Bis[(amidomethyl)pyridine] Zirconium(IV) Complexes: Synthesis, Characterization, and Activity as Olefin Polymerization Catalysts†

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This contribution describes the synthesis, characterization, and olefin polymerization reactivity of bis(chelate)zirconium complexes bearing (amidomethyl)pyridine ligands [(6-X-C_5H_3N)$CH_2NC_6F_5$, X = CH_3 (Lig^1H), Br (Lig^2H), H (Lig^3H)]. Metathesis reaction, alkane elimination, and amine elimination provided routes to compounds $(Lig^1)_2ZrCl_2$ (**1**), $(Lig^1)_2ZrBz_2$ (**4**; Bz = $CH_2C_6H_5$), and $(Lig^2)_2Zr(NMe_2)_2$ (**5**). Attempts to prepare $(Lig^1)_2Zr(NMe_2)_2$ in a reaction between $Zr(NMe_2)_4$ and Lig^1H led instead to compound $(Lig^1)(Lig^1*)ZrF(NMe_2)$ (**2**), in which one dimethylamino group had been exchanged with one ortho fluoride on the perfluorophenyl ring of the ligand via an aromatic nucleophilic substitution reaction. Halide displacement reaction performed on compound **2** afforded the dichloride compound $(Lig^1)(Lig^1*)ZrCl_2$ (**3**). Reaction between $Zr(NMe_2)_4$ and Lig^3H provided a mixture of $(Lig^3)_2Zr(NMe_2)_2$ and $(Lig^3)(Lig^3*)ZrF(NMe_2)$, the latter being analogous to **2**. X-ray crystallographic analysis showed for compound **1** a distorted octahedral geometry with C_1 symmetry and for compound **2** a 7-coordinate species. Variable-temperature NMR studies established for compound **1** an inversion of metal configuration through dynamic interchange of the all-cis enantiomers. Fluxional behaviors in solution were also observed for compounds **2**, **3**, and **4**. Treatment of complexes with Al^iBu_2H and methylalumoxane (MAO) yields active, multisite ethylene and propylene polymerization catalysts.

Introduction

The search for noncyclopentadienyl ancillary ligands for homogeneous olefin polymerization catalysts has significantly grown in the past decade, and a new generation of polymerization catalyst precursors with excellent performance, with respect to activity, selectivity, living behavior, and stability has been developed.[1] The family of octahedral bis(chelate) group 4 metal complexes based on monoanionic ligands emerged as an important and versatile class of olefin polymerization catalysts, after the remarkable results obtained with phenoxy-imine ligands.[2−5]

The rapid expansion of this area, stimulated by the promising catalytic activity of the complexes, resulted also in considerable contributions to coordination chemistry. Nitrogen-based polydentate ligands (for instance, amidinates,[6] pyrrolide-imine,[7] 2,6-bis(*N*-aryliminomethyl)pyridine,[8] α-diimine[9]) have attracted particular interest for their advantageous feasibility and flexibility in design to introduce sterically and electronically demanding features. Recently a new family of high-performance pyridylamidohafnium(IV) complexes was discovered by Dow and Symyx, adopting a high-throughput parallel screening approach. A most notable feature of these catalysts is the ortho-metalation of the aryl substituent on the pyridine ring, resulting in tridentate ligation of the pyridyl-amido moiety and a slightly distorted trigonal bipyramidal Hf coordination.[10−12]

In this regard, the simple aminopyridinato ligand derived from deprotonated 2-aminopyridines was also largely studied (model I in Chart 1). As a consequence of the relatively simple and

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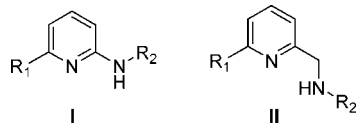
Chart 1

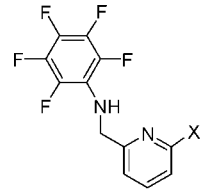


I II

high-yield synthesis, combined with easy modification of steric and electronic properties of the precursor aminopyridines, these compounds have led to a wide variety of mono-, bis-, tris-, and tetrakisaminopyridinato derivatives.[13,14] For the synthesis of bis(amidopyridine) zirconium complexes, the control of the ligand number about each metal center to two, avoiding formation of complexes bearing one or three ligands, is challenging. To address this problem, Scott emphasized the importance of the choice of the amido *N*-substituents and described bis(*N*-adamantyl-2-aminopyridinato) zirconium dichloride as a moderately active catalyst for ethylene polymerization.[15] Following this result, highly active bis(chelate) zirconium complexes stabilized by bulky aminopyridinato ligands were reported.[14d]

In this context, we pursued an alternative approach to the synthesis of bis(aminopyridinato) zirconium complexes featuring an increased size of the chelating ring by the introduction of one more carbon atoms. Herein we report the synthesis of new pentafluoro-*N*-((pyridin-2-yl)methyl)aniline ligands (model II in Chart 1), the synthesis of bis(chelate) zirconium complexes obtained thereof, and preliminary results on their olefin polymerization catalysis.[16]

Chart 2



(Lig^1H) X= CH_3
(Lig^2H) X= Br
(Lig^3H) X= H

Results and Discussion

Synthesis and Characterization of the Complexes. The ligands [(6-X-C_5H_3N)$CH_2NC_6F_5$, X = CH_3 (**Lig^1H**), Br (**Lig^2H**), H (**Lig^3H**)] were prepared by condensation reactions between the pentafluoroaniline and the appropriate pyridinecarboxaldehyde, followed by reduction of the imine functionality by $NaBH_3CN$ (Chart 2). The preparation of bis-chelate zirconium complexes was achieved by different synthetic approaches, producing in some cases unexpected ligand structure rearrangements. The obtained zirconium complexes were characterized by NMR spectroscopy, elemental analysis, and, in some cases, also single-crystal X-ray diffraction analysis.

The dichloro bis(Lig^1) zirconium(IV) compound (**1**) was prepared via metathesis reaction of the lithium salt of Lig^1 and zirconium tetrachloride in tetrahydrofurane solvent (Scheme 1). Reaction proceeded cleanly with good yield (89%), producing **1** as a pale yellow solid, which was characterized by X-ray diffraction analysis. Suitable crystals were grown from dichloromethane/hexane at room temperature. Selected bond lengths and angles for compound **1** are listed in Table 1.

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Scheme 1

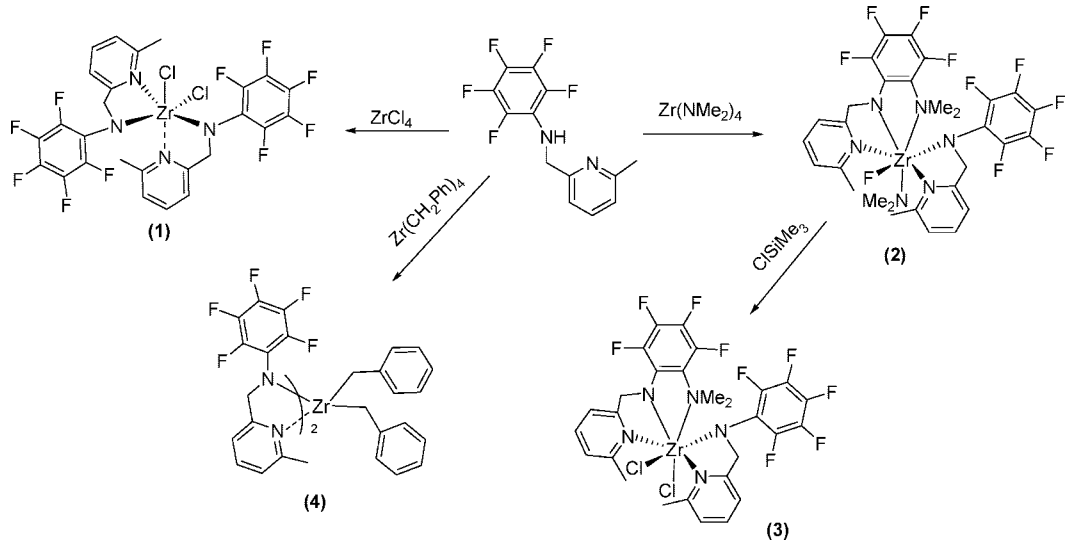


Table 1. Selected Bond Lengths (Ångstroms) and Angles (Degrees) for Compounds 1 and 2

compound **1**	compound **2**
Cl1−Zr 2.433(2)	Zr−F1 1.972(3)
Cl2−Zr 2.440(2)	Zr−N1 2.449(4)
Zr−N1 2.096(6)	Zr−N2 2.205(4)
Zr−N3 2.114(6)	Zr−N3 2.177(4)
Zr−N4 2.375(6)	Zr−N4 2.605(4)
Zr−N2 2.460(6)	Zr−N5 2.085(4)
	Zr−N6 2.629(4)
N1−Zr−N3 102.5(3)	F1−Zr−N5 112.95(15)
N1−Zr−N4 83.5(2)	F1−Zr−N3 123.05(14)
N3−Zr−N4 72.5(2)	N5−Zr−N3 103.93(17)
N1−Zr−Cl1 107.46(19)	F1−Zr−N2 126.37(14)
N3−Zr−Cl1 86.31(19)	N5−Zr−N2 101.48(15)
N4−Zr−Cl1 157.99(16)	N3−Zr−N2 83.76(15)
N1−Zr−Cl2 141.44(19)	F1−Zr−N1 74.36(12)
N3−Zr−Cl2 105.3(2)	N5−Zr−N1 83.75(15)
N4−Zr−Cl2 80.07(17)	N3−Zr−N1 153.55(14)
Cl1−Zr−Cl2 100.44(8)	N2−Zr−N1 69.85(14)
N1−Zr−N2 70.4(2)	F1−Zr−N4 78.96(13)
N3−Zr−N2 166.3(3)	N5−Zr−N4 79.61(15)
N4−Zr−N2 117.1(2)	N3−Zr−N4 66.55(14)
Cl1−Zr−N2 84.85(15)	N2−Zr−N4 149.36(14)
Cl2−Zr−N2 86.55(16)	N1−Zr−N4 139.82(13)
	F1−Zr−N6 71.73(12)
	N5−Zr−N6 171.26(15)
	N3−Zr−N6 67.63(14)
	N2−Zr−N6 80.33(13)
	N1−Zr−N6 104.83(13)
	N4−Zr−N6 94.46(13)

Compound **1** displayed a distorted octahedral geometry with two chlorine atoms located in cis position (Cl1−Zr−Cl2 100.44(8)°), and both the *N*-pyridine (N2−Zr−N4 117.1(2)°) and the *N*-aniline atoms (N1−Zr−N3 102.5(3)°) in a cis relationship to each other (Figure 1). The distances between the Zr atom and the N aniline atoms are, respectively, Zr−N1 2.096(6) Å and Zr−N3 2.114(6) Å, whereas the distances between the Zr atom and the N pyridine atoms are, respectively, Zr−N2 2.460(6) Å and Zr−N4 2.375(6) Å. Zr−N distance values reflect those observed in the analogous zirconium (amidomethyl)pyridine monochelate complexes.[16]

Of the five possible octahedral structures for $(Lig^1)_2ZrCl_2$ complexes, compound **1** reflects the coordination geometry depicted by model C in Chart 3 for the related dimethylamido complex. This C_1 symmetry with all-cis configuration differs from the geometry usually observed for octahedral bis(phenoxyimine) zirconium complexes, where the two chelating ligands are related by a crystallographic C_2 symmetry, the trans positions are occupied by the O atoms, and the cis positions are occupied by N atoms (both at 2.355(2) Å from the Zr atom).[2e] For compound **1**, on the contrary, a C_2 coordination geometry would imply steric repulsion between the two ortho methyl groups. Moreover, a closer inspection of the structure showed that the five-atom rings Zr−N1−N2−C7−C8 and Zr−N3−N4−C19−C20 are planar within rmsd values of 0.079 and 0.038 Å, respectively, with an angle between planes of 64.6(2)°; in this way the two aforementioned rings result in the two planes being almost perpendicular to each other. Both pyridine moieties lie in the previously defined 5-atom ring planes, whereas the fluorinated aromatic rings are tilted with respect to the coordination planes with angles of 67.5(3)° and 79.5(2)°, respectively.

With the aim of exploring the feasibility of a largely pursued synthetic route for the preparation of zirconium bisamide derivatives, two equivalents of Lig^1H were allowed to react with tetrakis(dimethylamido) zirconium(IV) in dry hexane, giving the new compound **2** as a light yellow solid. Elemental analysis of **2** was in good agreement with the expected $(Lig^1)_2Zr(NMe_2)_2$ formulation. The ^1H NMR spectrum at room temperature showed broad signals, an indication of a fluxional equilibrium

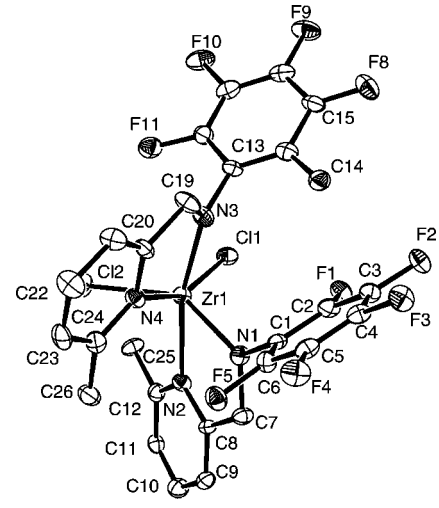
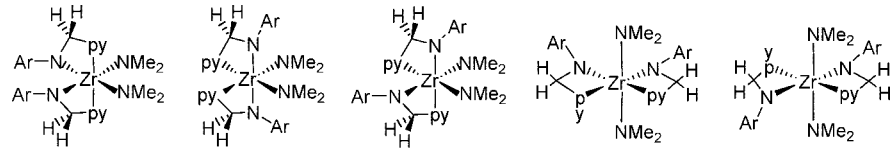


Figure 1. ORTEP drawing for compound **1**. Ellipsoids are drawn at 30% probability level.

Chart 3



A, C_2 **B**, C_2 **C**, C_1 **D**, C_2v **E**, C_2h

Ar = C_6F_5

in solution and, at lower temperature, the presence of two sets of signals in a 1:1 ratio, attributable to the ligand hydrogen atoms (see below). More information came from the ^{19}F NMR spectrum at room temperature: seven broad signals were observed in the region from −180 to −145 ppm, accounting for nine aryl fluorine atoms, and one singlet at +52.21 ppm accounting for one fluorine atom. The last signal was attributed to a fluorine atom directly bonded to zirconium, on the basis of the literature data,[17] suggesting a possible structural modification of the ligands. Hydrolysis of compound **2** followed by NMR analysis of the organic fraction of the hydrolyzed product resulted in identification of a pristine pyridyl-amino ligand Lig^1H in a 1:1 ratio with a modified form of the ligand (Lig^1*H) (see the Supporting Information). The structure of compound **2** was definitively elucidated by single-crystal X-ray diffraction analysis (Figure 2), disclosing a 7-coordinate zirconium bearing the modified ligand (Lig^1*), in which one fluorine atom of the aryl group was replaced by a dimethylamino group, the pristine Lig^1 ligand, one fluorine atom, and one NMe_2 group. The substitution of an ortho aryl fluoride of the ligand by a dimethylamino group bound to a metal center has precedent in the literature and can be justified by aromatic nucleophilic substitution reaction (SN_{Ar}) occurring during the formation of complexes (Scheme 1).[18] Deck et al. described the partial defluorination of pentafluorophenyl-substituted cyclopentadienyl or indenyl ligands by titanium amide.[19] Schrock et al. reported a structurally characterized 7-coordinate pyridyldiamine hafnium complex in which two aromatic fluorines were substituted with two dimethylamino groups,[20a] and documented also this type of exchange in a molybdenum system.[20b] Cyclopentadienyl-iminophosphinamide zirconium(IV) complexes in which two fluorine atoms of the *N*-aryl group were replaced by dimethylamino groups have been also reported by Scott.[20c] Among main group elements, Bochmann reported a structurally characterized zwitterionic aminoborane formed via nucleophilic substitution attack on an ortho F.[20d]

Selected bond lengths and angles for compound **2** are listed in Table 1. The geometry of **2** can be roughly described as a distorted octahedron with an extra atom at the center of a face. More in detail, the Lig^1 ligand displays the pyridine nitrogen atom at 2.205(4) Å and the aniline nitrogen atom at 2.449(4) Å, the Lig^1* behaves as a tridentate ligand with two nitrogen atoms (N4 and N6), providing a dative bond at 2.605(4) Å and 2.629(4) Å and a sigma-bonded N3 atom at 2.177(4) Å. The fluorine atom is at a distance of 1.972(3) Å. These values agree with those observed for analogous 7-coordinate Hf and Mo compounds; notably the two dative bonds show considerably longer distances with respect to the literature compounds ($Hf-N_{donor}$ distances are 2.355(14) Å and 2.459(11) Å; $Mo-N_{donor}$ distances are 2.330(5), 2.482(5), and 2.440(5) Å).[18] In addition, the N3 atom deviates considerably from the plane defined by the Zr atom and the pyridine moiety (rmsd = 0.048 Å), being displaced by −0.680(6) Å. The plane formed by the fluorinated aromatic ring and N3 and N6 atoms (rmsd = 0.018 Å) forms an angle of 62.5(1)° with the previously defined plane. As for the other ligand, the N1 and N2 nitrogen atoms deviate from the 5-atom plane Zr−N1−N2−C7−C8 (rmsd = 0.096 Å) by, respectively, 0.11 and 0.13 Å. The fluorinated aromatic rings are tilted with respect to this plane by 52.28(15)°.

The reaction of compound **2** with an excess of Me_3SiCl afforded in good yield compound **3** where both the Zr−F and $Zr-NMe_2$ groups were replaced by chlorides (Scheme 1). The absence in the ^{19}F NMR spectrum of the signal relative to the Zr−F bond indicated that the reaction was complete.

With the aim of preparing a bis(Lig^1)zirconium dialkyl derivative, the reaction of tetrabenzylzirconium with 2 equiv of Lig^1H in benzene was performed. The zirconium dibenzyl compound (**4**) was obtained straightforwardly (Scheme 1). The product was stable as a solid but easily underwent degradation reaction in solution with formation of the "free" ligand.

The sterically and electronically different (amidomethyl)pyridine ligands Lig^2H and Lig^3H were also used for the synthesis of bis(chelate) zirconium(IV) complexes. The reaction of 2 equiv of *N*-[(6-bromopyridin-2-yl)methyl]-2,3,4,5,6-pentafluoroaniline (Lig^2H) with tetrakis(dimethylamido) zirconium(IV) resulted in the formation of the octahedral $(Lig^2)_2Zr(NMe_2)_2$ compound **5** (Scheme 2). This species showed at room temperature a ^1H NMR spectrum with very sharp signals and a pattern compatible with the presence of a symmetric structure in solution. Hydrolysis experiments were also performed and resulted in the isolation of the intact amino-pyridine ligand (Lig^2H). The SN_{Ar} reaction, observed for compound **2** (see above), did not occur in this case. A previous paper highlighted that the SN_{Ar} reaction preferentially occurs on CF bonds positioned in close proximity to the inner coordination sphere of early transition metal amides, suggesting an intermediate species in which both the fluorine atom and the dimethylamino group are coordinated to the metal.[19] In the case of compound **5** the presence of a bromine atom in the ortho position of the pyridine ring may play a competitive role, electronically stabilizing the observed structure.

The reaction of 2 equiv of the simplest ligand Lig^3H and tetrakis(dimethylamido) zirconium(IV) was also attempted. NMR analysis of the obtained solid displayed at room temperature broad signals. A detailed NMR investigation, based on ^1H, ^{13}C, and ^{19}F NMR analysis, also performed at lower temperatures (see the Supporting Information), disclosed that the solid was a mixture of two bis(chelate) zirconium com-

(17) (a) O'Connor, P. E.; Berg, D. J.; Barclay, T. *Organometallics* **2002**, *21*, 3947–3954. (b) Jager-Fiedler, U.; Arndt, P.; Baumann, W.; Spannenberg, A.; Burlakov, V.; Rosenthal, U. *Eur. J. Inorg. Chem.* **2005**, 2842–2849. (c) Il'in, E. G.; Kovalev, V. V.; Aleksandrov, G. G.; Grenthe, I. *Dokl. Chem.* **2005**, *401*, 42–46 (part 1).

(18) Monitoring the reaction between two equivalents of Lig1H and tetrakis(dimethylamido) zirconium(IV) by variable-delay ^{19}F NMR experiments in C_6D_6 minor signals were observed around−50 ppm, in the characteristic region for bridging fluoride of the type Zr-F-Zr. Cfr.:(a) O'Connor, P. E.; Berg, D. J.; Barclay, T. *Organometallics* **2002**, *21*, 3947–3954, and references therein.

(19) Deck, P. A.; Konatè, M. M.; Kelly, B. V.; Slebodnick, C. *Organometallics* **2004**, *23*, 1089–1097.

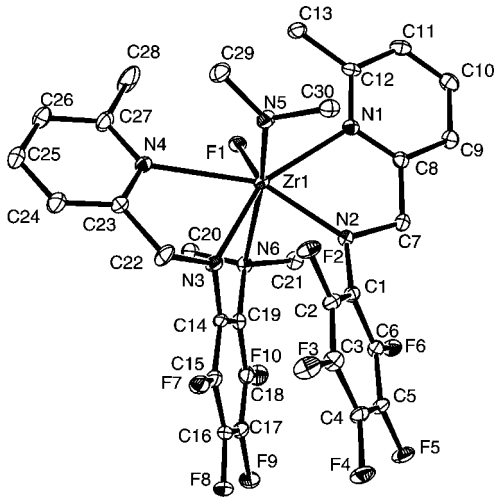
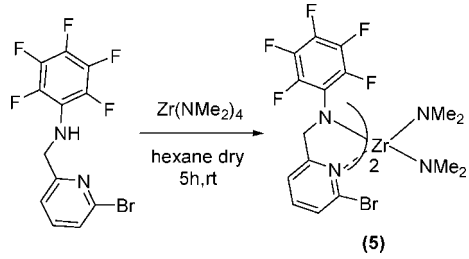


Figure 2. ORTEP drawing for compound **2**. Ellipsoids are drawn at 30% probability level.

Scheme 2



pounds in about a 1: 1 ratio (Scheme 3). The first compound was the octahedral bis(dimethylamido) zirconium(IV) compound bearing two intact Lig[3] ligands; the second was a 7-coordinate

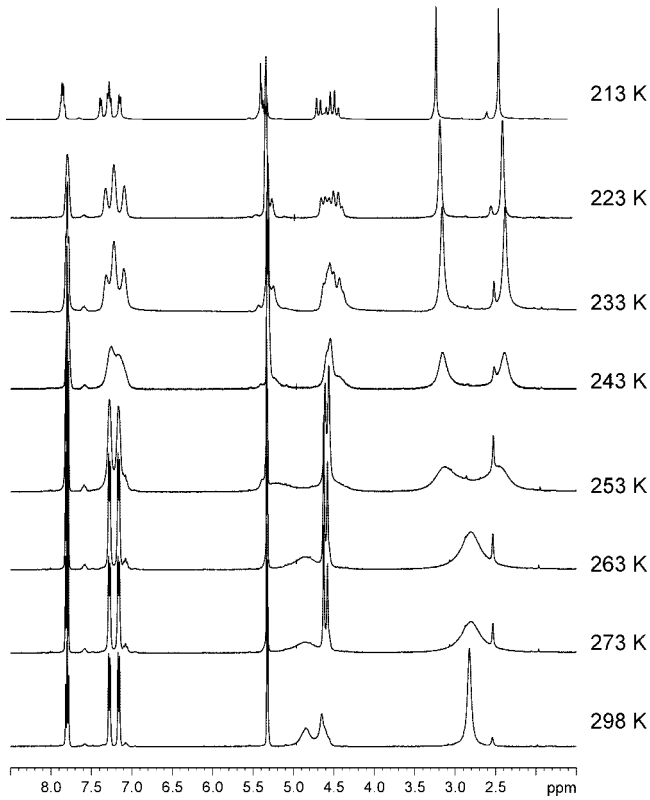


Figure 3. ^{1}H NMR spectra of compound **1** at various temperatures (CD_2Cl_2).

zirconium compound, of formula (Lig[3]*)(Lig[3])ZrF(NMe_2) analogous to compound **2**, bearing one intact Lig[3] ligand and one modified ligand (Lig[3]*) by the substitution of an ortho aryl fluoride with a dimethylamino group. To support this hypothesis, the ^{19}F NMR spectrum displayed two signal sets in about a 3:1 ratio; the main set was constituted by five signals attributable to the intact C_6F_5 ring of Lig[3], and the minor set was constituted by four signals in the region of perfluorinated aryl group and one singlet at +42.17 ppm, attributable to the fluorine atom directly bound to zirconium. In nice agreement with this result, the ^{1}H NMR analysis of the organic fraction of the hydrolyzed product displayed the presence of the pristine pyridyl-amino ligand (Lig[3]H) in a 3:1 ratio with a modified pyridyl-amino ligand (Lig[3]*H), where one fluorine atom of the aryl group was replaced by a dimethylamino group. The exchange reaction of one ortho fluoride on the pentafluorophenyl ring of the ligand with a dimethylamino group can be also operating in this system through SN_{Ar}. Although several attempts of crystallization were performed, we were unable to separate the two species.

Solution Structure of the Complexes. The configurations of compounds **1**−**5** in solution were determined by variable-temperature NMR spectroscopy.

The ^{1}H NMR spectrum of **1** at room temperature in CD_2Cl_2 displayed very broad signals, suggesting a fluxional equilibrium in solution. To verify if the C_1 symmetry species observed in the solid state was preserved in solution, variable-temperature ^{1}H NMR experiments were performed (Figure 3). As matter of fact, at lower temperatures the broad signals split up: at 213 K two sets of signals in a 1:1 ratio for the inequivalent hydrogen atoms of the ligands were observed (i.e., two singlets at 2.3 and 3.1 ppm for the methyl on the pyridine moiety, two AB patterns for methylenic hydrogen atoms at 4.3 and 4.6 ppm, and two sets of signals in the aromatic region). A dynamic interchange of the all-cis enantiomers could be occurring, probably through a mechanism involving dissociation of a pyridine nitrogen. The free energy of activation associated with this process was calculated to be 11.91 kcal mol^{-1}.[21] The *N*-pyridinic bond cleavage and the formation of a configurationally labile 5-coordinate intermediate were previously proposed by Serpone for bis(8-quinolato) titanium alkoxide complexes[22] and by Jordan for analogous bis(8-quinolato) alkyl group 4 metal complexes.[23]

A fluxional behavior in solution was also observed for compound **2** by variable-temperature ^{1}H NMR analysis (Figure 4). The aromatic region of the ^{1}H NMR spectrum recorded at room temperature was per se indicative, presenting one set of well-defined sharp signals at 7.04 (d), 7.09 (d), and 7.57 (t) ppm, attributed to the pyridine hydrogen atoms of an apparently more strongly coordinated ligand, and a second set of broad

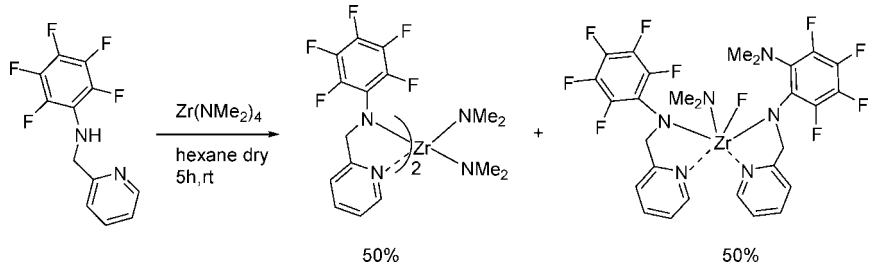
(20) (a) Schrock, R. R.; Adamchuck, J.; Ruhland, K.; Lopez, L. P. H. *Organometallics* **2003**, *22*, 5079–5091. (b) Cochran, F. V., Jr.; Schrock, R. R. *Organometallics* **2000**, *19*, 2414–2416. (c) Vollmerhaus, R.; Tomaszewski, R.; Shao, P.; Taylor, N. J.; Wiacek, K. J.; Lewis, S. P.; Al-Humydi, A.; Collins, S. *Organometallics* **2005**, *24*, 494–507. (d) Hannant, M. H.; Wright, J. A.; Lancaster, S. J.; Hughes, D. L.; Horton, P. N.; Bochmann, M. *Dalton Trans.* **2006**, 2415–2426.

(21) The free energy of activation has been calculated using the Eyring equation, $\Delta G_c^{\ddagger} = 4576T_c[10319 + \log T_c/K_c]$, where T_c is the coalescence temperature and K_c is the exchange rate constant at coalescence, which is given by $K_c = \pi\Delta\nu/\sqrt{2}$. $\Delta G^{\ddagger}$ was determined from the coalescence of methyl proton on the pyridine ring in the ^{1}H NMR spectra (T_c = 263 K). See: (a) Gunther, H. *NMR Spectroscopy*, 2nd ed.; Wiley: New York, 1995; pp 241245. (b) Grutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

(22) Bickley, D. G.; Serpone, N. *Inorg. Chem.* **1979**, *18*, 2200.

(23) Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282–3302.

Scheme 3



signals at 7.15, 7.19, and 7.70 ppm attributable to a fluxional second ligand. Lowering the temperature sharpened the second set of broad signals, too, indicating a locked coordination of both ligands to the zirconium. The $\Delta G^{\ddagger}$ associated with this process was 13.10 kcal mol^{-1}.[21,24] Perusal of the Zr−N bond distances in the solid state (cfr. Table 1) disclosed that the Zr−N pyridinic bond was significantly longer for the tridentate ligand Lig[1]* than for the bidentate ligand Lig[1] (cfr. Zr−N4 2.605(4) Å against Zr−N1 2.449(4) Å). Reasonably, the fluxional equilibrium observed could involve the dissociation of the Zr−pyridinic nitrogen bond of the weaker coordinated ligand Lig[1]*. A similar fluxional behavior in solution was also observed for compound **3**.

The dibenzyl compound **4** showed in the ^{1}H NMR spectrum at room temperature very broad signals. In this case variable-temperature ^{1}H NMR experiments evidenced the presence of at least two isomeric species in fluxional equilibrium. The ^{1}H NMR spectrum registered at 233 K evidenced a signal pattern compatible with the presence of one C_1 symmetric main species plus other minor isomeric species.

The ^{1}H NMR spectrum at room temperature of compound **5** showed very sharp signals and a pattern compatible with the presence of a highly symmetric structure in solution. Variable-temperature (from 193 to 353 K) NMR studies did not show significant change in the spectra. As pointed out above, for octahedral bis(chelate)Zr(NMe$_2$)$_2$ complexes five isomers are possible (Chart 3). The NMR spectroscopic data are compatible with the higher symmetries associated with two of them (D or E), having the NMe$_2$ groups in trans. Alternatively, these data could be compatible with the presence of the C_2 symmetry isomers (A or B), in the Λ−Δ fast exchange regime within the range of the explored temperatures. It is worth noting that the analogous bis(chelate) zirconium dichloride complex **1** bearing the pentafluoro-*N*-((6-methylpyridin-2-yl)methyl)anilinato ligand displayed a C_1 symmetry with all-cis configuration.

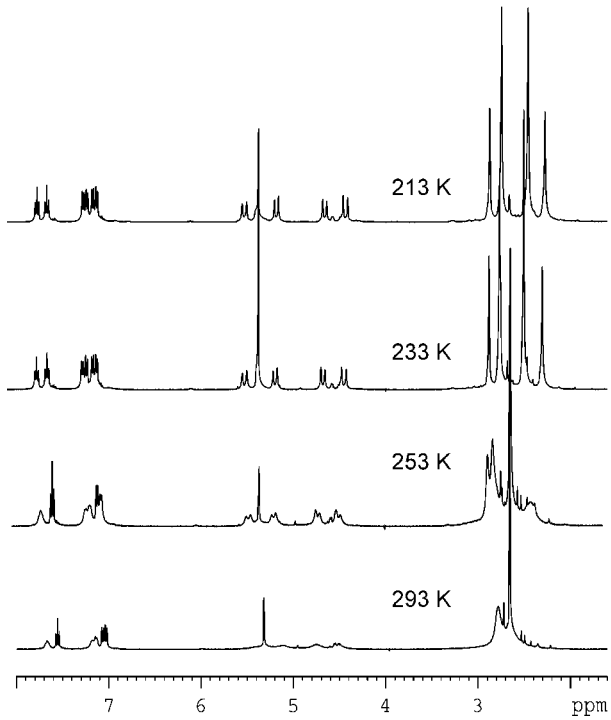


Figure 4. ^{1}H NMR spectra of compound **2** at various temperatures (CD_2Cl_2).

The coordination chemistry of this family of ligand seems to be variable and poorly predictable, because slight differences in their steric and electronic features dramatically influence the coordination environment at the central Zr atom.

Olefin Polymerization Studies. Complexes **1**−**5** were tested as catalysts for the polymerization of ethylene and higher olefins using different cocatalysts and under variable conditions. Polymers were characterized by ^{1}H and ^{13}C NMR, DSC, and GPC analyses.

Compounds **1**−**5** were able to promote polymerization of ethylene under 6 atm of monomer pressure, by using MAO or Al^{i}Bu$_2$H/MAO as cocatalysts. Activities, melting temperatures of the polymers, and molecular weight data are collected in Table 2. In all cases linear polyethylenes were produced (T_m = 132−136 °C), with moderate activities. As a general trend, the Al^{i}Bu$_2$H/MAO cocatalyst system was a more efficient activator than MAO alone. This effect was particularly evident in the case of the less reactive dimethylamido zirconium derivatives **2** and **5**, which reasonably require the presence of Al^{i}Bu$_2$H to generate the Zr−H or Zr−alkyl bonds where the polyinsertion may start, as previously observed for other dimethylamido zirconium catalysts.[25] On the contrary, for the zirconium dichloride compound **3**, comparable polymerization activities were obtained with both activation systems (cfr. runs 10 and 11 in Table 2).

A variety of cocatalyst combinations, including the ionizing agents commonly used for homogeneous polymerization catalysts, were also tested for compound **2**. Use of Al^{i}Bu$_2$H in combination with either [CPh$_3$][B(C$_6$F$_5$)$_4$] or [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] or B(C$_6$F$_5$)$_3$ resulted in comparable polymerization activities. Al^{i}Bu$_3$ in combination with MAO gave similar results, whereas Al^{i}Bu$_2$H/MAO at 50 °C gave significantly higher polymerization activity (cfr. runs 6 and 8 in Table 2). A screening of the effect of the temperature in the presence of the latter activator system showed that when the temperature increased from 25 to 50 °C, the catalytic activity became 15-fold higher; a further rise to 75 °C was instead deleterious, suggesting a partial catalyst deactivation.

(24) $\Delta G^{\ddagger}$ for compound **2** was determined from the coalescence of the methyl proton on the pyridine ring in the ^{1}H NMR spectra (T_c = 283 K).

(25) (a) Kim, I.; Nishihara, Y.; Jordan, R. F.; Rogers, R. D.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1997**, *16*, 3314–3323. (b) Kim, I.; Choi, C. S. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 1523–1539.

Table 2. Ethylene Polymerization Results for Complexes 1−5

run[a]	precatalyst	cocatalyst	T (°C)	activity[b]	T_m (°C)	M_w (× 10^3)	M_w/M_n
1	**1**	MAO	25	6.8	135.3	nd[c]	nd
2	**1**	MAO	50	34.3	136.0	208.6	60.8
3	**1**	Al^{i}Bu$_2$H/MAO	50	22.6	135.8	2485.8	128.9
4	**2**	MAO	50	0.3	133.6	1065.3	22.8
5	**2**	Al^{i}Bu$_2$H/MAO	25	5.8	133.0	244.7	70.1
6	**2**	Al^{i}Bu$_2$H/MAO	50	83.2	134.3	549.6	69.7
7	**2**	Al^{i}Bu$_2$H/MAO	75	32.9	133.0	345.3	110.3
8[d]	**2**	Al^{i}Bu$_2$H/[CPh$_3$][B(C$_6$F$_5$)$_4$]	50	5.5	134.8	360.0	60.0
9	**3**	MAO	25	3.7	133.9	189.9	62.0
10	**3**	MAO	50	65.5	132.6	1444.6	14.6
11	**3**	Al^{i}Bu$_2$H/MAO	50	72.7	133.9	nd	nd
12	**4**	Al^{i}Bu$_2$H/MAO	50	18.6	134.9	172.4	78.2
13	**4**	MAO	50	3.8	134.8	288.0	70.7
14	**5**	Al^{i}Bu$_2$H/MAO	50	20.0	133.5	267.6	53.3

[a] Conditions: precatalyst = 20 μmol; Al^{i}Bu$_2$H/Zr = 30; Al$_{(MAO)}$/Zr =1000; ethylene pressure = 6 atm; toluene = 90 mL; time = 60 min. MAO dried obtained by distilling off the solvent from the commercial solution. [b] Activity = kg of polymer × (mol of Zr × h × atm)$^{-1}$. [c] nd = not determined. [d] Compound **2** = 40 μmol; time = 90 min.

Table 3. Propylene Polymerization Results

run[a]	complex	cocatalyst	T (°C)	time (h)	activity[b]	[*mm*] %	[*mr*] %	[*rr*] %	M_w (× 10^3)	M_w/M_n
1	**1**	Al^{i}Bu$_2$H/MAO	0	5	436	38	33	29	1623.9	318
2	**1**	Al^{i}Bu$_2$H/MAO	50	1	1016	34	38	28	394.1	106.1
3	**1**	MAO	50	1	1666	41	30	29	1639.1	58.4
4	**2**	Al^{i}Bu$_2$H/MAO	0	4	520	18	45	36	62.0	17.2
5	**2**	Al^{i}Bu$_2$H/MAO	50	1	2083	24	47	29	107.25	24.7
6	**5**	Al^{i}Bu$_2$H/MAO	50	1	333	56	25	19	301.50	84.2

[a] Conditions: precatalyst = 20 μmol; Al^{i}Bu$_2$H/Zr = 30; Al$_{(MAO)}$/ Zr =1000; propylene pressure = 6 atm; toluene = 90 mL; time = 60 min. MAO dried obtained by distilling off the solvent from the commercial solution. [b] Activity = g of polymer × (mol of Zr × h × atm)$^{-1}$.

Analysis of the polymer samples by GPC revealed in any case high molecular weights with bi- or trimodal molecular weight distributions, an indication of a non-single-center catalyst nature. Although the mechanism causing multimodality is still elusive and care must be taken in extrapolating the solution structures of the precatalysts to the real active species, we propose that the multimodal MWDs of polymers could be connected to the highly fluxional character of the precatalysts. A similar behavior was previously observed for an analogous bis(phenoxy-imine) zirconium complex, which, as a consequence of the unusual C_1 symmetric geometry was highly fluxional in solution and produced bi- and trimodal polyethylenes.[2j] However, it is worth mentioning that ligand redistribution could also occur during the formation of the catalytic species and/or during the polymerization process, giving rise to additional polymerization species that could cause the multimodality of molecular weight distribution as previously observed by Kempe for bis(aminopyridinato) zirconium(IV) complexes[14d] and by Scott for iminophosphonamide zirconium complexes.[26] To avoid the ligand redistribution reaction, following the suggestion of a reviewer, an ethylene polymerization run was performed according to previous literature data[26] by adding the dialkyl catalyst precursor **4**, preactivated with [Ph$_3$C][B(C$_6$F$_5$)$_4$], to a toluene solution containing triisobutylaluminum as a scavenger and saturated with the monomer.[27] GPC analysis disclosed a monomodal, although still broad, molecular weight distribution of the polymer.

Propylene polymerizations were also carried out at a monomer pressure of 6 atm, by using Al^{i}Bu$_2$H/MAO as the activator. In Table 3 are collected the main results of the propylene polymerization runs. Catalyst **1** produced at 50 °C a stereoirregular, slightly isotactic-enriched polypropylene ([*mm*] = 34%). The polymer was prevailingly regioregular, having 3.2% of regioirregularly arranged monomers units, indicated in the ^{13}C NMR spectrum by the methyl resonances of the tail-to-tail units observed between 12.6 and 15.0 ppm.[28] At lower temperature (0 °C), the activity decreased, but a slight increase in the fraction of *mm* triads was observed by ^{13}C NMR, and an ultrahigh molecular weight was disclosed by GPC analysis (cfr. Table 3, run 1).

In the ^{13}C NMR spectrum of the polypropylene sample obtained at 50 °C, the exclusive presence of isobutyl end groups

Table 4. Crystal Data and Structure Refinement Details for Compounds 1 and 2

	compound **1**	compound **2**
formula	$C_{26}H_{16}Cl_2F_{10}N_4ZrCH_2Cl_2$	$C_{30}H_{28}F_{10}N_6Zr$
formula weight	821.47	753.80
crystal system	monoclinic	triclinic
space group	P 2$_1$/*n*	P −1
a (Å)	10.752(3)	9.463(2)
b (Å)	13.018(3)	12.446(3)
c (Å)	22.022(5)	12.821(3)
α (deg)		90.499(6)
β (deg)	90.512(7)	93.571(7)
γ (deg)		96.789(6)
V (Å^3)	3082.3(13)	1496.3(6)
Z	4	2
D_c (g cm^{-3})	1.770	1.673
μ (mm^{-1})	0.791	0.463
F(000)	1624	760
independent reflections measured	6912	5033
param/restraints	417	430
R1 [$F_o > 4\sigma(F_o)$]	0.101	0.070
$_w$R2 (all refl)	0.2922	0.2182
GooF	1.021	1.133
$\Delta\rho_{min}$ (eÅ^{-3})	−0.839	1.512
$\Delta\rho_{max}$ (e Å^{-3})	2.065	1.410

(26) Tomaszewski, R.; Vollmerhaus, R.; Al-Humydi, A.; Wang, Q.; Taylor, N. J.; Scott, C. *Can. J. Chem.* **2006**, *84*, 214.

(27) Polymerization conditions: compound **4** = 20 μmol; [CPh$_3$][B(C$_6$F$_5$)$_4$] = 20 μmol; Al^{i}Bu$_3$H = 600 μmol; ethylene pressure = 1 atm; toluene = 35 mL; temperature = 50 °C; time = 120 min. Activity = 2.5 kg of polymer × (mol of Zr × h × atm)$^{-1}$. T_m = 135.3 °C. GPC analysis M_n = 398.466, M_w = 1.610.409, M_w/M_n = 4.04.

(28) (a) Zambelli, A.; Gatti, G. *Macromolecules* **1978**, *1*, 1–1485. (b) Zambelli, A.; Bajo, G.; Rigamonti, E. *Makromol. Chem.* **1978**, *179*, 1249.

was observed. The isobutyl end groups were selectively observed also in a polymer sample obtained at 50 °C in the presence of MAO alone, thus suggesting a primary propene insertion operating both in the initiation and in the termination steps. The reasonable polymerization mechanism should involve primary insertion into $Zr-CH_3$ bonds, followed by prevailingly primary insertion during the propagation and termination via chain transfer of the primary growing chain to MAO, generating a new $Zr-CH_3$ bond for reinsertion.

Catalyst **2** at 50 °C showed the highest activity toward propylene polymerization and produced stereoirregular polypropylene having 5.2% of regioirregularly arranged monomer units. At 0 °C the same catalyst produced a stereoirregular, slightly sindiotactic, regioregular polymer. In the ^{13}C NMR spectrum of the sample obtained at 50 °C, resonances attributable to isobutyl end-groups were observed and, in very low amount (1:15 ratio to isobutyl group), also resonances due to vinylidene end-groups. Thus, chain termination by β-hydrogen transfer is of only marginal significance.

Compound **5** produced highly regioregular polypropylene with a prevailingly isotactic microstructure ([*mm*] = 56%), although with low activity. In the ^{13}C NMR spectrum no signals of regioirregular monomer units or end-groups were detected. Full pentad analysis disclosed that the relative intensities of the *mmmr*, *mmrr*, and *mrrm* stereochemical pentads are roughly 2:2:1, as expected from the statistical model of the "enantiomorphic sites" of the stereospecific propagation.[29]

Compounds **1**−**5** were also tested in the polymerization of 1-hexene. All of the compounds were inactive, at least under the explored conditions (i.e., Al^iBu_2H/MAO as activator, 50 °C, toluene solvent), apart from compound **2**. Albeit with low activity, compound **2** produced a prevailingly isotactic poly-1-hexene, having a higher degree of isotacticity than the polypropylene obtained with the same catalyst under analogous conditions. It is worth noting that the increase in the isospecificity in the polymerization of higher α-olefins with respect to propylene has been previously observed for a binaphthyl bridged salen zirconium catalyst.[30]

As far as the polymerization activities are concerned, the synthesized bischelate zirconium(IV) complexes bearing (amidomethyl)pyridine ligands were less active than the analogous bis(aminopyridinato) zirconium complexes in ethylene polymerization. On the contrary, they exhibited some activity in the polymerization of propylene and higher α-olefins, where these latter were inactive.[14d]

Conclusions

The new pentafluoro-*N*-((pyridin-2-yl)methyl)aniline ligands described in this paper were suitable for the preparation of bis(chelate) zirconium(IV) complexes. In fact, the dichloride (**1**), the dibenzyl (**4**), and the diamide (**5**) zirconium derivatives were prepared via traditional routes, straightforwardly and in high yields. Quite surprisingly, attempts to prepare $(Lig^1)_2Zr(NMe_2)_2$ in a reaction between $Zr(NMe_2)_4$ and Lig^1H led to the 7-coordinate compound $(Lig^1)(Lig^1*)ZrF(NMe_2)$ (**2**), where the modified tridentate Lig^1* ligand was generated by exchange reaction of one ortho fluoride on the pentafluorophenyl ring of the ligand with a dimethylamino group. Compound **2** was fully characterized by X-ray diffraction analysis. X-ray crystallographic analysis was also performed on compound **1** and disclosed a distorted octahedral geometry, with a C_1 symmetry deriving from all-cis configuration. Variable-temperature NMR studies established for compound **1** an inversion of metal configuration through dynamic interchange of the all-cis enantiomers. Fluxional behaviors in solution were also observed for compounds **2**, **3**, and **4**. Treatment of complexes with Al^iBu_2H and methylalumoxane (MAO) yields active, multisite ethylene and propylene polymerization catalysts. In the screening of their olefin polymerization reactivity several promising aspects emerged (i.e., the ultrahigh molecular weight polypropylene obtained with compound **1**, the highly regioregular, prevailingly isotactic polypropylene obtained with **5**, or the prevailingly isotactic poly-1-hexene obtained with compound **2**). In conclusion, the preliminary polymerization results obtained with this new class of bis(chelate) zirconium compounds encourage the search in this field; future work will extend the study to other group 4 transition metals and/or to different (amidomethyl)pyridine ligands, in order to study the effects on their structures and catalytic behavior.

Experimental Section

General Procedure. Manipulation of sensitive materials was carried out under nitrogen using Schlenk or glovebox techniques. Hexane, tetrahydrofurane, benzene, and toluene were refluxed over sodium/benzophenone, methylene chloride over calcium hydride, then distilled under nitrogen prior to use. $CDCl_3$, CD_2Cl_2, and C_6D_6 were dried over calcium hydride, distilled prior to use, and stored on molecular sevies. 1,1,2,2-Tetrachloroethane-d_2 was used as received for polymer sample analysis. Methylaluminoxane (MAO) 10% wt in toluene solution was purchased from Sigma-Aldrich; the residual $AlMe_3$ contained in it was removed by distilling the volatile under reduced pressure, washing the resulting solid with dry hexane, and drying the obtained white powder in vacuo. Ethylene and propene were purchased from SON and used without further purification; 1-hexene was distilled over calcium hydride prior to use. NMR spectra were recorded on a Bruker Advanced 400 MHz spectrometer (^1H, 400 MHz; ^{13}C, 100 MHz; ^{19}F 376 MHz). ^{13}C NMR polymer spectra were recorded on an AM Bruker 62.5 MHz spectrometrer in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) at 100 °C and reported relative to hexamethyldisiloxane (HDMS). Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 series C,H,N,S Analyzer.

Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) of polyethylene and polypropylene were determined by high-temperature gel permeation chromatography (GPC) using PL-GPC210 with PL-Gel Mixed A columns, a RALLS detector (Precison Detector, PD2040 at 800 nm), an H502 viscometer (Viscotek,), a refractive detectorn and a DM400 data manager. The measurements were recorded at 150 °C using 1,2,4-trichlorobenzene as solvent and narrow molecular weight distribution polystyrene standards as reference. Some GPC measurements were performed on a Waters GPC-V200 RI detector at 135 °C using 1,2-dichlorobenzenea solvent and Styragel columns (range of 10^7-10^3). The molecular weight and the molar mass distribution of the poly-1-hexene sample was measured by GPC at 30 °C, using $CHCl_3$ as solvent, flow rate of eluant of 1 mL/min, and narrow polystyrene standards as reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range of 1 000−1 000 000 Å). Every value was the average of two independent measurements.

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Polymer melting points (T_m) were measured by differential scanning calorimetry (DSC) using a DSC 2920 TA instrument in nitrogen flow with a heating and cooling rate of 10 °C min^{-1}. Melting temperatures were reported for the second heating cycle.

Synthesis of 2,3,4,5,6-Pentafluoro-N-((6-methylpyridin-2-yl)-methyl)aniline (Lig^{1}H). To a solution of 6-methyl-2-pyridinecarboxaldehyde (1.50 g, 12 mmol) and 2,3,4,5,6-pentaluoroaniline (2.61 g, 14.0 mmol) in THF (100 mL), containing 3 Å molecular sieves was added *p*-toluenesulfonic acid (200 mg) at room temperature. The resulting solution was refluxed for 18 h. After filtration, the solvent was distilled off by rotary evaporation. The crude product was purified from dichlorometane/hexane, obtaining a pale yellow solid (yield = 65%). Reduction of the imine function of ligand was carried out by using $NaBH_3CN$ in methanol, following a previously reported procedure,[31] obtaining Lig^{1}H as a light yellow powder (yield = 95%): ^{1}H NMR ($CDCl_3$; 293 K) δ 2.55 (3H, s, $-CH_3$), 4.55 (2H, br d, $-CH_2$), 5.14 (1H, br s, NH), 7.05 (2H, m, ArH), 7.54 (1H, t, *p*-ArH); ^{13}C NMR ($CDCl_3$; 293 K) δ 24.62 (CH_3), 50.66 (CH_2), 118.85, 122.22, 124.25, 132.52, 134.89, 137.15, 139.57, 156.19, 158.39 (Ar−*C*); ^{19}F NMR ($CDCl_3$, 293 K) δ −172.4 (t, 1F, *p*-F), −165.14 (t, 2F, *m*-F), −159.96 (d, 2F, *o*-F). Anal. Calcd for $C_{13}H_9F_5N_2$ (288.21): C, 54.17; H, 3.15; N, 9.72. Found: C, 53.75; H, 3.17; N, 9.48.

Synthesis of N-((6-Bromopyridin-2-yl)methyl)-2,3,4,5,6-pentafluoroaniline (Lig^{2}H). The imine ligand was obtained as above by reacting 6-bromo-2-pyridine-carboxaldehyde (1.0 g, 5.3 mmol) and 2,3,4,5,6-pentaluoroaniline (1.10 g, 6.0 mmol). The crude product was purified by column chromatography on neutral alumina, using hexane/diethyl ether (yield = 64%). The subsequent reduction reaction with $NaBH_3CN$ gave amino ligand in good yield (75%): ^{1}H NMR ($CDCl_3$; 293 K) δ 4.55 (2H, br d, $-CH_2$), 4.76 (1H, br s, NH), 7.22−7.56 (3H, m, ArH); ^{13}C NMR ($CDCl_3$; 293 K) δ 50.44 (CH_2), 120.64, 127.22, 139.30, 142.20, 159.13 (Ar−*C*); ^{19}F NMR ($CDCl_3$, 293 K) δ −171.2 (t, 1F, *p*-F), −164.6 (t, 2F, *m*-F), −159.45 (d, 2F, *o*-F). Anal. Calcd for $C_{12}H_6BrF_5N_2$ (353.08): C, 40.82; H, 1.71; N, 7.93. Found: C, 39.99; H, 1.81; N, 6.98.

Synthesis of 2,3,4,5,6-Pentafluoro-N-((pyridin-2-yl)methyl)aniline (Lig^{3}H). The imine ligand was obtained as above by reacting 2-pyridinecarboxaldehyde (1.5 mL, 15.7 mmol) and 2,3,4,5,6-pentafluoroaniline (2.9 g, 16 mmol) (yield = 80%). The subsequent reduction reaction with $NaBH_3CN$ gave the amino ligand as a light brown powder in good yield (98%): ^{1}H NMR (C_6D_6; 293 K) δ 4.21 (2H, br d, $-CH_2$), 5.31 (1H, br s, NH), 6.48−6.94 (3H, m, ArH), 8.29 (1H, br d, *o*-ArH); ^{13}C NMR (C_6D_6; 293 K) δ 49.97 (CH_2), 121.44, 122.22, 136.16, 149.15, 156.76 (Ar−*C*); ^{19}F NMR (C_6D_6, 293 K) δ −173.5 (t, 1F, *p*-F), −165.6 (t, 2F, *m*-F), −161.2 (d, 2F, *o*-F). Anal. Calcd for $C_{12}H_7F_5N_2$ (274.18): C, 52.57; H, 2.57; N, 10.22. Found: C, 52.34; H, 2.42; N, 9.89.

Synthesis of Complex 1. To a stirred solution of Lig^{1}H (1.0 g, 3.47 mmol) in THF (50 mL) at −78 °C was added a butyllithium hexane solution (1.45 mL, 2.5 M, 3.62 mmol). The mixture was allowed to warm to room temperature and stirred for 3 h. The resulting yellow solution was added dropwise to a stirred solution of $ZrCl_4 \cdot 2THF$ (0.652 g, 1.73 mmol) in 50 mL of THF at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. Removal of the solvent in vacuo gave a dark yellow powder. The crude product was extracted in dichloromethane, and the solution was filtered, concentrated, and layered with hexane. A pale yellow powder deposited overnight (1.14 g, 89%). Suitable crystals for X-ray crystal structure determination were grown from dichloromethane/hexane at room temperature: ^{1}H NMR (CD_2Cl_2; 293 K) δ 2.82 (6H, br s, $-CH_3$), 4.65 (2H, br s, $-CH_2$), 4.84 (2H, br s, $-CH_2$), 7.16 (2H, br d, ArH), 7.27 (2H, br d, ArH), 7.80 (2H, br t, *p*-ArH); ^{13}C NMR ($CDCl_3$; 293 K) δ 24.98 (CH_3), 63.40 (CH_2), 118.70, 124.70, 136.08, 139.13, 142.04, 145.26, 160.68 (Ar-*C*); ^{19}F NMR (CD_2Cl_2, 293 K) δ −174.0 (1F, br t), −166.3 (2F, br t), −160.7 (2F, br d). Anal. Calcd for $C_{26}H_{16}Cl_2F_{10}N_4Zr$ (736.54): C, 42.40; H, 2.19; N, 7.61. Found: C, 41.81 H, 2.22; N, 6.94.

Synthesis of Complex 2. Lig^{1}H (0.800 g, 2.77 mmol) and tetrakis(dimethylamido)zirconium (0.370 g, 1.38 mmol) were dissolved in 30 mL of hexane. The solution was stirred for 5 h at room temperature. The solvent was then distilled off in vacuo and the resulting powder washed twice with hexane. The complex was crystallized from dichloromethane/hexane. Suitable crystals for X-ray analysis were grown from dichloromehane/pentane at room temperature (0.870 g, 84%): ^{1}H NMR (CD_2Cl_2; 293 K) δ 2.60 (18H, br s, $-CH_3$), 4.75 (2H, br s, $-CH_2$), 5.12 (2H, br s, $-CH_2$), 6.9−7.3 (4H, br m, ArH), 7.5−7.8 (2H, br t, *p*-ArH); ^{13}C NMR (CD_2Cl_2; 293 K) δ 23.44, 24.65 (CH_3), 42.43, 45.91 ($N(CH_3)_2$), 58.2, 61.1 (CH_2), 117.9, 123.3, 137.5 (Ar−*C*); ^{19}F NMR ($CDCl_3$, 293 K) δ −177.1 (1F, br s), −168.88 (1F, br s), −167.39 (2F, br s), −162.94 (1F, br s), −157.35 (1F, br s), −151.70 (1F, br s), − 148.15 (2F, br s), 52.21 (1F, s, Zr−F). Anal. Calcd for $C_{30}H_{28}F_{10}N_6Zr$ (753.79): C, 47.80; H, 3.74; N, 11.15. Found: C, 47.50; H, 3.62; N, 10.98.

Hydrolysis of Complex 2. To a solution of 30 mg of complex **2** in dichloromethane (2 mL) was added 5 mL of water. The organic product was extracted with diethyl ether and dried over Na_2SO_4, and the solvent was removed by rotary evaporation. Product was characterized by NMR spectroscopy, disclosing Lig^{1}H and Lig^1*H in a 1:1 ratio. Lig^1*H: ^{1}H NMR ($CDCl_3$; 293 K) δ 2.53 (3H, s, $-CH_3$), 2.70 (6H, s, Ar−$N(CH_3)_2$), 4.51 (2H, br d, $-CH_2$), 5.90 (1H, br s, NH), 7.00 (2H, m, ArH), 7.50 (1H, t, *p*-ArH); ^{13}C NMR ($CDCl_3$; 293 K) δ 29.91 (CH_3), 43.73 (Ar−N(*C*H_3)$_2$), 51.27 (CH_2), 118.91, 121.96, 124.38, 137.04, 139.57, 156.16, 158.29 (Ar−*C*); ^{19}F NMR ($CDCl_3$, 293 K) δ −173.93 (t, 1F, *p*-F), −162.19 (t, 1F, *m*-F), −160.16 (d, 1F, *o*-F), −150.80 (d, 1F, *o*-F).

Synthesis of Complex 3. Complex **2** (200 g, 0.3 mmol) and Me_3SiCl (0.195 g, 1.8 mmol) were dissolved in 20 mL of dry toluene, and the solution was stirred at room temperature for 24 h. The light yellow precipitate was filtered off, washed with dry hexane, and dried in vacuo (yield 90%): ^{1}H NMR ($CDCl_3$; 298 K) δ 2.68 (6H, br s, $-CH_3$), 2.72 (6H, br s, $-CH_3$), 4.56 (2H, br s, $-CH_2$), 4.59(2H, br s, $-CH_2$), 7.04−7.7 (6H, br m, ArH); ^{13}C NMR (CD_2Cl_2; 293 K) δ 24.69, 25.13 (CH_3), 43.88 (Ar−$N(CH_3)_2$), 50.77, 51.27 (CH_2), 119.08−138.91 (Ar−*C*); ^{19}F NMR (CD_2Cl_2, 293 K) δ −168.48 (2F, br s), −167.11 (1F, br s), −163.78 (1F, br s), −159.00 (1F, br s), −151.68 (1F, br s), −149.04 (2F, br s), −147.83 (1F, br s). Anal. Calcd for $C_{28}H_{22}Cl_2F_9N_5Zr$ (761.62): C, 44.16; H, 2.91; N, 9.20. Found: C, 43.98; H, 2.86; N, 9.15.

Synthesis of Complex 4. To a solution of Lig^{1}H (0.500 g, 1.76 mmol) in benzene (20 mL) was slowly added a solution of tetrabenzylzirconium (0.400 g, 0.88 mmol) in benzene (10 mL). The solution was stirred for 3 h at room temperature, the solvent was distilled off in vacuo, and the resulting crude product was washed with hexane and crystallized from toluene (yield = 68%): ^{1}H NMR (C_6D_6; 293 K) δ 2.60 (6H, br s, $-CH_3$), 2.34 (4H, br m, CH_2Ph), 4.75 (4H, br m, $-CH_2$), 6.05−6.99 (16H, br m, ArH); ^{13}C NMR (C_6D_6; 293 K) selected resonances δ 25.35, 26.24 (CH_3), 45.67 (CH_2), 58.69 (CH_2Ph), 118.65−160.10 (Ar−*C*); ^{19}F NMR (C_6D_6, 293 K) δ main resonances δ −166.4 (1F, br s), −166.0 (2F, br t), −147.0 (2F, br d), minor resonances −179.5 (br s), −167.2 (br s), −159.4 (br s), −155.0 (br s). Anal. Calcd for $C_{40}H_{30}F_{10}N_4Zr$ (847.90): C, 56.66; H, 3.57; N, 6.61. Found: C, 56.50; H, 3.42; N, 6.60.

Synthesis of Complex 5. Lig^{2}H (0.625 g, 1.77 mmol) and tetrakis(dimethylamido)zirconium (0.235 g, 0.88 mmol) were dissolved in 30 mL of dry hexane. The resulting solution was stirred for 5 h at room temperature. The solvent was then distilled off in vacuo, and the resulting powder was washed with hexane. The complex was crystallized from dichloromethane (0.670 g, 86%):

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^{1}H NMR ($CDCl_3$; 293 K) δ 2.79 (12H, s, $-N(CH_3)_2$), 5.09 (4H, s, $-CH_2$), 7.06 (2H, d, ArH), 7.31 (2H, d, ArH), 7.43 (2H, t, *p*-ArH); ^{13}C NMR ($CDCl_3$; 293 K) δ 42.55 ($N(CH_3)_2$), 58.08 (CH_2), 119.65, 126.76, 139.83, 164.71 (Ar$-C$); ^{19}F NMR ($CDCl_3$, 293 K) δ -166.3 (2F, br d), -153.3 (2F, br s), -148.3 (1F, br s). Anal. Calcd for $C_{28}H_{22}Br_2F_{10}N_6Zr$ (883.53): C, 38.06; H, 2.51; N, 9.51. Found: C, 38.62; H, 2.36; N, 8.99.

Reaction between Lig^{3}H and Zr(NMe$_2$)$_4$. Lig^{3}H (0.700 g, 2.55 mmol) and tetrakis(dimethylamido)zirconium (0.330 g, 1.25 mmol) were dissolved in 30 mL of hexane. The solution was stirred for 6 h at room temperature, the solvent was distilled off in vacuo, and the resulting powder was washed with hexane (0.750 g, 82%): ^{1}H NMR (C_6D_6; 293 K) δ 2.63 (12H, s, $-N(CH_3)_2$), 4.66 (4H, br s, $-CH_2$), 6.3 (4H, br m, ArH), 6.3 (2H, br t, ArH), 8.7 (2H, br d, *o*-Py-H); ^{13}C NMR ($CDCl_3$; 293 K) δ 43.29 ($N(CH_3)_2$), 61.31 (CH_2), 121.27, 121.95, 137.84, 149.17, 163.61 (Ar$-C$); ^{19}F NMR (C_6D_6, 293 K) δ -168.8 (3F, br t), -166.8 (6F, br t), -149.77 (6F, br d); minor resonances -169.5 (1F, br s), -162.9 (1F, br s), -158.5 (1F, br s), -151.3 (1F, br s), 42.17 (1F, s, Zr$-$F). Anal. Calcd for $C_{28}H_{24}F_{10}N_6Zr$ (724.09): C, 46.34; H, 3.33; N, 11.58. Found: C, 45.87; H, 3.21; N, 11.08.

Hydrolysis of the Reaction Product between Lig^{3}H and Zr(NMe$_2$)$_4$. Thirty milligrams of the obtained sample was dissolved in dichloromethane (2 mL) and treated with water (5 mL). The organic fraction was extracted with diethyl ether and dried over Na_2SO_4; volatiles were removed by rotary evaporation. The resulting solid product was characterized by NMR spectroscopy, disclosing a mixture of Lig^{3}H and Lig^3*H in a 3:1 ratio. Lig^3*H: ^{1}H NMR ($CDCl_3$; 293 K) δ 2.70(6H, s, Ar$-N(CH_3)_2$), 4.56 (2H, br d, $-CH_2$), 5.81 (1H, br s, NH), 7.20 (2H, m, ArH), 7.63 (1H, t, *p*-ArH), 8.55 (1H, d, *o*-ArpyH); ^{13}C NMR ($CDCl_3$; 293 K) δ 44.00 (Ar$-N(CH_3)_2$) 51.3 (CH_2), 116.4, 123.3, 136.8, 149.6 (Ar$-C$); ^{19}F NMR ($CDCl_3$, 293 K) δ -173.69 (t, 1F, *p*-F), -162.10 (t, 1F, *m*-F), -160.09 (d, 1F, *o*-F), -150.67 (d, 1F, *o*-F).

Polymerizations. Ethylene and propylene polymerizations were performed in a magnetically stirred reactor (100 cm^3) or in a 500 mL Büchi glass autoclave. The reactor vessels were charged sequentially with MAO and a toluene solution of the precatalyst. The mixture was thermostated at the required temperature, and the monomer gas feed was started. After the required polymerization time, the mixture was poured into acidified ethanol. The precipitated polymer was recovered by filtration and dried at 40 °C in a vacuum oven. Details and results of polymerization are reported in Tables 2 and 3.

1-Hexene Polymerization. Polymerization was performed in a magnetically stirred reactor (50 °C) that was charged sequentially with dried MAO (20 mmol), 4 mL of toluene, and 8 mL of 1-hexene and warmed to 50 °C. Then a solution of complex **2** (20 μmol) in toluene (2 mL), preaged for 10 min with a solution of Al*i*Bu$_2$H in toluene (2.15 mL, 0.28 M in), was added. After 5 h, the polymerization mixture was poured into acidified ethanol. Polymer was recovered and dried in a vacuum oven (yield = 0.060 g). From ^{13}C NMR spectrum [*mmmm*] = 84%. From GPC: $M_w/M_n = 4.54$; $M_n = 46700$.

X-ray Crystallography. Suitable crystals of both compounds **1** and **3** were selected and mounted on a cryoloop with paratone oil and measured at 100 K with a Rigaku AFC7S diffractometer equipped with a Mercury^2 CCD detector using graphite monochromated MoKα radiation (λ = 0.71069 Å). Data reduction was performed with the crystallographic package CrystalClear.[32] Data have been corrected for Lorentz, polarization, and absorption. The structures were solved by direct methods using the program SIR97[33] and refined by means of full-matrix least-squares based on F^2 using the program SHELXL97.[34]

For both compounds all non-hydrogen atoms were refined anisotropically; hydrogen atoms were positioned geometrically and included in structure factor calculations but not refined. As for compound **1** the crystallographic asymmetric unit consists of one molecule of **1** and one molecule of CH_2Cl_2. The difficulties in modeling the disorder of the CH_2Cl_2 molecule could account for the lower quality of the X-ray analysis of **1**.

Crystal data and refinement details are reported in Table 4. Crystal structures are drawn by means of the program ORTEP32.[35]

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Supporting Information Available: X-ray crystallographic information files in CIF format for compounds **1** and **2**; ^{1}H, ^{13}C, and ^{19}F NMR spectra of the ligands and of complexes **1**$-$**5**, ^{1}H NMR of hydrolysis products, and ^{13}C NMR spectra of polyhexene and polypropylene samples. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800736W

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