Synthesis, Characterization, and Ethylene Polymerization of Group IV Metal Complexes with Mono-Cp and Tridentate Aryloxide or Arylsulfide Ligands

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Half-sandwich titanium and zirconium complexes with tridentate dianionic aryloxide or arylsulfide ligands [R-2-{(2-XC_6H_4)N═CH}C_6H_2O]$^{2-}$ ([XNO^R]$^{2-}$, R = H, X = O (**L1**); R = 4-Me-6-Bu^t (R′), X = O (**L2**); R = H, X = S (**L3**); R = 4-Me-6-Bu^t (R′), X = S (**L4**)) have been prepared. Reactions of $CpMCl_3$ (M = Ti, Zr) with sodium salts of the aryloxide or arylsulfide ligands (**L1**−**L4**) afford CpTi[XNO^R]Cl [R = H, X = O (**1**); R = 4-Me-6-Bu^t (R′), X = O (**2**); R = H, X = S (**3**); R = 4-Me-6-Bu^t (R′), X = S (**4**)] and CpZr[ONO^R]Cl [R = H (**5**)], respectively. Complexes **1**−**5** were characterized by IR and ^{1}H NMR spectra and elemental analyses, and their molecular structures have been determined by X-ray diffraction methods. The coordination properties of these complexes have been investigated in the solid state and compared to related systems. When activated by excess methylaluminoxane (MAO), these complexes can be used as catalysts for ethylene polymerization and exhibited moderate activities. The activities of arylsulfide complexes **3** and **4** are higher than those of their analogues, aryloxide complexes **1** and **2**, and zirconium complex **5** is much more active than titanium complexes **1**−**4**.

Introduction

Since the discovery of homogeneous Ziegler−Natta catalysis by group IV metallocenes in 1980,[1] considerable effort has been devoted to catalyst modification in order to improve olefin polymerization activity and control polymer properties such as stereoregularity, co-monomer incorporation, and microstructure.[2] Despite the ongoing research on metallocene catalysts, the search for alternatives to the metallocene catalysts that can produce polymers with novel properties has been one of the major goals of transition metal coordination chemistry over the last two decades.[3]

A number of groups have explored the use of catalysts with one cyclopentadienyl and a second, non-Cp ligand with an oxygen and/or nitrogen donor in recent years. Monoanionic salicylaldimines are among the most versatile non-Cp ligands to have emerged in olefin polymerization catalysis over the past 10 years.[4] These salicylaldiminato ligands are obtained by easy synthetic routes, and hence their steric and electronic properties can be readily tuned, via substitution of the aromatic ring or modification of the imino nitrogen substitutent. However, despite extensive investigation of group IV metal complexes of salicylaldiminato ligands and their utilities in olefin polymerization chemistry, few monocyclopentadienyl salicylaldiminato group IV metal derivatives of the type Cp′M[ON]$_n$X$_{3-n}$ (M = Ti, Zr; Cp′ = substituted or unsubstituted cyclopentadienyl ring; L = bidentate monoanionic salicylaldiminato ligand; X = anionic donor ligand) have been reported.[5]

Monocyclopentadienyl dichloro group IV metal complexes CpM[ON]Cl_2 containing a bidentate monoanionic salicylaldiminato ligand have been reported. When activated by MAO, they are active for the polymerization of ethylene, but give multimodal molecular weight distributions consistent with multiple active sites. The most active systems were demonstrated to be effective for the copolymerization of 1-hexene and ethylene. In the absence of ethylene, 1-hexene is oligomerized.[5b] Half-sandwich monochloro group IV metal complexes CpM[ON]$_2$Cl containing two bidentate monoanionic salicylaldiminato ligands have been also synthesized and were used as catalysts for the polymerization of ethylene.[5a,c] Recently, half-sandwich

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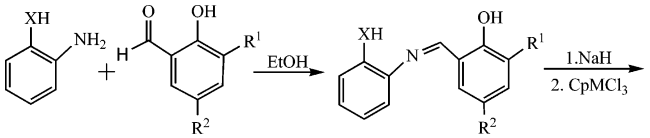
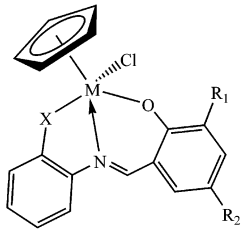
Scheme 1. Synthetic Routes to Complexes of the Type CpM[XNO^R]Cl, 1−5



L1 R^1 = H, R^2 = H, X= O
L2 R^1 = ^{t}Bu, R^2 = Me, X= O
L3 R^1 = H, R^2 = H, X= S
L4 R^1 = ^{t}Bu, R^2 = Me, X= S



1 R^1 = H, R^2 = H, X= O, M = Ti
2 R^1 = ^{t}Bu, R^2 = Me, X= O, M = Ti
3 R^1 = H, R^2 = H, X= S, M = Ti
4 R^1 = ^{t}Bu, R^2 = Me, X= S, M = Ti
5 R^1 = H, R^2 = H, X= O, M = Zr

monochloro and monoalkyl group IV metal complexes CpZr[ONNO]Cl ([ONNO] = [C_6H_4-1,2-{N=CH(3,5-^{t}Bu$_2C_6H_2$-2-O)}$_2$]) containing tetradentate dianionic salicylaldiminato ligands have been developed. The zirconium complexes are catalyst precursors for the polymerization of ethylene when activated with MAO under mild conditions.[5c] Half-sandwich monochloro titanium and zirconium complexes CpM[ONO]Cl ([ONO] = [2-{(2-OC_6H_2)N=CH}C_6H_3O]; M = Ti, Zr)[5a,d] containing tridentate dianionic salicylaldiminato ligands, derived from condensation of *o*-aminophenol and salicyaldehyde, have been recently reported, exhibiting moderate activities for the polymerization of ethylene. However these complexes containing a bulky *ortho*-substituent have not been reported, and there is no crystal structure data reported for this species. Recently, much attention has been paid to sulfur-containing ligands and several reports on their use as catalysts for olefin polymerization,[6] but few arylsulfide complexes have been reported for olefin polymerization.[7] Herein, we describe the synthesis, X-ray crystallographic characterization, and ethylene polymerization chemistry of five monocyclopentadienyl monochloro titanium and zirconium complexes CpM[XNO^R]Cl ([XNO^R] = [R-2-{(2-XC_6H_4)N=CH}C_6H_2O]; M = Ti, Zr; R = H, R′ (4-Me-6-Bu^t); X = O, S) containing tridentate dianionic aryloxide or arylsulfide ligands derived from condensation of salicyaldehyde with aminophenols or aminothiophenols.

Results and Discussion

Synthesis and Characterization of Half-Sandwich Titanium and Zirconium Aryloxide or Arylsulfide Complexes. The salicylaldimine derivatives **L1**−**L4** were prepared in good yields by condensation reactions of the corresponding salicyaldehyde with *o*-aminophenol or *o*-aminothiophenol in boiling ethanol. Previous papers described the synthesis of complexes **1** and **3** by reactions of Cp_2TiCl_2 or $CpTiCl_3$ with **L1** or **L3** in the presence of NEt_3.[8] Attempts to apply the method to the preparation of half-sandwich titanium aryloxide or arylsulfide complexes gave thick red oils that would not produce pure products. The ^{1}H NMR spectrum showed the product to be a mixture. Now we present here an alternative synthetic route in good yields for these half-sandwich group IV complexes consisting in the reaction of $CpMCl_3$ with disodium salts of ligands, obtained by deprotonation in the presence of NaH. This synthetic procedure was more accurate and convenient than that using dilithium salts of ligands.[5d]

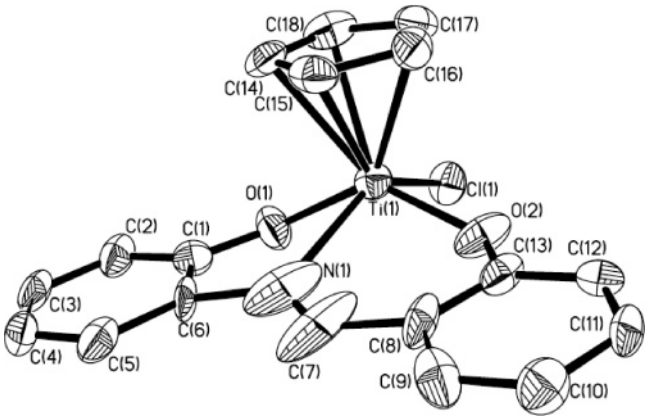


Figure 1. ORTEP drawing of the molecular structure of CpTi[ONO^H]Cl (**1**). The hydrogen atoms are omitted for clarity.

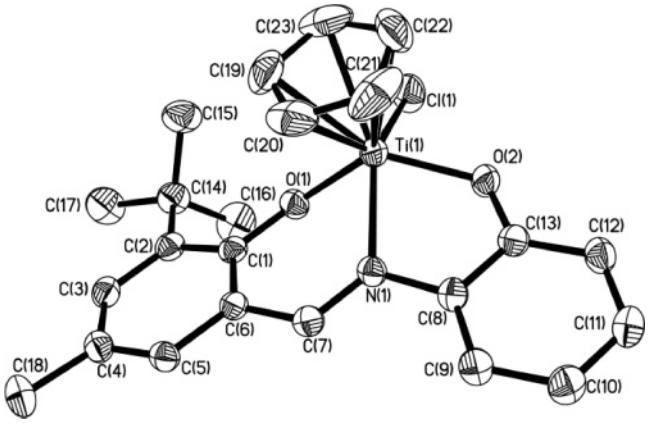


Figure 2. ORTEP drawing of the molecular structure of CpTi[ONO$^{R'}$]Cl (**2**). The hydrogen atoms are omitted for clarity.

The complexes are fully characterized by ^{1}H NMR and IR spectra and elemental analysis (see Experimental Section). The ^{1}H NMR spectra of Ti complexes **1**, **2**, and **3** show the CH=N protons, which are shifted downfield approximately 0.24−0.50 ppm relative to free ligands. However, the CH=N proton in Ti thiolato complex **4** is shifted upfield approximately 0.20 ppm relative to free ligand. The chemical shift difference for the CH=N proton in Zr complex **5** and free ligand is only −0.03 ppm.

The solid-state structures of **1**, **2**, **3**, and **4** were determined by single-crystal X-ray diffraction studies. Their solid-state structures are quite similar and will be discussed first (Figures 1−4). Selected structural parameters, along with those for related $CpTiYCl_2$ derivatives (Y = OAr, SAr), are collected in Table 1. If the centroid of the cyclopentadienyl ring is considered as a single coordination site, these complexes all adopt five-

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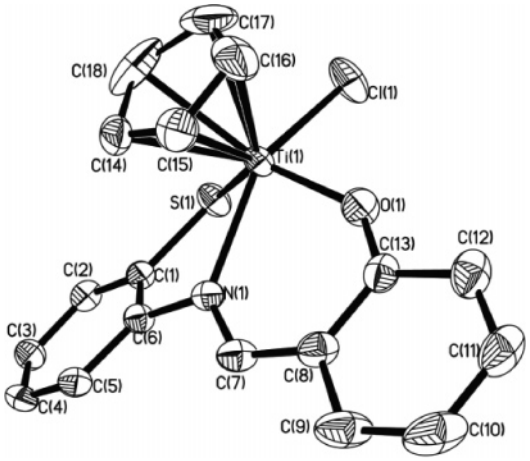

Figure 3. ORTEP drawing of the molecular structure of CpTi[SNO^{H}]Cl (**3**). The hydrogen atoms are omitted for clarity.

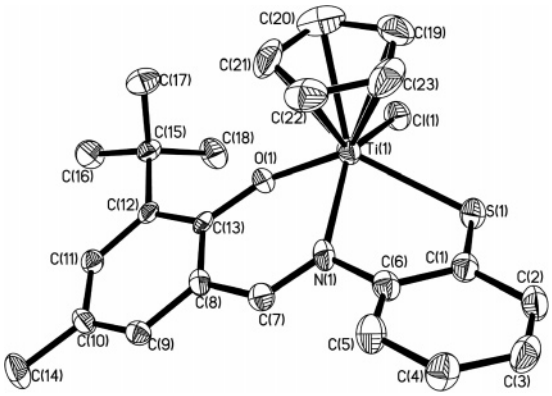

Figure 4. ORTEP drawing of the molecular structure of CpTi[SNO$^{R'}$]Cl (**4**). The hydrogen atoms are omitted for clarity.

coordinate, distorted square-pyramidal structures in which the equatorial positions are occupied by the two oxygen atoms or one sulfur atom and one oxygen atom of the chelating dianionic aryloxide and arylsulfide ligands, the nitrogen atom, and the chlorine atom. The cyclopentadienyl group is coordinated on the axial position.

In the monochloro titanium aryloxides and arylsulfides of **1**, **2**, **3**, and **4**, the Ti−X (X = O, S) bond distances are longer than those in the related dichloro titanium aryloxides and arylsulfide CpTi(2,6-^{i}Pr$_2$C$_6$H$_3$O)Cl$_2$,[9] CpTi[2-Bu^{t}-6-(2,4,6-Me$_3$C$_6$H$_2$N═CH)C$_6$H$_3$O]Cl$_2$,[5b] and CpTi(4-MeC$_6$H$_4$S)Cl$_2$,[10] respectively. The Ti−N bond distances (2.171(2)−2.185(5) Å) in **2**, **3**, and **4** are shorter than in **1** (2.317(9) Å) and CpTi[2-Bu^{t}-6-(2,4,6-Me$_3$C$_6$H$_2$N═CH)C$_6$H$_3$O]Cl$_2$[5b] (2.268(4) Å), indicative of significant coordination of an imino nitrogen atom to the metal center in the solid state. A somewhat shorter Ti−Cl bond distance is observed in **4** (2.317(9) Å), possibly reflecting the lower electron density at the metal center. In these titanium aryloxides (**1**, **2**) and arylsulfides (**3**, **4**) shown in Table 1, the Ti−S−C bond angle is significantly smaller than the Ti−O−C bond angles. The largest Ti−S−C bond angle observed in these systems is 100.25(12)° (**3**), while the smallest Ti−O−C angle is 121.40(16)° (CpTi(2,6-^{i}Pr$_2$C$_6$H$_3$O)Cl$_2$[9]). In addition, the Ti−S−Ar angles lie within a small range (98.7(2)−100.25(12)°), while the Ti−O−Ar angles cover a much wider range (approximately (121.40(16)−173.0(3)°).

The solid-state structure of zirconium complex **5** is determined by single-crystal X-ray diffraction studies. Selected structural parameters are collected in Table 2. If the centroid of the cyclopentadienyl ring is considered as a single coordination site, the complex adopts a six-coordinate, distorted octahedral structure in which the equatorial positions are occupied by the two oxygen atoms of the chelating aryloxide ligand, an additional oxygen atom of THF, and the chlorine atom. The cyclopentadienyl group is coordinated on the axial position, and the nitrogen atom occupies another axial position. The Zr−O (2.028(4), 2.048(4) Å), Zr−N (2.439(8) Å), and Zr−Cl (2.4994(17) Å) bond distances in zirconium complex **5** are longer than those in its analogous titanium complex **1**, respectively. These results are to be expected when the atomic radii of the two metal atoms are considered. The Zr−N bond distance (2.439(8) Å) is slightly longer than that of FI zirconium catalysts (2.355−2.38 Å),[4b] which indicates less donating ability of imino nitrogen atom to the metal center.

Ethylene Polymerization. The prepared complexes were briefly investigated in ethylene polymerization. Titanium and zirconium complexes CpM[XNO^{R}]Cl **1**−**5** were activated with MAO. The results are summarized in Table 3.

Titanium complexes **1**−**4** show moderate activities for the polymerization of ethylene. The activity of arylsulfide complexes **3** and **4** is higher than that of their analogues aryloxide complexes **1** and **2**, possibly reflecting the higher rate of alkylation by MAO in **3** and **4**/MAO systems. In the **1**−**4**/MAO systems, no discoloration of the orange-red reaction mixture was observed over 60 min and ethylene consumption continued over this period, suggesting that the active species are quite stable under these conditions. The activity of complexes **2** and **4**, having a bulky *tert*-butyl group, is somewhat higher than that of corresponding complexes **1** and **3**. It can be seen from the results in Table 3 that **3**/MAO gave the highest activity at 70 °C, and increasing the temperature of polymerization led to a decrease in the molecular weight of the polymer. Zirconium complex **5** is much more active than titanium complexes **1**−**4**.

Conclusions

A series of monocyclopentadienyl monochloro titanium and zirconium complexes of tridentate dianionic aryloxide or arylsulfide ligands [XNO^{R}]$^{2-}$ have been prepared. The routes employed proved to be effective with both aryloxide ligands and arylsulfide ligands. The coordination properties of these complexes have been investigated compared to related systems. The Ti−S−C bond angle is significantly smaller than the Ti−O−C bond angles. The Ti−S−Ar angles lie within a small range, while the Ti−O−Ar angles cover a much wider range. A longer Zr−N bond distance is observed in the zirconium comples CpZr[ONO^{H}]Cl, indicative of less donating ability of the imino nitrogen atom to the metal center. When activated by excess methylaluminoxane (MAO), these complexes can be used as catalysts for ethylene polymerization. The activities of arylsulfide complexes CpTi[SNO^{R}]Cl are higher than those of their analogues, aryloxide complexes CpTi[ONO^{R}]Cl, and zirconium complex CpZr[ONO^{H}]Cl is much more active than titanium complexes CpTi[XNO^{R}]Cl. The activity of titanium complexes CpTi[XNO^{R}]Cl increases as the R group is replaced from H to 4-Me-6-Bu^{t}.

Experimental Section

General Considerations. All the operations were carried out under pure nitrogen atmosphere using standard Schlenk techniques.

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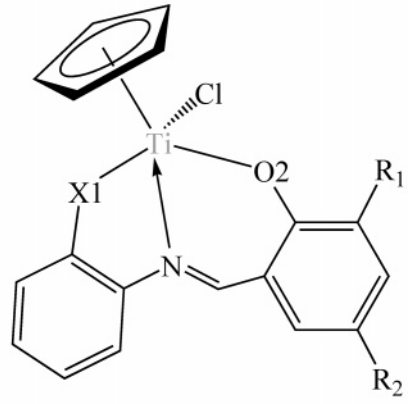
Table 1. Summary of Crystallographic Data for 1−4 and Related Complexes $CpTiYCl_2$ (Y = OAr, SAr)



1 R^1 = H, R^2 = H, X1= O1
2 R^1 = ^{t}Bu, R^2 = Me, X1= O1
3 R^1 = H, R^2 = H, X1= S1
4 R^1 = ^{t}Bu, R^2 = Me, X1= S1

complex	Ti−X1	Ti−O2	Ti−N	Ti−Cl	Ti−Cp	Ti−X1−C	Ti−O2−C	X1−Ti−O2
$CpTi(O\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_2$[9]	1.760(4)			2.262(av)		173.0(3)		
$CpTi[2\text{-}Bu^t\text{-}6\text{-}(2,4,6\text{-}Me_3C_6H_2N{=}CH)C_6H_3O]Cl_2$[10]	1.875(3)		2.268(4)	2.347(av)		136.5(2)		
$CpTi(SC_6H_4Me\text{-}4)Cl_2$[11]	2.2924(5)			2.245(av)	2.014	99.60(5)		
$CpTi[ONO^H]Cl$ (**1**)	1.893(5)	1.876(5)	2.317(9)	2.320(2)	2.0298	127.0(5)	131.3(5)	134.7(2)
$CpTi[ONO^{R'}]Cl$ (**2**)	1.9103(17)	1.8805(18)	2.171(2)	2.3514(10)	2.0547	121.40(16)	136.27(16)	129.51(8)
$CpTi[SNO^H]Cl$ (**3**)	2.4014(12)	1.862(2)	2.197(3)	2.3419(11)	2.0435	100.25(12)	137.4(2)	126.21(9)
$CpTi[SNO^{R'}]Cl$ (**4**)	2.448(2)	1.866(4)	2.185(5)	2.185(5)	2.0889	98.7(2)	144.7(4)	130.34(14)

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $CpZr[ONO^H]Cl$ (5)

Zr(1)−O(1)	2.028(4)	O(1)−Zr(1)−O(2)	149.25(17)
Zr(1)−O(2)	2.048(4)	O(2)−Zr(1)−O(3)	83.00(14)
Zr(1)−O(3)	2.312(4)	O(1)−Zr(1)−N(1)	81.8(2)
Zr(1)−N(1)	2.439(8)	O(2)−Zr(1)−N(1)	68.4(2)
Zr(1)−Cl(1)	2.4994(17)	O(3)−Zr(1)−N(1)	76.37(18)
Zr(1)−C(18)	2.512(6)	O(1)−Zr(1)−Cl(1)	92.89(13)
Zr(1)−Cp	2.263	N(1)−Zr(1)−Cl(1)	79.67(16)
Zr(1)−O1−C(1)	129.5(4)	O(1)−Zr(1)−C(18)	124.7(2)
Zr(1)−O2−C(13)	134.7(4)	O(2)−Zr(1)−C(18)	86.0(2)

Tetrahydrofuran (THF), hexane, and toluene were distilled from sodium−benzophenone. Commercial reagents, namely, NaH (60%), $CpTiCl_3$, $CpZrCl_3$, methylaluminoxane (MAO), and salicylaldehyde with *o*-aminophenol or *o*-aminothiophenol were purchased from ACROS Co. 3-(*tert*-Butyl)-5-methylsalicylaldehyde was prepared according to the literature.[11]

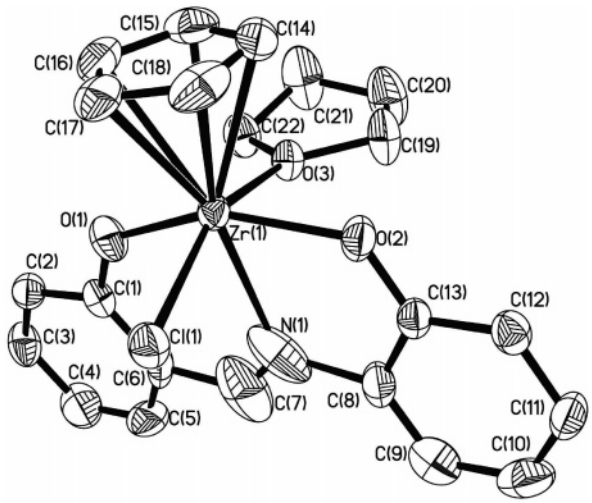


Figure 5. ORTEP drawing of the molecular structure of $CpZr[ONO^H]Cl$ (**5**). The hydrogen atoms are omitted for clarity.

Table 3. Results of Ethylene Polymerization[a]

entry	catalyst	temp (°C)	time (min)	activity[b]	M_v[c] (10^{-4})
1	$CpTi[ONO]Cl$ (**1**)	70	60	31	53
2	$CpTi[ONO^{R'}]Cl$ (**2**)	70	60	50	51
3	$CpTi[SNO]Cl$ (**3**)	25	60	7.1	49
4	$CpTi[SNO]Cl$ (**3**)	50	60	37	61
5	$CpTi[SNO]Cl$ (**3**)	70	60	61	31
6	$CpTi[SNO]Cl$ (**3**)	90	60	43	11
7	$CpTi[SNO]Cl$ (**3**)	70	30	15	9
8	$CpTi[SNO^{R'}]Cl$ (**4**)	70	60	77	27
9	$CpZr[ONO]Cl$ (**5**)	70	60	150	10

[a] Conditions: [M] = 10 μmol, Al/M = 1500, toluene = 50 mL, ethylene pressure = 1 atm. [b] Activity in kgPE·mol M^{-1}·h^{-1}. [c] M_v was measured by the Ubbelohde calibrated viscosimeter technique.

^{1}H (500 MHz) NMR measurements were obtained on a Bruker AC500 spectrometer in $CDCl_3$ solution. IR (KBr) spectra were recorded on a Nicolet FT-IR spectrophotometer. Elemental analyses for C and H were carried out on an Elementar III Vario EI analyzer.

$[ONO^H]H_2$ (L1). A mixture of salicylaldehyde (5 mL, 0.0478 mol) and 30 mL of ethanol was heated to 80 °C, and then a solution of *o*-aminophenol (5.21 g, 0.0478 mol) in 20 mL of ethanol was dropwise added. The reaction mixture was refluxed for 2 h and cooled to room temperature. The product was recrystallized from ethanol to afford fine dark red needles in 85% (8.66 g) yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.29 (s, 1H, OH), 8.69 (s, 1H, CH=N), 7.45−6.98 (m, 8H, Ar−H), 5.81 (s, 1H, OH).

$[ONO^{R'}]H_2$ (L2). Using the same procedure as for the synthesis of **L1**, **L2** (0.91 g) was obtained as red crystals by the reaction of

(11) Kasumov, V. T.; Tas, E.; Yakar, Y.; Koeksal, F.; Koeseoglu, R. *Z. Naturforsch. Teil. B: Chem. Sci.* **2002**, *57*, 495.

Table 4. Summary of Crystallographic Data for 1, 2, 3, 4, and 5

	1	2	3	4	5·C_4H_8O
formula	$C_{18}H_{14}ClNO_2Ti$	$C_{23}H_{24}ClNO_2Ti$	$C_{18}H_{14}ClNOSTi$	$C_{23}H_{24}ClNOSTi$	$C_{22}H_{22}ClNO_3Zr$
fw	359.68	429.81	375.71	445.84	475.10
T, K	298(2)	293(2)	293(2)	293(2)	293(2)
cryst syst	triclinic	monoclinic	tetragonal	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$	$I\bar{4}$	$Pna2(1)$	$P2(1)/n$
a, Å	10.1760(19)	12.360(3)	21.043(4)	22.415(11)	8.572(3)
b, Å	10.457(2)	12.831(3)	21.043(4)	13.398(6)	14.639(4)
c, Å	15.517(3)	13.710(4)	7.488(2)	7.215(4)	15.940(5)
α, deg	107.959(3)	90	90	90	90
β, deg	94.315(3)	105.316(4)	90	90	93.075(5)
γ, deg	94.627(3)	90	90	90	90
volume, Å^3	1557.0(5)	2097.1(10)	3315.6(13)	2166.9(18)	1997.2(10)
Z	2	6	8	2	4
D_{calc}, Mg/m^3	1.165	1.537	1.505	0.683	1.320
absorp coeff, mm^{-1}	0.387	0.824	0.805	0.314	0.689
F(000)	570	978	1536	464	808
cryst size, mm	0.02 × 0.05 × 0.05	0.04 × 0.05 × 0.08	0.15 × 0.10 × 0.08	0.06 × 0.08 × 0.10	0.05 × 0.10 × 0.15
2*θ* range, deg	2.78−50.02	3.94−54.26	2.74−52.00	3.54−55.02	3.78−50.02
no. of reflns collected/unique	6567/5410 [R_{int} = 0.0505]	10 386/4577 [R_{int} = 0.0359]	7656/3214 [R_{int} = 0.0316]	10 204/3768 [R_{int} = 0.1033]	8310/3523 [R_{int} = 0.0463]
no. of data/restraints/params	5410/11/415	4577/0/257	3214/0/208	3768/1/257	3523/3/253
goodness of fit on F^2	0.655	0.913	0.957	0.805	0.869
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0567 wR2 = 0.0950	R1 = 0.0482 wR2 = 0.1020	R1 = 0.0419 wR2 = 0.0787	R1 = 0.0539 wR2 = 0.0855	R1 = 0.0502 wR2 = 0.1147
lgst diff peak and hole, e/Å^3	0.578 and −0.278	0.403 and −0.242	0.298 and −0.204	0.514 and −0.306	1.364 and −0.743

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

3-(*tert*-butyl)-5-methylsalicyaldehyde (0.783 g, 4.08 mmol) and *o*-aminophenol (0.448 g, 4.08 mmol) in a yield of 79%. ^{1}H NMR ($CDCl_3$, 500 MHz): *δ* 12.69 (s, 1H, OH), 8.64 (s, 1H, CH═N), 7.26−7.03 (m, 6H, Ar−H), 5.95 (s, 1H, OH), 2.33 (s, 3H, CH_3), 1.45 (s, 9H, $C(CH_3)_3$).

[SNO^H]H$_2$ (L3). Using the same procedure as for the synthesis of **L1**, **L3** (3.29 g) was obtained as red crystals by the reaction of salicyaldehyde (2.39 mL, 22.8 mmol) and *o*-aminothiophenol (2.85 g, 22.8 mmol) in a yield of 63%. ^{1}H NMR ($CDCl_3$, 500 MHz): *δ* 12.90 (s, 1H, SH), 8.83 (s, 1H, CH═N), 7.25−6.50 (m, 8H, Ar−H), 4.61 (s, 1H, OH).

[SNO$^{R'}$]H$_2$ (L4). Using the same procedure as for the synthesis of **L1**, **L4** (1.09 g) was obtained as red crystals by the reaction of 3-(*tert*-butyl)-5-methylsalicyaldehyde (1.40 g, 7.3 mmol) and *o*-aminothiophenol (0.914 g, 7.3 mmol) in a yield of 50%. ^{1}H NMR ($CDCl_3$, 500 MHz): *δ* 13.18 (s, 1H, SH), 9.20 (s, 1H, CH═N), 7.03−6.56 (m, 6H, Ar−H), 2.35 (s, 3H, CH_3), 1.43 (s, 9H, $C(CH_3)_3$).

CpTi[ONO^H]Cl (1). To a stirred suspension of NaH (0.048 g, 2.0 mmol) in 10 mL of THF was added **L1** (0.129 g, 0.606 mmol) dropwise at −78 °C. Stirring was maintained for 2 h at room temperature. The mixture was filtered. The filtrate was cooled to −78 °C and added dropwise to a solution of $CpTiCl_3$ (0.133 g 0.606 mmol) in 15 mL of toluene. The resulting suspension was warmed to room temperature and kept stirring over night, and the solvent was removed under vacuum. The residue was extracted in 20 mL of toluene to remove NaCl salt. Removal of volatiles under vacuum left a dark red powder. Recrystallization of the product from toluene/hexane afforded **1** (0.163 g, 75%) as dark red crystals. ^{1}H NMR (500 Hz, $CDCl_3$, ppm): *δ* 9.19 (s, 1H, N═CH), 7.78−6.99 (m, 8H, Ph−H), 6.21 (s, 5H, Cp-H). IR (KBr): *ν* 1603, 1582, 1535, 1439, 1372, 1299, 1146, 1026, 850, 745 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_2NTiCl$: C, 60.11; H, 3.93; N, 3.89. Found: C, 60.29; H, 4.01; N, 3.81.

CpTi[ONO$^{R'}$]Cl (2). This complex was prepared as described above for **1**, starting from NaH (0.048 g, 2.0 mmol), **L2** (0.219 g, 0.77 mmol), and $CpTiCl_3$ (0.170 g, 0.77 mmol). Workup afforded **2** (0.215 g) as dark red crystals in a yield of 65%. ^{1}H NMR (500 Hz, $CDCl_3$, ppm): *δ* 9.13 (s, 1H, N═CH), 7.68−6.95 (m, 6H, Ph−H), 6.17 (s, 5H, Cp−H), 2.43 (s, 3H, CH_3), 1.51 (s, 9H, $C(CH_3)_3$). IR (KBr): *ν* 1607, 1588, 1540, 1439, 1399, 1375, 1309, 1150, 1025, 859, 751 cm^{-1}. Anal. Calcd for $C_{23}H_{24}ClNO_2Ti$: C, 64.27; H, 5.63; N, 3.26. Found: C, 64.30; H, 5.66; N, 3.21.

CpTi[SNO^H]Cl (3). This complex was prepared as described above for **1**, starting from NaH (0.053 g, 2.2mmol), **L3** (0.218 g, 0.951 mmol), and $CpTiCl_3$ (0.209 g, 0.951 mmol). Workup afforded **3** (0.246 g) as dark red crystals in a yield of 69%. ^{1}H NMR (500 Hz, $CDCl_3$, ppm): *δ* 9.067 (s, 1H, N═CH), 7.798−7.198 (m, 8H, Ph−H), 6.195 (s, 5H, Cp−H). IR (KBr) *ν*: 1604, 1543, 1439, 1372, 1295, 1149, 1025, 851, 735 cm^{-1}. Anal. Calcd for $C_{18}H_{14}ClNOSTi$: C, 57.54; H, 3.76; N, 3.73. Found: C, 57.59; H, 3.79; N, 3.71.

CpTi[SNO$^{R'}$]Cl (4). This complex was prepared as described above for **1**, starting from NaH (0.048 g, 2.0 mmol), **L4** (0.227 g, 0.760 mmol), and $CpTiCl_3$ (0.167 g, 0.760 mmol). Workup afforded **4** (0.206 g) as dark red crystals in a yield of 61%. ^{1}H NMR (500 Hz, $CDCl_3$, ppm): *δ* 9.00 (s, 1H, N═CH), 7.66−7.24 (m, 6H, Ph−H), 6.15 (s, 5H, Cp−H), 2.44 (s, 3H, CH_3), 1.49 (s, 9H, $C(CH_3)_3$). IR (KBr): *ν* 1610, 1540, 1439, 1401, 1380, 1311, 1159, 1020, 859 cm^{-1}. Anal. Calcd for $C_{23}H_{24}ClNOSTi$: C, 61.96; H, 5.43; N, 3.14. Found: C, 61.97; H, 5.46; N, 3.15.

CpZr[ONO^H]Cl·C$_4$H$_8$O (5). This complex was prepared as described above for **1**, starting from NaH (0.048 g, 2.0 mmol), **L1** (0.130 g, 0.610 mmol), and $CpZrCl_3$ (0.160 g, 0.610 mmol). Workup afforded **5** (0.125 g) as orange crystals in a yield of 51%. ^{1}H NMR (500 Hz, $CDCl_3$, ppm): *δ* 8.67 (s, 1H, N═CH), 7.47−6.78 (m, 8H, Ar−H), 6.18 (s, 5H, Cp−H), 3.75 (t, 4H, CH_2−O−CH_2), 1.85 (m, 4H, CH_2−CH_2). IR (KBr): *ν* 1609, 1585, 1550, 1481, 1455, 1396, 1302, 1261, 1173, 1121, 1040, 1011, 848, 753 cm^{-1}. Anal. Calcd for $C_{22}H_{22}ClNO_3Zr$: C, 55.61; H, 4.67; N,2.95. Found: C, 55.51; H, 4.71; N, 3.01.

Single-Crystal X-ray Structure Determination of Complexes 1−5. For complexes **1**−**5**, a single crystal suitable for X-ray analysis was sealed into a glass capillary, and the intensity data of the single crystal were collected on the CCD-Bruker Smart APEX system. All determinations of the unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (*λ* = 0.71073 Å). All data were collected at room temperature using the *ω*-scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares

method. All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included but not refined. Crystallographic data are summarized in Table 3.

Ethylene Polymerization. A 100 mL flask was equipped with an ethylene inlet, a magnetic stirrer, and a vacuum line. The flask was filled with 50 mL of freshly distilled solvent, MAO (10 wt % in toluene, 9 mL) was added, and the flask was placed in a bath at the desired polymerization temperature for 10 min. The polymerization reaction was started by adding a toluene solution of the catalyst precursor (0.010 mmol) with a syringe. The polymerization was carried out for the desired time and then quenched with 3% HCl in ethanol (250 mL). The precipitated polymer was filtered and then dried overnight in a vacuum oven at 80 °C.

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Supporting Information Available: X-ray crystallographic data for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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