Monocyclopentadienyl Bis(phenoxo-imino) Zirconium Complexes as Precatalyst Species for Olefin Polymerization. Stereospecific Methylation of an Imino Group with Formation of a Zirconium−amido Bond

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The Schiff base *N*,*N′*-*o*-phenylenebis(3,5-di-*tert*-butyl-salicylideneimine) (**1**; ^{t}Bu$_4$salophenH$_2$) reacts with 1 equiv of $Zr(\eta^5\text{-}C_5H_5)Cl_3\cdot DME$ in the presence of 2.2 equiv of NEt_3 in pentane to give the monocyclopentadienyl bis(phenoxo-imino) monochloro zirconium derivative $Zr(\eta^5\text{-}C_5H_5)[C_6H_4\text{-}1,2\text{-}\{N{=}CH(3,5\text{-}{}^tBu_2C_6H_2\text{-}2\text{-}O)\}_2]Cl$ (**2**). Moreover, 2 equiv of the monolithiated reagent derived from 3-*tert*-butyl-*N*-ethylsalicylaldimine by reaction with Li^{n}Bu in hexane reacts at −78 °C with 1 equiv of $Zr(\eta^5\text{-}C_5H_5)Cl_3\cdot DME$ in THF to yield the corresponding monocyclopentadienyl bis(phenoxo-imino) monochloro zirconium complex $Zr(\eta^5\text{-}C_5H_5)[CH_3CH_2N{=}CH\{(3\text{-}{}^tBuC_6H_3\text{-}2\text{-}O)\}]_2Cl$ (**5**) after elimination of LiCl. Methylation of **2** with MgClMe in pentane or toluene at −78 °C affords $Zr(\eta^5\text{-}C_5H_5)[1,2\text{-}C_6H_4\{N{=}CH(3,5\text{-}{}^tBu_2C_6H_2\text{-}2\text{-}O)\}\{NCH(Me)(3,5\text{-}{}^tBu_2C_6H_2\text{-}2\text{-}O)\}]$ (**3**) as a result of the reduction of one of the C=N bonds of the coligand. The hydrolysis of **3** gives the new organic compound $[C_6H_4\{N{=}CH(3,5\text{-}{}^tBu_2C_6H_2\text{-}2\text{-}OH)\}\{NCH(Me)(3,5\text{-}{}^tBu_2C_6H_2\text{-}2\text{-}OH)\}]$ (**4**), which was also quantitatively isolated by reaction of **1** with MgClMe followed by treatment with a saturated solution of NH_4Cl in water. All of the reported compounds were characterized by the usual analytical and spectroscopic methods, and the molecular structure of **5** was determined by X-ray diffraction analysis from suitable single crystals. The catalytic activities of **2**, **3**, and **5** for ethylene polymerization using MAO as cocatalyst were determined.

Introduction

The quest for new olefin polymerization catalysts displaying high activities similar to those of the group 4 metallocene complexes MCp_2X_2[1] is a highly topical research challenge. In this context, ligands with oxygen and nitrogen donors have been extensively investigated.[2] Chelating bidentate monoanionic ligands based on alkoxo-pyridino groups,[3] tridentate dianionic ligands based on dialkoxo-amino groups,[4] and tetradentate ligands based on dialkoxo-diamino[5] and dialkoxo-diimino groups[6] have received increasing attention for cyclopentadienyl-free halide or alkyl group 4 catalyst precur-

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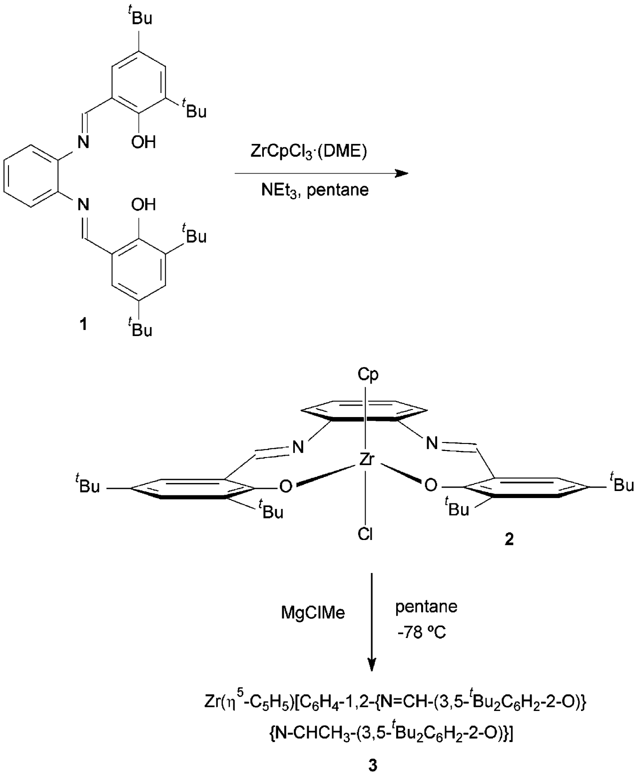
sors $M(N,O^-)_2X_2$, $M(N,O^-,O^-)X_2$, and $M(N,N,O^-,O^-)X_2$, which have proved to be active in olefin polymerizations upon activation with suitable activators. Monocyclopentadienyl dihalide or dialkyl group 4 metal complexes $MCp(N,O^-)X_2$ containing a bidentate N,O^- monoanionic chelate ligand have been also reported,[7] producing high-molecular-weight polyethylene[7d] when activated with methylaluminoxane (MAO). The polymerization process using these complexes can be rationalized by the accepted Ziegler–Natta model,[1] since two coordination sites in cis positions are available.

Very recently, new types of cyclopentadienyl-amido[8] and monocyclopentadienyl-alkoxo[9] monochloro or monoalkyl group 4 complexes have been reported. The double-silylamido-bridged cyclopentadienyl zirconium benzyl complex $Zr[\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N^tBu)_2]Bz$ reacts with $B(C_6F_5)_3$ to give the isolated ion pair $\{Zr[\eta^5\text{-}C_5H_3(SiMe_2\text{-}\eta^1\text{-}N^tBu)_2]\}^+[PhCH_2B(C_6F_5)_3]^-$, which is active in ethylene polymerizations, even though it does not apparently contain a Zr–alkyl ligand.[8c]

The use of tetradentate Schiff bases H_2L to synthesize group 4 metal coordination compounds has been studied in order to explore their reactivity with ammonium salts[10] or trimethylaluminum[11] to generate cationic species, considered as the active species in the olefin polymerization processes. Compounds of the type $M(L)Cl_2$ (M = Ti, Zr, Hf; L = N,N,O^-,O^--donor Schiff base) have been described in which the "MCl_2" fragment exhibits a cis or trans geometry, depending on the nature of the metal and the ligand (L).[12] In this context, we have focused our efforts on the preparation of monocyclopentadienyl monochloro and monoalkyl group 4 metal complexes of the type MCp(L)X (X = halo and alkyl ligands), incorporating one tetradentate or two bidentate Schiff base ancillary ligands, and we were interested in exploring the reactivity of such complexes toward aluminum alkyls and $B(C_6F_5)_3$. Herein we report the synthesis and characterization of some monocyclopentadienyl phenoxo-imino monochloro zirconium compounds, the results of alkylation reactions involving a ligand C=N bond, and the application of these complexes in ethylene polymerizations in the presence of MAO.

Scheme 1



Results and Discussion

1. Monocyclopentadienyl Derivatives Containing a Bis(phenoxo-imino) Tetradentate Ligand. The tetradentate Schiff base **1** (Scheme 1) was prepared in high yield from 1,2-diaminobenzene and 3,5-di-*tert*-butyl-salicylaldehyde in cold methanol following a modified literature procedure.[13] NMR data of **1** are in accord with a C_{2v}-symmetric molecule.

Compound **1** reacts with 1 equiv of $Zr(\eta^5\text{-}C_5H_5)Cl_3\cdot DME$[14] (DME = 1,2-dimethoxyethane) in the presence of 2.2 equiv of NEt_3 in pentane under reflux to form the monocyclopentadienyl bis(phenoxo-imino) monochloro complex $Zr(\eta^5\text{-}C_5H_5)[C_6H_4\text{-}1,2\text{-}\{N{=}CH(3,5\text{-}^tBu_2C_6H_2\text{-}2\text{-}O)\}_2]Cl$ (**2**). The reaction of **2** with methylmagnesium chloride (3 M solution in THF) in pentane or toluene at −78 °C does not give a zirconium methyl species but results in alkylation of one of the C=N bonds, with

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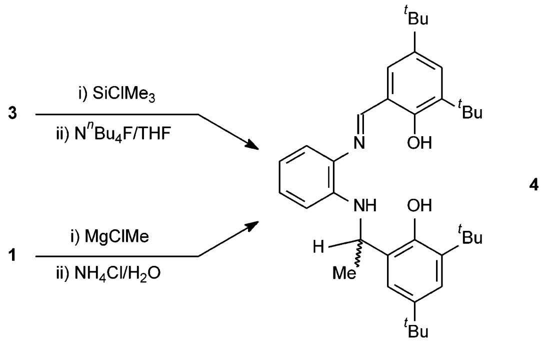
Scheme 2



formation of the diphenoxo-imino-amido zirconium complex [Zr(η^5-C_5H_5)[C_6H_4-1,2-{N═CH(3,5-^{t}$Bu_2C_6H_2$-2-O)}-{$NCHCH_3$(3,5-^{t}$Bu_2C_6H_2$-2-O)}] **3** (Scheme 1).

The reaction of **3** with an excess of $SiClMe_3$ followed by treatment with a 3 M solution of N^nBu_4F in THF resulted in the hydrolysis of the zirconium complex and liberation of the new imine-amine substance **4**. Alternatively, **4** can be also synthesized in quantitative yield by reaction of **1** with 3.2 equiv of MgClMe followed by treatment with a saturated aqueous solution of NH_4Cl (Scheme 2).

Compounds **2** and **3** are obtained as yellow and red solids, respectively, which are soluble in aromatic, aliphatic, and chlorinated hydrocarbon solvents. They can be stored for months under an inert atmosphere without decomposition and remain air stable for some weeks in the solid state. The analytical composition fits well the proposed formulations. The ^{1}H NMR spectra ($CDCl_3$, 25 °C) of **1** and **2** show, respectively, singlets assignable to the N═CH protons, AA′BB′ spin systems for the phenylene ring, AB spin systems for the phenoxo protons, and two signals for the *tert*-butyl groups. A singlet for the cyclopentadienyl ring protons in the expected region of the spectrum for compound **2** and one singlet due to O*H* resonances in the spectrum of **1** are also observed. The ^{1}H NMR spectra ($CDCl_3$, 25 °C) of compounds **3** and **4** exhibit four singlets for the nonequivalent *tert*-butyl groups, ABCD spin systems for the phenylene rings, and two AB spin systems for the phenoxo protons. The spectrum of **3** also shows the typical resonances at δ 5.0 (q, 1H) and δ 1.18 (d, 3H) with the coupling constant $^3J = 6.3$ Hz for the NCH-(CH_3) fragment, while for **4** the characteristic signals for the NHCH(CH_3) group are observed at δ 4.57 (d, 1H), 4.49 (dq, 1H), and 1.65 (d, 3H) with coupling constants of 2.9 and 6.8 Hz. The resonances of the imine protons appear at δ 8.9 and 8.62 for **3** and **4**, respectively. Characteristic resonances for methyl groups bonded to the zirconium atom are not observed in the spectrum of compound **3**. These spectroscopic features are consistent with a C_s symmetry for compound **2** and C_1 symmetry for compounds **3** and **4** and indicate that one of the two C═N bonds has been methylated.

The ^{13}C NMR spectroscopic data corroborate the methylation of **2**, proceeding through the reduction of one of the salophen imino groups with the stereospecific formation of the zirconium amido chiral complex **3**. A significant spectroscopic feature associated with the ^{13}C NMR spectra of the substances described here is the resonance for the imino carbon atom −HC═N−, which is observed at δ 164.4 and 164.9 for **1** and **4**. Almost identical chemical shifts are observed for compounds **2** and **3** (δ 164.2 and 159.3, respectively), which suggests that in solution the imino N atom is not coordinated or interacts only very weakly with the metal center, with coordination being disfavored in compound **3** due to folding of the diphenoxo-imino-amido ligand. Comparison of the chemical shifts for the carbon atoms in compounds **3** and **4** shows that in **3** there is a very slight π-interaction between the amido nitrogen free electron pair and the metal atom (δ_{NCHMe} 58.2 and 57.7 for **3** and **4**, respectively; $\Delta\delta_{NCHMe} = 0.5$ ppm). This effect contributes to the conjugation of the amido nitrogen free electron pair with the phenylene ring system, as indicated by the shielding of the *ipso*-*C*(phenylene)−N(sp^3) resonance in **3** (δ 134.9) with respect to that in **4** (δ 138.8; $\Delta\delta = 4$ ppm). The small deshielding of the *C*O resonances in compounds **2** and **3** compared with the signal for **1** (δ 158.3) indicates $\sigma + \pi$ coordination of alkoxo ligands in the zirconium complexes. Taking into account the nature of the alkoxo group as three-electron ($\sigma + \pi$) and the amido as one-electron (σ) donor ligands, a 16-electron metal environment for these zirconium compounds can be achieved by coordination of the cyclopentadienyl, the two alkoxo, and the chloro (or amido) ligands.

The formation of **3** can be explained by two possible pathways (Scheme 3). In pathway **A**, compound **2** reacts with MgClMe to give a zirconium methyl intermediate which may undergo a stereospecific migration of the methyl ligand to an imino moiety. Alternatively, the Grignard reagent may react directly with the C═N bond, a sequence that may be favored by the coordination of magnesium to the chloro ligand (pathway **B**). The formation of the zirconium−amido bond in **3** is favored by the "*class a*" (hard acid) character of the zirconium atom.[15]

When the reaction of **2** with MgClMe/THF (1:1.2 ratio) in rigorously dried toluene-d_8 solution was monitored by NMR spectroscopy at low temperatures, the formation of an asymmetric species was detected at −50 °C, which was converted to **3** at room temperature. However, the formation of an intermediate zirconium methyl complex (**A**) was never observed. It seems likely, therefore, that the formation of **3** takes place through direct methylation of the imino function. We have also studied this reaction under the same conditions on a preparative scale, varying the molar ratio of **2** to MgClMe. When **2** is allowed to react with 0.8 equiv of MgClMe, we observed in the final product the presence of starting material and **3** as the major product. Treatment of **2** with an excess of the Grignard reagent (4 equiv) leads exclusively and cleanly to **3**; there is no alkylation of zirconium or attack on the second imino function.

Reduction of an phenoxo-imino functionality to give a phenoxo-amido group has been shown during the olefin polymerization process catalyzed by a family of zirconium complexes containing two phenoxo-imino chelate ligands[16] using $Ph_3CB(C_6F_5)_4/Al^iBu_3$ as activator. Kinetic studies demonstrating similar behavior of cyclopentadienyl-free Schiff-base dibenzyl complexes of

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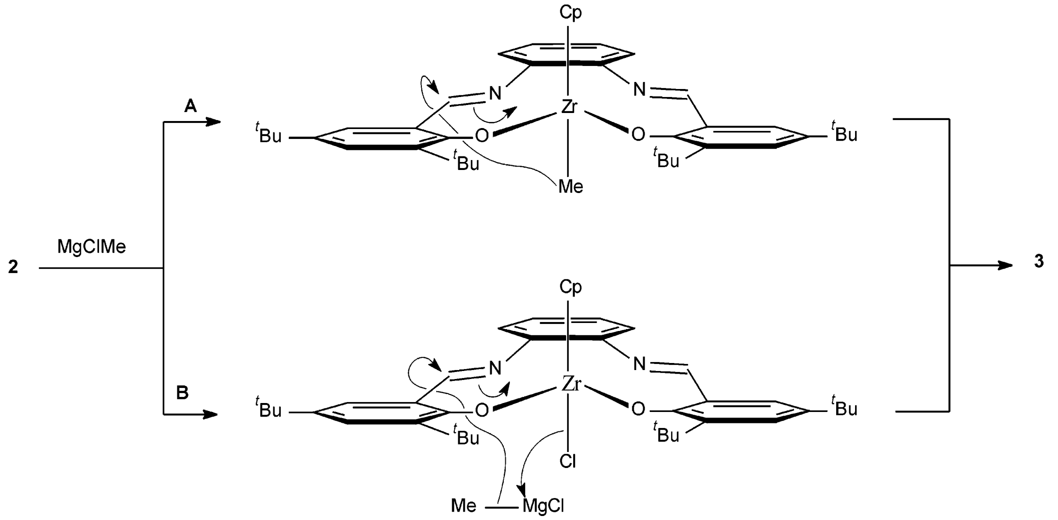
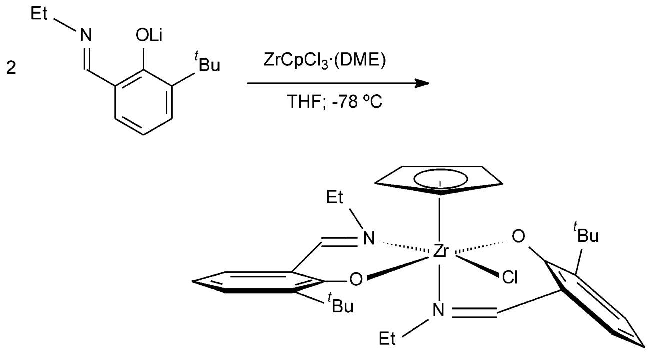
Scheme 3



titanium and zirconium have also been reported.[17] It has been pointed out that the neutral group 4 diimino dibenzyl complexes are unstable with respect to a 1,2-migratory insertion of a benzyl ligand to the imino C=N bond. This reaction constitutes a catalyst deactivation mechanism in the olefin polymerization process catalyzed by these compounds. However, Zr($^{\text{bis}-t\text{Bu}}$Salfen)($CH_2Ph)_2$ ($^{\text{bis}-t\text{Bu}}$Salfen = [Fe{η^5-C_5H_4N=CH(3,5-^{t}Bu$_2$-C_6H_2)O}$_2$]), in which both zirconium benzyl and imino ligands are present, has been isolated as a stable substance at room temperature.[18] Alternatively, direct nucleophilic attack has been proposed to occur at the electrophilic carbon atom of one of the imino bonds.[19] The nucleophilic attack on carbonyl functions (aldehydes and ketones) as well as imino groups due to coordination to transition metals[20] as well as Lewis acids[21] is, of course, a well-known process.

2. Monocyclopentadienyl Derivatives Containing Two Phenoxo-imino Ligands. The reaction of Li[EtN=CH(3-^{t}BuC_6H_3-2-O)], obtained by addition of Li^n-Bu in hexane to the corresponding iminophenol in dry THF at −78 °C under argon, with the cyclopentadienyl zirconium compound Zr(η^5-C_5H_5)Cl_3·DME, in THF at −78 °C, gives the monocyclopentadienyl bis(phenoxo-imino) monochloro derivative Zr(η^5-C_5H_5)[CH_3CH_2N=CH{(3-^{t}BuC_6H_3-2-O)}]$_2$Cl (**5**) (Scheme 4). An analytically pure sample was obtained by layering a concentrated dichloromethane solution with light petroleum and cooling. The compound was obtained as a gray powder in good yield. Related titanium and zirconium monophenoxo-imino complexes as well as some CpTi compounds containing two Schiff base ligands embedding the Ti(IV) in a six-coordinate environment have been recently reported.[22] Attempts to alkylate compound **5** did not give isolable products.

Scheme 4



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In the ^{1}H NMR spectrum of **5**, the imino protons appear at δ 8.05 and 7.99, while the ^{13}C chemical shift of the imino carbon atoms indicates deshielding compared with the free ligand ($\Delta\delta \approx 7$ ppm), indicating that the nitrogen atoms are coordinated to the metal center, in contrast with the observations for **2** and **3**. These spectroscopic data are consistent with an asymmetric geometry for this compound in solution.

The structure of complex **5** was confirmed by a single-crystal X-ray diffraction study (Figure 1). Selected bond distances and angles are listed in Table 1. The compound crystallized with a solvent molecule that could not be resolved (elemental analysis suggests 0.25 CH_2Cl_2).

If the centroid of the cyclopentadienyl ring is considered as a single coordination site, the geometry around the titanium center can be well described as octahedral. The structure shows a trans arrangement of oxygen atoms, with the Cp ligand in a cis position with respect to the chlorine atom, and the two nitrogen atoms located in cis positions. Similar trans oxygen disposition has been previously observed for bis(phenoxo-imino) titanium and zirconium derivatives,[6c,23] and this is the expected structural trend for the favored geometry

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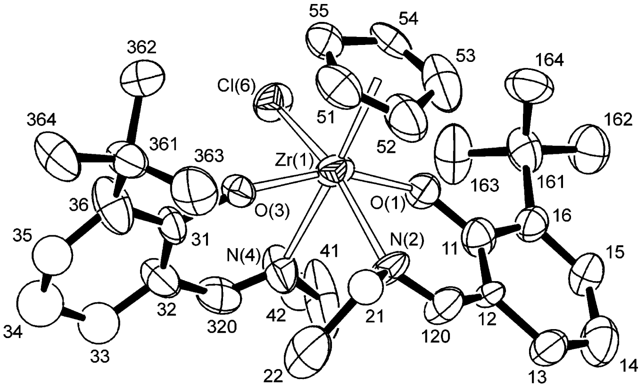

Figure 1. Molecular structure of **5**, showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 5[a]

Zr(1)−O(1)	2.040(9)	Zr(1)−N(2)	2.307(8)
Zr(1)−O(3)	2.038(7)	Zr(1)−N(4)	2.380(12)
Zr(1)−Cl(6)	2.537(3)	Zr(1)−C(52)	2.58(2)
Zr(1)−C(51)	2.628(6)	Zr(1)−C(53)	2.646(7)
Zr(1)−C(54)	2.590(10)	Zr(1)−C(55)	2.581(12)
Zr(1)−C(5x)	2.314	O(1)−C(11)	1.341(14)
O(3)−C(31)	1.368(12)	C(120)−N(2)	1.258(15)
C(11)−C(12)	1.399(14)	C(320)−N(4)	1.226(16)
N(2)−C(21)	1.495(18)	N(4)−C(41)	1.516(14)

O(1)−Zr(1)−N(2)	78.2(3)	O(3)−Zr(1)−Cl(6)	94.2(3)
O(3)−Zr(1)−O(1)	157.8(3)	N(4)−Zr(1)−Cl(6)	78.7(3)
O(1)−Zr(1)−N(4)	83.7(4)	O(1)−Zr(1)−C(5x)	100.0
O(1)−Zr(1)−Cl(6)	89.5(2)	N(2)−Zr(1)−C(5x)	100.9
O(3)−Zr(1)−N(2)	90.2(4)	O(3)−Zr(1)−C(5x)	100.7
N(2)−Zr(1)−N(4)	80.0(4)	N(4)−Zr(1)−C(5x)	176.3
N(2)−Zr(1)−Cl(6)	156.3(3)	Cl(6)−Zr(1)−C(5x)	101.1
O(3)−Zr(1)−N(4)	75.7(3)	C(11)−O(1)−Zr(1)	143.8(7)
C(31)−O(3)−Zr(1)	145.5(7)	O(1)−C(11)−C(12)	117.9(10)
O(3)−C(31)−C(32)	117.8(9)	O(1)−C(11)−C(16)	121.1(9)
O(3)−C(31)−C(36)	121.5(9)	C(120)−N(2)−C(21)	112.7(11)
C(320)−N(4)−C(41)	113.4(12)	C(120)−N(2)−Zr(1)	127.9(8)
C(320)−N(4)−Zr(1)	128.1(9)	C(21)−N(2)−Zr(1)	118.7(7)
C(41)−N(4)−Zr(1)	118.2(8)		

[a] Esd's are given in parentheses. C(5x) is the centroid of the Cp ring, C(51−55).

Table 2. Ethylene Polymerizations Catalyzed with Complexes 2, 3, and 5/MAO[a]

entry	cat.	T (°C)	t (min)	yield (mg)	activity[b]	M_w[c]	M_n[c]	M_w/M_n	T_f[d] (°C)	T_c[d] (°C)
1	**2**	25	5	5	5.2					
2	**3**	25	5	1	1.1					
3	**2**	50	5	11	11.4	234 600	113 500	2.1	139	123
4	**3**	50	5	2	2.2					
5	**2**	50	15	49	17.9	321 200	155 400	2.1	139	123
6	**3**	50	15	63	22.9	307 400	144 000	2.1	139	124
7	**2**	50	30	82	15	386 000	177 000	2.2	140	123
8	**3**	50	30	140	25.5	376 300	197 000	1.9	139	122
9	**5**[e]	25	30	95	32					
10	**5**[e]	50	15	310	207					
11	**5**[e]	50	30	1385	462					

[a] Conditions: ethylene pressure 1 atm; solvent toluene, 50 mL; MAO:Zr = 1000:1; catalyst 11.0 μmol. [b] In units of kg of polymer (mol of Zr)$^{-1}$ h^{-1} atm^{-1}. [c] Determined by GPC. [d] Determined by DSC; T_f = melting point; T_c = crystallization point. [e] Catalyst 6 μmol.

investigated for zirconium complexes containing bis-[N,O] bidentate ligands, $Zr[N,O]_2X_2$.[24] The two trans components N(2)−Zr(1)−Cl(6) and O(3)−Zr(1)−O(1) with angle values of 156.3(3) and 157.8(3)°, respectively, are bent away from the Cp plane, while the Cp(centroid)−Zr(1)−N(4) angle is almost linear (176.3°). The plane of one of the phenoxo-imino ligands, O(1)−C(11)−C(12)−C(120)−N(2), is nearly parallel to the Cp plane, while the plane of the second phenoxo-imino ligand, O(3)−C(31)−C(32)−C(320)−N(4), is nearly perpendicular to the Cp plane. The sum of the angles around N(2) and N(4) are approximately 360°, indicating sp^2 hybridization at both nitrogen atoms. The zirconium−imino bond distances Zr−N(2) and Zr−N(4) (2.307(8) and 2.380(12) Å, respectively) are analogous in length to other reported $Zr-N(sp^3)_{amino}$[25] and other $Zr-N(sp^2)_{imino}$ bonding interactions and are consistent with a Zr−N single bond, indicating significant coordination, in the solid state, of the imino nitrogen atom to the metal center, similar to that observed in solution according to the spectroscopic data. The average Zr(1)−O distance of 2.039 Å is as expected for Zr−O bonds with partial double-bond character due to oxygen π-donation[26] and correlates with a wide average Zr−O−C bond angle of 144.7°. These Zr−O bond lengths are intermediate between the ranges observed for bridging and terminal Zr−OR distances.[27]

3. Polymerization Studies. The zirconium complexes **2**, **3**, and **5** have been studied as catalyst precursors for olefin polymerizations upon activation with methylaluminoxane (MAO). Since each complex contains only one Cl ligand, we assume that MAO reacts under Zr−O bond cleavage, presumably by reaction with the $AlMe_3$ component of MAO, to generate an active cationic zirconium alkyl species. Polymerization of ethylene was investigated in toluene as solvent at 25 and 50 °C under 1 atm of ethylene pressure (Al:Zr = 1000:1). The results are summarized in Table 2. There was no polymerization of propylene under identical conditions. The catalytic activities of all three compounds increase when the temperature is raised from 25 to 50 °C, with the highest activity being observed after 30 min of polymerization time. Compound **5** is about an order of magnitude more active than **2** and **3**; this may reflect the less favorable reduction of the imino functionality reaction and the more facile metal−ligand cleavage and MAO activation of complexes containing bidentate rather than tetradentate ligands. The activity of the amido complex **3** is roughly twice that of **2** under comparable conditions (entries 7 and 8). The GPC data indicate small differences in molecular weight of the resulting polymers with M_w values in the range of 200 000−400 000 and polydispersities close to 2.0. For **2** and **3** the M_w values increased with polymerization time. The polymers produced by these catalysts exhibit single DSC endotherms, with melting point $T_f \approx 140$ °C.

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Concluding Remarks

In this contribution we describe the synthesis and characterization of the monocyclopentadienyl bis(phenoxo-imino) monochloro zirconium derivative $Zr(\eta^5\text{-}C_5H_5)[C_6H_4\text{-}1,2\text{-}\{N{=}CH(3,5\text{-}^tBu_2C_6H_2\text{-}2\text{-}O)\}_2]Cl$ (**2**), which contains a tetradentate Schiff base ligand, and the analogous complex $Zr(\eta^5\text{-}C_5H_5)[EtN{=}CH(3\text{-}^tBuC_6H_3\text{-}2\text{-}O)]_2Cl$ (**5**), containing two Schiff base ligands. The coordination of the phenoxo-imino ligand to the metal center in the complexes depends on the nature of the Schiff base studied. When the tetracoordinate ligand is used, NMR spectroscopy suggests a weak coordination of the imino nitrogen atom, while significant coordination is observed in the compound with the bidentate ligand. The diphenoxo-imino-amido zirconium compound $Zr(\eta^5\text{-}C_5H_5)[C_6H_4\text{-}1,2\text{-}\{N{=}CH(3,5\text{-}^tBu_2C_6H_2\text{-}2\text{-}O)\}\{NCH(Me)(3,5\text{-}^tBu_2C_6H_2\text{-}2\text{-}O)\}]$ (**3**) is formed in the methylation reaction of compound **2** by reduction of the corresponding imino functionality. The nature of the tetracoordinated ligand in compound **3** is confirmed by a hydrolysis reaction, giving a diphenol-amine-imine compound. The zirconium complexes are catalyst precursors for the polymerization of ethylene when activated with MAO under mild conditions.

Experimental Section

General Considerations. All manipulations were performed under argon using Schlenk and high-vacuum-line techniques or in an inert-atmosphere glovebox. The solvents were of reagent grade and were purified by distillation under argon before use by employing the appropriate drying/deoxygenated agent. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. 1,2-Diaminobenzene, 3,5-di-*tert*-butyl-salicylaldehyde, formic acid, triethylamine, methylmagnesium chloride, and chlorotrimethylsilane (Aldrich) were used as received or purified by literature methods.[28] $Zr(\eta^5\text{-}C_5H_5)Cl_3\cdot DME$[14] was prepared by a known procedure. C, H, and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. The IR spectra were recorded at room temperature on a Perkin-Elmer Spectrum-2000 FT-IR spectrophotometer. The NMR spectra were recorded on Varian Mercury VX-300 PFG and PFG WFG Unity Plus 500 spectrometers. The chemical shifts were referenced with respect to residual proton and carbon resonances of the solvent ($CDCl_3$: ^1H, 7.24 ppm; ^{13}C, 77.0 ppm). The assignment of the signals in NMR spectra was made by using PFG WFG TOCSY1D, PFG WFG NOESY1D, PFG WFG HSQC, and PFG HMBC pulse sequences. Polymerization grade ethylene from Air Liquide was purified by passage through two columns packed with activated 4 Å molecular sieves. Methylaluminoxane (MAO; 10% solution in toluene) was purchased from CROMPTON GmbH.

Polymer melt endotherms were determined using a Perkin-Elmer DSC-4 differential scanning calorimeter and heating rate of 10 °C/min. Melting points of solid samples placed in a dried capillary tube sealed under high vacuum are determined using Thiele's method (thermometer Fernandez 75 mm immersion, range −10 to +200 °C, 1 °C graduation). The GPC measurements were performed on a Polymer Laboratories PL-220 instrument, equipped with a refractive index detector. The samples were analyzed in trichlorobenzene (TCB) stabilized with 0.0125% BHT at 160 °C. The flow was 1.0 mL/min. Two columns of PLgelMIXED B (length 600 mm) were used.

Synthesis of ^{t}Bu$_4$salophenH$_2$ (1). A solution of 3,5-di-*tert*-butyl-salicylaldehyde (14.26 g, 60.84 mmol) in MeOH (340 mL) was treated successively with formic acid (0.35 mL) and 1,2-diaminobenzene (3.29 g, 30.47 mmol) with vigorous stirring at 0 °C. The reaction mixture was stirred at room temperature overnight, and a yellow solid was formed. After filtration, the solid was washed twice with cold MeOH and further dried at 64 °C in vacuo overnight (15.28 g, 93%). IR (KBr): ν (cm^{-1}): 3430 (OH), 1617 (C=N). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 13.50 (2H, s, O*H*), 8.65 (2H, s, N=C*H*), 7.42 (2H, AB spin system, ^4J = 2.5 Hz, C*H* phenol), 7.30 (2H, AA′BB′ spin system, C*H* phenylene), 7.23 (2H, AA′BB′ spin system, C*H* phenylene), 7.20 (2H, AB spin system, ^4J = 2.1 Hz, C*H* phenol), 1.42 (18H, s, ^{t}Bu), 1.31 (18H, s, ^{t}Bu). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 14.03 (2H, s, O*H*), 8.11 (2H, s, N=C*H*), 7.62 (2H, AB spin system, C*H* phenol), 7.04 (2H, AB spin system, C*H* phenol), 6.98 (2H, AA′BB′ spin system, C*H* phenylene), 6.72 (2H, AA′BB′ spin system, C*H* phenylene), 1.42 (18H, s, ^{t}Bu), 1.31 (18H, s, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 164.4 (N=*C*H), 158.3 (*C*-OH), 142.5 (*ipso*-phenylene), 140.1, 137.0, 118.2 (*ipso*-phenol), 128.0, 127.2, 126.6, 119.7 (phenol + phenylene), 35.4, 34.4 (*ipso*-^{t}Bu), 31.7, 29.7 (^{t}Bu). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ 165.1 (N=*C*H), 158.3 (*C*−OH), 143.1 (*ipso*-phenylene), 140.4, 137.6, 119.1 (*ipso*-phenol), 128.2, 127.4, 127.3, 120.1 (phenol + phenylene), 35.5, 34.3 (*C*Me$_3$), 31.6, 29.8 (C*Me$_3$*). Anal. Calcd for $C_{36}H_{48}N_2O_2$: C, 79.96; H, 8.95; N, 5.18. Found: C, 79.97; H, 9.00; N, 5.33.

$Zr(\eta^5\text{-}C_5H_5)[C_6H_4\text{-}1,2\text{-}\{N{=}CH(3,5\text{-}^tBu_2C_6H_2\text{-}2\text{-}O)\}_2]Cl$ (2). ^{t}Bu$_4$salophenH$_2$ (1.51 g, 2.80 mmol) and freshly purified triethylamine (0.825 mL, 6.03 mmol) in pentane (120 mL) were added at room temperature to a pentane solution (40 mL) of $Zr(\eta^5\text{-}C_5H_5)Cl_3\cdot DME$ (1 g, 2.82 mmol). The mixture was refluxed with vigorous stirring for 23 h. After it was cooled to room temperature, the mixture was evaporated to dryness and the remaining solid was Soxhlet-extracted with ether. The resulting solution was evaporated in vacuo, and a yellow-orange solid was obtained, which was recrystallized from cold pentane to give an analytically pure yellow solid, characterized as **2** (0.26 g, 13%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.57 (2H, s, N=C*H*), 7.68 (2H, AA′BB′ spin system, C*H* phenylene), 7.62 (2H, AB spin system, ^4J = 2.5 Hz, C*H* phenoxo), 7.49 (2H, AA′BB′ spin system, C*H* phenylene), 7.34 (2H, AB spin system, ^4J = 2.1 Hz, C*H* phenoxo), 6.06 (5H, s, Cp), 1.47 (18H, s, C*Me$_3$*), 1.34 (18H, s, C*Me$_3$*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 164.2 (N=CH), 162.8 (C−O), 143.4 (*ipso*-phenylene), 139.2, 139.1, 122.1 (*ipso*-phenoxo), 132.7, 130.7, 128.4, 117.4 (phenoxo + phenylene), 114.6 (Cp), 35.5, 34.4 (*C*Me$_3$), 31.6, 30.2 (C*Me$_3$*). Anal. Calcd for $C_{41}H_{51}N_2O_2ClZr$: C, 67.41; H, 7.04; N, 3.83. Found: C, 67.51; H, 7.50; N, 3.88.

$Zr(\eta^5\text{-}C_5H_5)[C_6H_4\text{-}1,2\text{-}\{N{=}CH(3,5\text{-}^tBu_2C_6H_2\text{-}2\text{-}O)\}\{N{-}CHCH_3(3,5\text{-}^tBu_2C_6H_2\text{-}2\text{-}O)\}]$ (3). Methylmagnesium chloride (0.2 mL of a 3 M solution in THF, 0.6 mmol) was added dropwise to a solution of **2** (0.34 g, 0.47 mmol) in pentane (20 mL) at −78 °C. The reaction mixture was slowly warmed to room temperature with vigorous stirring. The dark red solution was filtered, and the volatiles were removed in vacuo to give a red solid, which was recrystallized from cold toluene and characterized as **3** (0.23 g, 69%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.90 (1H, s, N=C*H*), 7.65 (1H, ABCD spin system, phenylene), 7.62 (1H, AB spin system, phenoxo), 7.45 (1H, AB spin system, phenoxo), 7.29 (1H, ABCD spin system, phenylene), 7.23 (1H, AB spin system, phenoxo), 7.05 (1H, AB spin system, phenoxo), 6.98 (1H, ABCD spin system, phenylene), 6.69 (1H, ABCD spin system, phenylene), 5.85 (5H, s, Cp), 5.00 (1H, q, ^3J = 6.3 Hz, NC*H*), 1.59, 1.57, 1.38, 1.36 (36H, s, C*Me$_3$*), 1.18 (3H, d, ^3J = 6.3 Hz, NCHC*H$_3$*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 159.3 (N=*C*H), 157.7, 154.7, 153.3, 141.0, 140.6, 138.6, 137.5, 134.9, 133.9, 122.3 (*ipso*-phenoxo + phenylene), 130.0, 129.0, 128.2, 123.3, 122.1, 115.5, 115.2, 114.6 (phenoxo + phenylene), 112.9 (Cp), 58.2 (N*C*HCH$_3$), 35.9, 35.8, 34.6, 34.5 (*C*Me$_3$), 32.1, 31.8, 30.5, 30.1 (C*Me$_3$*), 25.9 (NCH*C*H$_3$).

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Anal. Calcd for $C_{42}H_{54}N_2O_2Zr$: C, 71.04; H, 7.66; N, 3.94. Found: C, 70.84; H, 7.63; N, 4.01.

[C_6H_4-1,2-{N=CH(3,5-$^tBu_2C_6H_2$-2-OH)}{NCH(CH_3)(3,5-$^tBu_2C_6H_2$-2-OH)}] (4). Method 1. Methylmagnesium chloride (0.22 mL of a 3 M solution in THF, 0.66 mmol) was added dropwise to a solution of **1** (0.11 g, 0.20 mmol) in pentane (10 mL) at −78 °C. The reaction mixture was slowly warmed to room temperature with vigorous stirring overnight. The dark red solution was neutralized with saturated solutions of NH_4Cl in water (5 mL) and NaCl in water (2 mL). The organic layer was washed with water (5 mL) and a saturated solution of NaCl in water (2 mL), dried over $MgSO_4$, and filtered. All volatiles were removed in vacuo to give a crude yellow solid, which was purified by flash column chromatography on silica gel (40−63 μm), elution with hexane, and recrystallization in ether, affording yellow crystals which were characterized as **4** (0.10 g, 90%), mp 197 °C dec. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 13.01 (1H, s, O*H*), 9.50 (1H, s, O*H*), 8.62 (1H, s, N=C*H*), 7.48 (1H, AB spin system, phenol), 7.25 (1H, AB spin system, phenol), 7.23 (1H, AB spin system, phenol), 7.07 (1H, ABCD spin system, phenylene), 7.03 (1H, ABCD spin system, phenylene), 7.00 (1H, AB spin system, phenol), 6.93 (1H, ABCD spin system, phenylene), 6.85 (1H, ABCD spin system, phenylene), 4.57 (1H, d, J = 2.9 Hz, N*H*), 4.49 (1H, dq, J = 6.8 Hz; 2.9 Hz, NC*H*), 1.65 (3H, d, J = 6.8 Hz, NCHC*H*$_3$), 1.47, 1.38, 1.33, 1.32 (36H, s, C*Me*$_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 164.9 (N=CH), 158.2, 153.4 (C−OH), 141.3 (*ipso*-phenylene−N_{imido}), 138.8 (*ipso*-phenylene−N_{amine}), 140.9, 140.8, 136.9, 136.2, 126.5, 118.5 (*ipso*-phenol), 128.4, 127.7, 126.9, 122.7, 121.7, 121.0, 118.4, 115.9 (CH, phenol + phenylene), 57.7 (N*C*HCH$_3$), 35.4, 35.3, 34.5, 34.4 (*C*Me$_3$), 32.0, 31.7, 30.0, 29.7 (C*Me*$_3$), 22.9 (NCH*C*H$_3$). Anal. Calcd. for $C_{37}H_{52}N_2O_2$: C, 79.81; H, 9.41; N, 5.03. Found: C, 79.67; H, 9.97; N, 4.99.

Method 2. A 0.05 mL portion of chlorotrimethylsilane (0.43 mmol) was added dropwise to a solution of compound **3** (13 mg, 16.3 μmol) in $CHCl_3$ (0.5 mL), and the reaction mixture was stirred at room temperature overnight. After completion (12 h), all volatiles were removed in vacuo to eliminate the excess of trimethylchlorosilane. The residue was dissolved in 0.5 mL of $CHCl_3$, 1 mL of a 3 M solution of N^nBu_4F in THF (3 mmol) was added, and the resulting solution was stirred for 30 min. The solvent was completely removed at 50 °C, and the residue was dissolved in 2 mL of CH_2Cl_2 and washed with water (2 mL) and a saturated solution of NaCl in water (1 mL). The organic layer was washed twice with water (2 mL) and a saturated solution of NaCl in water (1 mL), dried over $MgSO_4$, and filtered. All volatiles were removed in vacuo to give a crude yellow solid, which was purified by flash column chromatography on silica gel (40−63 μm); elution with hexane afforded compound **4** as a yellow solid (ca. 10 mg, 100%) after solvent removal by evaporation.

Zr(η^5-C_5H_5)[CH_3CH_2N=CH{(3-$^tBuC_6H_3$-2-O)}]$_2$Cl·0.25CH_2Cl_2 (5). A solution of Li^nBu (1.6 M in hexanes, 3.15 mmol, 2.0 mL) was added dropwise to a stirred solution of 3-*tert*-butyl-*N*-ethyl-salicylaldimine (0.62 g, 3 mmol) in THF (100 mL) at −78 °C. The mixture was stirred at −78 °C for 15 min, allowed to reach room temperature, stirred for a further 1 h, and then cooled to −78 °C. $ZrCpCl_3$·DME was added as a suspension in THF (50 mL). The resulting solution was warmed to room temperature and stirred overnight. The volatiles were removed under vacuum to give a brown foam, which was extracted with dichloromethane and the extract filtered to remove LiCl. The solution was then concentrated to ∼5−10 mL, carefully layered with light petroleum, and left at 5 °C to afford yellow crystals of the title compound and some residual $ZrCpCl_3$ as a gray powder. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.05 (1H, s, N=C*H*), 7.99 (1H, s, N=C*H*), 7.55 (1H, dd, J = 7.7 and 1.7 Hz, aryl), 7.52 (1H, dd, J = 7.7 and 1.7 Hz, aryl), 7.17 (1H, dd, J = 7.7 and 1.6 Hz, aryl), 7.15 (1H, dd, J = 7.7 and 1.6 Hz, aryl), 6.80 (1H, t, J = 7.6 Hz, aryl), 6.78 (1H, t, J = 7.6 Hz, aryl), 6.39 (5H, s, Cp), 5.28 (0.5H, s, CH_2Cl_2), 3.62 (2H, m, NC*H*$_2$CH$_3$), 3.43 (2H, m, NC*H*$_2$CH$_3$), 1.56 (9H, s, C*Me*$_3$), 1.49 (9H, s, C*Me*$_3$), 1.05 (3H, t, J = 7.3 Hz, NCH$_2$C*H*$_3$), 0.93 (3H, t, J = 7.3 Hz, NCH$_2$C*H*$_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 167.8 (N=CH), 165.9 (N=CH), 159.7−117.3 (phenoxo), 115.1 (Cp), 53.7 (N*C*H$_2$CH$_3$), 53.1 (N*C*H$_2$CH$_3$), 35.0 (*C*Me$_3$), 34.7 (*C*Me$_3$), 30.3 (C*Me*$_3$), 29.7 (C*Me*$_3$), 16.2 (NCH$_2$*C*H$_3$), 15.7 (NCH$_2$*C*H$_3$). Anal. Calcd for $C_{31}H_{41}N_2O_2ClZr\cdot0.25CH_2Cl_2$: C, 60.38; H, 6.73; N, 4.51; Cl, 8.56. Found: C, 60.31; H, 6.97; N, 4.15; Cl, 8.50 (these numbers are very sensitive to the exact amount of CH_2Cl_2 present in the analysis sample). M^+: *m/z* 599.4.

Crystal Structure Analysis of Zr(η^5-C_5H_5)[CH_3CH_2N=CH{(3-$^tBuC_6H_3$-2-O)-κO}]$_2$Cl·(solvent). Crystal data: $C_{31}H_{41}ClN_2O_2Zr$, solvent (unresolved), fw = 685.5*, orthorhombic, space group $Pna2_1$ (No. 33), a = 24.474(5) Å, b = 16.284(3) Å, c = 8.623(2) Å, V = 3436.6(12) Å^3. Z = 4, D_c = 1.325 g cm^{-3}*, F(000) = 1452*, T = 140(1) K, μ(Mo Kα) = 4.3 cm^{-1}*, λ(Mo Kα) = 0.710 69 Å. N.B.: asterisks denote values which do not include any solvent contribution.

Crystals are pale yellow and tetrahedral. A crystal of dimensions 0.30 × 0.20 × 0.20 mm was coated with oil and mounted on a glass fiber in the cold nitrogen stream on a Rigaku R-Axis IIc image plate diffractometer equipped with a rotating-anode X-ray source (Mo Kα radiation) and graphite monochromator. Using 4° oscillations, 48 exposures of 45 min each were made. The total number of reflections recorded (not including absences), to θ_{max} = 25.4°, was 11 201, of which 6049 were unique (R_{int} = 0.048) and 4270 were “observed” with $I > 2\sigma_I$.

Data were processed using the DENZO/SCALEPACK programs.[29] The structure was determined by the direct methods routines in the SHELXS program and refined by full-matrix least-squares methods, on F^2 values, in SHELXL.[30] Refinement with the Zr, Cl, and O atoms anisotropic gave R1 = 0.234 and some poor molecular dimensions. The top difference peaks were at 4.3 and 4.1 e Å^{-3} and were recognized as alternative sites for the Zr and Cl atoms. Extension and refinement of the alternative structure showed pseudo mirror plane symmetry of the two structures at z = ∼0.18 and ∼0.68 and a ratio of major to minor component molecules of ca. 63:37. Some atom sites are common to both molecules. Atoms in sites of at least 0.63 occupancy were refined anisotropically; for lower site occupancies, atoms were refined isotropically. Further disorder was found in the major component in the phenyl ring of C(31−36) and in both ethyl groups; in the minor component, the atoms of the ethyl groups were not located. A region, believed to be of solvent (the crystals were recrystallized from a mixture of CH_2Cl_2 and hexanes), remains unresolved; 10 carbon atoms with site occupancies of 0.23−0.78, corresponding to ca. 5 carbon atoms overall, were included in the refinement. Hydrogen atoms were included in the major molecule in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. At the conclusion of the refinement, wR2 = 0.243 and R1 = 0.104[30b] for all 6049 reflections weighted with $w = [\sigma^2(F_o^2) + (0.176P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the “observed” data only, R1 = 0.081. In the final difference map, the highest peak (ca. 0.8 e Å^{-3}) was close to O(3).

Scattering factors for neutral atoms were taken from ref 31. Computer programs used in this analysis have been noted above or in Table 4 of ref 32 and were run on a Silicon Graphics Indy computer at the University of East Anglia or a DEC-Alpha Station 200 4/100 computer at the Biological Chemistry Department, John Innes Centre.

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Polymerization Procedure. Dried toluene (50 mL) was introduced under argon into the glass reactor equipped with a magnetic stirrer and was externally thermostated at the desired temperature with vigorous stirring over 30 min. MAO (8 mL, 12.19 mmol) was then injected and the mixture stirred for 15 min. The argon was replaced by ethylene (1 atm), the solution was degassed in vacuo, and the reactor was refilled with the ethylene. This procedure was repeated and the solution saturated with ethylene (1 atm) over 15 min. The zirconium complex (6−11 μmol in 1 mL^{-1} of toluene) was injected. The polymerization was terminated by methanol injection. The polymer was precipitated with 100 mL of a 5% HCl solution in MeOH, stirred, filtered, washed successively with 50 mL of a 5% HCl solution in MeOH, 100 mL of water, and 100 mL of MeOH, and finally dried in vacuo at 50 °C for 24 h to constant weight.

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Supporting Information Available: Tables giving X-ray crystallographic data for $Zr(\eta^5\text{-}C_5H_5)[CH_3CH_2N{=}CH\{(3\text{-}^tBuC_6H_3\text{-}2\text{-}O)\}]_2Cl\cdot(solvent)$ and a figure giving an additional view of the structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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