Organometallics **2000,** *19,* 2837−2843

Articles

Synthesis of Zirconium(IV) Monocyclopentadienyl−Aryloxy Complexes and Their Use in Catalytic Ethylene Polymerization. X-ray Structure of $(\eta^5\text{-}C_5Me_5)Zr\{2,6\text{-}OC_6H_3(CH_3)_2\}_3$

A. Antiñolo,[†] F. Carrillo-Hermosilla,[†] A. Corrochano,[†] J. Fernández-Baeza,[†] A. Lara-Sanchez,[†] M. R. Ribeiro,[‡] M. Lanfranchi,[§] A. Otero,*,[†] M. A. Pellinghelli,[§] M. F. Portela,[‡] and J. V. Santos[‡]

Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, Campus de Ciudad Real, 13071-Ciudad Real, Spain, and Departamento de Engenharia Quimica, Instituto Superior Tecnico de Lisboa, Avenue Rovisco Pais, 1096-Lisboa Codex, Portugal, and Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffractometrica del CNR, Viale delle Scienze 78, 43100-Parma, Italy

Received March 6, 2000

The complex $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)Cl_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**) has been prepared by the reaction of the starting material Cp^*ZrCl_3 and 1 equiv of the lithium salt of the phenol compound. The reactions of **1** and the appropriate Grignard reagents afford the alkyl derivatives $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)Me_2$ (**2**) and $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)(Bz)(Cl)$ (**3**). This and other dimethyl derivatives, namely, $Cp^*Zr(2,6\text{-}OC_6H_3Me_2)Me_2$ (**4**), $Cp^*Zr(O\text{-}2\text{-}{}^tBu\text{-}6\text{-}MeC_6H_3)Me_2$ (**5**), and $Cp^*Zr(O\text{-}2\text{-}C_3H_5\text{-}6\text{-}MeC_6H_3)Me_2$ (**6**), can be obtained by reaction of Cp^*ZrMe_3 and the corresponding phenol. When an excess of the less bulky $2,6\text{-}Me_2C_6H_3OH$ phenol was used, the completely substituted complex $Cp^*Zr(2,6\text{-}OC_6H_3Me_2)_3$ (**7**) was obtained. The reactivity of $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)Me_2$ in the insertion process of isocyanide compounds was studied. In all cases, the corresponding η^2-iminoacyl compounds, $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)(\eta^2\text{-}MeC{=}NR)(Me)$ [R = Xy (**8**); ^{n}Bu (**9**), Cy (**10**), TMB = 1,1,3,3-tetramethylbutyl (**11**)], were obtained. Similar reactivity was found for $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)(Bz)(Cl)$ and $Cp^*Zr(O\text{-}2\text{-}{}^tBu\text{-}6\text{-}MeC_6H_3)Me_2$. The complexes were characterized by spectroscopic methods, and in some cases, variable-temperature ^{1}H NMR spectroscopy studies were carried out. In addition, the molecular structure of $Cp^*Zr(2,6\text{-}OC_6H_3Me_2)_3$ has been determined by X-ray diffraction methods. Finally, complexes $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)Cl_2$ and $Cp^*Zr(2,6\text{-}OC_6H_3Me_2)_3$ were tested as ethylene polymerization catalysts in the presence of MAO as cocatalyst. While the former complex shows a high activity similar to that found for classical metallocene catalysts, the latter is much less active. The different activities found for these complexes can be explained in terms of the different activation processes.

Introduction

Alkene polymerization by homogeneous metallocene catalysts has been the object of both fundamental and applied studies, especially after it was reported that the presence of partially hydrolyzed trimethylaluminum (MAO: methylalumoxane) has a favorable effect on the process.[1] Development of new “single-site” group 4 catalyst precursors for optimizing polymerization catalysis is one of the most attractive subjects in the field of organometallic chemistry.[2] There are many reports regarding this chemistry that involve metallocene derivatives, but few examples of monocyclopentadienyl derivatives bearing aryloxy ligands[3] have been reported even though complexes containing titanium as the metal center have been known for a number of years.[3b] Recently, Nomura and co-workers[4] described similar

---

[†] Universidad de Castilla-La Mancha.

[‡] Instituto Superior Tecnico de Lisboa.

[§] Università degli Studi di Parma.

(1) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(2) Cornils, B., Herrmann, W. A., Eds. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, 1996.

(3) (a) Steven, J. C.; Neitlamer, D. R. U.S. Patent, *5064*, 802, 1991. (b) Gómez-Sal, P.; Martín, A.; Mena, M.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1991**, *419*, 77. (c) Sarsfield, M. J.; Ewart, S. W.; Tremblay, T. L.; Roszak, A.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3097. (d) Firth, A. V.; Stephan, D. W. *Inorg. Chem.* **1998**, *37*, 4726. (e) Firth, A. V.; Stephan, D. W. *Inorg. Chem.* **1998**, *37*, 4732.

(4) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152.

10.1021/om000209l CCC: $19.00 © 2000 American Chemical Society
Publication on Web 06/20/2000

monocyclopentadienyl derivatives of titanium-containing bulky disubstituted aryloxy ligands. These complexes play an active role in the polymerization reaction of α-olefins, such as ethylene, 1-hexene, or propylene, using MAO as cocatalyst.

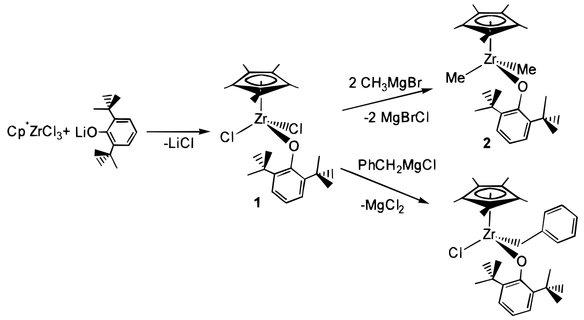
Furthermore, many alkyl or hydride derivatives of group 4 metallocenes are involved in a number of applications that are of great interest in organic synthesis, including carbon monoxide or isocyanide insertions into metal−hydride or metal−alkyl bonds.[5] This migratory insertion leads to acyl and iminoacyl functions for most of the early d-block metals. In the case of η^2-iminoacyl derivatives, many examples are known that are more stable than their oxygen counterparts, especially for complexes that do not contain a Cp ligand. In fact, alkyl- or aryloxides of the group 4 metals have been reported[6] to react with isocyanides, and such reactions have enabled the isolation and characterization of a large number of η^2-iminoacyl derivatives.

In this paper we wish to extend this chemistry to include the synthesis of zirconium analogues of the type $Cp^*Zr(OAr)_nX_{3-n}$ ($Cp^* = \eta^5\text{-}C_5Me_5$; OAr = aryloxy group; X = halogen, alkyl; $n = 1, 3$). The reactivity of these compounds toward isocyanide insertion and their use in the catalysis of ethylene polymerization, in the presence of MAO as a cocatalyst, were also studied.

Results and Discussion

Synthesis. Complex $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)Cl_2$ (**1**) was prepared from Cp^*ZrCl_3 by adding 1 equiv of the corresponding lithium phenoxide as a hexane/toluene suspension (see Experimental Section) (Scheme 1).

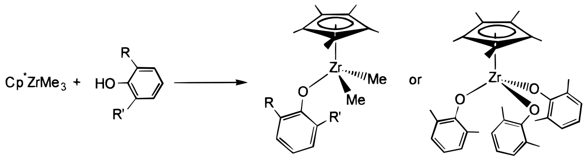
Scheme 1



Compound **1** was obtained as an air-sensitive yellow microcrystalline solid that is soluble in dichloromethane, THF, or toluene, but is scarcely soluble in hexane.

This complex was used as the starting material for the synthesis of new alkyl derivatives (see Scheme 1). Thus, the reaction of complex **1** with 2 equiv of MeMgBr in diethyl ether afforded the complex $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)Me_2$ (**2**), whereas the reaction with one or more equivalents of BzMgCl afforded the monoalkyl derivative $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)(Bz)(Cl)$ (**3**). The compounds were isolated as off-white (**2**) or yellow (**3**) microcrystalline solids that are very air-sensitive. It is interesting to note that the analogous complex $Cp^*Ti(2,6\text{-}OC_6H_3{}^iPr_2)Me_2$ cannot be obtained by the same procedure starting from $Cp^*Ti(2,6\text{-}OC_6H_3{}^iPr_2)Cl_2$.[3] Alternatively, complex **2** could be obtained by the reaction of Cp^*ZrMe_3 with 2,6- $^tBu_2C_6H_3OH$ in hexane. This procedure was extended to other phenols. In this way (see Scheme 2), complexes $Cp^*Zr(2,6\text{-}OC_6H_3Me_2)Me_2$ (**4**), $Cp^*Zr(O\text{-}2\text{-}{}^tBu\text{-}6\text{-}MeC_6H_3)Me_2$ (**5**), and $Cp^*Zr(O\text{-}2\text{-}C_3H_5\text{-}6\text{-}MeC_6H_3)Me_2$ (**6**) were obtained in good yields by reacting 1 equiv of Cp^*ZrMe_3 with 1 equiv of the corresponding phenol. Only when an excess of the less bulky $2,6\text{-}Me_2C_6H_3OH$ phenol was used was the completely substituted complex $Cp^*Zr(2,6\text{-}OC_6H_3Me_2)_3$ (**7**) obtained.

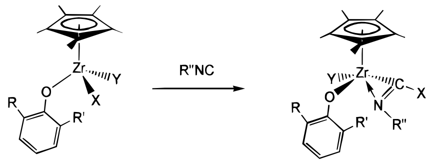
Scheme 2



R	R'	Complex
^tBu	tBu	**1**
Me	Me	**4**(1:1) or **7**(1:3)
^tBu	Me	**5**
C_3H_5	Me	**6**

Due to its relative stability and ease of preparation, complex **2** was chosen to study the reactivity toward isocyanide insertion at the metal−carbon bonds. This complex reacted smoothly with 1 equiv of different isocyanides, namely, XyNC (Xy = xylyl = $2,6\text{-}Me_2C_6H_3$), ^nBuNC, CyNC (Cy = cyclohexyl), or TMBNC (TMB = 1,1,3,3-tetramethylbutyl), to give chiral η^2-iminoacyl derivatives (see below for characterization) $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)(\eta^2\text{-}MeC{=}NR)(Me)$ [R = Xy (**8**); ^nBu (**9**), Cy- (**10**), TMB (**11**)] (see Scheme 3).

Scheme 3



R	R'	R''	X	Y	Complex
^tBu	^tBu	Xy	Me	Me	**8**
^tBu	^tBu	^nBu	Me	Me	**9**
^tBu	^tBu	Cy	Me	Me	**10**
^tBu	^tBu	TMB	Me	Me	**11**
^tBu	^tBu	Xy	Bz	Cl	**12**
^tBu	Me	Xy	Me	Me	**13**

In a similar fashion (see Scheme 3), complexes **3** and **5** reacted with XyNC to give the corresponding η^2-iminoacyl compounds $Cp^*Zr(2,6\text{-}OC_6H_3{}^tBu_2)(\eta^2\text{-}BzC{=}NXy)(Cl)$ (**12**) and $Cp^*Zr(O\text{-}2\text{-}{}^tBu\text{-}6\text{-}MeC_6H_3)(\eta^2\text{-}MeC{=}NXy)(Me)$ (**13**). These complexes were synthesized in order to evaluate the different reactivities of the methyl (**2**) and benzyl (**3**) derivatives toward the insertion process and also to assess the influence of an asymmetric bulky aryloxy ligand (**5**) on the chirality of the η^2-iminoacyl compound.

These complexes were obtained as off-white (**8**, **11**, **12**) microcrystalline solids or as light brown oily materi-

---

(5) (a) Collman, P.; Hegedus, L. S.; Norton, J. R.; Finke, R. B. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450. (c) Evans, W. J.; Meadows, J. H.; Hunter, E.; Atwood, J. L. *Organometallics* **1987**, *6*, 295.

(6) (a) McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1985**, *107*, 1072. (b) Durfee, L. D.; Hill, J. E.; Fanwich, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75.

als (**9**, **10**, **13**), all of which are extremely air-sensitive. A second insertion into the remaining zirconium methyl group was not observed, even when stoichiometries other than 1:1 were tested. When carbon monoxide was used as the reagent in the insertion process, only an intractable mixture of products was obtained.

Characterization. The complexes were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and elemental analysis (see Experimental Section). The ^{1}H NMR spectra of **1** and **2** in $CDCl_3$ show a single peak near 1.4 ppm, which integrates for 18 protons and corresponds to the *tert*-butyl groups of the aryloxy ligand. A similar spectrum was found for compound **4**, which shows a single peak for the methyl group protons of the phenoxy substituent. In addition, peaks corresponding to the Cp* ligand and aromatic protons of the aryloxy group were observed (see Experimental Section). In contrast, complex **3** shows a very broad peak for the methyl groups of the ^{t}Bu substituents in its ^{1}H NMR spectrum at room temperature. This behavior indicates that for complexes **1**, **2**, and **4** free rotation about the O−C bond occurs, while this rotation is partially blocked in compound **3**. To study the dynamic behavior in solution, variable-temperature ^{1}H NMR experiments were performed for these complexes. Complexes **1**, **2**, and **4** show a single peak for the ^{t}Bu or Me groups of the aryloxy ligand, even at low temperatures. In contrast, complex **3** shows splitting of the broad signal at low temperature, and this gives rise to two single peaks at 223 K. When the temperature was raised to 373 K, a single sharp peak was found for complex **3**, indicating that free rotation had been achieved. The coalescence temperature (293 K) and the two site exchange equations[7] can be used to estimate the value of $\Delta G_c^\ddagger$ to be 14.5 ± 0.2 kcal mol^{-1}. It is noteworthy that both complexes **5** and **6**, which contain an asymmetric phenoxy group, show a single peak for their zirconium-bonded methyl groups in their ^{1}H NMR spectra over a wide range of temperatures. This result is in accordance with free rotation of the phenoxy groups even at low temperature, a situation that has previously been described for complexes **1**, **2**, and **4**. Finally, the ^{1}H NMR spectrum of **7** in C_6D_6 shows a single peak at 2.24 ppm, which integrates for 18 protons and can be assigned to the six equivalent methyl groups of the aryloxy ligands. This equivalence can again be explained in terms of the free rotation of these aryloxy groups around the O−C bonds, even though the metal center is in a more crowded environment in this case. A single-crystal X-ray analysis of compound **7** was carried out in order to provide precise structural details of this compound.

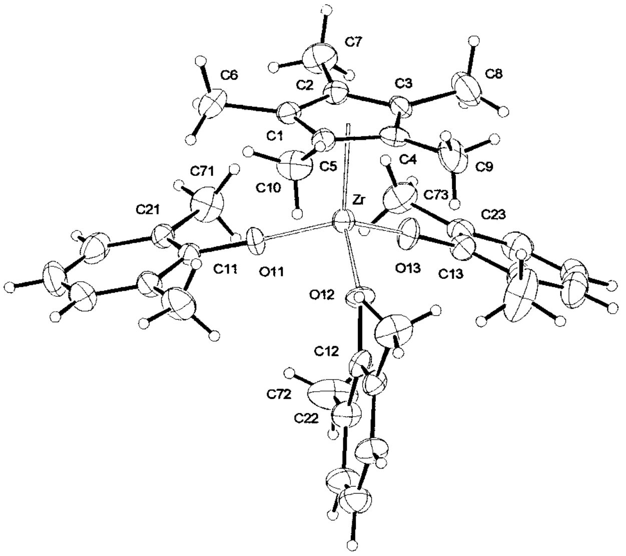


Figure 1. ORTEP drawing of **7**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 7

Zr−O(11)	1.940(4)	Zr−C(3)	2.531(6)
Zr−O(12)	1.947(4)	Zr−C(4)	2.516(7)
Zr−O(13)	1.950(4)	Zr−C(5)	2.523(7)
Zr−CE[a]	2.220(7)	O(11)−C(11)	1.355(7)
Zr−C(1)	2.525(7)	O(12)−C(12)	1.359(6)
Zr−C(2)	2.541(7)	O(13)−C(13)	1.350(7)

O(11)−Zr−O(12)	103.29(16)	O(13)−Zr−CE	113.0(2)
O(11)−Zr−O(13)	105.82(17)	C(11)−O(11)−Zr	167.5(4)
O(12)−Zr−O(13)	103.54(16)	C(12)−O(12)−Zr	155.3(4)
O(11)−Zr−CE	112.6(2)	C(13)−O(13)−Zr	166.1(5)
O(12)−Zr−CE	117.4(2)		

[a] CE is the centroid of the cyclopentadienyl ring

The molecular structure of complex **7** is shown in Figure 1 together with the atomic labeling scheme. The second digit of the phenoxy labels refers to moiety 1, 2, or 3 accordingly. Selected bond distances and angles are summarized in Table 1. The Zr atom coordinates a Cp* ring in a η^5 and symmetric fashion, as well as three 2,6-dimethylphenoxy oxygen atoms. The complex presents a three-legged piano stool coordination and can also be described as pseudo-tetrahedral if the centroid of the Cp* ring is considered as occupying one coordination site. The 2,6-dimethylphenoxy ligand 2 lies roughly on a pseudo mirror plane passing through the Zr atom, the centroid, and the C(2) and C(7) carbon atoms of the cyclopentadienyl ring. The phenoxy ligand 2 is quasi-orthogonal [83.2(3)°], and the other two ligands are nearly parallel to the pentatomic ring [16.6(2)° and 22.3(2)° for 1 and 3, respectively]. The O(11)O(12)O(13) plane is almost parallel to the Cp ring [2.4(2)°]. Owing to the orientation of the three phenoxy ligands, an enlargement of the O(11)−Zr−O(13) and CE−Zr−O(12) bond angles is observed due to the existence of steric hindrance between the C(71) and C(73), the C(82) and C(9), and the C(82) and C(10) methyl carbon atoms. The two phenoxy ligands related by the pseudo mirror plane show a Zr−O−C bond angle of nearly 180° [167.5(4)° and 166.1(5)° for 1 and 3, respectively], whereas for phenoxy ligand 2 the bond angle is 155.3(4)°. Despite the difference in the Zr−O−C bond angles, the Zr−O bond distances are practically equal and are shorter than those found in several [$Cp_2Zr(O{-}Ar)_2$] or [$Cp^*_2Zr(O{-}Ar)_2$] complexes.[8] As found in these latter complexes, there is no correlation between the Zr−O bond lengths and the Zr−O−C bond angles. Howard et al.[8] proposed that the M−O−Ar bond angles do not provide a good indication of the extent of M−O π-interactions, and it is most probable that the linearity at the oxygen atom

---

(7) Abrahams, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy*; John Wiley and Sons: New York, 1988.

(8) Howard, W. A.; Trnka, T. M.; Parkin, G. *Inorg. Chem.* **1995**, *34*, 5900, and references therein.

Table 2

complex	ν(C=N) (cm^{-1})	δ ^{13}C NMR (ppm) for quaternary iminoacyl carbon atom
8	1567	246.55
9	1580	240.62
10	1589	238.39
11	1580	237.84
12	1597	242.37
13	1585	239.62

Table 3. Activity in Ethylene Polimerization

complex	Al/Zr	T (°C)	activity (kg PE/mol Zr·h·bar)
1[a]	499	29	2440
	503	40	2930
	505	58	2170
	1093	29	4260
	1504	29	4030
	1083	40	3910
	1509	40	2770
	1500	25	3260
7[b]	499	25	28
	1537	25	25
	1026	25	27
	508	35	34
	508	50	74
Cp_2ZrCl_2[c]	2000	25	5260
Cp^*ZrCl_3[d]	1500	24	82
$Cp^*Ti(Cl)_2(O\text{-}2,6^iPrC_6H_3)$[e]	2000	60	1240

[a] Experimental conditions: P(ethylene) = 3.5 bar; 300 mL of toluene; t = 2.5 min. [b] Experimental conditions: P(ethylene) = 3.5 bar; 300 mL of toluene; t = 45 min. [c] Experimental conditions: P(ethylene) = 1 bar; 300 mL of toluene; t = 8 min. [d] Experimental conditions: P(ethylene) = 3.5 bar; 300 mL of toluene; t = 45 min. [e] From ref 4.

is attributable mainly to steric interactions.[9,10] A comparison with other Zr(IV) complexes containing only one η^5-coordinated Cp ring was not possible because, after a bibliographic search on the Cambridge Structural Database, we believe that compound **7** is the first example of this type of complex to be structurally characterized. In any case, on the basis of the short Zr−O distances we can propose a strong interaction between the metal center and the surrounding oxygen atoms.

The migratory insertion of alkyl groups toward isocyanide ligands allows the introduction of iminoacyl groups, which are present in different coordination modes. In fact, for high-valent oxophilic early transition metals, the iminoacyl group typically adopts a η^2-coordination mode through both the nitrogen and the carbon atoms.[11] Similarly, a η^2-coordination mode was proposed for the iminoacyl ligand in complexes **8**−**13** on the basis of their IR and ^{13}C NMR spectra. In fact, these complexes show characteristic[11] ν(C=N) stretching vibrations at ca. 1580 cm^{-1}. In addition, iminoacyl quaternary carbon atoms resonate at ca. 240 ppm (see Table 2).

These complexes contain a chiral center at the zirconium atom, and this results in diastereotopic groups in **9**−**12**, as shown by the NMR spectra (see Experimental Section). In fact, the ^{1}H NMR spectrum of **9** shows a complex spin system for the hydrogen atoms of the *n*-Bu group, of the type *AA′BB′CC′X*$_3$; complex **10** shows broad multiplets for the hydrogen atoms of the cyclohexyl group; in complex **11** the methyl groups in position *1* of the TMB group also appear to be diastereotopic, and the $-CH_2-$ group in position *2* leads to a broad peak; finally, in complex **12** the presence of a diastereotopic group in the benzyl substituent of the iminoacyl ligand is also observed.

A remarkable feature of the ^{1}H NMR spectra of these iminoacyl complexes at room temperature is the difference observed in the peaks assigned to the *tert*-butyl groups of the aryloxy ligand. Whereas complexes **9** and **10** both show a single peak, integrating for 18 protons, complexes **8** and **12** show two peaks, both of which integrate for 9 protons, and complex **11** displays a very broad peak in this region of the spectrum. In addition, complexes **8** and **12** show two different peaks for the methyl groups of the xylyl moiety. To explain these features, we propose that in complexes **8**, **11**, and **12** the rotation of the phenoxy group about the O−C bond is partially or totally blocked at room temperature, whereas in complexes **9** and **10** this rotation is free. To confirm this behavior, a variable-temperature ^{1}H NMR study was carried out using toluene-d_8 as the solvent. Complexes **8** and **12** do not show any equivalence of the *tert*-butyl groups even at 373 K. In contrast, complexes **9** and **10** show a single peak at temperatures as low as 183 K. Complex **11** shows, at 203 K, two peaks corresponding to two inequivalent ^{t}Bu groups. When the temperature was raised to 273 K, the peaks coalesced, and at 373 K, a single peak was observed. The $\Delta G_c^{\ddagger}$ value for the rotation process was estimated to be 14.2 ± 0.2 kcal mol^{-1}, which is similar to that found previously for the blocked rotation of the phenoxy group in complex **3** (see above). This blocked rotation could be due to the steric hindrance caused by the bulky iminoacyl nitrogen substituent (e.g., Xy, TMB) acting on the aryloxy group.

As previously mentioned, the presence of a chiral center allowed us to prepare an iminoacyl complex (**13**) with a second center of asymmetry in the phenoxy group. The aim of this was to observe the two possible diastereoisomers in the NMR spectra. In fact, complex **13** has, in addition to the zirconium chiral center, a phenoxy ligand with two different groups at the *2* and *6* positions. If the rotation of the phenoxy group is blocked, as discussed for complexes **8** and **12**, it would be possible to detect two rotameric diasteroisomers. Unfortunately, this rotation was not blocked even at 183 K, as was the case for the parent complex **5**. However, a broadening of the signals corresponding to the 2-^{t}Bu and 6-Me substituents was observed at this temperature, indicating that the rotation is beginning to be blocked, and thus the two isomers would be observable.

Catalytic Activity in Ethylene Polymerization Processes. The catalytic activity in ethylene polymerization of the aryloxy derivatives **1** and **7**, in association with MAO, was studied, and the results are explained in terms of the influence of the number of the substituents on the activity. Polymerization reactions were carried out in the temperature range 25−55 °C and at several Al/Zr molar ratios. The results are summarized in Table 3. For comparison, the results obtained by us

---

(9) (a) Adachi, T.; Hughes, D. L.; Ibrahim, S. K.; Okamoto, S.; Pickett, C. J.; Yabanouchi, N.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1081. (b) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1978**, *17*, 668.

(10) Heyn, R. H.; Stephan, D. W. *Inorg. Chem.* **1995**, *34*, 2804.

(11) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

in the presence of the classical Cp_2ZrCl_2/MAO system or the monocyclopentadienylzirconium precursor, $Cp*ZrCl_3$,[12] under similar conditions are also reported.

The activity of both new catalytic systems depends on the Al/Zr ratio, but this effect was much more pronounced for the system based on complex **1**. In this case, the polymerization activity reaches a maximum at an Al/Zr ratio near 1000 and then remains constant or decreases slightly, depending of the reaction temperature. It can be seen from the results in Table 3 that, at a constant Al/Zr ratio, increasing the temperature up to 40 °C leads to an increase in the polymerization rate. This is due to the increase of the propagation rate with temperature. At higher temperatures a decrease in the activity was observed, and this is probably related to the thermal instability of the active species. This is common behavior for the metallocene systems, and the optimal temperature for each system depends on the balance between the propagation rate and the thermal instability.

For instance, the polymerization activity of the system based on complex **7** was still increasing at the highest temperature used (i.e., 50 °C).

In any case, it was also found that polymerization activity of complex **1** was much higher than that observed for complex **7** (almost 100 times) and also than that of the previously described analogous titanium compound,[4] $Cp*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$, or the precursor, $Cp*ZrCl_3$. In contrast, the activity was on the same order as that of the known Cp_2ZrCl_2/MAO system (see Table 3).

The stability of complex **7** could explain the different deactivation rate found and the decrease of activity observed for the more thermally unstable system based on complex **1**.

Conclusions

Monocyclopentadienyl−aryloxy derivatives of zirconium can be easily prepared by the reaction of the appropriate monocyclopentadienyl zirconium trichloride or trialkyl precursors and lithium phenoxide or phenol. Alkyl derivatives undergo insertion of one isocyanide molecule into a zirconium−carbon bond, giving rise to the corresponding chiral η^2-iminoacyl compounds. Similar reactivity was found for methyl or benzyl zirconium derivatives. The dynamic behavior of some of these complexes was studied by means of variable-temperature ^1H NMR studies. The dichloride and triphenoxy complexes **1** and **7** catalyze ethylene polymerization in the presence of MAO as cocatalyst. Complex **1**, $Cp*Zr(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)Cl_2$, was found to be more active by 100 times than the trisubstituted complex **7**, $Cp*Zr(O\text{-}2,6\text{-}Me_2C_6H_3)_3$, and 10 times more active than similar titanium complexes described previously.

Experimental Section

General Procedures. All reactions were carried out using Schlenk techniques or a glovebox (model VAC HE-2). Solvents were distilled from the appropriate drying agents and deoxygenated prior to use. Complexes $Cp*ZrCl_3$ and $Cp*ZrMe_3$ were prepared by literature procedures.[12] Different phenols and isocyanides were purchased from Aldrich and Fluka, stored over molecular sieves, and deoxygenated before use.

^1H and ^{13}C NMR spectra were obtained on a 300 Unity Varian spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in parts per million relative to $SiMe_4$. IR spectra of iminoacyl derivatives were obtained in the region 500−4000 cm^{-1} using an FT-IR Nicolet Magna Spectra spectrophotometer.

Synthesis of $Cp*Zr(OC_6H_3(C(CH_3)_3)_2)Cl_2$ (1). To a solution of 2,6-di-*tert*-butylphenol (3.10 g, 15.02 mmol) in 50 mL of hexane was added a 1.6 M solution of ^nBuLi in hexane (9.38 mL, 15.02 mmol). A cloudy white precipitate was obtained immediately. After 2 h of reaction, the liquor was decanted and the precipitate was filtered off, washed with 50 mL of hexane, and dried in vacuo. The solid was mixed with $Cp*ZrCl_3$ (5.00 g, 15.02 mmol), and the mixture was suspended in hexane/toluene (1:1) and stirred, at room temperature, for 4 h. The yellow suspension obtained was dried in vacuo, and the residue was extracted with 250 mL of hexane. The volume of the solution was reduced to 25 mL, and it was cooled to −20 °C for 24 h. Complex **1** was obtained as a light yellow microcrystalline solid (50%). ^1H NMR (300 MHz, C_6D_6): δ 1.41 (s, 18H, ^tBu), 2.09 (s, 15H, Cp*), 6.87 (t, $J = 7.93$ Hz, 1H, H4), 7.21 (d, $J = 7.93$ Hz, 2H, H3 and H^5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 12.57 (Cp*), 31.85 ($C(CH_3)_3$), 35.27 ($C(CH_3)_3$), 120.98 (C4), 124.83 (C3 and C5), 127.78 (Cp*), 139.23 (C2 and C6), 160.76 (C1). Anal. Calcd for $C_{24}H_{36}O_3Cl_2Zr$: C, 57.35; H, 7.22. Found: C, 57.60; H, 7.46.

Synthesis of $Cp*Zr(OC_6H_3(C(CH_3)_3)_2)(CH_3)_2$ (2). Method A. To a solution of $Cp*ZrMe_3$ (0.30 g, 1.10 mmol) in 10 mL of hexane was added a solution of 2,6-di-*tert*-butylphenol (0.19 g, 0.94 mmol) in 5 mL of hexane at room temperature. After stirring for 4 h, the solvent was removed in vacuo and the residue was extracted with 10 mL of pentane and cooled at −30 °C for 24 h. Complex **2** was obtained as a white microcrystalline solid (91% yield).

Method B. To a solution of $Cp*Zr(OC_6H_3{}^tBu_2)Cl_2$ (0.29 g, 0.57 mmol) in 25 mL of diethyl ether, at −80 °C, was added 0.38 mL (1.14 mmol) of a solution of MeMgBr in diethyl ether. The mixture was stirred for 6 h at room temperature. The solvent was removed under vacuum, the residue was extracted with 30 mL of hexane, and, after filtration, the solvent was evaporated to afford a white solid (95% yield). ^1H NMR (300 MHz, C_6D_6): δ 0.39 (s, 6H, ZrMe), 1.42 (s, 18H, ^tBu), 1.75 (s, 15H, Cp*), 6.89 (t, 1H, $J = 7.81$ Hz, H4), 7.29 (d, 2H, $J = 7.81$ Hz, H3 and H5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 11.60 (Cp*), 31.71 ($C(CH_3)_3$), 35.22 ($C(CH_3)_3$), 45.37 (ZrMe), 120.19 (C3 and C5), 120.66 (C4), 125.20 (Cp*), 139.11 (C2 and C6), 161.62 (C1). Anal. Calcd for $C_{26}H_{42}OZr$: C, 67.62; H, 9.17. Found: C, 67.18; H, 9.87.

Synthesis of $Cp*Zr(OC_6H_3(C(CH_3)_3)_2)(CH_2Ph)(Cl)$ (3). To a solution of $Cp*Zr(OC_6H_3(C(CH_3)_3)_2)Cl_2$ (0.34 g, 0.68 mmol) in 25 mL of diethyl ether, at −80 °C, was added 0.68 mL (0.68 mmol) of a solution of $PhCH_2MgCl$ in diethyl ether. The mixture was allowed to react at 25 °C for 6 h. The solvent was removed under vacuum, and the yellow oily residue was extracted with 40 mL of hexane. After filtration, the solution was concentrated to 10 mL and cooled at −30 °C overnight to afford complex **3** as a yellow microcrystalline solid (81% yield). ^1H NMR (300 MHz, C_6D_6): δ 1.40 (br s, 18H, ^tBu), 1.74 (s, 15H, Cp*), 2.55 (AB spin system, 2H, J_{AB}=11.95 Hz, CH_2Ph), 6.84 (t, 1H, $J = 7.70$ Hz, H4), 7.20 (m, 5H, CH_2Ph), 7.38 (d, 2H, $J = 7.70$ Hz, H3 and H5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 12.07 (Cp*), 32.40 ($C(CH_3)_3$), 35.60 ($C(CH_3)_3$), 72.41 (CH_2-Ph), 120.84 (C3 and C5, from $C_6H_3{}^tBu_2$), 122.47 (C4, from $C_6H_3{}^tBu_2$), 124.37 (C4, from CH_2Ph), 125.41 (Cp*), 128.79, 128.94 (C2, C6, C3, C5, from CH_2Ph), 138.60 (C1, from CH_2Ph), 145.20 (C2, C6, from $C_6H_3{}^tBu_2$), 161.28 (C1, from $C_6H_3{}^tBu_2$). Anal. Calcd for $C_{31}H_{43}OClZr$: C, 66.69; H, 7.76. Found: C, 66.37; H, 7.52.

Synthesis of $Cp*Zr(OC_6H_3RR')(CH_3)_2$ [$RR' = (CH_3)_2$ (4);

---

(12) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.

R = CH$_3$, R′ = C(CH$_3$)$_3$ (5); R = CH$_3$, R′ = C$_3$H$_7$ (6)]. Complexes **4**−**6** were synthesized using the method described for complex 2 (*method A*) with the corresponding phenol.

4: light brown solid, 95% yield. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.26 (s, 6H, ZrMe), 1.76 (s, 15H, Cp*), 2.19 (s, 6H, C$_6$H$_3$*Me*$_2$), 6.82 (t, 1H, J = 7.61 Hz, H4), 7.10 (d, 2H, J = 7.61 Hz, H3 and H5). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 10.92 (Cp*), 17.54 (C$_6$H$_3$*Me*$_2$), 38.40 (ZrMe), 119.69 (C3 and C5), 120.46 (C4), 120.69 (Cp*), 128.32 (C2 and C6), 159.10 (C1). Anal. Calcd for C$_{20}$H$_{30}$OZr: C, 63.60; H, 8.01. Found: C, 63.25; H, 8.45.

5: white solid, 95 yield. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.33 (s, 6H, ZrMe), 1.49 (s, 9H, ^{t}Bu), 1.79 (s, 15H, Cp*), 2.10 (s, 3H, Me), 6.87 (pt, 1H, J = 7.77 Hz, J = 7.33 Hz, H4), 7.05 (d, 1H, J = 7.77 Hz, H3 or H5), 7.25 (d, 1H, J = 7.33 Hz, H3 or H5). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 11.23 (Cp*), 19.09 (Me), 30.47 (C(*C*H$_3$)$_3$), 34.93 (*C*(CH$_3$)$_3$), 41.26 (ZrMe), 120.04 (C3 or C5), 120.63 (C3 or C5), 124.96 (Cp*), 128.74 (C4), 128.78 (C2 or C6), 137.52 (C2 or C6), 159.80 (C1). Anal. Calcd for C$_{23}$H$_{26}$OZr: C, 65.81; H, 8.64. Found: C, 65.47; H, 8.31.

6: brown oil, 95% yield. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.25 (s, 6H, ZrMe), 1.77 (s, 15H, Cp*), 2.17 (s, 3H, Me), 3.39 (d, 2H, J = 6.31, C*H*$_2$CH=CH$_2$), 5.09 (m, 2H, CH$_2$CH=C*H*$_2$), 6.06 (m, 1H, CH$_2$C*H*=CH$_2$), 6.84 (pt, 1H, J = 7.93 Hz, J = 7.40 Hz, H4), 7.01 (d,1H, J = 7.93 Hz, H3 or H5), 7.07 (d, 1H, J = 7.40 Hz, H3 or H5). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 10.97 (Cp*), 17.79 (Me), 34.91 (*C*H$_2$CH=CH$_2$), 39.25 (ZrMe), 115.77, 119.73 (C3 and C5), 120.85 (Cp*), 127.28 (CH$_2$*C*H=CH$_2$), 127.80 (C4), 128.31 (CH$_2$CH=*C*H$_2$), 128.87, 137.36 (C2 and C6), 158.45 (C1). Anal. Calcd for C$_{22}$H$_{32}$OZr: C, 65.45; H, 7.99. Found: C, 65.50; H, 7.67.

Synthesis of Cp*Zr(OC$_6$H$_3$(CH$_3$)$_2$)$_3$ (7). To a solution of Cp*ZrMe$_3$ (0.15 g, 0.55 mmol) in 10 mL of hexane was added 2,6-dimethylphenol (0.20 g, 1.66 mmol) in 10 mL of hexane. The mixture was stirred for 3 h to afford a yellow precipitate. The solid was filtered off, washed with 15 mL of hexane, and recrystallized from CH$_2$Cl$_2$/hexane to afford complex **7** as a white microcrystalline solid (87% yield). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.93 (s, 15H, Cp*), 2.24 (s, 18H, OC$_6$H$_3$*Me*$_2$), 6.75 (t, 3H, J = 7.33 Hz, H4), 6.93 (d, 6H, J = 7.33 Hz, H3 and H5). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 11.56 (Cp*), 18.30 (OC$_6$H$_3$*Me*$_2$), 120.88 (C3 and C5), 122.94 (C4), 126.99 (Cp*), 129.42 (C2 and C6), 159.81 (C1). Anal. Calcd for C$_{34}$H$_{42}$O$_3$Zr: C, 69.22; H, 7.18. Found: C, 69.74; H, 7.08.

Synthesis of Cp*Zr(OC$_6$H$_3$RR′)(R″C=NX)(Y) [R = R′ = ^{t}Bu, X = Y = Me, R″ = Xy (8), ^{n}Bu (9), Cy (10), TMB (11); R = R′ = ^{t}Bu, X = CH$_2$Ph, Y = Cl, R″ = Xy (12); R = ^{t}Bu, R′ = Me, X = Y = Me, R″ = TMB (13)]. To a solution of Cp*Zr(OC$_6$H$_3$RR′)(X)(Y) (0.60 mmol) in 5 mL of hexane was added a solution of the corresponding isocyanide, RNC (0.60 mmol), in 5 mL of hexane. The solution was stirred at room temperature for 5 h, and the solvent was removed under vacuum. Complexes **8**, **11**, and **12** were obtained as off-white solids after recrystallization from pentane. Complexes **9**, **10**, and **13** were obtained as spectroscopically pure light-brown oily materials after several attempts at recrystallization.

8: 90% yield. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.53 (s, 3H, ZrMe), 1.42 (s, 9H, ^{t}Bu), 1.52 (s, 9H, ^{t}Bu), 1.62 (s, 3H, Me from Xy), 1.86 (s, 15H, Cp*), 2.09 (s, 3H, Me from Xy), 2.0.11 (s, 3H, MeC=N), 6.90 (m, 4H, H3 and H5, from C$_6$H$_3$^{t}Bu$_2$ and Xy), 7.26 (dd, 1H, J = 5.10 Hz, J = 4.40 Hz, H4 from C$_6$H$_3$^{t}Bu$_2$ or Xy), 7.30 (dd, 1H, J = 4.80 Hz, H=5.60 Hz, H4 from C$_6$H$_3$^{t}Bu$_2$ or Xy). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 11.92 (Cp*), 18.91, 19.09 (Me from Xy), 22.10 (MeC=N), 32.79 (ZrMe), 31.81, 32.45 (C(*C*H$_3$)$_3$), 35.40, 35.52 (*C*(CH$_3$)$_3$), 118.50, 119.34, 125.30, 125.40, 125.73, 128.19, 128.31 (C3, C4, C5 from C$_6$H$_3$^{t}Bu$_2$ and Xy, and from Cp*), 129.03, 131.14 (C2 and C6 from Xy), 138.51, 139.02 (C2 and C6 from C$_6$H$_3$^{t}Bu$_2$), 144.72 (C1 from Xy), 161.73 (C1 from C$_6$H$_3$^{t}Bu$_2$), 246.55 (C=N). Anal. Calcd for C$_{35}$H$_{51}$NOZr: C, 70.89; H, 8.67; N, 2.36. Found: C, 69.42; H, 9.15; N, 2.33.

9: 90% yield. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.56 (s, 3H, ZrMe), 0.80 (t, 3H, J = 7.30 Hz, CH$_3$(δ), from ^{n}Bu), 1.15 (m, 2H, CH$_2$(γ), from ^{n}Bu), 1.43 (s, 18H, ^{t}Bu$_2$), 1.60 (m, 2H, CH$_2$(β), from ^{n}Bu), 1.81 (s, 15H, Cp*), 2.16 (s, 3H, MeC=N), 3.46 (m, 2H, CH$_2$(α), from ^{n}Bu), 6.81 (t, 1H, J = 7.80 Hz, H4), 7.25 (d, 2H, J = 7.80 Hz, H3 and H5). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 11.56 (Cp*), 13.89 (CH$_3$(δ)), 19.12 (*Me*C=N), 20.96 (CH$_2$(γ)), 30.25 (ZrMe), 31.56 (C(*C*H$_3$)$_3$), 31.68 (CH$_2$(β)), 35.34 (*C*(CH$_3$)$_3$), 48.02 (CH$_2$(α)), 117.66 (Cp*), 118.82 (C4), 124.93 (C3 and C5), 138.49 (C2 and C6), 162.06 (C1), 240.62 (C=N). Anal. Calcd for C$_{31}$H$_{61}$NOZr: C, 68.32; H, 9.43; N, 2.57. Found: C, 68.77; H, 9.28; N, 2.69.

10: 90% yield. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.67 (s, 3H, ZrMe), 1.10 (m, 2H, CH$_2$(4), from Cy), 1.44 (s, 18H, ^{t}Bu$_2$), 1.62 (br s, 4H, CH$_2$(3) and CH$_2$(5), from Cy), 1.72 (br s, 2H, CH$_2$(2) or CH$_2$(6), from Cy), 1.83 (s, 15H, Cp*), 2.01 (br s, 2H, CH$_2$(2) or CH$_2$(6), from Cy), 2.18 (s, 3H, MeC=N), 3.81 (s, 1H, CH(1), from Cy), 6.83 (t, 1H, J = 7.80 Hz, H4), 7.27 (d, 2H, J = 7.80 Hz, H3 and H4). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 11.64 (Cp*), 18.90 (MeC=N), 24.91 (CH$_2$(4)), 25.20, 25.24 (CH$_2$(3) and CH$_2$(5)), 29.91 (ZrMe), 31.15 (C(*C*H$_3$)$_3$), 32.07, 32.95 (CH$_2$(2) and CH$_2$(6)), 35.36 (*C*(CH$_3$)$_3$), 60.28 (CH(1)), 117.74 (Cp*), 118.86 (C4), 124.92 (C3 and C5), 138.54 (C2 and C6), 162.07 (C1), 238.39 (C=N). Anal. Calcd for C$_{33}$H$_{53}$NOZr: C, 69.41; H, 9.36; N, 2.45. Found: C, 68.95; H, 9.44; N, 2.72.

11: 90% yield. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.64 (s, 3H, ZrMe), 1.44 (br s, 18H, ^{t}Bu$_2$), 1.60 (s, 3H, N−C(C*H*$_3$)$_2$−), 1.83 (s, 15H, Cp*), 1.76 (s, 2H, −C*H*$_2$−), 2.48 (s, 3H, MeC=N), 6.83 (t, 1H, J = 7.69 Hz, H4), 7.27 (d, 2H, J = 7.69 Hz, H3 and H5). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 11.57 (Cp*), 21.96 (MeC=N), 29.75, 30.58 (N−C(*C*H$_3$)$_2$−), 31.20 (ZrMe), 31.75 (−CH$_2$C(*C*H$_3$)$_3$), 31.82 (C(*C*H$_3$)$_3$), 31.89 (−CH$_2$*C*(CH$_3$)$_3$), 35.32 (*C*(CH$_3$)$_3$), 54.19 (−CH$_2$−), 68.35 (N−C(CH$_3$)$_2$−), 117.73 (Cp*), 118.72 (C4), 124.91 (C3 and C5), 138.38 (C2 and C6), 162.07 (C1), 237.84 (C=N). Anal. Calcd for C$_{35}$H$_{59}$NOZr: C, 69.94; H, 9.89; N, 2.33. Found: C, 69.53; H, 9.65; N, 2.25.

12: 85% yield. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.41 (s, 9H, ^{t}Bu), 1.61 (s, 9H, ^{t}Bu), 1.76 (s, 3H, Me from Xy), 1.89 (s, 15H, Cp*), 2.02 (s, 3H, Me from Xy), 3.97 (AB spin system, 2H, J_{AB} = 14.65 Hz, C*H*$_2$Ph), 7.27 (m, 2H, H4). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 11.92 (Cp*), 19.39, 19.42 (Me from Xy), 32.32, 32.77 (C(*C*H$_3$)$_3$), 35.66, 35.74 (*C*(CH$_3$)$_3$), 44.82 (*C*H$_2$Ph), 120.10, 122.64, 125.05, 125.44, 126.00, 127.22, 128.61 (C3, C4, C5 from C$_6$H$_3$^{t}Bu$_2$ and Xy, and from Cp*), 122.84 (C4, CH$_2$Ph), 128.10, 128.40 (C2 or C6, C3 or C5, CH$_2$Ph), 134.40 (C1, CH$_2$Ph), 129.76, 130.49 (C2 and C6, Xy), 138.60, 139.90 (C2 and C6, C$_6$H$_3$^{t}Bu$_2$), 144.37 (C1, Xy), 161,63 (C1, C$_6$H$_3$^{t}Bu$_2$), 242.37 (C=N). Anal. Calcd for C$_{40}$H$_{52}$NOClZr: C, 69.68; H, 7.60; N, 2.03. Found: C, 69.30; H, 7.44; N, 1.98.

13: 90% yield. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.51 (s, 3H, ZrMe), 0.89 (s, 9H, −CH$_2$C(C*H*$_3$)$_2$), 1.40 (s, 3H, N−C(CH$_3$)$_2$−), 1.46 (s, 3H, N−C(CH$_3$)$_2$−), 1.51 (s, 9H, ^{t}Bu), 1.73 (AB spin system, 2H, J_{AB} = 14.65 Hz, −CH$_2$−), 1.96 (s, 15H, Cp*), 2.14 (s, 3H, C$_6$H$_3$^{t}Bu$_2$), 2.55 (s, 3H, MeC=N), 6.79 (pt, 1H, J = 7.81 Hz, J = 7.33 Hz, H4), 7.04 (d, 1H, J = 7.33 Hz, H3 or H5), 7.21 (d, 1H, J = 7.81 Hz, H3 and H5). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 11.36 (Cp*), 19.29 (C$_6$H$_3$^{t}Bu$_2$), 22.04 (MeC=N), 27.91 (ZrMe), 30.51, 30.81 (N−C(*C*H$_3$)$_2$−), 31.61 (C(*C*H$_3$)$_3$), 31.90 (−CH$_2$C(*C*H$_3$)$_2$), 32.06 (−CH$_2$*C*(CH$_3$)$_3$), 35.02 (*C*(CH$_3$)$_3$), 53.74 (−CH$_2$−), 67.80 (N-*C*(CH$_3$)$_2$−), 117.46 (Cp*), 118.99, 124.78 (C3 and C5), 127.17 (C4), 128.63, 136.93 (C2 and C6), 160.54 (C1), 239.62 (C=N). Anal. Calcd for C$_{32}$H$_{50}$NOZr: C, 68.76; H, 9.56; N, 2.51. Found: C, 68.36; H, 9.73; N, 2.38.

Single-Crystal X-ray Diffraction Experimental Data. Details of the crystal data and a summary of data collection parameters for compound **7** are given in Table 4. Data were collected on a Philips PW 1100 diffractometer using graphite-monochromated Mo Kα radiation. A set of 24 carefully centered reflections in the range 7.0° < θ < 12.4° was used for determining the lattice constants. No decay was observed during the data collection. The data were corrected for Lorentz and polarization effects. The structure was solved by direct

Table 4. Crystal Data and Structure Refinement for 7

empirical formula	$C_{34}H_{42}O_3Zr$
fw	589.90
temperature	293(2) K
wavelength	0.71073 Å
cryst syst, space group	monoclinic, $P2_1/n$
unit cell dimens	$a = 15.935(5)$ Å $b = 22.262(8)$ Å $c = 8.645(3)$ Å $\beta = 91.44(2)°$
volume	3066(2) $Å^3$
Z, calcd density	4, 1.278 Mg/m^3
abs coeff	0.389 mm^{-1}
$F(000)$	1240
cryst size	0.18 × 0.25 × 0.28 mm
θ range for data collection	3.03−24.00°
index ranges	$-18 \leq h \leq 18$, $0 \leq k \leq 25$, $0 \leq l \leq 9$
no. of reflns collected/unique	5134/4791 [R(int) = 0.0943]
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	4791/0/354
goodness-of-fit on F^{2a}	0.705
final R indices [$I > 2\sigma(I)$]	R1 = 0.0392, wR2 = 0.0427
R indices (all data)	R1 = 0.2111, wR2 = 0.0731
largest diff peak and hole	0.313 and −0.399 $e·Å^{-3}$

[a] $GOOF = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

methods (SIR-92)[13] and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 using the SHELXL-97 program.[14] All the hydrogen atoms were geometrically fixed using the riding model. All calculations were carried out on the Digital AlphaStation 255 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma. The programs PARST[15] and ORTEP[16] were also used.

Polymerization Test. Reactions were carried out under a controlled atmosphere. High-purity ethylene (Air Liquide) was purified over 3A and 13A molecular sieves. Methylalumoxane was used without further purification as received from Witco GmbH. Ethylene polymerizations were carried out in a 1 L glass autoclave reactor. Toluene was used as solvent, and the reaction time, monomer pressure, and the amount of catalyst introduced were chosen carefully in order to avoid mass transfer limitations. In a typical procedure, ethylene was first introduced into the reactor at the polymerization temperature until saturation of toluene was achieved. The prescribed amount of zirconium complex precatalyst and MAO were first mixed and allowed to react during 15 min. The mixture was then introduced into the reaction vessel, in a nitrogen stream, and the polymerization was started. Ethylene pressure and temperature were recorded at different polymerization times. The polymerization rate was calculated by measuring the pressure drop. The use of an ethylene reservoir (14 L volume) ensured a final ethylene pressure drop of less than 5% in order to maintain a constant monomer concentration.

The tests were performed twice, and the results were in well agreement, with differences less than 5%. The average values were showed in Table 3.

Acknowledgment. A.A.G., F.C.H., A.C., J.F.B., and A.O. gratefully acknowledge financial support from the Acciones Integradas Hispano-Portuguesas, Spain (HP 97-0036) and the Dirección General de Enseñanza Superior e Investigación Científica, Spain (Grant No. PB95-0023-C01-02). M.R.R., J.V.S., and M.F.P. gratefully acknowledge financial support from the Conselho de Reitores Universidades Portuguesas (Acções Integradas Luso-Espanholas LE-25/98), Fundação para a Ciencia e Tecnologia (Project Praxis PCEX/C/QUI/75/96), and the sub-Programa Ciência e Tecnologia do 2° Quadro Comunitário de Apoio for Grant BD13551/97. M.L. and M.A.P. gratefully acknowledge financial support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and Consiglio Nazionale delle Ricerche (CNR, Rome, Italy).

Supporting Information Available: Crystal structure data for **7**, including tables of atomic positional parameters, anisotropic thermal parameters, full listing of bond distances and angles, and hydrogen atomic coordinates. The material is available free of charge via the Internet at http://www.pubs.acs.org.

OM000209L

---

(13) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Gualiardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(14) Sheldrick, G. M., *SHELXL-97*, Program for the refinement of crystal structures; University of Göttingen, 1997.

(15) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

(16) Zolnai, L.; Pritzkow, H. *ZORTEP*. ORTEP original program modified for PC, University of Heidelberg, 1994.