe the synthesis of a new chiral, nonracemic, fluorous diamino-diol $(ON^{Cy}NO)H_2$ based on a 1,2-cyclohexanediamine backbone. The objectives of this work were to define the coordination properties of $(ON^{Cy}NO)^{2-}$ in simple titanium(IV) and zirconium(IV) $[MX_2(ON^{Cy}NO)]$ complexes, to prepare $[M(R)(ON^{Cy}NO)]^+$ and $[M(R)(ON^2NO)]^+$ alkyl species, and to explore the ethylene and 1-hexene polymerization properties of these ionic species.

Results and Discussion

Proligand synthesis: The chiral fluorous diamino-diol $(1R,2R)$-$C_6H_{10}[N(Me)CH_2C(CF_3)_2OH]_2$ $[(ON^{Cy}NO)H_2$, **2**] was prepared by the ring-opening of two equivalents of the fluorinated oxirane $CF_3)_2\overline{COC}H_2$, generated in situ from hexafluoroacetone and diazomethane,[15] with one equivalent of the corresponding (*R*,*R*)-*N*,*N'*-dimethyl-1,2-cyclohexanediamine [Eq. (1)].[16] This one-pot procedure leads to a mixture of the desired disubstituted product **2** (ca. 35 %) and the monosubstituted alcohol **1** (ca. 65 %). Fractional sublimation and subsequent recrystallization afforded pure **1** and **2** in 60 and 28 % (unoptimized) yields, respectively, as crystalline solids.

The ^1H and ^{19}F NMR spectra of **2** at room temperature (298 K) in $[D_6]$benzene or $[D_1]$chloroform solution feature broadened resonances (Figure 1). This observation is indicative of a dynamic phenomenon, which likely reflects restricted fluxionality due to intramolecular O−H···N hydrogen bonding. The ^1H and ^{19}F NMR spectra at 323 K in $[D_1]$chloroform or at 338 K in $[D_6]$benzene (Figure 1) show much sharper resonances, in particular for the acidic OH groups ($\delta_H = 6.94$ ppm), indicative of fast exchange on the NMR timescale.



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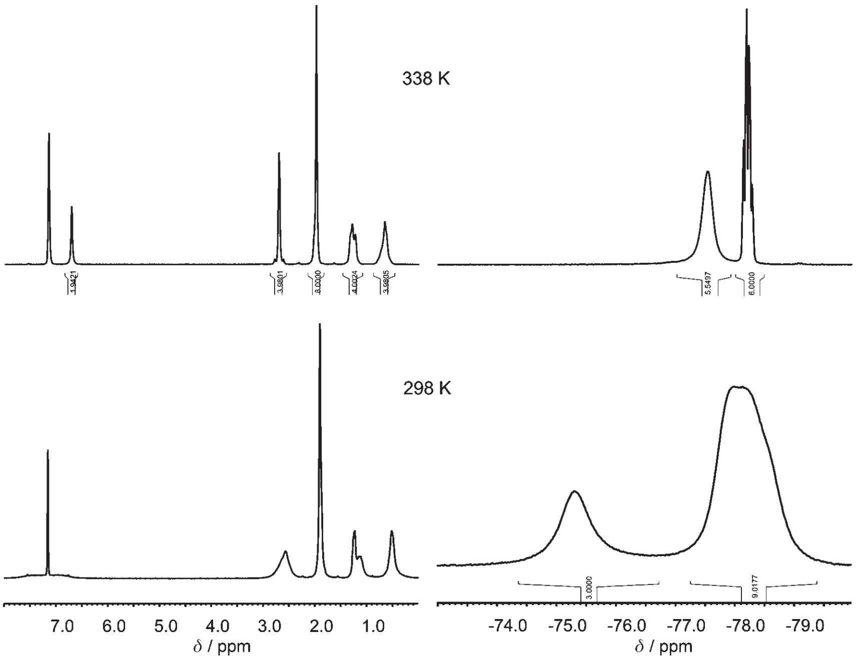
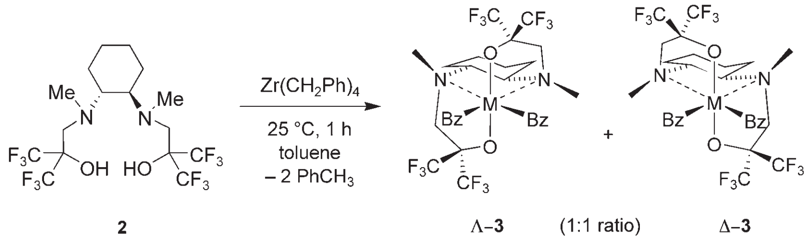


Figure 1. ^1H (left) and ^{19}F (right) NMR spectra of $(ON^{Cy}NO)H_2$ (**2**) in $[D_6]$benzene at different temperatures.

Synthesis and structures of $[Zr(CH_2Ph)_2(ON^{Cy}NO)]$ (3) and $[Ti(O\textit{i}Pr)_2(ON^{Cy}NO)]$ (4): The dibenzylzirconium complex $[Zr(CH_2Ph)_2(ON^{Cy}NO)]$ (**3**) was prepared by alkane elimination from the 1:1 reaction of $[Zr(CH_2Ph)_4]$ and chiral diamino-diol **2** [Eq. (2)]. ^1H NMR spectroscopy indicated that the reaction in $[D_6]$benzene at room temperature takes place within minutes and leads to the quantitative formation of **3** with clean release of two equivalents of toluene. A gram-scale synthesis carried out in toluene, followed by standard work up, afforded **3** in 91% yield. The hexafluoro complex **3** is only poorly soluble in aromatic solvents and readily soluble in chlorinated solvents.



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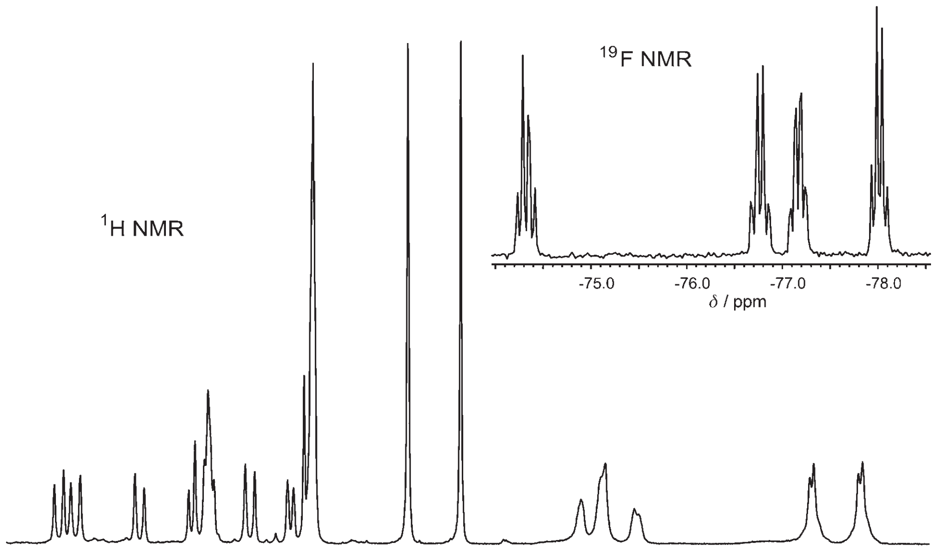


Figure 2. NMR spectra of $[Zr(CH_2Ph)_2(ON^{Cy}NO)]$ (**3**). Bottom: Aliphatic region of the ^1H NMR spectrum (500 MHz, $[D_8]$toluene, 298 K). Top: ^{19}F NMR spectrum (182 MHz, $[D_8]$toluene, 298 K).

The ^1H, ^{19}F, and ^1H–^{13}C HETCOR NMR spectra of **3** recorded in $[D_8]$toluene at 298 K showed the formation of two C_2-symmetric species in an approximately 1:1 ratio (Figure 2). As demonstrated by X-ray diffraction studies (vide infra), these isomers arise because of different configurations at the nitrogen and metal centers, that is, they are Δ and Λ diastereomers (see [Eq. (2)]). The ^1H NMR spectrum of the Λ-**3** and Δ-**3** diastereomers features one singlet for the $NCHCHN$ bridge, one singlet for the NCH_3 groups, two doublets for the $NCH_2C(CF_3)_2$ groups ($^2J_{H,H} = 15.0$ and 15.6 Hz, respectively), and one doublet for the two $ZrCHHPh$ groups ($^2J_{H,H} = 9.8$ and 10.3 Hz, respectively). The cyclohexyl hydrogen atoms appear as two multiplets of equal intensity in one diastereomer and as three multiplets (0.5:0.5:1 ratio) in the other diastereomer. The ^{13}C resonances for the C_{ipso} atoms of the benzylic groups are found at low fields ($\delta =$

145.9 and 144.9 ppm), which is indicates that the two benzyl groups in each diastereomer are η^1-coordinated to the metal center in solution.[10a,17] In the ^{19}F NMR spectrum, both species exhibit two sharp quartets of equal intensity ($^4J_{F,F}$ = 10.3 Hz) (Figure 2).

The thermodynamic barrier to the racemization of **3** by interconversion between the Λ and Δ stereoisomers was assessed by variable-temperature ^{19}F NMR studies in [D$_8$]toluene. However, no change in the shape or intensity of the resonances was observed upon heating up to 383 K. By assuming, quite reasonably, that coalescence does not appear up to 403 K, the lower limit for the racemization barrier was estimated to be 19 kcal mol^{-1}.[18] When compared with the racemization energy barriers determined for related dibenzylzirconium complexes **G** (8–9 kcal mol^{-1})[11] and **H** (17 kcal mol^{-1}),[12] this value suggests, as expected, a more stereorigid character of the cyclohexyl-bridged ligand system compared with unbridged and ethylene-bridged complexes, respectively.

Crystals of **3** suitable for X-ray studies were obtained from a toluene solution at room temperature. Selected bond lengths and angles and crystallographic details are summarized in Table 1 and Table 2. The crystal unit contains four molecules composed of one pair of diastereomers, that is, Δ-**3** and Λ-**3**, which arise from chirality at the octahedral metal center (Figure 3).[2] Both Λ-**3** and Δ-**3** feature distorted hexacoordinate geometry with a noncrystallographic C_2-symmetry axis. Except for the *trans* O-Zr-O angles, which differ by around 14°, the geometrical parameters (bond lengths and angles) are nearly the same for both diastereomers and, therefore, the structure of only one of these isomers will be described. The overall geometry of Λ-**3** is reminiscent of that of the related ethylene-bridged complex **H** previously characterized (Λ diastereoisomer described).[12] The *trans*-like O231-Zr2-O251 angle in Λ-**3** (148.68°) is only 6° larger than that in Λ-**H**. The *cis* angles between the oxygen and nitrogen atoms of the coordinated ligand and the benzylic groups are within the range observed for complex Λ-**H**. Also, the Zr–O (2.008(2), 2.005(2) Å) and Zr–N (2.411(2), 2.618(2) Å) distances are similar to those observed in Λ-**H**. Note the approximate 0.2 Å difference between the Zr2–N241 and Zr2–N261 bond lengths, which may be caused by either unequal *trans* influence of the benzylic groups positioned *trans* to the nitrogen atoms and/or steric congestion within the coordinated ligand. The unequivocal nonequivalence of the benzylic groups in Λ-**3** is evidenced by the difference in the Zr–C$_{ipso}$ distances (Zr2–C212 2.971(3) Å versus Zr2–C222 3.192(3) Å) and angles (Zr2-C211-C212 101.09(16)° versus Zr2-C221-C222 114.07(18)°), which are indicative of a significant Zr···Ph interaction for one of the benzyl moieties. The formal electron count is 16, by considering the alkoxides as four-electron donors.

Table 1. Selected bond lengths [Å] and angles [°] for the diastereomers of [Zr(CH$_2$Ph)$_2$(ON^{Cy}NO)] (**3**).

Δ isomer		Λ isomer	
Zr1–O131	2.005(2)	Zr2–O231	2.0077(19)
Zr1–O151	2.0603(18)	Zr2–O241	2.0577(17)
Zr1–N141	2.448(2)	Zr2–N241	2.411(2)
Zr1–N161	2.570(2)	Zr2–N261	2.618(2)
Zr1–C111	2.285(3)	Zr2–C211	2.294(2)
Zr1–C121	2.274(3)	Zr2–C221	2.283(3)
Zr1–C112	2.960(3)	Zr2–C212	2.971(3)
Zr1–C122	3.290(3)	Zr2–C222	3.192(3)
N141-Zr1-N161	71.11(7)	N241-Zr2-N261	71.32(7)
C111-Zr1-C121	105.39(10)	C211-Zr2-C221	102.18(10)
O131-Zr1-O151	162.45(9)	O231-Zr2-O251	148.68(8)
N161-Zr1-C111	148.89(8)	N261-Zr2-C212	149.19(8)
N141-Zr1-C112	137.81(9)	N241-Zr2-C211	137.23(9)
O131-Zr1-C111	94.40(11)	O231-Zr2-C221	95.98(9)
O131-Zr1-C121	89.34(10)	O231-Zr2-C211	91.78(9)
O151-Zr1-C121	108.20(10)	O251-Zr2-C211	118.89(9)
Zr1-C111-C112	120.59(19)	Zr2-C221-C222	114.07(18)
Zr1-C121-C122	101.74(17)	Zr2-C211-C212	101.09(16)

Table 2. Summary of the crystallographic data for [Zr(CH$_2$Ph)$_2$(ON^{Cy}NO)] (**3**).

	3
formula	$C_{30}H_{34}F_{12}N_2O_2Zr$
crystal size [mm]	0.20 × 0.15 × 0.04
M_r [g mol^{-1}]	773.81
crystal system	monoclinic
space group	$P2_1$
a [Å]	11.0996(6)
b [Å]	14.4130(10)
c [Å]	20.1886(12)
α [°]	90
β [°]	100.942(3)
γ [°]	90
V [Å^3]	3171.0(3)
Z	4
ρ_{calcd} [g cm^{-3}]	1.621
T [K]	100(2)
θ range [°]	1.03–29.6
μ [mm^{-1}]	0.71073
no. of measured reflections	37737
no. of independent reflections	17706
reflections with $I > 2\sigma(I)$	14260
parameters	847
goodness of fit	1.006
R [$I > 2\sigma(I)$]	0.036
wR^2	0.0739
largest difference [e Å^{-3}]	0.589/−0.659

The above NMR and X-ray data confirm the formation of diastereomers Δ-**3** and Λ-**3** in equal amounts and indicate that the chiral *N*-methyl-substituted ligand backbone is not effective at dictating the configurations at the nitrogen atoms during the Zr–N bond-forming process. These results are in line with recent reports by the groups of Walsh[19] and Kol[20] on the synthesis of titanium isopropoxide complexes with chiral *N*-methyl-tetrahydrosalen (salan) ligands, in which poor or no diastereoselectivity was observed. Nevertheless, for NH (i.e., non-methylated) salan ligands, Kol and co-workers did observe perfect chiral induction from the ligand to the metal center with the formation of a single C_2 diastereomeric complex. The low chiral induction observed in the *N*-methyl ligands was tentatively rationalized in terms of steric interactions between the nitrogen substituents and

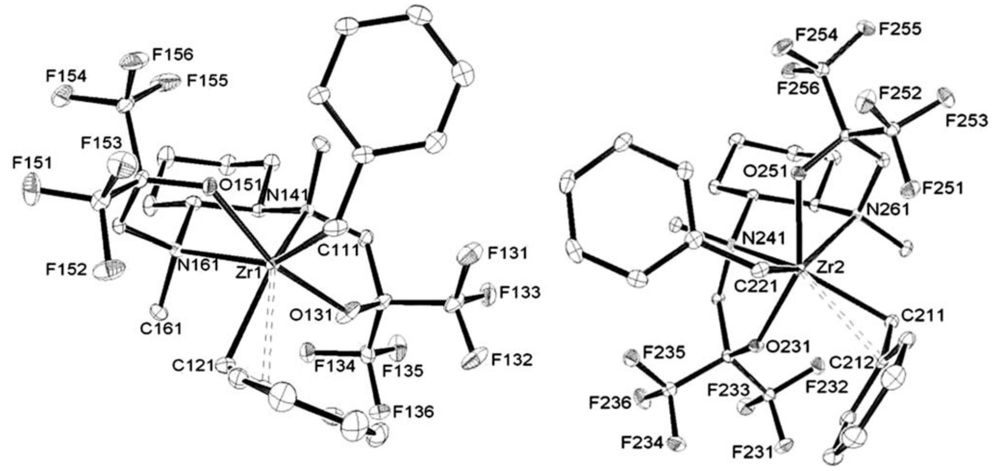


Figure 3. ORTEP views of the two diastereomers of the complex $[Zr(CH_2Ph)_2(ON^{Cy}NO)]$ (left: Δ-**3**; right: Λ-**3**), depicted with 30 % thermal ellipsoids; all hydrogen atoms have been omitted for clarity.

the axial hydrogen atoms of the adjacent cyclohexane carbon atoms. We were therefore also interested in preparing the titanium isopropoxide complex of ligand $(ON^{Cy}NO)H_2$ (**2**).

In line with the synthesis of parent ethylene-bridged complexes $[TiX_2(ON^{Cy}NO)]$ (X = O*i*Pr, Cl),[12] and, as is common for simple exchange reactions between titanium alkoxide complexes and alcohols,[20,21] the addition of titanium tetraisopropoxide to ligand **2** in toluene solution proceeded readily. The expected complex $[Ti(OiPr)_2(ON^{Cy}NO)]$ (**4**) was isolated in quantitative yield [Eq. (3)]. The ^1H and ^{19}F NMR spectra of **4** feature sharp resonances and are also consistent with the formation of two C_2 diastereomers (**4a**, **4b**). This is particularly evident from the observation of two sets of two quartets in the ^{19}F NMR spectrum (Figure 4), which lie in the same chemical shift area of the spectrum as those of **3**. However, in contrast to **3**, the room temperature (298 K) spectrum of **4** indicates an approximate 1:6 ratio between the diastereomers (Figure 4).[22] One may assume that the titanium complex **4** adopts an arrangement similar to the related (and structurally characterized) complexes $[Zr(CH_2Ph)_2(ON^{Cy}NO)]$ (**3**) and $[TiX_2(ON^2NO)]$ (X = Cl, O*i*Pr),[12] as well as Walsh's[19] and Kol's[20] diaminobis(phenolate) diisopropoxy titanium complexes; that is, the two isomers observed in the NMR spectra correspond to chiral-at-metal Δ-**4** and Λ-**4**, with a *trans*-O,O, *cis*-N,N, *cis*-O*i*Pr,O*i*Pr disposition of the ligands (Scheme 3). However, one cannot discard other configurational isomers such as *cis*-O,O, *cis*-N,N, *trans*-O*i*Pr,O*i*Pr (Scheme 3). The latter type of isomer has been proposed to co-exist in minor amounts beside the former type of isomer at a low temperature in the case of $[Zr(CH_2Ph)_2(ON^{Cy}NO)]$ (**H**).[12] Unfortunately,

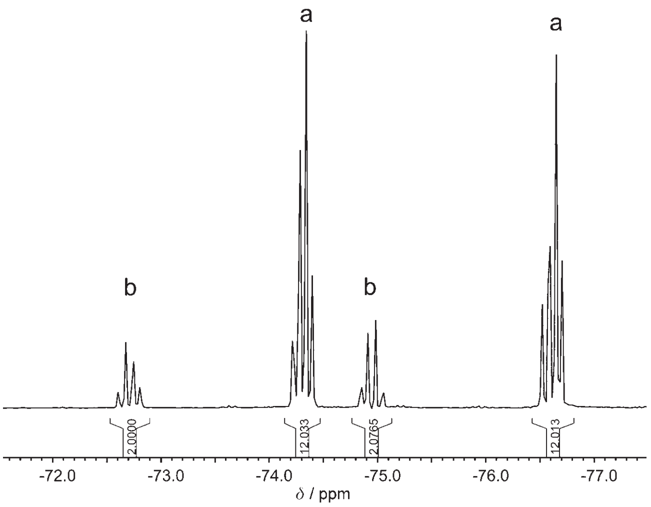
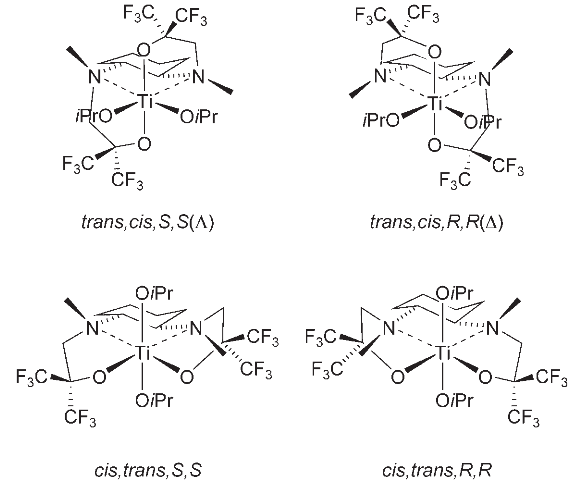


Figure 4. ^{19}F NMR spectrum (182 MHz, [D$_8$]toluene, 298 K) of $[Ti(OiPr)_2(ON^{Cy}NO)]$ (**4**). Descriptors **a** and **b** refer to the two observed isomers of **4**.



trans,cis,S,S(Λ)

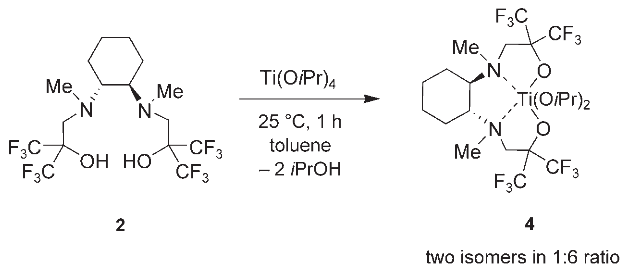
trans,cis,R,R(Δ)

cis,trans,S,S

cis,trans,R,R

Scheme 3. Possible C_2-symmetric isomers of $[Ti(OiPr)_2(ON^{Cy}NO)]$ (**4**). The four entries in the descriptor (e.g. *trans,cis,S,S*) refer to the arrangement of alkoxide and isopropoxide ligands and the configuration of N^a and N^b, respectively. Note that the amine ligands must be *cis*. For the top two isomers, the descriptor in parentheses (Λ, Δ) refers to the absolute configuration of the metal.

no single crystal of **4** suitable for X-ray studies has been obtained to date and NOESY data proved uninformative, and so the exact nature of the isomers of **4** and their interconversion remain unclear.



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Generation of cationic benzylzirconium species from [Zr(CH$_2$Ph)$_2$(ON^{2}NO)] (H) and [Zr(CH$_2$Ph)$_2$(ON^{Cy}NO)] (3): The structural investigation of the cationic species formed upon reaction of neutral Group 4 metal complexes with molecular activators is a difficult task owing to the high sensitivity of these species, but it may provide valuable information. In the field of olefin polymerization, it is thus possible to establish relationships for the catalytic performances of the neutral precursor/activator binary system, in particular, its single-site character, thermal stability, and sometimes its stereospecificity. We were therefore interested in investigating the generation of cationic benzylzirconium species from the neutral achiral complex [Zr(CH$_2$Ph)$_2$(ON^{2}NO)] (**H**, Scheme 2) and the chiral complex [Zr(CH$_2$Ph)$_2$(ON^{Cy}NO)] (**3**).

Reactions of complex **H** with $[Ph_3C]^+[B(C_6F_5)_4]^-$, $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$, and $B(C_6F_5)_3$, were monitored by NMR spectroscopy. In all cases, benzyl abstraction proceeded quantitatively at −40 °C in [D$_2$]dichloromethane or [D$_5$]chlorobenzene. For instance, the ^{1}H NMR spectrum (298 K) for the reaction of **H** with $[Ph_3C]^+[B(C_6F_5)_4]^-$ showed the formation of one equivalent of Ph_3CCH_2Ph ($\delta(Ph_3CCH_2Ph) = 3.96$ ppm).[23] The corresponding ^{19}F and ^{11}B NMR spectra (298 K) contained a single set of resonances for the free borate anion $[B(C_6F_5)_4]^-$, suggesting the formation of the cationic species [Zr(CH$_2$Ph)(ON^{2}NO)]$^+$ (**5**), which is possibly coordinated by solvent molecules [Eq. (4)]. Variable-temperature ^{1}H and ^{19}F NMR spectroscopy showed that this species exhibits fluxional behavior (Figure 5).[24] The ^{19}F NMR spectrum of **5** at 305 K features a single broad resonance for the CF$_3$ groups of the ligand. When the sample is cooled, this signal decoalesces to give four multiplets of equal intensity at 220 K. In parallel, the ^{1}H NMR spectrum at 305 K contains three AB systems for the C(CF$_3$)$_2$C*HH*, ZrC*HH*Ph, and NC*HH* groups, and the NCH$_3$ groups appear as a broad singlet ($\delta = 2.56$ ppm). Partial decoalescence is observed at 220 K, in particular with two singlets of equal intensity observed for the NC*H*$_3$ groups, while the ZrC*HH*Ph hydrogen atoms remain as an AB system. All these features are reversible upon warming or cooling. The high-field ^{13}C resonance for the *ipso*-carbon atom in ZrCH$_2$Ph ($\delta(220\,K) = 133.4$ ppm) is consistent with a η^2 coordination mode.[25] Clearly, **5** adopts C_1 symmetry at low temperatures that averages on the NMR timescale to C_2 symmetry at high temperatures, a phenomenon that likely involves rapid exchange of the η^2-benzyl group at the metal coordination sites.

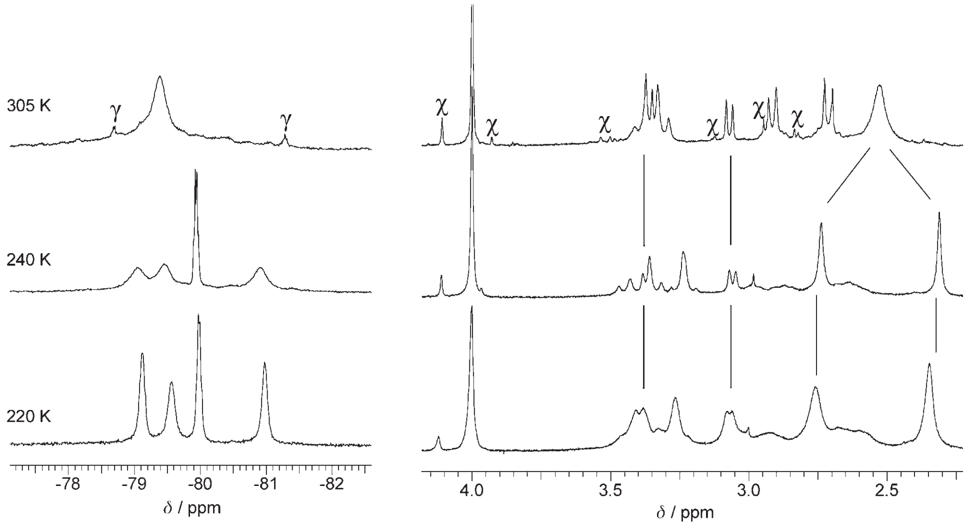
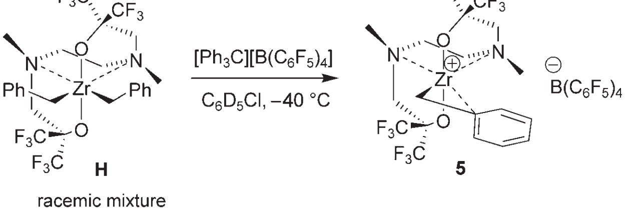


Figure 5. Variable-temperature NMR spectra of the 1:1 reaction mixture of [Zr(CH$_2$Ph)$_2$(ON^{2}NO)] (**H**) with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in [D$_5$]chlorobenzene at −30 °C which generates "[Zr(CH$_2$Ph)(ON^{2}NO)]$^+$[B(C$_6$F$_5$)$_4$]$^-$" (**5**). Left: Low-field region of the ^{19}F NMR spectra (470 MHz) (resonances for the $[B(C_6F_5)_4]^-$ anion are not shown). Right: Aliphatic region of the ^{1}H NMR spectra (500 MHz). The symbols γ et χ represent resonances of unidentified byproducts or impurities.

Reaction of **1** with (THF)•B(C$_6$F$_5$)$_3$ in [D$_2$]dichloromethane resulted in the clean formation of the cationic THF adduct [Zr(CH$_2$Ph)(ON^{2}NO)(THF)]$^+$ $[PhCH_2B(C_6F_5)_3]^-$ (**6**) [Eq. (5)]. Complex **6** is stable for days up to −10 °C in [D$_2$]dichloromethane, at which temperature



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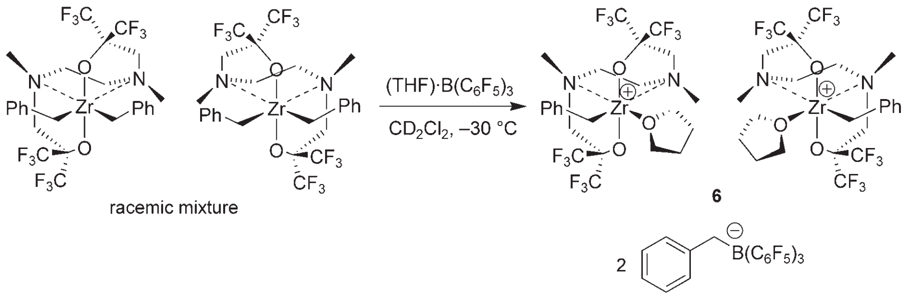


(5)

it exists as a fully separated ionic pair, as evidenced by NMR spectroscopy. The characteristic resonances of the free $[PhCH_2B(C_6F_5)_3]^-$ ion are found in the ^1H NMR spectrum at $\delta = 2.78$ ppm (BCH_2Ph) and in the $^{13}C\{^1H\}$ spectrum at $\delta = 148.4$ ppm (*ipso*-carbon atom of the benzyl group),[26] as well as in the ^{19}F and ^{11}B NMR spectra. The cationic part possesses C_1 symmetry and is represented in the ^1H NMR spectrum by four doublets for the $CHHC(CF_3)$ hydrogen atoms, two singlets for the NCH_3 groups, multiplets for each $ZrCHHPh$ moiety, and by the NCH_2CH_2N AB-type hydrogen system (Figure 6). The coordinated THF molecule also features as a C_1-symmetric pattern, with each pair of α- and β-hydrogen atoms appearing as a multiplet. The ^{19}F NMR spectrum at 243 K contains, besides the resonances due to a free $[PhCH_2B(C_6F_5)_3]^-$ ion, four quartets ($^4J_{F,F} = 9.7$ Hz) in a 1:1:1:1 ratio (of which two overlap) arising from the cation.

The reaction of $[Zr(CH_2Ph)_2(ON^{Cy}NO)]$ (**3**) in $[D_2]$dichloromethane at −40 °C with the aforementioned molecular activators, including also $(THF){\cdot}B(C_6F_5)_3$, unexpectedly led to complex mixtures of products, as indicated by very complicated ^1H NMR spectra in the temperature range 233–298 K. No unambiguous assignments were possible. When $(THF){\cdot}B(C_6F_5)_3$ was used to generate the putative "$[Zr(CH_2Ph)(ON^{Cy}NO)(THF)]^+$ $[PhCH_2B(C_6F_5)_3]^-$" (**7**), the ^{19}F NMR spectra at 243 and 298 K both revealed four different sets of signals that account for >90 % of the products, of which two major sets in a 1:1.2 ratio were attributed to C_1- and C_2- or C_s-symmetric species, respectively (see the Supporting Information). Attempts to identify the cationic entities have so far failed.

To gain a better insight into the solution structure of the cationic species generated in situ from **H** and **3**, a theoretical DFT study was performed.[27] Eight possible limit structures of the cations $[Zr(CH_2Ph)(ON^2NO)(THF)]^+$ (**I**, as in **6**) and $[Zr(CH_2Ph)(ON^{Cy}NO)(THF)]^+$ (**II**, as in **7**), with different arrangements of the ligands and overall symmetry, were constructed and optimized at the BP86-RI/SV(P) level of theory. The stable geometries obtained were then used in a single-point energy calculation at the B3LYP/TZVP level of theory (see the Supporting Information). In total agreement with the experimental observations for **6**, only one ***c***-type structure of **I** (as one pair of enantiomers) was found to be reasonable (Figure 7); the total electronic energy minima of all the other calculated structures are 11–26 kcal mol^{-1} higher. On the other hand, four different structures for **II** were found to lie within 0–4.6 kcal mol^{-1} of the total electronic energy range (Figure 7), which is also consistent with

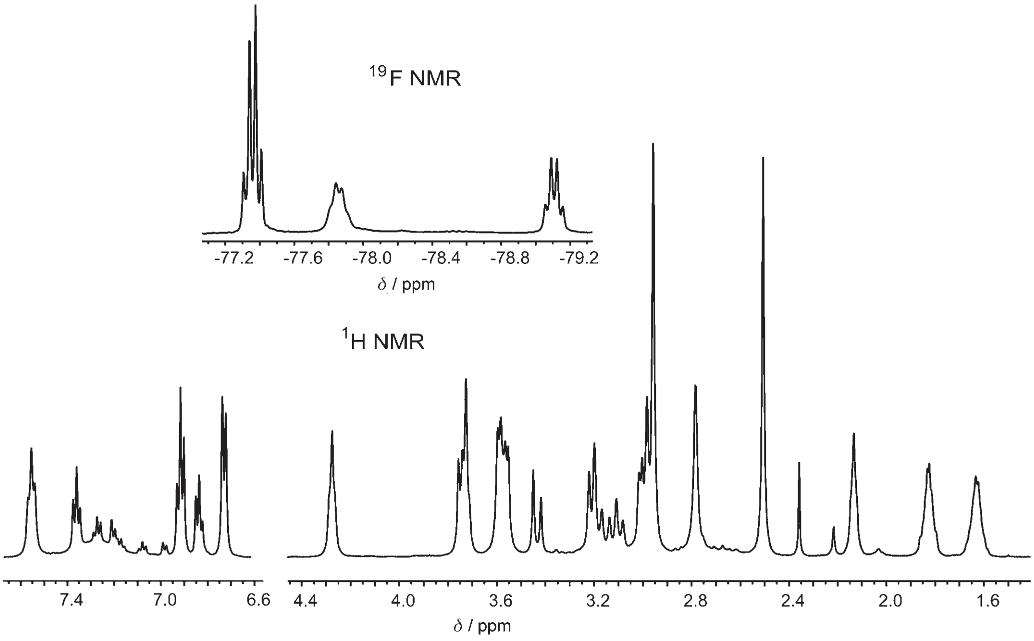


Figure 6. NMR spectra of $[Zr(CH_2Ph)(ON^2NO)(THF)][PhCH_2B(C_6F_5)_3]$ (**6**) in $[D_2]$dichloromethane at 243 K. Bottom: Aliphatic region of the ^1H NMR spectrum (500 MHz). Top: Low-field region of the ^{19}F NMR spectrum (282 MHz) (resonances for the $[PhCH_2B(C_6F_5)_3]^-$ anion are not shown).

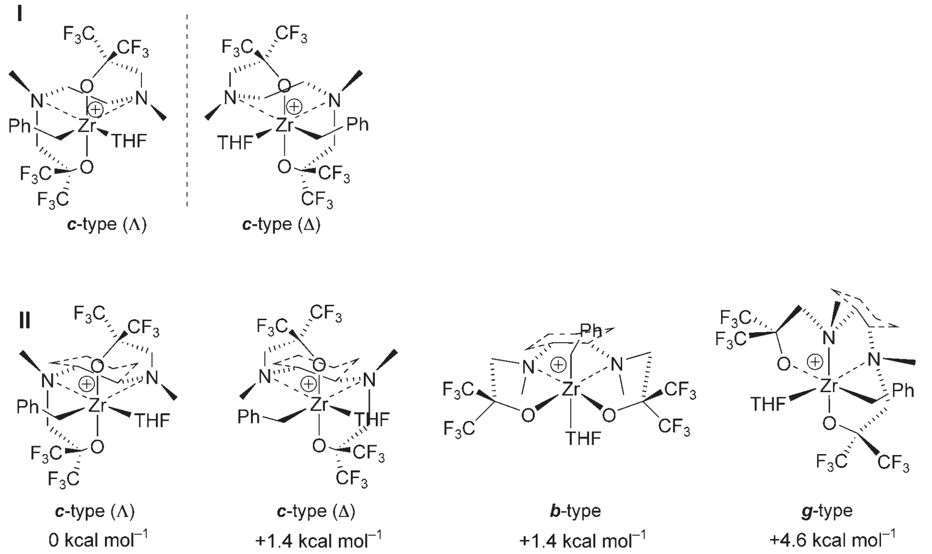


Figure 7. DFT-predicted geometries of the cationic species **I** and **II** derived from **6** and **7**, respectively; only the most stable structures (0–5 kcal mol^{-1} range) are shown (see the Supporting Information for further details).

the experimental observation of several species in solution for **7**.

Polymerization catalysis: Combinations of neutral dibenzyl complexes [Zr($CH_2Ph)_2$(ON^{2}NO)] (**H**) and [Zr($CH_2Ph)_2$(ON^{Cy}NO)] (**3**) with molecular activators were evaluated in the polymerization of ethylene and 1-hexene.[28] Representative results are summarized in Table 3.

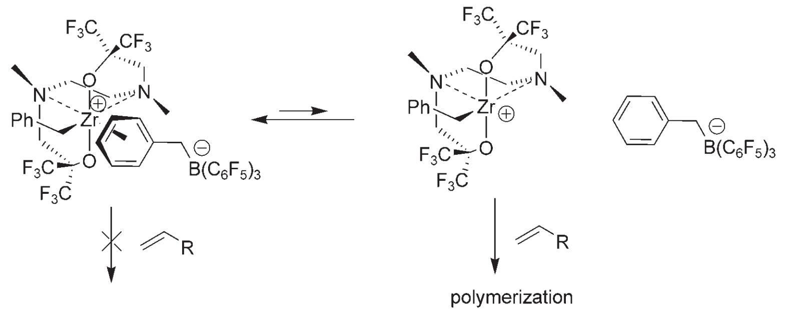
A 1:1 combination of $[Ph_3C]^+[B(C_6F_5)_4]^-$ and **H** exhibits moderate catalytic activity in ethylene polymerization at room temperature (196 kg PE mol Zr^{-1} h^{-1}, Table 3, entry 1). An activity about twice as high was observed when the polymerization was conducted at 0 °C (401 kg PE mol Zr^{-1} h^{-1}, Table 3, entry 2), which may reflect the increased stability of the cationic species under these conditions. These activity data are slightly higher than those reported by Jordan and co-workers for related fluorous alkoxide-pyridino catalysts [Zr($CH_2Ph)_2$({pyC($CF_3)_2$O}$_2$)] (**G**),[29] but significantly lower than those obtained with imino-phenolate catalysts.[4a] Low-molecular-weight materials with somewhat broad polydispersities and low melting temperatures (ca. 116 °C) were isolated in the experiments conducted both at room temperature and at 0 °C, a behavior which is also similar to that of the catalyst system based on **G**.[11]

The polymerization of 1-hexene catalyzed by **H**/activator binary systems appears to be strongly dependent on the reaction conditions; that is, the nature of the solvent and activator and the order of introduction of reagents play a crucial role in the catalytic performances and polymer characteristics. We first observed that dissolving separately the catalyst precursor and activator (trityl, Turner's, or borane), each in bulk 1-hexene, and mixing the resulting solutions (protocol **I**,[6i] Table 3, entry 3) failed to give any polymer.

Table 3. Ethylene and 1-hexene polymerization promoted by [Zr($CH_2Ph)_2$(ON^{2}NO)] (**H**)/activator and [Zr($CH_2Ph)_2$(ON^{Cy}NO)] (**3**)/activator binary systems.[a]

Entry	Monomer	Complex ([mol])	Activator	Protocol[b]	*T* [°C]	Time [min]	Polymer [g]	Yield [%]	Activity[c]	M_w [kg mol^{-1}][d]	M_w/M_n[d]	[*mm*] [%][e]
1	ethylene	**H** (40.6)	trityl	**IV**	25	10	1.32	–	196	1940	3.16	–
2	ethylene	**H** (29.0)	trityl	**IV**	0	10	1.93	–	401	2960	3.09	–
3	1-hexene	**H** (13.8)	any type	**I**	25	30	0	0	0	–	–	–
4	1-hexene	**H** (16.7)	trityl	**II**	25	30	0.52	15	62	5.2	1.17	50
5	1-hexene	**H** (16.7)	trityl	**II**	0	30	0.13	4	16	14.1	2.15	54
6	1-hexene	**H** (41.3)	BF15	**II**	25	60	0.47	14	11	4.8	1.49	nd
7	1-hexene	**H** (41.3)	BF15	**II**	50	60	0.21	6	5	4.6	1.49	nd
8	1-hexene	**H** (41.3)	BF15	**III**	25	60	2.20	65	53	5.8	1.21	nd
9	1-hexene	**H** (41.3)	BF15	**III**	0	180	traces	<1	–	–	–	–
10[f]	1-hexene	**H** (41.3)	trityl	**III**	25	60	traces	<1	–	–	–	–
11	1-hexene	**3** (41.3)	BF15	**III**	25	60	2.63	76	63	41.0	1.76	83
12	1-hexene	**3** (41.3)	trityl	**III**	25	60	traces	<1	–	–	–	–
13[g]	1-hexene	**3** (41.3)	BF15	**III**	25	60	0.21	6	5	47.2	1.64	84
14	1-hexene	**3** (41.3)	BF15	**III**	50	10	3.36	99	488	39.9	1.77	nd
15	1-hexene	**3** (41.3)	BF15	**III**	50	5	3.34	98	969	39.8	1.79	nd
16	1-hexene	**3** (41.3)	BF15	**III**	50	1	3.12	92	4527	40.1	1.77	nd

[a] General conditions unless otherwise stated: Ethylene polymerization reactions were carried out in toluene (50 mL) at 6 bar pressure; [1-hexene]/[Zr] = 1000–3000, [B]/[Zr] = 1, total volume = 10 mL. [b] **I**: the precatalyst and activator were each dissolved in 1-hexene (5 mL) and the solutions mixed. **II**: The cation was pregenerated in toluene (1 mL) and then added to 1-hexene (10 mL). **III**: The cation was pregenerated in hexane (5 mL) and then 1-hexene (5 mL) was added. **IV**: The cation was pregenerated in toluene (1 mL) and added to a saturated solution of ethylene in toluene. [c] Average activity in kg PH mol Zr^{-1} h^{-1}. [d] Determined by GPC in THF versus PSt standards. [e] Determined by ^{13}C{^{1}H} NMR spectroscopy. [f] Cationic species were completely insoluble. [g] The temperature was kept to 25 °C by using a water bath.



Scheme 4. Dissociation of tight ion pairs as a possible way to produce active polymerization species (the backbone of the ligand is omitted for clarity).

Also, the use of toluene as solvent significantly decreases the polymerization activity of catalyst systems based on **H** (protocol **II**, Table 3, entries 4–7). Better results were obtained by activating the precatalyst with $B(C_6F_5)_3$ in hexane solution and by performing the polymerization reaction with this mixture (protocol **III**, Table 3, entry 8). 1-Hexene polymerization proceeds instantaneously under these conditions and is accompanied by substantial warming to yield low-molecular-weight oily materials with narrow polydispersity. Adequate conditions for effective polymerization are, however, strict. No polymer was recovered when the reaction was performed at 0 °C (Table 3, entry 9), which indicates that the exothermicity released in the very first stages of the reaction is mandatory for activity (vide infra). Also, the use of $[Ph_3C]^+[B(C_6F_5)_4]^-$ as activator in place of $B(C_6F_5)_3$ led to completely insoluble ionic species (an orange precipitate formed while the supernatant solution remained colorless) and no polymerization took place (Table 3, entry 10). The same observation was made when the cyclohexyl-bridged precursor **3** was used in combination with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (Table 3, entry 12). The average activities determined with precatalyst **H** (16–62 kg PH mol Zr^{-1} h^{-1}) are of the same order of magnitude as those observed with $[Zr(CH_2Ph)_2(\{pyC(CF_3)_2O\}_2)]$ (**G**)/$B(C_6F_5)_3$ (90 kg PH mol Zr^{-1} h^{-1}, $M_n = 840$ g mol^{-1}).[11]

The **3**/$B(C_6F_5)_3$ system exhibits much higher activity towards 1-hexene than was observed with precursor **H** (Table 3, entry 11). Strong exothermicity was also noticed for polymerization reactions carried out at "room temperature" with this system. In fact, conducting the reaction with effective temperature control at 25 °C led to modest polymerization activity (Table 3, entry 13). On the other hand, improved performances were observed by heating at 50 °C, with overall activities of up to 4500 kg PH mol Zr^{-1} h^{-1} (Table 3, entries 14–16). Note that molecular weights (M_w = 39 800–42 500 g mol^{-1}) and polydispersities ($M_w/M_n = 1.69$–1.79) were almost invariable in this series of experiments. These observations suggest that for both the **H**/$B(C_6F_5)_3$ and **3**/$B(C_6F_5)_3$ systems 1) the same catalytic species operate(s) at "25–50 °C", 2) the first formed cationic species such as $[Zr(CH_2Ph)(ONNO)]^+[(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]^-$ are not the true active species, and 3) the "true" catalytic species responsible for the initiation is generated in an endothermic step. We suggest that the additional energy required may be associated with dissociation of the tight ion pair $[Zr(CH_2Ph)(ONNO)][(\eta^6\text{-}PhCH_2)B(C_6F_5)_3]$ to form active free cationic species $[Zr(CH_2Ph)(ONNO)]^+$ (Scheme 4).[27b]

The microstructures of the poly(1-hexene)s were investigated by ^1H and ^{13}C NMR spectroscopy. As expected for low-molecular-weight polymers, resonances attributed to end-groups, mostly of the vinylidene type, were observed in all cases. Integration of the resonances in the C3 region of the $^{13}C\{^1H\}$ NMR spectra of the poly(1-hexene)s obtained from precatalyst **H** (entries 3–10) (Figure 8a)[30] reveals an isotactic-enriched microstructure with 50–54 % *mm* triads fitting an enantioselectivity parameter σ of around 0.79–0.81.[31] The higher intensity of the *mrrm* pentad (δ = 33.8 ppm) relative to the *mmrm*, *rmmr*, and *mmrr* pentads (δ = 34.4 ppm) is consistent with enantiomorphic site control rather than chain-end control,[6i,30a,32] that is, that the symmetry of the active species and not the last inserted monomeric unit is responsible for the stereoselectivity of the polymer. In addition, 2,1-regioerrors (δ = 34.8 ppm) are visible in these polymers. Gratifyingly, the poly(1-hexene)s obtained from chiral precursor **3** (Table 3, entries 11–16) do not contain such regioerrors (or in a very low amount) and feature an improved isotacticity of 84 % of *mm* triad abundance (σ = 0.94), which is evidenced by the intense resonance at δ = 34.5 ppm assigned to the *mmmm* pentad (74 % content) (Figure 8). The similar degree of isotacticity found for the polymers obtained both at 25 °C (84 % *mm*) and 50 °C (83 % *mm*) suggest that the stereoerrors arise from enantiofacial misinsertion and not from chain epimerization reactions.[6i,33]

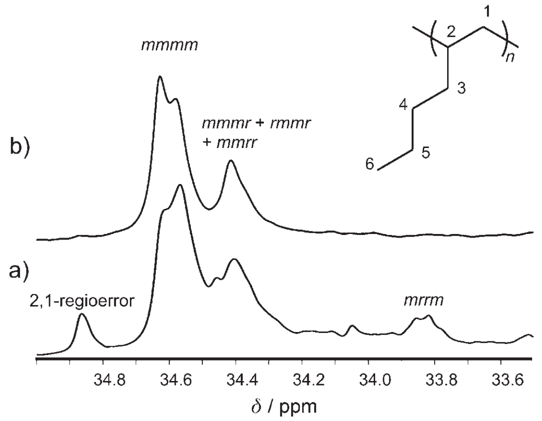


Figure 8. C3 region of the $^{13}C\{^1H\}$ NMR spectra (125 MHz, [D$_1$]chloroform, 313 K) of isotactic-enriched poly(1-hexene)s obtained with precursors a) **H** and b) **3**.

Conclusion

Dibenzylzirconium complexes with fluorous diamino-dialkoxy ligands have been converted into the corresponding cationic species and their use as catalysts has been investigated in 1-hexene polymerization. In the presence of THF as a stabilizing Lewis base, benzyl abstraction from the neutral 1,2-ethylenediamino complex **H** leads to a single cationic species, as determined by NMR spectroscopy. Unexpectedly, benzyl abstraction from the neutral complex **3**, which bears a configurationally more rigid *trans*-1,2-cyclohexyl bridge, generates a mixture of cationic species. DFT studies conducted on a variety of possible cationic structures for both achiral and chiral systems corroborate these observations. This suggests, in turn, that the co-existence of several isomeric cations with the 1,2-cyclohexanediamino ligand is an intrinsic feature of this system and does not result from the instability/decomposition of the cationic species first generated.

The role of the fluorous diamino-dialkoxy ligand in determining the regio- and stereoselectivity of 1-hexene polymerization has been evidenced. Contrary to catalyst systems based on **H**, those derived from **3** show almost no 2,1-regioerrors. Also, the level of isotacticity of catalyst systems based on **3** (up to 84% *mm*), though somewhat lower than that achieved with related systems based on diamino-bis-(phenolate)-zirconium catalysts such as **D** (up to 95% *mm*),[6h] is significantly improved in comparison to that obtained with the parent ethylene-bridged system **H** (up to 54% *mm*). Thus, the chiral *trans*-1,2-cyclohexyl systems, despite the possible co-existence of active cationic species, proved more stereoselective, which is evidently related to the effect of the bridge on the stereorigidity of the catalyst. In fact, the level of isotacticity in this series of fluorous diamino-dialkoxy-zirconium complexes is related to the ease of Δ,Λ interconversion: Jordan's unbridged fluorous bis(alkoxide-pyridino) catalysts $[Zr(CH_2Ph)_2(\{pyC(CF_3)_2O\}_2)]$ (**G**) readily undergo such an interconversion ($\Delta G^{\neq}=8$–$9\,kcal\,mol^{-1}$) and yield atactic poly(1-hexene)s.[11] Catalysts derived from **H** ($\Delta G^{\neq}=17\,kcal\,mol^{-1}$) are less isotactic than those derived from **3**, which is stereorigid on the NMR timescale at temperatures up to 100 °C ($\Delta G^{\neq}\geqslant 19\,kcal\,mol^{-1}$).

Experimental Section

General considerations: All manipulations were performed under purified nitrogen or argon using standard high-vacuum Schlenk techniques or in a glove box. Solvents (toluene, hexane, and diethyl ether) were freshly distilled from Na/K alloy under nitrogen and degassed thoroughly by freeze-thaw-vacuum cycles prior to use. Deuterated solvents (>99.5% D, Eurisotop) were freshly distilled from Na/K amalgam under argon and degassed prior to use. Anhydrous hexafluoroacetone was purchased from SynQuest Fluorochemicals and used as received. $[Ti(OiPr)_4]$ and $[Zr(CH_2Ph)_4]$ were purchased from Strem Chemicals and used as received. Complex $[Zr(CH_2Ph)_2(ON^2NO)]$ (**H**) was synthesized as previously reported.[12]

The NMR spectra of complexes were recorded on Bruker AC-300 and AM-500 spectrometers in Teflon-valve NMR tubes at ambient probe temperature (298 K) unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ and were determined by reference to the residual solvent peaks. Assignment of ^{13}C signals was made from ^1H–^{13}C HMQC and HMBC NMR experiments. ^{19}F and ^{11}B chemical shifts were determined by reference to external neat $BF_3{\cdot}Et_2O$ and an aqueous solution of $NaBF_4$, respectively. All coupling constants are given in hertz. Elemental analyses were performed at the Microanalytical Laboratory at the Institute of Chemistry of Rennes or at the NSC Regional Instrumentation Center at National Chiao Tung University, Hsinchu, Taiwan, and are the average of two independent determinations. Mass spectra were obtained on a JEOL SX-102A instrument operating in fast atom bombardment (FAB) mode. Gel permeation chromatography (GPC) of polyethylene samples was performed on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene as solvent (stabilized with 125 ppm butylated hydroxytoluene (BHT)) at 150 °C with a set of three PLgel 10 μm Mixed-B or Mixed-B LS columns. Polyethylene molecular weights were determined by reference to polystyrene (PSt) standards and are reported relative to polyethylene standards, as calculated by the universal calibration method using Mark–Houwink parameters ($K=14.1\times10^{-5}$, $\alpha=0.70$ for PSt, $K=14.1\times10^{-5}$, $\alpha=0.70$ for PE).[34] GPC of poly-1-hexenes was performed on a Waters instrument equipped with the double detection methods of UV spectrometry and differential refractometry using THF as solvent ($1\,mL\,min^{-1}$) at ambient temperature. The molecular weights of poly-1-hexene were determined by reference to polystyrene standards. ^{13}C NMR analysis of poly(1-hexene)s was performed on a Bruker AM 500 spectrometer equipped with a 5 mm probe at 40 °C in $[D_1]$chloroform (number of scans = 25 600).

$(ON^{Cy}NO)H_2$ (2): Anhydrous hexafluoroacetone (1.00 g, 7.03 mmol) was slowly added to a diethyl ether solution of diazomethane etherate (0.89 g, 21.2 mmol) in a 100-mL reaction flask equipped with a dry ice condenser to produce the anticipated 2,2-bis(trifluoromethyl)oxirane. The resulting solution was continuously stirred at room temperature for 6 h and then (1*R*,2*R*)-1,2-bis(methylamino)cyclohexane (0.50 g, 3.51 mmol) in diethyl ether (10 mL) was added dropwise over a period of 5 min and the solution stirred for a further 12 h. Volatiles were removed under vacuum and the oily residue was separated by repeated fractional sublimation. The monosubstituted product (**1**, 1.36 g, 60% based on HFA) was collected at 50–55 °C (200 mm Hg), and the expected disubstituted compound (**2**, 0.99 g, 28%) was obtained at 70–75 °C. Subsequent crystallization from CH_2Cl_2/diethyl ether (1:1) afforded colorless crystalline solids.

Analytical data for **1**: ^1H NMR (500 MHz, $[D_1]$chloroform, 298 K): $\delta=5.90$ (br, 2H; NH+OH), 3.02 (d, $J_{H,H}=16$ Hz, 1H), 2.84 (d, $J_{H,H}=16$ Hz, 1H), 2.41 (t, $J_{H,H}=12$ Hz, 1H), 2.40 (s, 3H; Me), 2.37 (s, 3H; Me), 2.31 (t, $J_{H,H}=12$ Hz, 1H), 2.05 (d, $J_{H,H}=12$ Hz, 1H), 1.89–1.74 (m, 3H), 1.18 ppm (m, 4H).

Analytical data for **2**: ^1H NMR (500 MHz, $[D_1]$chloroform, 333 K): $\delta=6.84$ (br s, 2H; OH), 2.98 (br, 4H), 2.39 (m, 2H), 2.37 (s, 6H; Me), 1.92 (br, 2H; CH_2), 1.83 (d, $J_{H,H}=2.5$ Hz, 2H; CH_2), 1.35 (br, 2H), 1.21 ppm (m, $J_{H,H}=3.5$ Hz, 2H); ^1H NMR (500 MHz, $[D_6]$benzene, 338 K): $\delta=6.80$ (s, 2H; OH), 2.80 (s, 4H; CH_2), 2.05 (m+s, 8H; CH+Me), 1.35 (m, 4H; CH_2), 0.65 ppm (m, 4H; CH_2); ^{19}F NMR (188 MHz, $[D_6]$benzene, 333 K): $\delta=-78.2$ (q, $^4J_{F,F}=10.4$ Hz, 6F), −77.5 ppm (br, 6F); MS (FAB): *m*/*z* observed (actual) [assignment]: 503 (502) $[M^++1]$, 433 (433) $[M^+-CF_3]$, 335 (335) $[M^+-C_3F_6OH]$; elemental analysis calcd (%) for $C_{16}H_{22}F_{12}N_2O_2$: C 38.26, H 4.41, N 5.58; found: C 38.27, H 4.47, N 5.49.

$[Zr(CH_2Ph)_2(ON^{Cy}NO)]$ (3): In a glove box, solid diamino-diol **2** (0.383 g, 0.762 mmol) was added in small portions under vigorous stirring to a solution of $[Zr(CH_2Ph)_4]$ (0.347 g, 0.761 mmol) in toluene (30 mL) cooled to −30 °C. The reaction mixture was allowed to warm to room temperature and then stirred for a further 5 h. During this period of time, a yellowish precipitate formed. Volatiles were removed under vacuum, the residue was washed with hexane (2×5 mL) and dried under vacuum to give **3** as a pale yellow microcrystalline powder (0.54 g, 91%). Crystals suitable for X-ray diffraction were obtained from a concentrated benzene solution at room temperature. The ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra at 298 K each show two sets of resonances, consistent with the existence of two diastereomers of **3** (**a** and **b**) in approximately equal ratio.

^{1}H NMR (500 MHz, [D$_8$]toluene, 298 K): $\delta=7.32$ (m, 8H; *o*-H, **a** and **b**), 7.18 (m, 8H; *m*-H, **a** and **b**), 6.92 (t, $^3J=7.3$ Hz, 1H; *p*-H, **a** or **b**), 6.88 (t, $^3J=7.3$ Hz, 1H; *p*-H, **a** or **b**), 2.97 (d, $^2J=15.0$ Hz, 2H; NCHHC(CF$_3$)$_2$, **a**), 2.91 (d, $^2J=15.6$ Hz, 2H; NCHHC(CF$_3$)$_2$, **b**), 2.70 (d, $^2J=15.0$ Hz, 2H; NCHHC(CF$_3$)$_2$, **a**), 2.52 (d, $^2J=10.3$ Hz, 2H; ZrCHHPh, **a** or **b**), 2.50 (d, overlaps the signals from the benzylic protons of the other diastereomer and protons of the NCH$_3$ group, $^2J=10.3$ Hz, 2H; ZrCHHPh, **a** or **b**), 2.49–2.47 (d, $^2J=10.3$ Hz, 2H; ZrCHHPh, **a** or **b**), 2.49–2.47 (d, overlaps the signal from the benzylic protons of the other diastereomer, $^2J=9.8$ Hz, 2H; ZrCHHPh, **a** or **b**), 2.49–2.47 (m, overlaps the signals from the benzylic protons, 2H; NC*H*C*H*N, **a**), 2.33 (d, $^2J=15.6$ Hz, 2H; NCHHC(CF$_3$)$_2$, **a** or **b**), 2.16 (m, overlaps the signals from toluene, 2H; NCHCHN, **b**), 1.81 (s, 6H; NCH$_3$, **b**), 1.64 (s, 6H; NCH$_3$, **a**), 1.24 (br m, 2H; Cy, **a**), 1.16 (br m, 4H; Cy, **b**), 1.05 (br m, 2H; Cy, **a**), 0.48 (br m, 4H; Cy, **A**), 0.32 ppm (br m, 4H; Cy, **b**); {^{1}H}^{13}C NMR (125 MHz, [D$_8$]toluene, 298 K): $\delta=145.9$ (C$_{ipso}$, **a** or **b**), 144.9 (C$_{ipso}$, **a** or **b**), 128.8 (*o*-C, *m*-C, **a** or **b**), 128.4 (*o*-C, *m*-C, **a** or **b**), 128.2 (*o*-C, *m*-C, **a** or **b**), 127.9 (*o*-C, *m*-C, **a** or **b**), 125.5 (CF$_3$, signals from **a** overlap signals from **b**), 122.8 (*p*-C, **a** or **b**), 122.1 (*p*-C, **a** or **b**), 85.0 (*C*(CF$_3$)$_2$, **a**), 84.9 (*C*(CF$_3$)$_2$, **b**), 72.5 (*C*H$_2$Ph, **a** or **b**), 69.8 (*C*H$_2$Ph, **a** or **b**), 66.1 (N*C*H*C*HN, Cy, **b**), 62.9 (N*C*H*C*HN, Cy, **a**), 57.5 (N*C*H$_2$C(CF$_3$)$_2$, **a**), 54.7 (N*C*H$_2$C(CF$_3$)$_2$, **b**), 44.2 (NCH$_3$, **b**), 38.1 (NCH$_3$, **A**), 24.2 (Cy, **a**), 23.3 (Cy, **b**), 23.1 (Cy, **a**), 22.7 ppm (Cy, **b**); ^{19}F NMR (188 MHz, [D$_8$]toluene, 298 K): $\delta=-74.3$ (q, $^4J_{\rm F,F}=10.3$ Hz, 6F; **a** or **b**), −76.7 (q, $^4J_{\rm F,F}=10.3$ Hz, 6F; **a** or **b**), −77.1 (q, $^4J_{\rm F,F}=10.3$ Hz, 6F; **a** or **b**), −78.0 ppm (q, $^4J_{\rm F,F}=10.3$ Hz, 6F; **a** or **b**); elemental analysis calcd (%) for $C_{30}H_{34}F_{12}N_2O_2Zr$: C 46.56, H 4.43, N 3.62; found: C 45.98, H 4.12, N 3.54.

[Ti(O*i*Pr)$_2$(ON$^{\rm Cy}$NO)] (4): A solution of diamino-diol **2** (0.100 g, 0.199 mmol) in toluene (2 mL), cooled to −30 °C, was added dropwise over 5 min under vigorous stirring to a solution of [Ti(O*i*Pr)$_4$] (0.056 g, 0.199 mmol) in toluene (2 mL) cooled to −30 °C. The clear mixture was slowly warmed to room temperature over 12 h under magnetic stirring. Volatiles were removed under vacuum and the solid residue was washed with pentane and dried in vacuo to give **4** as a white solid (0.121 g, 92 %). Elemental analysis calcd (%) for $C_{22}H_{34}F_{12}N_2O_4Ti$: C 39.65, H 5.14; found: C 40.11, H 5.05. At 298 K, two sets of signals were observed in the ^{1}H, {^{1}H}^{13}C, and ^{19}F NMR spectra, consistent with the existence of two isomers of **4** (**a** and **b**) formed in a ratio 1:6. ^{1}H NMR (500 MHz, [D$_8$]toluene, 298 K): $\delta=4.94$ (sept, $^2J_{\rm H,H}=6.2$ Hz, 2H; CH O*i*Pr, **b**), 4.91 (sept, $^2J_{\rm H,H}=6.2$ Hz, 2H; CH O*i*Pr, **a**), 3.07 (d, $^2J_{\rm H,H}=16.0$ Hz, 2H; NCH$_2$C(CF$_3$)$_2$, **a**), 3.04 (d, $^2J_{\rm H,H}=14.8$ Hz, 2H; NCH$_2$C(CF$_3$)$_2$, **b**), 2.98 (d, $^2J_{\rm H,H}=14.8$ Hz, 2H; NCH$_2$C(CF$_3$)$_2$, **b**), 2.80 (m, 2H; (Me)NCHCHN(Me), **b**), 2.67 (m, 2H; (Me)NCHCHN(Me), **a**), 2.60 (d, $^2J_{\rm H,H}=16.0$ Hz, 2H; NCH$_2$C(CF$_3$)$_2$, **a**), 2.50 (s, 6H; NCH$_3$, **a**), 2.23 (s, 6H; NCH$_3$, **b**), 1.45 (br m, CH$_2$ Cy, **a** and **b**), 1.38 (d, $^2J_{\rm H,H}=6.3$ Hz, 6H; CH$_3$ O*i*Pr, **a**), 1.37 (d, $^2J_{\rm H,H}=5.6$ Hz, 6H; CH$_3$ O*i*Pr, **b**), 1.31 (d, $^2J_{\rm H,H}=6.3$ Hz, 6H; CH$_3$ O*i*Pr, **a**), 1.26 (d, $^2J_{\rm H,H}=5.6$ Hz, 6H; CH$_3$ O*i*Pr, **b**), 0.65 ppm (br m, CH$_2$ Cy, **a** and **b**); {^{1}H}^{13}C NMR (125 MHz, [D$_8$]toluene, 298 K): $\delta=125.2$ (q, $^1J_{\rm C,F}=299$ Hz, CF$_3$, **a** and **b**), 85.5 (br, C(CF$_3$)$_2$, **a** and **b**), 79.5 (CH O*i*Pr, **a**), 79.2 (CH O*i*Pr, **b**), 65.3 (N*C*H*C*HN Cy, **a**), 60.4 (N*C*H*C*HN Cy, **b**), 58.1 (N*C*H$_2$C(CF$_3$)$_2$, **b**), 54.0 (N*C*H$_2$C(CF$_3$)$_2$, **a**), 45.7 (NCH$_3$, **a**), 39.3 (NCH$_3$, **b**), 25.0 (CH$_3$ O*i*Pr, **a**), 24.5 (CH$_3$ O*i*Pr, **a**), 24.4 (CH$_3$ O*i*Pr, **b**), 23.6 (CH$_2$ Cy, **a**), 22.5 (CH$_2$ Cy, **b**), 22.3 ppm (CH$_2$ Cy, **a**). ^{19}F{^{1}H} NMR (188 MHz, [D$_8$]toluene, 298 K): $\delta=-72.7$ (q, $^4J_{\rm F,F}=12.1$ Hz, 6F; **b**), −74.4 (q, $^4J_{\rm F,F}=11.9$ Hz, 6F; **a**), −75.0 (q, $^4J_{\rm F,F}=12.1$ Hz, 6F; **b**), −76.6 ppm (q, $^4J_{\rm F,F}=11.9$ Hz, 6F; **a**).

Reaction of [Zr(CH$_2$Ph)$_2$(ON^{2}NO)] (H) with [Ph$_3$C][B(C$_6$F$_5$)$_4$]—Generation of ionic complex of [Zr(CH$_2$Ph)(ON^{2}NO)][B(C$_6$F$_5$)$_4$] (5): A Teflon-valved NMR tube was charged with [Zr(CH$_2$Ph)$_2$(ON^{2}NO)] (**H**, 0.015 g, 18.9 μmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.017 g, 18.9 μmol), and [D$_5$]chlorobenzene (ca. 0.5 mL) was vacuum transferred into this mixture at −50 °C. The tube was sealed and kept at −40 °C. A yellow solution formed within 5 min. Its ^{1}H NMR spectrum was recorded at 220 K and indicated quantitative conversion of **H** to give mainly (>90 %) **5**. Compound **5** is not soluble in hydrocarbons (toluene, pentane, hexanes). ^{1}H NMR (500 MHz, [D$_5$]chlorobenzene, 290 K): $\delta=3.39$ (d, $^2J=14.4$ Hz, 2H; NCH$_2$C(CF$_3$)$_2$), 3.34 (d, $^2J=9.3$ Hz, 1H; ZrC*H*$_2$Ph), 3.31 (d, $^2J=14.4$ Hz, 2H; NCH$_2$C(CF$_3$)$_2$), 3.07 (d, $^2J=9.3$ Hz, 1H; ZrC*H*$_2$Ph), 2.91 (d, $^2J=11.4$ Hz, 2H; C*H*$_2$C*H*$_2$), 2.71 (d, $^2J=11.4$ Hz, 2H; C*H*$_2$C*H*$_2$), 2.56 ppm (br s, 6H; NCH$_3$); ^{1}H resonances due to ZrC*HH*Ph overlap those of Ph$_3$CCH$_2$Ph; ^{19}F{^{1}H} NMR (376 MHz, [D$_5$]chlorobenzene, 290 K): $\delta=-79.5$ (br m, 12F; CF$_3$), −134.2 (m, 8F; *o*-F B(C$_6$F$_5$)$_4^-$), −164.6 (q, $^3J_{\rm F,F}=20.4$ Hz, 4F; *p*-F B(C$_6$F$_5$)$_4^-$), −168.6 ppm (t, $^3J_{\rm F,F}=19.0$ Hz, 8F; *m*-F B(C$_6$F$_5$)$_4^-$); ^{1}H NMR (400 MHz, [D$_5$]chlorobenzene, 220 K): $\delta=8.00$ (m, 1H; *p*-H(ZrBn)), 7.80 (m, 2H; *m*-H(ZrBn)), 3.36 (d, $^2J=9.4$ Hz, 1H; ZrC*H*$_2$Ph), 3.06 (d, $^2J=9.4$ Hz, 1H; ZrC*H*$_2$Ph), 2.74 (s, 3H; NCH$_3$), 2.36 ppm (s, 3H; NCH$_3$); resonances due to CH$_2$CH$_2$ are observed in the range of 3.01–2.59 ppm and those of NCH$_2$C(CF$_3$)$_2$ in the range of 3.47–3.34 ppm, but are too broad to be attributed, resonances arising from *o*-H(ZrBn) overlap those from Ph$_3$CCH$_2$Ph; ^{13}C{^{1}H} NMR (100 MHz, [D$_5$]chlorobenzene, 220 K): $\delta=144.8$ (*p*-C(ZrBn)), 139.7 (*o*-C(ZrBn)), 133.4 (*ipso*-C(ZrBn)), 130.3 (*m*-C(ZrBn)), 123.8 (q, $^1J_{\rm C\text{-}F}=291$ Hz, 2C; CF$_3$), 121.5 (q, $^1J_{\rm C\text{-}F}=291$ Hz, 2C; CF$_3$), 81.5 (Zr*C*H$_2$Ph), 62.7 (2C; N*C*H$_2$C(CF$_3$)$_2$), 65.7 (1C; CH$_2$*C*H$_2$), 58.9 (1C; *C*H$_2$CH$_2$), 55.6 (1C; NCH$_3$), 50.9 ppm (1C; NCH$_3$); resonances arising from *C*(CF$_3$)$_2$, *o*-C$_6$F$_5$, *m*-C$_6$F$_5$, and *p*-C$_6$F$_5$ were not observed; ^{11}B NMR (128 MHz, [D$_5$]chlorobenzene, 220 K): $\delta=-17.0$ ppm (br s, B(C$_6$F$_5$)$_4^-$); ^{19}F{^{1}H} NMR (376 MHz, [D$_5$]chlorobenzene, 220 K): $\delta=-79.2$ (m, 3F; CF$_3$), −79.6 (m, 3F; CF$_3$), −80.1 (m, 3F; CF$_3$), −81.1 (3F; CF$_3$), −134.4 (m, 8F; *o*-F B(C$_6$F$_5$)$_4^-$), −163.8 (m, 4F; *p*-F B(C$_6$F$_5$)$_4^-$), −167.9 ppm (m, 8F; *m*-F B(C$_6$F$_5$)$_4^-$); resonances for Ph$_3$CCH$_2$Ph:[24] ^{1}H NMR: $\delta=7.40$ (m, 12H; *o*-H and *m*-H(CPh$_3$)), 7.31 (m, 3H; *p*-H(CPh$_3$)), 7.18 (t, $^3J=8.0$ Hz, 1H; *p*-H(Bn)), 7.10 (t, $^3J=8.0$ Hz, 2H; *m*-H(Bn)), 6.72 (d, $^3J=8.0$ Hz, 2H; *o*-H(Bn)), 3.96 ppm (s, 2H; CH$_2$(Bn)); ^{13}C{^{1}H} NMR: $\delta=146.6$ (*ipso*-C(CPh$_3$)), 141.2 (*ipso*-(Bn)), 135.1 (*o*-C(Bn)), 132.1 (*o*-C(CPh$_3$)), 129.2 (*m*-C(CPh$_3$)), 128.5 (*m*-C(Bn)), 127.0 (*p*-C(Bn and CPh$_3$)), 58.0 (*C*Ph$_3$CH$_2$Ph), 45.6 ppm (CPh$_3$*C*H$_2$Ph).

Reaction of [Zr(CH$_2$Ph)$_2$(ON^{2}NO)] (H) with B(C$_6$F$_5$)$_3$—generation of ionic complex [Zr(CH$_2$Ph)(ON^{2}NO)(THF)][PhCH$_2$B(C$_6$F$_5$)$_3$] (6): A Teflon-valved NMR tube was charged with complex **H** (0.030 g, 41.68 μmol) and (THF)·B(C$_6$F$_5$)$_3$ (0.025 g, 42.80 μmol), and [D$_2$]dichloromethane (ca. 0.5 mL) was vacuum-transferred into the mixture at −50 °C. The tube was sealed and kept at −40 °C for 1 h. The NMR data indicated quantitative and clean conversion of **H** to ionic species **6**. ^{1}H NMR (500 MHz, [D$_2$]dichloromethane, 243 K): $\delta=7.55$ (br t, $^2J=7.2$ Hz, 2H; *m*-H, cation), 7.36 (t, $^2J=7.2$ Hz, 1H; *p*-H, cation), 7.23 (m, 2H; *o*-H, cation), 6.91 (t, $^2J=7.3$ Hz, 2H; *m*-H, borate), 6.83 (t, $^2J=7.3$ Hz, 1H; *p*-H, borate), 6.72 (d, $^2J=7.3$ Hz, 2H; *o*-H, borate), 3.75 (d, overlaps the signal from THF, 1H; NCH$_2$C(CF$_3$)$_2$), 3.72 (br m, 2H; α-CH$_2$, THF), 3.59 (d, overlaps the signal from THF, 1H; NCH$_2$C(CF$_3$)$_2$), 3.58 (br m, 2H; α-CH$_2$, THF), 3.56 (d, overlaps the signal from THF, $^2J=15.8$ Hz, 1H; NCH$_2$C(CF$_3$)$_2$), 3.43 (d, $^2J=15.8$ Hz, 1H; NCH$_2$C(CF$_3$)$_2$), 3.20 (m, overlaps the resonances from the ZrCH$_2$ group, 2H; NCH$_2$CH$_2$N), 3.13–3.10 (m, 1H; ZrCH$_2$Ph), 3.00 (m, overlaps the signals from NCH$_2$CH$_2$N and NCH$_3$, 1H; ZrCH$_2$Ph), 3.98 (m, overlaps the resonances from NCH$_3$, 2H; NCH$_2$CH$_2$N), 2.95 (s, 3H; NCH$_3$), 2.78 (br s, 2H; BC*H*$_2$Ph), 2.51 (s, 3H; NCH$_3$), 1.83 (br m, 2H; β-CH$_2$, THF), 1.63 ppm (br m, 2H; β-CH$_2$, THF); ^{13}C{^{1}H} HMBC/HMQC NMR (125 MHz, [D$_2$]dichloromethane, 233 K): $\delta=148.4$ (C$_{ipso}$, Ph, borate), 131.1 (Ph, cation), 129.4 (Ph, cation), 128.6 (Ph, borate), 126.9 (Ph, borate), 124.8 (CF$_3$), 124.7 (CF$_3$), 123.8 (CF$_3$), 122.5 (Ph, borate), 121.2 (CF$_3$), 85.0 (*C*(CF$_3$)$_2$), 84.8 (*C*(CF$_3$)$_2$, 80.3 (ZrCH$_2$Ph), 77.1 (α-CH$_2$, THF), 64.5 (N*C*H$_2$C(CF$_3$)$_2$), 62.7 (N*C*H$_2$C(CF$_3$)$_2$), 62.4 (N*C*H$_2$*C*H$_2$N), 57.6 (N*C*H$_2$*C*H$_2$N), 53.4 (NCH$_3$), 46.9 (NCH$_3$), 26.0 ppm (β-CH$_2$, THF); the quaternary *ipso*-C and another signal from the benzyl group of the cation as well as C$_6$F$_5$ carbon signals were not observed; ^{19}F NMR (282 MHz, [D$_2$]dichloromethane, 243 K): $\delta=-77.3$ (q, $^4J_{\rm F,F}=9.7$ Hz, 6F), −77.8 (br q, 3F), −79.1 (q, $^4J_{\rm F,F}=9.7$ Hz, 3F), −131.5 (d, $^3J_{\rm F,F}=20.8$ Hz, 3F), −164.3 (t, $^3J_{\rm F,F}=20.8$ Hz, 6F), −167.3 ppm (t, $^3J_{\rm F,F}=20.8$ Hz, 6F); ^{11}B NMR (128 MHz, [D$_2$]dichloromethane, 243 K): $\delta=-13.2$ ppm (br s, [PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$).

Reaction of [Zr(CH$_2$Ph)$_2$(ON$^{\rm Cy}$NO)] (3) with B(C$_6$F$_5$)$_3$—generation of ionic complex “[Zr(CH$_2$Ph)(ON$^{\rm Cy}$NO)(THF)][PhCH$_2$B(C$_6$F$_5$)$_3$]” (7): A Teflon-valved NMR tube was charged with complex **3** (0.020 g, 25.85 μmol) and (THF)·B(C$_6$F$_5$)$_3$ (0.016 g, 27.39 μmol), and [D$_2$]dichloromethane (ca. 0.5 mL) was vacuum-transferred into the mixture at −50 °C. The tube was sealed and kept at −40 °C for 1 h. ^{1}H and ^{19}F NMR spectroscopy indicated quantitative conversion of **3** to a mixture of several species/isomers; characteristic data for only the two major species/isomers (**a** and **b**, ca. 1:1.2 ratio) are given. ^{19}F NMR (282 MHz, [D$_2$]dichloromethane, 243 K): $\delta = -73.3$ (q, ${}^{4}J_{F,F} = 11.3$ Hz, 3F; **a**), -76.1 (q, ${}^{4}J_{F,F} = 11.3$ Hz, 3F; **a**), -77.2 (q, ${}^{4}J_{F,F} = 9.9$ Hz, 6F; **b**), -77.9 (q, overlaps a signal from species **A**, ${}^{4}J_{F,F} = 9.9$ Hz, 6F; **b**), -78.0 (q, overlaps a signal from species **b**, ${}^{4}J_{F,F} = 11.3$ Hz, 3F; **a**), -78.5 (q, ${}^{4}J_{F,F} = 11.3$ Hz, 3F; **a**), -131.6 (d, ${}^{3}J_{F,F} = 22.5$ Hz, 3F), -164.4 (t, ${}^{3}J_{F,F} = 22.5$ Hz, 6F), -167.4 ppm (t, ${}^{3}J_{F,F} = 22.5$ Hz, 6F).

Crystal structure determination of 3: A suitable single-crystal was mounted onto a glass fiber using the "oil-drop" method. Diffraction data were collected at 100 K using a Bruker APEX CCD diffractometer with graphite-monochromatized Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A combination of ω and ϕ scans were carried out to obtain at least a unique data set. The crystal structure was solved by means of the Patterson method, remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F^2 (programs SHELXS-97 and SHELXL-97).[35] Many hydrogen atoms could be found from the Fourier difference analysis. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Crystal data and details of data collection and structure refinement for compound **3** are given in Table 2.

CCDC-611997 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Typical procedure for the polymerization of ethylene: Polymerization experiments were performed in a 150-mL high-pressure glass reactor equipped with a mechanical stirrer (Pelton turbine) and externally heated with a double mantle with a circulating oil/water bath as desired. In a typical experiment (see Table 3), the reactor was filled with toluene (60 mL) under argon and pressurized at 6 atm of ethylene (Air Liquide, 99.99 %). The reactor was thermally equilibrated at the desired temperature for 1 h. The ethylene pressure was reduced to 1 atm and the catalyst precursor (30.0–40.0 μmol) in toluene (1.0 mL) was added through a syringe. The ethylene pressure was immediately increased to 6 atm and the solution stirred for the desired time. Ethylene consumption was monitored with an electronic manometer connected to a secondary 100-mL ethylene tank, which feeds the reactor by maintaining a constant total pressure. The polymerization reaction was stopped by making a vent in the vessel and quenching the mixture with a 10 % HCl solution in methanol (30 mL). The polymer was collected by filtration, washed with methanol (2 × 100 mL), and dried under vacuum overnight.

Typical procedure for the polymerization of 1-hexene: Polymerization experiments were performed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. In a typical experiment (Table 3, entry 8) in the glove box, a Schlenk flask was charged with a solid precatalyst (13.8–41.0 μmol), an activator (13.8–41.0 μmol), and a solvent (hexane or toluene, 5 mL). The mixture was stirred at room temperature for 1–2 min and then 1-hexene (5.0 mL) was added to the flask through a syringe. The reactor was thermally equilibrated immediately at the desired temperature and the solution was stirred for the desired time. The polymerization reaction was quenched by injecting a 10 % HCl solution in methanol (10 mL) into the reaction mixture. The polymer was collected by filtration, washed with methanol (2 × 500 mL), and dried under reduced pressure overnight.

The ^{1}H NMR spectrum of the poly(1-hexene) samples indicated that the polymer was isotactic-rich (see Results and Discussion section) with vinylidene type end-groups: ^{1}H NMR (500 MHz, [D$_1$]chloroform) $\delta = 5.6$, 4.0–3.9 ppm.

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[1] a) D. C. Bradley, R. M. Mehrotra, I. P. Rothwell, A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic Press, London, **2001**; b) R. M. Mehrotra, A. Singh, *Prog. Inorg. Chem.* **1997**, *46*, 239–545; c) L. G. Hubert-Pfalzgraf, *Coord. Chem. Rev.* **1998**, *178–180*, 967–997.

[2] U. Knof, A. Von Zelewsky, *Angew. Chem.* **1999**, *111*, 312–333; *Angew. Chem. Int. Ed.* **1999**, *38*, 302–322.

[3] For reviews on post-metallocene complexes related to polymerization, see: a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; b) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283–315; c) P. Corradini, G. Guerra, L. Cavallo, *Acc. Chem. Res.* **2004**, *37*, 231–241.

[4] a) S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2001**, *123*, 6847–6856; b) S. Kojoh, T. Matsugi, J. Saito, M. Mitani, T. Fujita, N. Kashiwa, *Chem. Lett.* **2001**, 822–823; c) J. Saito, M. Mitani, S. Matsui, J. Y. Mohri, S. Kojoh, N. Kashiwa, T. Fujita, *Angew. Chem.* **2001**, *113*, 3002–3004; *Angew. Chem. Int. Ed.* **2001**, *40*, 2918–2920; d) M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S.-I. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2002**, *124*, 3327–3336; e) J. Saito, M. Mitani, J. Mohri, S. Ishii, Y. Yoshida, T. Matsugi, S. Kojoh, N. Kashiwa, T. Fujita, *Chem. Lett.* **2001**, 576–577; f) M. Mitani, R. Furuyama, J.-I. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2002**, *124*, 7888–7889.

[5] a) J. Tian, G. W. Coates, *Angew. Chem.* **2000**, *112*, 3772–3775; *Angew. Chem. Int. Ed.* **2000**, *39*, 3626–3629; b) J. Tian, P. D. Hustad, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 5134–5135; c) A. F. Mason, G. W. Coates, *J. Am. Chem. Soc.* **2004**, *126*, 16326–16327.

[6] a) E. Y. Tshuva, M. Versano, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Inorg. Chem. Commun.* **1999**, *2*, 371–373; b) E. Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Chem. Commun.* **2000**, 379–380; c) E. Y. Tshuva, S. Groysman, I. Goldberg, M. Kol, Z. Goldschmidt, *Organometallics* **2002**, *21*, 662–670; d) E. Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Organometallics* **2001**, *20*, 3017–3028; e) E. Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Inorg. Chem.* **2001**, *40*, 4263–4270; f) E. Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Inorg. Chem. Commun.* **2000**, *3*, 611–614; g) E. Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Chem. Commun.* **2001**, 2120–2121; h) E. Y. Tshuva, I. Goldberg, M. Kol, *J. Am. Chem. Soc.* **2000**, *122*, 10706–10707; i) S. Segal, I. Goldberg, M. Kol, *Organometallics* **2005**, *24*, 200–202; j) A. Yeori, S. Groysman, I. Goldberg, M. Kol, *Inorg. Chem.* **2005**, *44*, 4466–4468.

[7] a) C. Capacchione, A. Proto, H. Ebeling, R. Mülhaupt, K. Möller, T. P. Spaniol, J. Okuda, *J. Am. Chem. Soc.* **2003**, *125*, 4964–4965; b) C. Capacchione, M. D'Acunzi, O. Motta, L. Oliva, A. Proto, J. Okuda, *Macromol. Chem. Phys.* **2004**, *205*, 370–373; c) C. Capacchione, A. Proto, H. Ebeling, R. Mülhaupt, K. Möller, R. Manivannan, T. P. Spaniol, J. Okuda, *J. Mol. Catal. B* **2004**, *213*, 137–140; d) K. Beckerle, C. Capacchione, H. Ebeling, R. Manivannan, R. Mülhaupt, A. Proto, T. P. Spaniol, J. Okuda, *J. Organomet. Chem.* **2004**, *689*, 4636–4641; e) C. Capacchione, R. Manivannan, M. Barone, K. Beckerle, R. Centore, L. Oliva, A. Proto, A. Tuzi, T. P. Spaniol, J. Okuda, *Organometallics* **2005**, *24*, 2971–2982; f) K. Beckerle, R. Manivannan, T. P. Spaniol, J. Okuda, *Organometallics* **2006**, *25*, 3019–3026.

[8] a) J. P. Corden, W. Errington, P. Moore, M. G. H. Wallbridge, *Chem. Commun.* **1999**, 323–324; b) P. D. Knight, A. J. Clarke, B. S. Kimber-

ley, R. A. Jackson, P. Scott, *Chem. Commun.* **2002**, 352–353; c) T. Repo, M. Klinga, P. Pietikäinen, M. Leskelä, A.-M. Uusitalo, T. Pakkanen, K. Hakala, P. Aaltonen, P. B. Löfgren, *Macromolecules* **1997**, *30*, 171–175; d) J. Balsells, P. J. Caroll, P. J. Walsh, *Inorg. Chem.* **2001**, *40*, 5568–5574.

[9] I. J. Munslow, A. J. Clarke, R. J. Deeth, I. Westmoreland, P. Scott, *Chem. Commun.* **2002**, 1868–1869.

[10] For Group 4 metal complexes that incorporate tridentate $(OZO)^{2-}$ dialkoxide ligands, see: a) L. Lavanant, L. Toupet, C. W. Lehmann, J.-F. Carpentier, *Organometallics* **2005**, *24*, 5620–5633; b) L. Lavanant, A. Silvestru, A. Faucheux, L. Toupet, R. F. Jordan, J.-F. Carpentier, *Organometallics* **2005**, *24*, 5604–5619, and references therein.

[11] T. Tsukahara, D. C. Swenson, R. F. Jordan, *Organometallics* **1997**, *16*, 3303–3313.

[12] L. Lavanant, T.-Y. Chou, Y. Chi, C. W. Lehmann, L. Toupet, J.-F. Carpentier, *Organometallics* **2004**, *23*, 5450–5458.

[13] A. Amgoune, L. Lavanant, C. M. Thomas, Y. Chi, R. Welter, S. Dagorne, J.-F. Carpentier, *Organometallics* **2005**, *24*, 6279–6282.

[14] For other Group 3 and 4 and lanthanide complexes bearing fluorinated alkoxide ligands, see: a) D. C. Bradley, H. Chudszynska, M. B. Hursthouse, M. Motevalli, *Polyhedron* **1994**, *13*, 1907–1918; b) D. C. Bradley, H. Chudszynska, M. B. Hursthouse, M. Motevalli, *Polyhedron* **1994**, *13*, 7–14; c) J. A. Samuels, E. B. Lobkovsky, W. E. Streib, K. Folting, J. C. Huffman, J. W. Zwanziger, K. G. Caulton, *J. Am. Chem. Soc.* **1993**, *115*, 5093–5104.

[15] I. S. Chang, J. T. Price, A. J. Tomlinson, C. J. Willis, *Can. J. Chem.* **1972**, *50*, 512–520.

[16] The synthetic procedure is identical to that of related fluoro amino alcohol ligands $HO(CF_3)_2CH_2NH(CH_2CH_2OMe)$ and $HO(CF_3)_2CH_2N(CH_2CH_2OMe)_2$, which have been utilized in preparation of the Sr^{II} , Ba^{II}, and Cu^{II} CVD source reagents: a) Y. Chi, S. Ranjan, T.-Y. Chou, C.-S. Liu, S.-M. Peng, G.-H. Lee, *J. Chem. Soc. Dalton Trans.* **2001**, 2462–2466; b) P.-F. Hsu, Y. Chi, T.-W. Lin, C.-S. Liu, A. J. Carty, S.-M. Peng, *Chem. Vap. Deposition* **2001**, *7*, 28–34; c) Y. Chi, S. Ranjan, P.-W. Chung, H.-Y. Hsieh, S.-M. Peng, G.-H. Lee, *Inorg. Chim. Acta* **2002**, *334*, 172–182; for ring-opening of $(CF_3)_2\overline{COC}H_2$ by alcohol nucleophiles see also: d) V. A. Petrov, *Synthesis* **2002**, 2225–2231.

[17] R. F. Jordan, R. E. Lapointe, C. S. Bajgur, S. F. Echols, R. Willett, *J. Am. Chem. Soc.* **1987**, *109*, 4111–4113.

[18] a) The lower limit for the racemization barrier $\Delta G^{\ddagger}_{(\mathrm{racemization})}$ was estimated by using the following equations: $\Delta G^{\ddagger}_{(\mathrm{racemization})} = 4.576T_c[10.319+\log(T_c/k_c)]$, where T_c is the (estimated) coalescence temperature and k_c is the exchange rate constant at coalescence, which is given by $k_c = \pi[(\Delta\nu^2_{AB} + 6J^2_{AB}]^{1/2}/2^{1/2}$. For $C(CF_3)_2CH_2$: $\Delta\nu_{AB} = 162$ Hz, $J_{AB} = 10.3$ Hz, $T_c = 403$ K. See: b) S. Alexander, *J. Chem. Phys.* **1962**, *37*, 967–974; c) R. J. Kurland, M. B. Rubin, W. B. Wise, *J. Chem. Phys.* **1964**, *40*, 2426–2427; d) D. Kost, A. Zeichner, *Tetrahedron Lett.* **1974**, *15*, 4533–4536.

[19] J. Balsells, P. J. Carroll, P. J. Walsh, *Inorg. Chem.* **2001**, *40*, 5568–5574.

[20] A. Yeori, S. Groysman, I. Goldberg, M. Kol, *Inorg. Chem.* **2005**, *44*, 4466–4468.

[21] D. C. Bradley, R. C. Mehrotra, I. P. Rothwell, A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic Press, New York, **2001**.

[22] No broadening of the ^{19}F NMR quartets was observed upon warming, but the diasteromeric ratio changed to about 1:2 at 338 K. The phenomenon is reversible upon cooling.

[23] E. J. Stoebenau, R. F. Jordan, *J. Am. Chem. Soc.* **2003**, *125*, 3222–3223.

[24] Complex **5** is stable overnight at 220 K and decomposes within 6 h at 270 K, and more rapidly at room temperature.

[25] a) S. L. Latesky, A. K. McMullen, G. P. Niccolai, I. P. Rothwell, J. C. Huffman, *Organometallics* **1985**, *4*, 902–908; b) R. F. Jordan, R. E. Lapointe, C. S. Bajgur, S. F. Echols, R. Willett, *J. Am. Chem. Soc.* **1987**, *109*, 4111–4113; c) M. Bochmann, S. J. Lancaster, M. B. Hursthouse, K. M. Abdul Malik, *Organometallics* **1994**, *13*, 2235–2243.

[26] a) C. Pellecchia, A. Grassi, A. Immirzi, *J. Am. Chem. Soc.* **1993**, *115*, 1160–1162; b) C. Pellecchia, A. Immirzi, A. Grassi, A. Zambelli, *Organometallics* **1993**, *12*, 4473–4478; c) A. D. Horton, J. De With, *Organometallics* **1997**, *16*, 5424–5436.

[27] A similar DFT study was also performed on the neutral complexes **H** and **3**, and gave results consistent with spectroscopic observations.

[28] Catalytic combinations based on MAO activator were not explored because of the possible transfer of $(OZZO^R)^{2-}$ ligands between group 4 metal and aluminum centers; see reference [10b].

[29] At 45 °C and 8 atm, $[Zr(CH_2Ph)_2(\{pyC(CF_3)_2O\}_2)]$ (**G**) combined with $[Ph_3C][B(C_6F_5)_4]$ affords 56 kg PE mol^{-1} h^{-1}, $M_w = 21\,800$ g mol^{-1} and $M_w/M_n = 3.7$; with $B(C_6F_5)_3$, 32 kg PE mol^{-1} h^{-1}, $M_w = 16\,100$ g mol^{-1} and $M_w/M_{n=}2.6$. See reference [11].

[30] a) T. Asakura, M. Demura, Y. Nishiyama, *Macromolecules* **1991**, *24*, 2334–2340; b) X. Zhao, G. Odian, A. Rossi, *J. Polym. Sci. A: Polym. Chem.* **2000**, *38*, 3802–3811; c) G. Galland, L. F. Da Silva, A. Nicolini, *J. Polym. Sci. A: Polym. Chem.* **2005**, *43*, 4744–4753.

[31] V. Busico, R. Cipullo, *Prog. Polym. Sci.* **2001**, *26*, 443–533.

[32] G. N. Babu, R. N. Newmark, J. C. W. Chien, *Macromolecules* **1994**, *27*, 3383–3388.

[33] V. Busico, D. Brita, L. Caporaso, R. Cipullo, M. Vacatello, *Macromolecules* **1997**, *30*, 3971–3977.

[34] T. G. Scholte, N. L. J. Meijerink, H. M. Schofelleers, A. M. G. Brands, *J. Appl. Polym. Sci.* **1984**, *29*, 3763–3782.

[35] a) G. M. Sheldrick, SHELXS-97, Program for the Determination of Crystal Structures, University of Goettingen (Germany), **1997**; b) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Goettingen (Germany), **1997**.

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