Chiral Zirconium Complexes with Bianiline-Based N_4-Donor Ligands

Mika Kettunen,[†] Christoph Vedder,[‡] Frank Schaper,[‡] Markku Leskelä,[†]
Ilpo Mutikainen,[†] and Hans-Herbert Brintzinger*,[‡]

*Laboratory of Inorganic Chemistry, University of Helsinki, FIN-00014 Helsinki, Finland, and
Fachbereich Chemie, Universität Konstanz, D-78457 Konstanz, Germany*

Received January 26, 2004

Syntheses of new tetradentate ligands, containing a bianiline backbone and two additional heterocyclic N-donors, and of chiral zirconium complexes containing these ligands as dianions are reported. Crystal structures of some of these complexes show a preference for coordinating the two remaining ligands in a *trans*- rather than *cis*-orientation. Nevertheless, these complexes are moderately active in MAO-activated olefin polymerization in toluene solution at 50 °C. With propene, partly isotactic polypropene (55% mmmm) is obtained. These observations indicate that in cationic species generated in these reaction systems, the growing polymer chain and the olefin substrate occupy *cis*-coordination sites, while the heterocyclic N ligands adopt a screw-like *trans* orientation suitable to favor one of the enantiofacial orientations of the entering olefin substrate.

Introduction

Earlier studies on olefin polymerization catalysts based on group IV metal complexes with substituted, annelated, and/or bridged cyclopentadienyl ligands[1,2] have been followed more recently by investigations on polymerization catalysts derived from a great variety of other transition metal complexes.[3] For group IV transition metals, various complexes with two bidentate N,N ligands[4] or O,N ligands or with a tetradentate O,N,N,O ligand have been studied with regard to MAO-activated olefin polymerization catalysis,[5] some with remarkable activities,[4a,6] recently even without MAO activation.[7] Nevertheless, the polymerization activities for MAO-activated titanium and zirconium complexes with Schiff-base O,N,N,O ligands containing a chiral bianiline backbone, prepared by Scott and co-workers,[8] have been reported only once.[9]

Other complexes containing ligands with N-donor atoms only, which include amidinato,[10] diamido,[11] triamidoamine,[12] and diamido-diamine[13] complexes, among these also chiral zirconium complexes containing bidentate[14] and tetradentate[15] diamido ligands with a bi-

---

[†] University of Helsinki.

[‡] Universität Konstanz.

(1) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(2) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(3) (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 285. (c) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(4) (a) Yoshida, Y.; Matsui, S.; Takagi, Y.; Mitani, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *Organometallics* **2001**, *20*, 4793. (b) Tsurugi, H.; Yamagata, T.; Tani, K.; Mashima, K. *Chem. Lett.* **2003**, *32*, 756. (c) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 1651.

(5) (a) Jones, D.; Cavell, K.; Keim, W. *J. Mol. Catal. A*: *Chem.* **2001**, *138*, 37. (b) Tian, J.; Hustad, P. D.; Coates, W. *J. Am. Chem. Soc.* **2001**, *123*, 5134. (c) Tian, J.; Hustad, P. D.; Coates, W. *J. Am. Chem. Soc.* **2002**, *124*, 3614. (d) Kim, J.; Hwang, J.-W.; Kim, Y.; Lee, M.; Han, Y.; Do, Y. *J. Organomet. Chem.* **2001**, *620*, 1. (e) Ishii, S.-I.; Furuyama, R.; Matsukawa, N.; Saito, J.; Mitani, M.; Tanaka, H.; Fujita, T. *Macromol. Rapid Commun.* **2003**, *24* (7), 452. (f) Bott, R. K. J.; Hughes, D. L.; Schormann, M.; Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **2003**, *665* (1−2), 135. (g) Repo, T.; Klinga, M.; Pietikäinen, P.; Leskelä, M.; Uusitalo, A.-M.; Pakkanen, T.; Hakala, K.; Aaltonen, P.; Löfgren, B. *Macromolecules* **1997**, *30* (2), 171. (h) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123* (28), 6847.

(6) (a) Matsui, S.; Fujita, T. *Catal. Today* **2001**, *66* (1), 63. (b) Mitani, M.; Mohri, J.-I.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.-I.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 3327. (c) Furuyama, R.; Saito, J.; Ishii, S.-I.; Mitani, M.; Matsui, S.; Tohi, Y.; Makio, H.; Matsukawa, N.; Tanaka, H.; Fujita, T. *J. Mol. Catal. A: Chem.* **2003**, *200*, 31.

(7) (a) Bando, H.; Nakayama, Y.; Sonobe, Y.; Fujita, T. *Macromol. Rapid Commun.* **2003**, *24* (12), 732. (b) Ishii, S.; Saito, J.; Matsuura, S.; Suzuki, Y.; Furuyama, R.; Mitani, M.; Nakano, T.; Kashiwa, N.; Fujita, T. *Macromol. Rapid Commun.* **2002**, *23* (12), 693. (c) Nakayama, Y.; Bando, H.; Sonobe, Y.; Kaneko, H.; Kashiwa, N.; Fujita, T. *J. Catal.* **2003**, *215* (1), 171. (d) Nakayama, Y.; Bando, H.; Sonobe, Y.; Kaneko, H.; Kashiwa, N.; Fujita, T. *J. Catal.* **2003**, *215* (1), 171. (e) Saito, J.; Suzuki, Y.; Fujita, T. *Chem. Lett.* **2003**, *32* (3), 236. (f) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460. (g) Zuideveld, M. A.; Wehrmann, P.; Röhr, C.; Mecking, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 869.

(8) (a) Woodman, P. R.; Alcock, N. W.; Munslow, I. J.; Sanders, C. J.; Scott, P. *J. Chem. Soc., Dalton Trans.* **2000**, 3340. (b) Woodman, P. R.; Sanders, C. J.; Alcock, N. W.; Munslow, I. J.; Hitchcock, P. B.; Scott, P. *New J. Chem.* **1999**, *23*, 815. (c) Knight, P. D.; O'Shaughnessy, P. N.; Munslow, I. J.; Kimberley, B. S.; Scott, P. *J. Organomet. Chem.* **2003**, *683*, 103.

(9) Knight, P. D.; Clarke, A. J.; Kimberley, B. S.; Jackson, R. A.; Scott, P. *Chem. Commun.* **2002**, 352.

(10) (a) Chen, C.-T.; Rees, L. H.; Cowley, A. R.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **2001**, *11*, 1761. (b) Fuhrmann, H.; Brenner, S.; Arndt, P.; Kempe, R. *Inorg. Chem.* **1996**, *35*, 6742.

(11) (a) Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487. (b) Ong, T.-G.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2003**, *22*, 387.

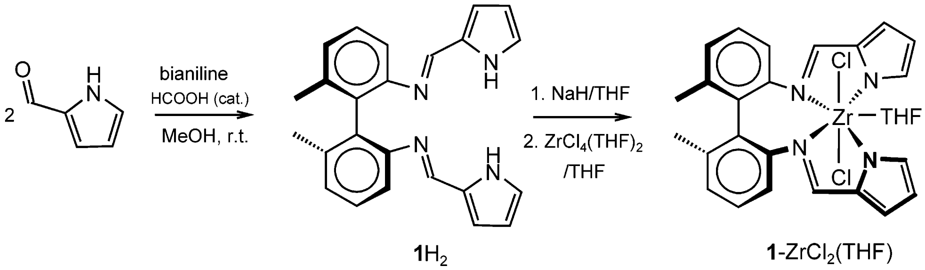
(12) (a) Morton, C.; Munslow, I. J.; Sanders, C. J.; Alcock, N. W.; Scott, P. *Organometallics* **1999**, *18*, 4608. (b) Morton, C.; Gillespie, K. M.; Sanders, C. J.; Scott, P. *J. Organomet. Chem.* **2000**, *606*, 141.

(13) (a) Skinner, M. E. G.; Cowhig, D. A.; Mountford, P. *Chem. Commun.* **2000**, 1167−1168. (b) Carpentier, J.-F.; Martin, A.; Swenson, D. C.; Jordan, R. F. *Organometallics* **2003**, *22*, 4999.

(14) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem* **1996**, *506*, 343.

10.1021/om040011r CCC: $27.50

Scheme 1



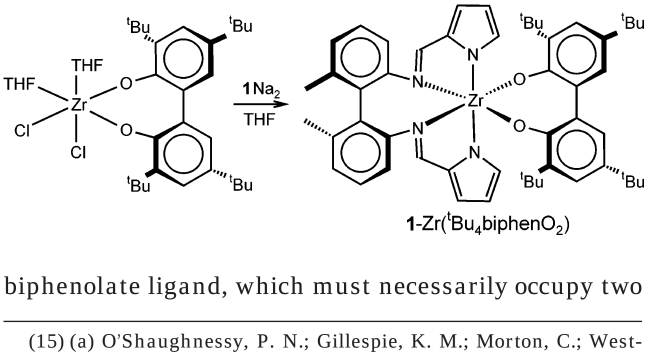
aniline backbone, as well as complexes with tetraazamacrocyclic ligands,[16] have been prepared but not always tested in polymerization. Here, we report on the synthesis of new 6,6′-dimethyl-bianiline-based tetradentate ligands containing two additional heterocyclic N-donors and the preparation of several chiral zirconium complexes derived from their dianionic deprotonation products, their structures, and their properties as precatalysts for olefin polymerization.

Results and Discussion

Complex Synthesis and Characterization. The dipyrrole diimine ligand **1**H_2 was readily prepared by condensation of 6,6′-dimethyl-bianiline with pyrrole aldehyde in methanol (Scheme 1). With a few drops of formic acid being added as a catalyst, the product was isolated with 85% yield after reacting 1 h at room temperature. Upon stirring the reaction mixture overnight in *n*-pentane, the product precipitated cleanly and no further purification was needed.

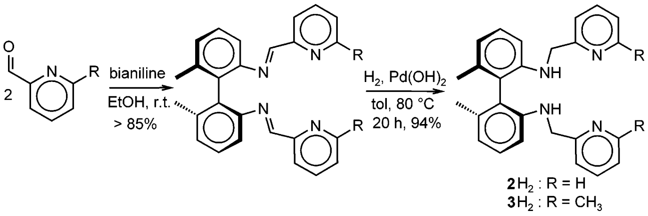
Deprotonation of the pyrrole rings of ligand **1**H_2 was achieved by reaction with NaH in THF. The disodium salt **1**Na_2 thus formed was reacted with $ZrCl_4(THF)_2$ in THF at room temperature to give complex **1**-$ZrCl_2$(THF) (Scheme 1). Washing the crude product with toluene, in which it is only slightly soluble, followed by extraction with CH_2Cl_2 gave analytically pure **1**-$ZrCl_2$(THF), the crystal structure of which is to be discussed below. The coordinated THF was not removable in vacuo at 100 °C or by coevaporation with toluene. To obtain a more soluble complex, **1**Na_2 was reacted also with ($^tBu_4$biphenO_2)-$ZrCl_2(THF)_2$,[17] to give the biphenolate complex **1**-Zr($^tBu_4$biphenO_2) (Scheme 2). Apparently, the bulky biphenolate ligand, which must necessarily occupy two *cis*-coordination sites, precludes the coordination of an extra THF ligand molecule.

Scheme 2



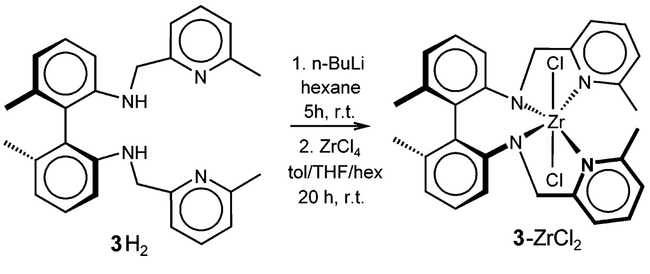
To study the effects of varying sidearm functionalities on structures and reactivities of these bianiline-based complexes, we next replaced the pyrrole by pyridyl moieties. The dipyridine diimines, obtained by condensation of dimethylbianiline with pyridine aldehyde and 6-methylpyridine aldehyde, respectively, had to be reduced to the diamines **2**H_2 and **3**H_2 first, to make dianionic ligands accessible from them. While attempts to reduce the dipyridine diimines with $NaBH_4$ or $LiAlH_4$ were unsuccessful or gave low isolated yields, complete conversion to the oily products **2**H_2 and **3**H_2, respectively, was achieved, as judged from ^1H NMR, by Pd-$(OH)_2$-catalyzed hydrogenation under H_2 pressure at 80 °C (Scheme 3).

Scheme 3



Reacting **2**H_2 or **3**H_2 with NaH and then with $ZrCl_4$ or $ZrCl_4(THF)_2$ did not allow isolation of any zirconium complexes. When ^{n}BuLi was used instead, a few crystals of **3**-$ZrCl_2$ were isolated (Scheme 4),[18] which allowed us to determine its structure by single-crystal X-ray diffractometry. The biphenolate complex **2**-Zr($^tBu_4$biphenO_2) was obtained by reacting ($^tBu_4$biphenO_2)Zr$(NMe_2)_2$ (**4**) with ligand **2**H_2 in toluene at room temperature for 2 days and then under reflux for 2 h (Scheme 5). Again, only a few crystals of **2**-Zr($^tBu_4$biphenO_2) were isolated from this reaction, but allowed determination of the

Scheme 4



---

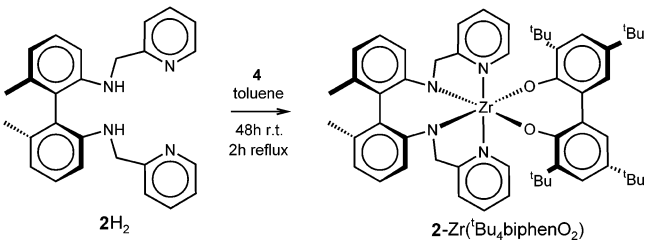
(15) (a) O'Shaughnessy, P. N.; Gillespie, K. M.; Morton, C.; Westmoreland, I.; Scott, P. *Organometallics* **2002**, *21* (21), 4496. (b) Westmoreland, I.; Munslow, I. J.; O'Shaughnessy, P. N.; Scott, P. *Organometallics* **2003**, *22* (14), 2972.

(16) (a) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493. (b) Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F. *Organometallics* **1998**, *17*, 382.

(17) Damrau, H.-R. H.; Royo, E.; Obert, S.; Schaper, F.; Weeber, A.; Brintzinger, H.-H. *Organometallics* **2001**, *20*, 5258.

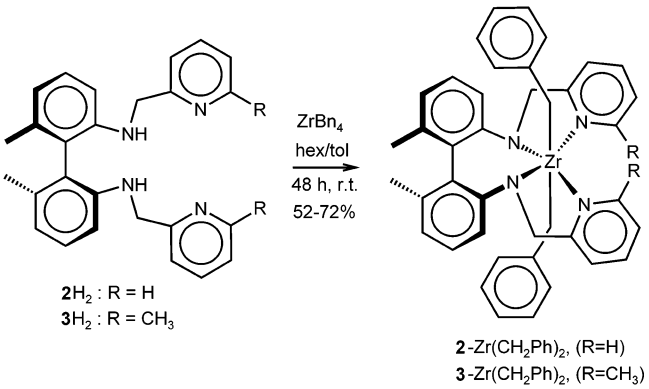
(18) Clegg, W.; Dunbar, L.; Horsburgh, L.; Mulvey, R. E. *Angew. Chem.* **1996**, *108*, 815.

Scheme 5



solid state structure of this complex by single-crystal X-ray diffraction. Finally, we observed that **2**H_2 and **3**H_2 readily reacted with $Zr(CH_2Ph)_4$ to give complexes **2**-$Zr(CH_2Ph)_2$ and **3**-$Zr(CH_2Ph)_2$, respectively, in acceptable yields (Scheme 6).

Scheme 6



All complexes containing ligands **1**, **2**, or **3** gave room-temperature NMR spectra in accord with a structure of time-averaged C_2-symmetry (see Experimental Section). NMR patterns of the AB type were observed for the diastereotopic N-CH_2 and Zr-CH_2 protons of **2**-$Zr(CH_2Ph)_2$ and **3**-$Zr(CH_2Ph)_2$, in accord with the chiral geometry of these complexes.

Molecular Structures of 1-$ZrCl_2$(THF), 3-$ZrCl_2$, 3-$Zr(CH_2Ph)_2$, and 2-Zr($^tBu_4biphenO_2$). In complex **1**-$ZrCl_2$(THF), the zirconium center is coordinated to the four nitrogen atoms of ligand **1**, to two chloride ions, and to the THF molecule (Figure 1, Table 1). The coordination polyhedron can be described as a distorted pentagonal bipyramid, where the chloride ions take the pseudoaxial positions with a Cl−Zr−Cl angle of 169°, while the four nitrogen atoms and the THF oxygen atom occupy a distorted N_4O mid-plane. The mean plane defined by the two pyrrole-N atoms and by the Zr and O atoms, which lie on the crystallographically imposed C_2 axis, is practically perpendicular to the $ZrCl_2$ plane and might thus be taken to be the base plane of a pentagonal bipyramide. The two imine-N atoms deviate by ±0.72 Å from this base plane due to a dihedral angle of 67° in the biphenyl backbone. Nevertheless, the O−Zr−N(pyrrole), N(pyrrole)−Zr−N(imine), and N(imine)−Zr−N(imine) angles (76°, 71°, and 77°, respectively) are all close to the value of 72° expected for a pentagonal coordination geometry. The Zr−N(imine) and Zr−N(pyrrole) bond lengths are close to those observed for Zr−Schiff-base and Zr−amido complexes, respectively.[8,10−16]

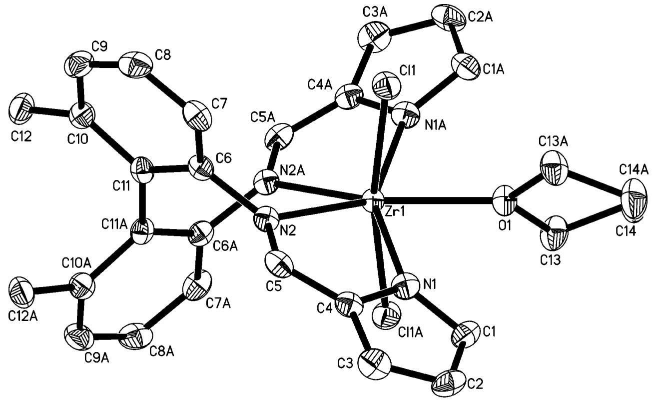


Figure 1. Molecular strucure of **1**-$ZrCl_2$(THF). Thermal ellipsoids are at 50% probability, hydrogen atoms omitted for clarity.

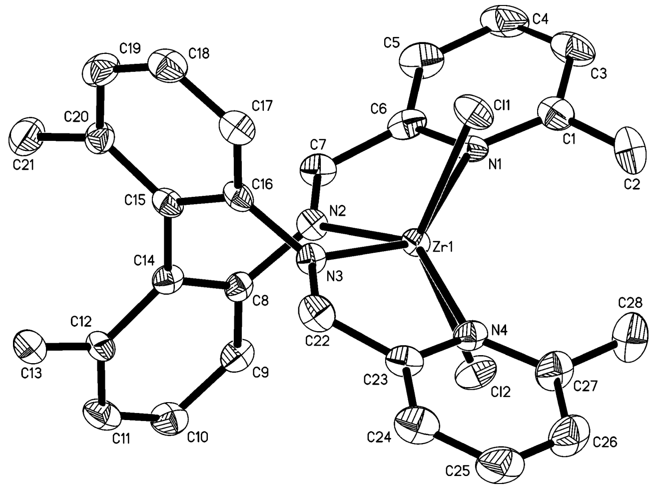


Figure 2. Molecular strucure of **3**-$ZrCl_2$. Thermal ellipsoids are at 50% probability, hydrogen atoms omitted for clarity.

Table 1. Bond Lengths (Å) and Angles (deg) at Zr Center for 1-$ZrCl_2$(THF)

Zr−N(1)	2.252(3)	N(1)−Zr−N(1A)	151.10(13)
Zr−N(2)	2.335(2)	N(1)−Zr−N(2)	71.03(9)
Zr−O(1)	2.268(3)	N(1)−Zr−O(1)	75.55(7)
Zr−Cl(1)	2.463(1)	N(2)−Zr−N(2A)	76.57(12)
		Cl(1)−Zr−Cl(1A)	169.08(4)

Surprisingly similar to the structure just discussed for **1**-$ZrCl_2$(THF) is that of **3**-$ZrCl_2$ (Figure 2, Table 2), except that the THF ligand is missing here, due to the steric shielding of the fifth in-plane position by the *o*-methyl groups on each of the pyridine ligand moieties. The absence of a fifth ligand in the base plane results in a somewhat smaller Cl−Zr−Cl angle of 138°, the Cl−Zr−Cl plane still being close to perpendicular to the N(pyridyl)−Zr−N(pyridyl) base plane. The two N(amido) atoms deviate again by ±0.6 Å from this base plane; the N(pyridyl)−Zr−N(amido) and N(amido)−Zr−N(amido) angles (71−72° and 84°) as well as the large N(pyridyl)−Zr−N(pyridyl) angle of 141° are again close to the values expected for pentagonal coordination. The Zr−N(pyridyl) and Zr−N(amido) bond distances of 2.45 and 2.07 Å, respectively, are in the range of those reported for other Zr-imine and Zr-amido complexes.[8,10−16] The interchange of anionic and neutral N ligand atoms between the inner and outer positions of the coordination base plane in **1**-$ZrCl_2$(THF) and **3**-$ZrCl_2$ thus seems to have little effect on the overall coordination geometries of these complexes.

Table 2. Bond Lengths (Å) and Angles (deg) at Zr Centers for 3-ZrCl$_2$, 3-Zr(CH$_2$Ph)$_2$, and 2-Zr(^{t}Bu$_4$biphenO$_2$)

	3-ZrCl$_2$	**3**-Zr(CH$_2$Ph)$_2$	**2**-Zr(^{t}Bu$_4$biphenO$_2$)
Zr−N(3, amide)	2.073(3)	2.114(2)	2.100(3)
Zr−N(2, amide)	2.079(3)	2.084(2)	2.097(3)
Zr−N(1, pyridyl)	2.446(3)	2.526(2)	2.406(3)
Zr−N(4, pyridyl)	2.446(4)	2.521(2)	2.412(3)
Zr−X	2.475(1), X = Cl(1)	2.322(3), X = C(36)	2.037(2), X = O(2)
Zr−X	2.470(1), X = Cl(2)	2.322(3), X = C(29)	2.070(2), X = O(1)
N(1)−Zr−N(4)	140.8(1)	136.0(1)	161.7(1)
N(2)−Zr−N(3)	84.1(1)	85.4(1)	86.5(1)
N(1)−Zr−N(2)	71.4(1)	70.7(1)	68.8(1)
N(3)−Zr−N(4)	72.0(1)	69.6(1)	69.1(1)
N(1)−Zr−N(3)	144.0(1)	154.0(1)	103.6(1)
N(2)−Zr−N(4)	144.9(1)	151.29(8)	125.7(1)
X−Zr−X	138.4(1), X = Cl(1), Cl(2)	134.5(1), X = C(36), C(29)	90.9(1), X = O(1), O(2)

Even more striking is the structural similarity between complexes **3**-ZrCl$_2$ and **3**-Zr(CH$_2$Ph)$_2$ (Figure 3, Table 2). The bipyramidal coordination geometries are very similar, with a C(benzyl)−Zr−C(benzyl) angle of 134° and N(pyridyl)−Zr−N(amido) and N(amido)−Zr−N(amido) angles of 71° and 85°, respectively, and a large N(pyridyl)−Zr−N(pyridine) angle of 136°. The Zr−N distances are in the same range as noted before for **3**-ZrCl$_2$.

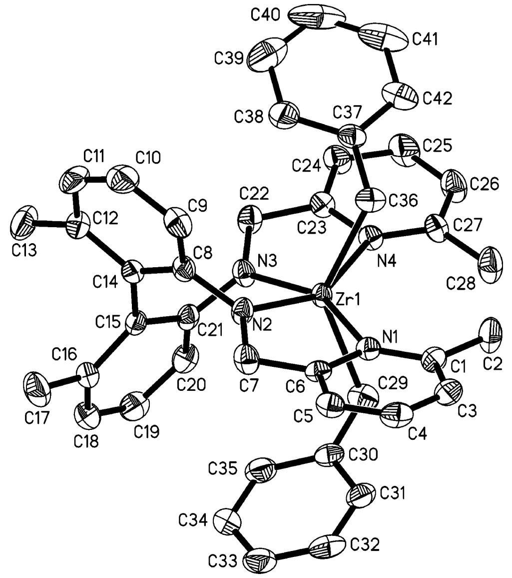


Figure 3. Molecular strucure of **3**-Zr(CH$_2$Ph)$_2$. Thermal ellipsoids are at 50% probability, hydrogen atoms omitted for clarity.

Bianiline-bridged N$_4$ ligands in complexes of the type N$_4$ZrX$_2$ thus tend to have all four N ligand atoms close to the mid-plane, which bisects the rather large X−Zr−X angle, so that the two X ligands occupy axial-type positions. Due to a rather short distance between the bianiline N atoms, associated with rather small dihedral angles of 62−67° between the two phenyl rings, the four N atoms leave a rather large open space in the molecular mid-plane, opposite the bridging biphenylene unit. This position, which corresponds to an equatorial corner of a distorted pentagonal bipyramide, can either be occupied by an additional ligand molecule, as in **1**-ZrCl$_2$(THF), or remain open, as in the sterically congested complexes of the type **3**-ZrX$_2$ (X = Cl, benzyl). While repulsive contacts (3.6 Å) between the methyl groups at the pyridyl rings might stabilize the large N(pyridyl)−Zr−N(pyridyl) angles, they are apparently not sufficient to displace the two pyridyl ligands from their positions close to the molecular mid-plane into axial positions.

A structure with axially placed pyridyl ligands is brought about, however, by the biphenolate ligand in **2**-Zr(^{t}Bu$_4$biphenO$_2$), in which the O ligand atoms must necessarily occupy *cis*-coordination positions (Figure 4, Table 2). This complex adopts a slightly distorted octahedral geometry, with an N(pyridyl)−Zr−N(pyridyl) angle of 162° and N−Zr−N, N−Zr−O, and O−Zr−O angles all close to 90°. Remarkably, the dihedral angle between the two phenyl rings in the bianiline backbone, 61°, is even smaller than in complexes that have all four N ligand atoms in equatorial positions. By analogy, we would assume that the bis-pyrrole complex **1**-Zr(^{t}Bu$_4$biphenO$_2$), discussed above, likewise has an octahedral geometry with pyrrole rings in axial positions.

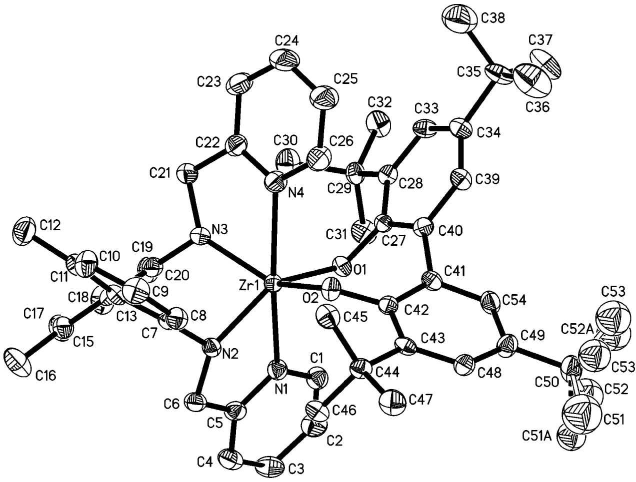


Figure 4. Molecular strucure of **2**-Zr(^{t}Bu$_4$biphenO$_2$). Thermal ellipsoids are at 50% probability, hydrogen atoms omitted for clarity.

Polymerization Studies. Complex **1**-ZrCl$_2$(THF) was found to catalyze, after activation with MAO, the polymerization of ethene (6.2 kg/mol·h·bar) and of propene (7.8 kg/mol·h·bar), under conditions that were not optimized (50 °C, 2 bar propene pressure, 20 bar ethene pressure, 5.8−20.8 μmol Zr, Al(MAO):Zr = 1000) (Table 3). The polypropene obtained with **1**-ZrCl$_2$(THF)/MAO was found to be partially isotactic with 55% mmmm pentads, in distinction to atactic polypropene obtained with a chiral zirconium complex containing a bidentate bianiline-diamido ligand.[14] After activation with [PhNMe$_2$H]$^+$[B(C$_6$F$_5$)$_4$]$^-$, complex **2**-Zr(CH$_2$Ph)$_2$

Table 3. Polymerization Results

complex	activator	monomer	activity[a]
1-$ZrCl_2(THF)$[b]	MAO	ethene	6.2
1-$ZrCl_2(THF)$[c]	MAO	propene	7.8
2-$Zr(CH_2Ph)_2$[d]	$[PhNMe_2H]^+[B(C_6F_5)_4]^-$	propene	0.4

[a] Given as kg polymer/[mol(catalyst)·h·bar]. [b] In toluene (100 mL) at 50 °C for 1 h, Al/Zr = 1000, *p*(ethene) = 20 bar. [c] In toluene (500 mL) at 50 °C for 2 h, Al/Zr = 1500, *p*(propene) = 2 bar. [d] In toluene (500 mL) at 50 °C for 2 h, anilinium borate/Zr = 1, *p*(propene) = 2 bar, Al(i-Bu)$_3$ added as scavanger.

catalyzed the polymerization of propene with rather low activity (0.44 kg/mol·h·bar). Complex **3**-$Zr(CH_2Ph)_2$, however, showed no propene polymerization activity at all when activated with $[PhNMe_2H]^+[B(C_6F_5)_4]^-$.[19]

The preliminary results presented above indicate that species of the type **1**- or **2**-Zr(pol)(olefin)$^+$ are generated in these reaction systems, in which the growing polymer chain and the olefin substrate occupy *cis*-coordination sites. This requires that the heterocyclic N ligands adopt a screw-like *trans*-orientation similar to that observed for **2**-Zr(^{t}Bu$_4$biphenO$_2$) and might thus be suitable to induce a preferential orientation of the last-inserted polymer-chain segment and/or the entering olefin substrate. This would explain the preference for isotactic enchainment observed in these reaction systems.

Molecular Modeling Studies. To investigate the accessibility of complex configurations with monodentate ligands in *cis*-position, we calculated the relative energies of *trans*-**2**-$ZrCl_2$ and of hypothetical *cis*-**2**-$ZrCl_2$ using molecular mechanics models (see Experimental Section). For our model complexes, the *cis*-configuration turned out to be less stable than the *trans*-configuration by only 4 kJ/mol. We thus conclude that isomerization into a *cis*-coordinated complex is a feasible process during polymerization with **2**-ZrX_2 as a precatalyst. For *cis*-**3**-$ZrCl_2$, on the other hand, we found a much greater energy difference of 23 kJ/mol relative to *trans*-**3**-$ZrCl_2$. One explanation for the lack of activity of **3**-$Zr(CH_2Ph)_2$ in polymerization might thus be that this complex is not able to adopt the *cis*-configuration required for the insertion reaction.

In further experimental and molecular modeling studies, we intend to investigate relative energies and interconversion rates for the *cis*- and *trans*-isomers of cationic complexes of the type (**2**,**3**)-Zr(alkyl)$^+$ as well as polymerization activities and polymer tacticities with respect to temperature, so as to corroborate the respective roles of alternative complex geometries in polymerization catalysis.

Experimental Section

General Comments. All reactions were performed under argon with Schlenk-line techniques or under N_2 in a glovebox. Solvents were dried prior to use by refluxing over and distillation from sodium (hydrocarbons), magnesium (alcohols), or calcium hydride (CH_2Cl_2). Deuterated solvents were dried over 4 Å molecular sieves and used without further purification. NMR spectra were recorded on Bruker AC 250 and DRX 600 spectrometers, ^{1}H NMR chemical shifts were calibrated by residual ^{1}H solvent peaks. Signals were assigned by HMQC and ROESY spectra. (3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate)$ZrCl_2(THF)_2$[17] and *N*,*N*′-(6,6′-dimethylbiphenyl-2,2′-diyl)diamine[20] were prepared according to literature procedures. $Zr(CH_2Ph)_4$ was obtained from MCAT GmbH (www.MCAT.de). All other chemicals were purchased from commercial suppliers and used without further purification.

***N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)bis(2-pyrrolemethyl)diimine (1H$_2$).** A solution of *N*,*N*′-(6,6′-dimethylbiphenyl-2,2′-diyl)diamine (1.0 g, 4.71 mmol), pyrrole-2-carboxaldehyde (0.90 g, 9.42 mmol), and HCOOH (0.25 mL) in methanol (40 mL) was stirred at room temperature for 1 h. Volatiles were evaporated, 30 mL of *n*-pentane added, and the reaction mixture stirred for another 12 h. The product, which precipitated in the form of a light red powder, was collected by filtration and washed with *n*-pentane to yield 1.46 g (85%) of **1**H$_2$ (mp 120 °C). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.97 (s, 6H, CH_3), 6.19 (m, 2H, pyrrole-CH), 6.50 (m, 2H, pyrrole-CH), 6.86 (m, 4H, NCC*H* and pyrrole-CH), 7.10 (d, $^3J = 7.5$ Hz, 2H, CH_3CCH), 7.24 (m, 2H, NCCHC*H*), 7.95 (s, 2H, N=CH) ppm. ^{1}H NMR (250 MHz, C_6D_6): δ 2.12 (s, 6H, CH_3), 6.04 (m, 4H, NHC*H*C*H*), 6.35 (m, 2H, NHCC*H*), 6.75 (d, $^3J = 7.7$ Hz, 2H, NCC*H*), 7.05 (d, $^3J = 7.2$ Hz, 2H, CH_3CCH), 7.16 (m, 2H, NCCHC*H*), 7.88 (s, 2H, N=CH) ppm. ^{13}C NMR (151 MHz, C_6D_6): 20.28 (*C*H$_3$), 110.11, 115.95, 116.59, 122.59, 126.86, 128.31, 133.54, 149.72, 152.06 ppm. Anal. Calcd for $C_{24}H_{22}N_4$ (366.44): C, 78.66; H, 6.05; N, 15.29. Found: C, 78.32; H, 6.04; N, 15.20.

***N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)bis(2-pyridylmethyl)diimine.** A solution of *N*,*N*′-(6,6′-dimethylbiphenyl-2,2′-diyl)diamine (6.03 g, 28.4 mmol) and pyridine-2-carboxaldehyde (5.40 mL, 6.08 g, 56.8 mmol) in ethanol (100 mL) was stirred at room temperature for 1 h. The volatiles were then evaporated, 100 mL of *n*-pentane was added, and the reaction mixture was stirred for another 12 h. During this time, a light yellow powder (mp 80 °C) precipitated, which was collected by filtration and washed with *n*-pentane. Yield: 10.1 g (91%). IR (KBr): ν 3053, 3014 (m, w, Ar-H), 2982, 2953, 2913, 2867 (w, m, m, w, C-H), 1632, 1585, 1567 (s, s, s, C=N, C=C), 1469, 1435 (s, s, C-H$_{def}$), 1219 (m), 993 (m) cm^{-1}. IR (PE): ν 597 (w), 590 (s), 580 (w), 570 (m), 549 (m), 530 (w), 520 (m), 475 (s), 440 (m), 404 (s), 381 (w), 368 (m), 316 (m), 260 (s), 241 (m) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.04 (s, 6H, CH_3), 6.92 (d, $^3J_{3/3'-4/4'}$ 7.7 Hz, 2H, 3-H/3′-H), 7.13 (d, $^3J_{5/5'-4/4'}$ 7.4 Hz, 2H, 5-H/5′-H), 7.22 (pt, $^3J_{5''-4''/6''}$ 5.8 Hz, 2H, 5″-H), 7.26 (pt, $^3J_{4/4'-3/3'/5/5'}$ 7.6 Hz, 2H, 4-H/4′-H), 7.59 (pt, $^3J_{4''-3''/5''}$ 7.4 Hz, 2H, 4″-H), 7.66 (d, $^3J_{3''-4''}$ 7.7 Hz, 2H, 3″-H), 8.37 (s, 2H, N=CH), 8.55 (d, $^3J_{6''-5''}$ 3.8 Hz, 2 H, 6″-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 19.87 (CH_3), 115.08 (C-3/C-3′), 121.32 (C-3″), 124.70 (C-5″), 127.36 (C-5/C-5′), 127.90 (C-4/C-4′), 132.64 (C-1/C-1′), 136.49 (C-4″), 137.10 (C-6/C-6′), 149.13 (C-6″), 149.73 (C-2/C-2′), 154.90 (s, C-2″), 159.52 (C=N) ppm. MS (EI, 70 eV): *m*/*z* 390 (100) [M$^+$], 312 (55) [$M^+ - C_5H_4N$], 285 (46) [312 − HCN], 208 (77) [$C_{14}H_{12}N_2^+$]. Anal. Calcd for $C_{26}H_{22}N_4$ (390.49 g/mol): C, 79.97; H, 5.68; N, 14.35. Found: C, 79.50; H, 5.75; N, 14.14.

***N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)bis[(6-methyl-2-pyridyl)methyl]diimine.** A solution of *N*,*N*′-(6,6′-dimethylbiphenyl-2,2′-diyl)diamine (3.50 g, 16.5 mmol) and 6-methylpyridine-2-carboxaldehyde (3.99 g, 32.9 mmol) in ethanol (60 mL) was stirred at room temperature for 1 h. Volatiles were evaporated, *n*-pentane was added, and the mixture was stirred for a further 12 h. The product, which precipitated as a white powder (mp 130 °C), was collected by filtration and washed with *n*-pentane. Yield: 6.15 g (89%). IR (KBr): ν 3058 (m, Ar-H), 2966, 2917 (m, m, C-H), 1649, 1627, 1590, 1569 (m, m, m, m, C=N, C=C), 1456 (m, C-H$_{def}$), 1218 (m) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.05 (s, 6H, 6-CH$_3$/6′-CH$_3$), 2.54 (s, 6 H, 6″-CH$_3$), 6.92 (d, $^3J_{3/3'-4/4'} = 7.8$ Hz, 2H, 3-H/3′-H), 7.10 (d, $^3J_{5''-4''} = 7.1$ Hz, 2H, 5″-H), 7.13 (d, $^3J_{5/5'-4/4'} = 7.5$ Hz, 2H,

---

(19) Since satisfactory elemental analyses were obtained for the catalyst precursors used, we can exclude that other complexes or starting materials, such as $ZrCl_4$ or $ZrCl_4(THF)_2$, were contributing to the observed polymerization catalysis.

(20) Kanoh, S.; Goka, S.; Murose, N.; Kubo, H.; Kondo, M.; Sugino, T.; Motoi, M.; Suda, H. *Polym. J.* **1987**, *19*, 1047.

5-H/5′-H), 7.26 (pt, $^3J_{4/4'-3/3'/5/5'} = 7.6$ Hz, 2H, 4-H/4′-H), 7.47 (d, $^3J_{3''-4''} = 7.4$ Hz, 2H, 3″-H), 7.49 (pt, $^3J_{4''-3''/5''}$ 7.5 Hz, 2H, 4″-H), 8.35 (s, 2H, N═CH) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 19.85 (6-CH_3/6′-CH_3), 24.21 (6″-CH_3), 114.95 (C-3/C-3′), 118.44 (C-3″), 124.30 (C-5″), 127.21 (C-5/C-5′), 127.84 (C-4/C-4′), 132.85 (C-1/C-1′), 136.66 (C-4″), 137.03 (C-6/C-6′), 149.92 (C-2/C-2′), 154.46 (C-2″), 157.74 (C-6″), 159.74 (C═N) ppm. MS (EI, 70 eV): *m/z* 418 (84) [M^+], 326 (29) [$M^+ - C_6H_6N$], 299 (56) [326 − HCN], 208 (100) [$C_{14}H_{12}N_2^+$]. Anal. Calcd for $C_{28}H_{26}N_4$ (418.54 g/mol): C, 80.35; H, 6.26; N, 13.39. Found: C, 80.03; H, 6.25; N, 13.38.

***N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)-*N*,*N*′-bis(2-pyridylmethyl)diamine (2H$_2$).** *N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)bis(2-pyridylmethyl)diimine (1.3 g, 3.33 mmol) was dissolved in toluene (20 mL) and transferred to a 30 mL autoclave. $Pd(OH)_2$ on charcoal (10 mg) was added as a catalyst, autoclave charged with 50 bar of H_2, and the reaction mixture stirred at 80 °C for 16 h. After venting the gases the mixture was filtered, the filtrate evaporated to dryness, and the residue dried in vacuo to yield a light yellow oil (1.24 g, 94%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.95 (s, 6H, CH_3), 4.39 (d, *J* 5.2 Hz, 4H, N-CH_2), 4.43 (t, *J* 5.5 Hz, 2H, NH), 6.47 (d, *J* 8.1 Hz, 2H, H-Ar), 6.69 (d, *J* 7.4 Hz, 2H, H-Ar), 7.10 (m, 4H, H-Ar), 7.23 (d, *J* 7.9 Hz, 2H, H-Ar) 7.49 (m, 2H, H-Ar), 8.44 (m, 2H, pyr-NC*H*) ppm. ^{1}H NMR (250 MHz, C_6D_6): δ 2.10 (s, 6H, CH_3), 4.14 (m, 4H, N-CH_2), 4.59 (m, 2H, NH), 6.52 (m, 2H, H-Ar), 6.56 (d, *J* 8.1 Hz, 2H, H-Ar), 6.79 (d, *J* 7.5 Hz, 2H, H-Ar), 6.95 (m, 2H, H-Ar) 7.13 (m, 4H, H-Ar), 8.34 (m, 2H, pyr-NC*H*) ppm. MS (FAB): *m/z* 395 (100) [$(M + H)^+$], 302 (31) [$M^+ - C_6H_6N$], 208 (18) [$C_{14}H_{12}N_2^+$]. Anal. Calcd for $C_{26}H_{26}N_4$ (394.51 g/mol): C, 79.15 H, 6.64; N, 14.21. Found: C, 77.44; H, 9.86; N, 13.75.

***N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)-*N*,*N*′-bis[(6-methyl-2-pyridyl)methyl]diamine (3H$_2$).** *N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)bis[(6-methyl-2-pyridyl)methyl]diimine (1.0 g, 2.39 mmol) was dissolved in toluene (20 mL) and transferred to a 30 mL autoclave. $Pd(OH)_2$ (10 mg) on charcoal was added as a catalyst, the autoclave charged with 10 bar of H_2, and the mixture stirred at 80 °C for 16 h. After venting the gases, the mixture was filtered, the filtrate evaporated to dryness, and the residue dried in vacuo to yield a colorless oil (0.95 g, 94%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 2.01 (s, 6H, bianiline-CH_3), 2.43 (s, 6H, pyridyl-CH_3), 4.35 (d, *J* = 5.5 Hz, 4H, N-CH_2), 4.69 (m, 2H, NH), 6.54 (d, *J* = 8.1 Hz, 2H, H-Ar), 6.74 (d, *J* = 7.6 Hz, 2H, H-Ar), 6.95 (d, *J* = 0.6 Hz, 2H, H-Ar), 7.03 (d, *J* = 7.6 Hz, 2H, H-Ar) 7.17 (m, 2H, H-Ar), 7.35 (m, 2H, H-Ar) ppm. ^{1}H NMR (250 MHz, C_6D_6): δ 2.15 (s, 6H, bianiline-CH_3), 2.31 (s, 6H, pyridyl-CH_3) 4.16 (m, 4H, N-CH_2), 4.86 (m, 2H, NH), 6.49 (d, *J* = 7.4 Hz, 2H, H-Ar), 6.64 (d, *J* = 8.1 Hz, 2H, H-Ar), 6.82 (m, 2H, H-Ar), 6.90 (m, 4H, H-Ar) 7.21 (m, 2H, H-Ar) ppm. MS (FAB): *m/z* 423 (98) [$(M + H)^+$], 316 (28) [$M^+ - C_7H_8N$], 208 (19) [$C_{14}H_{12}N_2^+$]. Anal. Calcd for $C_{26}H_{26}N_4$ (422.56 g/mol): C, 79.58; H, 7.16; N, 13.26. Found: C, 77.95; H, 7.52; N, 12.62.

[*N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)bis(2-pyrrolemethyl)diimine]Na$_2$ (1Na$_2$). A solution of **1**H$_2$ (2.7 g, 6.8 mmol) in THF (30 mL) was stirred with NaH (1.6 g, 67 mmol) at room temperature for 2 h and then filtered, the filtrate evaporated to dryness, and the residue dried in vacuo to yield a light yellow powder (2.6 g, 94%), which was used in the next step without purification. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.72 (s, 6H, CH_3), 1.80 (m, THF), 3.64 (m, THF), 6.32 and 6.36 (m, 4H, Ar-H), 6.77 (m, 4H, Ar-H), 6.89 (m, 2H, Ar-H), 8.20 (s, 2H, N═CH) ppm.

[*N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)bis(2-pyrrolemethyl)diimine]ZrCl$_2$(THF) (1-ZrCl$_2$(THF)). A solution of **1**Na$_2$ (0.52 g, 1.3 mmol) in THF (15 mL) was added to a stirred suspension of $ZrCl_4(THF)_2$ (0.48 g, 1.3 mmol) in THF (20 mL) at −78 °C. The reaction mixture was allowed to reach room temperature and stirred for another 20 h. The resulting dark red solution was evaporated to dryness, the solid residue washed with toluene and extracted with CH_2Cl_2, the filtrate evaporated, and the remaining yellow powder dried in vacuo. Yield: 0.38 g (50%). Crystals for X-ray diffraction were obtained by slow evaporation of a toluene solution at room temperature. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 1.99 (m, THF), 2.07 (s, 6H, CH_3), 4.13 (b, 4H, THF) 6.27 (s, 2H, pyrrole-NCHC*H*), 6.79 (s, 2H, pyrrole-NCC*H*), 7.14 (d, ^3J = 7.5 Hz, 2H, bianiline-NCC*H*), 7.23 (m, 2H, CH_3CC*H*), 7.23−7.29 (m, 2H H-Ar) 7.28 (m, 2H, bianiline-CHC*H*CH), 7.91 (s, 2H, N═CH) ppm. ^{13}C NMR (151 MHz, CD_2Cl_2): δ 19.6 (s, *C*H_3), 20.1, 26.2 (s, THF), 73.4 (b, THF), 114.0 (s, pyrrole-NCHC*H*), 121.5 (s, pyrrole-NC*C*H), 124.5 (s, bianiline-NC*C*H), 125.6, 128.3 (s, bianiline-CHC*H*CH), 128.5, 129.3 (s, bianiline-CH_3CC*H*), 132.3 (s, bianiline-NC*C*), 138.4, 139.7, 160.6 (s, C═N) ppm. Anal. Calcd for $C_{28}H_{28}Cl_2N_4OZr$ (598.66 g/mol): C, 56.17; H, 4.71; N, 9.36. Found: C, 55.86; H, 4.73; N, 9.23.

***N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)bis(2-pyrrolemethyl)diimine-Zr(3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate) (1-Zr(^{t}Bu$_4$biphenO$_2$)).** THF (30 mL) was added to a mixture of **1**Na$_2$ (0.30 g, 0.74 mmol) and (3,3′,5,5′-^{t}Bu$_4$-1,1′-bi-2-phenolate)-$ZrCl_2(THF)_2$ (0.53 g, 0.74 mmol) at −50 °C. The yellowish mixture was stirred at room temperature for 16 h, after which the volatiles were evaporated in vacuo and the residue extracted with CH_2Cl_2. The red extract was filtered and evaporated to dryness and the solid residue dried in vacuo to yield a yellow powder (0.48 g, 78%). ^{1}H NMR (600 MHz, C_6D_6): δ 1.30 (s, 18H, 5,5′-^{t}Bu), 1.62 (s, 18H, 3,3′-^{t}Bu), 1.92 (s, 6H, bianiline-CH_3), 5.91 (s, 2H, pyrrole-NCHC*H*), 6.26 (d, *J* 3.2 Hz, 2H, pyrrole-NCC*H*), 6.75 (m, 4H, bianiline-CH_3-CC*H*C*H*), 6.84 (s, 2H, *H*C═N), 7.18 (b, 2H, bianiline-NCC*H*), 7.27 (s, 2H, pyrrole-NC*H*), 7.37 (d, *J* 1.9 Hz, 2H, biphenolat-6,6′H-Ar) 7.49 (d, *J* 1.6 Hz, 2H, biphenolat-4,4′H-Ar) ppm. ^{13}C NMR (151 MHz, C_6D_6): δ 20.08, 25.6, 29.9, 30.8, 31.8, 34.4, 35.7, 67.8, 110.0, 114.0 (s, pyrrole-NCHC*H*), 121.4 (s, bianiline-NCC*H*), 121.9 (s, pyrrole-NC*C*H), 123.6 (biphenolate-4,4′C-Ar), 128.4 (bianiline-CH_3CHC*H*), 129.6 (biphenolate-6,6′C-Ar), 130.6, 132.4, 135.7, 138.5 (d), 142.5 142.8 (d, pyrrole-N*C*H), 147.6, 155.2, 161.8 (s, C═N) ppm. Anal. Calcd for $C_{52}H_{60}N_4O_2Zr$ (864.26 g/mol): C, 72.26; H, 7.00; N, 6.48. Found: C, 71.63; H, 7.55; N, 6.28.

***N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)-*N*,*N*′-bis(2-pyridylmethyl)diamido-Zr(CH$_2$Ph)$_2$ (2-Zr(CH$_2$Ph)$_2$).** A solution of **2**H$_2$ (0.40 g, 1.01 mmol) in hexane/toluene (13 + 5 mL) was added to a suspension of $Zr(CH_2Ph)_4$ (0.46 g, 1.01 mmol) in hexane (15 mL) at room temperature. The reaction mixture was stirred in the dark for 48 h, during which a yellow precipitate was formed. This was collected by filtration, washed three times with hexane (5 mL), and dried in vacuo. Yield: 0.35 g (52%). ^{1}H NMR (600 MHz, C_6D_6): δ 2.07 (d, *J* = 9.4 Hz, 2H, ZrCH_AH_B), 2.28 (s, 6H, CH_3), 2.39 (d, *J* = 9.4 Hz, 2H, ZrCH_AH_B), 4.42 (d, *J* 18.8 Hz, 2H, NCH_AH_B), 4.70 (d, *J* = 18.8 Hz, 2H, NCH_AH_B), 6.43 (m, 4H, ZrCH_2CC*H*), 6.45 (m, 2H, pyridine-NCC*H*), 6.64 (m, 4H, ZrCH_2Ph-*para-H* and pyridine-NCHC*H*), 6.86 (m, 4H, ZrCH_2Ph-*meta-H*), 6.91 (m, 2H, pyridine-*para-H*), 6.99 (m, 2H, bianiline-NCC*H*), 7.01 (m, 2H, bianiline-CH_3CC*H*), 7.23 (m, 2H, bianiline-NCCHC*H*), 8.40 (b, 2H, pyridine-NC*H*) ppm. ^{13}C NMR (151 MHz, C_6D_6): δ 20.9 (CH_3), 64.7 (N-CH_2), 66.2 (Zr-CH_2), 119.5 and 121.3 (ZrCH_2-Ph-*para-C* and pyridine-NCH*C*H), 120.9 (pyridine-NC*C*H), 121.1 (bianiline-NCC*H*), 123.9 (bianiline-CH_3C*C*H), 125.7 (ZrCH_2C*C*H), 127.5 (ZrCH_2Ph-*meta-C*), 127.6 (bianiline-NCCH*C*H), 129.3, 136.5 (pyridine-*para-C*), 136.8, 146.9 (pyridine-N*C*H), 149.9, 153.0, 165.1 ppm. Anal. Calcd for $C_{40}H_{38}N_4Zr$ (665.96 g/mol): C, 72.10; H, 5.75; N, 8.41. Found: C, 71.74; H, 5.77; N, 8.41.

***N*,*N*′-(6,6′-Dimethylbiphenyl-2,2′-diyl)-*N*,*N*′-bis[(6-methyl-2-pyridyl)methyl]diamido-Zr(CH$_2$Ph)$_2$ (3-Zr(CH$_2$Ph)$_2$).** This complex was prepared in the same manner as **2**-Zr(CH_2-Ph)$_2$ except that only hexane was used as solvent. Yield: 0.60 g, 72%. ^{1}H NMR (600 MHz, C_6D_6): δ 2.09 (d, *J* 9.2 Hz, 2H, ZrCH_AH_B), 2.28 (s, 6H, bianiline-CH_3), 2.53 (d, *J* = 9.2 Hz,

Table 4. Details of the Crystal Structure Determinations

	1-$ZrCl_2(THF)$	**2**-$Zr(^tBu_4biphenO_2)\cdot$ 0.5 $NHMe_2$	**3**-$ZrCl_2\cdot$toluene	**3**-$Zr(CH_2Ph)_2$
CCSD no.	228862	228865	228863	228864
formula	$C_{28}H_{28}Cl_2N_4OZr$	$C_{54}H_{64}N_4O_2Zr\cdot(C_2H_7N)_{0.5}$	$C_{28}H_{28}Cl_2N_4Zr\cdot C_7H_8$	$C_{42}H_{42}N_4Zr$
fw	598.66	914.85	674.80	694.02
temperature (K)	153	173(2)	173(2)	173(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$
unit cell a (Å)	16.754(3)	35.332(1)	10.7740(9)	17.6380(14)
b (Å)	13.906(3)	12.226(1)	12.3440(11)	13.8130(18)
c (Å)	12.633(3)	23.289(1)	12.7330(11)	15.9220(8)
α (deg)	90	90	106.110(6)	90
β (deg)	117.23(3)	92.950(1)	94.849(7)	116.330(6)
γ (deg)	90	90	95.488(7)	90
V ($Å^3$); Z	2617.2(9); 4	10046.8(11); 8	1608.5(2); 2	3476.7(6); 4
d_{calcd} (g/cm^3)	1.519	1.210	1.393	1.326
μ (mm^{-1}), $F(000)$	0.654; 1224	0.263; 3880	0.538; 696	0.352; 1448
cryst size (mm)	0. 5 × 0.1 × 0.1	0.24 × 0.2 × 0.2	0.1 × 0.1 × 0.1	0.2 × 0.2 × 0.15
θ range (deg)	2.00 to 25.02	5.02 to 27.51	5.03 to 27.50	5.00 to 27.50
no. of reflns collected/unique	4732/2295 [$R(int) = 0.0466$]	37 895/11 406 [$R(int) = 0.0961$]	17 704/5668 [$R(int) = 0.0659$]	36 747/7921 [$R(int) = 0.0687$]
T_{max}, T_{min}	0.940, 0.845[b]	0.949, 0.940[a]	0.948, 0.948[a]	0.949, 0.933[a]
no. of data/restraints/params	2295/0/164	11 406/36/565	5668/0/379	7921/0/424
GoF(F^2)	1.030	1.017	0.995	1.028
final R indices [$I > 2\sigma(I)$]	R1 = 0.0314, wR2 = 0.0692	R1 = 0.0636, wR2 = 0.1295	R1 = 0.0504, wR2 = 0.1003	R1 = 0.0452, wR2 = 0.0974
R indices (all data)	R1 = 0.0573, wR2 = 0.0765	R1 = 0.1389, wR2 = 0.1530	R1 = 0.0982, wR2 = 0.1203	R1 = 0.0856, wR2 = 0.1103
largest diff peak (e $Å^{-3}$)	0.375	0.753	0.572	0.507

[a] Absorption correction semiempirical from equivalents. [b] Absorption correction using psi-scan data.

2H, $ZrCH_AH_B$), 2.60 (s, 6H, pyridine-CH_3), 4.47 (d, J = 22.4 Hz, 2H, NCH_AH_B), 4.58 (d, J = 18.8 Hz, 2H, NCH_AH_B), 6.03 (m, 4H, $ZrCH_2CCH$), 6.24 (m, 2H, pyridine-NCC*H*), 6.42 (m, 2H, pyridine-CH_3CCH), 6.51 (m, 2H, $ZrCH_2Ph$-*para-H*), 6.66 (m, 4H, $ZrCH_2Ph$-*meta-H*), 6.81 (m, 2H, pyridine-*para-H*), 6.93 (m, 2H, bianiline-NCC*H*), 7.01 (m, 2H, bianiline-CH_3CCH), 7.18 (m, 2H, bianiline-NCCHC*H*) ppm. ^{13}C NMR (151 MHz, C_6D_6): δ 20.9 (bianiline-CH_3), 25.3 (pyridine-CH_3), 61.7 (Zr-CH_2), 67.2 (N-CH_2), 118.7 (pyridine-CH_2CCH), 119.3 ($ZrCH_2Ph$-*para-C*), 122.4 (pyridine-CH_3CCH), 122.7 (bianiline-NCC*H*), 124.2 (bianiline-CH_3CCH), 125.0 ($ZrCH_2CCH$), 127.5 ($ZrCH_2Ph$-*meta-C*), 127.8 (bianiline-NCCHC*H*), 134.3, 136.4, 136.9 (pyridine-*para-C*), 149.6, 155.7, 156.2, 163.6 ppm. Anal. Calcd for $C_{42}H_{42}N_4Zr$ (694.02 g/mol): C, 72.68; H, 6.10; N, 8.07. Found: C, 72.28; H, 6.26; N, 8.43.

***N,N′*-(6,6′-Dimethylbiphenyl-2,2′-diyl)-*N,N′*-bis[(6-methyl-2-pyridyl)methyl]diamido-$ZrCl_2$ (3-$ZrCl_2$).** A solution of ligand **3**H_2 (0.56 g, 1.3 mmol) in hexane (20 mL) was stirred with excess CaH_2 at room temperature for 0.5 h and filtered. N-BuLi (2.7 mmol) was added dropwise to the filtrate at 0 °C. The reaction mixture was stirred at room temperature for 5 h, diluted with 4 mL of THF, and added to a suspension of $ZrCl_4$ (0.3 g, 1.3 mmol) in toluene (20 mL). The reaction mixture was stirred at room temperature for 20 h and evaporated and the residue extracted with toluene. Only a few milligrams of yellow crystals were obtained from the toluene filtrate, which were subjected to X-ray crystallography. As judged from ^1H NMR, further extraction of the solid evaporation residue with CH_2Cl_2 yielded an inseparable mixture of products.

***N,N′*-(6,6′-Dimethylbiphenyl-2,2′-diyl)-*N,N′*-bis(2-pyridylmethyl)diamido-Zr(3,3′,5,5′-$^tBu_4$-1,1′-bi-2-phenolate) (2-Zr($^tBu_4biphenO_2$)).** 3,3′,5,5′-$^tBu_4$-1,1′-bi-2-phenol (0.39 g, 0.9 mmol) was added to a solution of $Zr(NMe)_4$ (0.25 g, 0.9 mmol) in toluene (20 mL), and the reaction mixture was stirred at room temperature for 20 h.The volatiles were evaporated, and the residue was dried in vacuo for 6 h. Without further purifications, the (3,3′,5,5′-$^tBu_4$-1,1′-bi-2-phenolate)$Zr(NMe_2)_2$ (**4**) thus obtained was dissolved in toluene (5 mL) and a toluene solution of ligand 2H_2 was added. The solution was stirred for 48 h at room temperature and refluxed for 2 h followed by evaporation to dryness. Judging from its ^1H NMR, the solid residue appeared to be a mixture of products. Recrystallization from toluene yielded only a few milligrams of crystalline **2**-Zr($^tBu_4biphenO_2$), which was identified by X-ray crystallography.

Crystal Structure Determinations. Single crystals of **3**-$Zr(CH_2Ph)_2$, **3**-$ZrCl_2$, and **2**-Zr($^tBu_4biphenO_2$) were selected for the X-ray measurements and mounted on a glass fiber using the oil drop method. Data were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation (71.073 pm) and a graphite monochromator. Data for **1**-$ZrCl_2(THF)$ were collected on a Enraf Nonius CAD4 four-circle diffractometer. The structures were solved by direct methods. All nonhydrogen atoms were refined anisotropically.[21] Hydrogen atoms were introduced at calculated positions and refined with fixed geometry with respect to their carrier atoms. Cell parameters and the specific data collection parameters are summarized in Table 4.

Molecular Modeling Calculations. All calculations were done using the MM+ force field in the Hyperchem 5.0 program package. The geometry of the ZrN_4 fragment was imported from the crystal structures of **3**-$ZrCl_2$ and **2**-Zr($^tBu_4biphenO_2$), respectively. The ZrN_4 fragment was kept frozen while the geometry of the remaining atoms, including the chloride atoms, was optimized. Energy differences for *cis*- and *trans*-coordinations were determined from single-point calculations, in which all interactions with zirconium were neglected.

Polymerization of Propene with 1-$ZrCl_2$(THF)/MAO. In a Büchi 1 L autoclave, 500 mL of toluene containing 2.75 mL (4.4 mmol) of methylaluminoxane (MAO, Witco, 1.6 M solution in toluene, 5.2 mass % Al, molar mass ca. 800) was saturated with propene (2 bar at 50 °C). In a Schlenk tube, complex **1**-$ZrCl_2(THF)$ (3.5 mg, 5.8 μmol) was stirred in 15 mL of toluene and 2.75 mL (4.4 mmol) of MAO for 15 min, after which it was transferred to the autoclave. During the polymerization reaction, the total pressure was kept constant at

---

(21) Sheldrick, G. M. *SHELXTL*; University of Göttingen: Germany, 1990, 1997. Sheldrick, G. M. *SADABS*; University of Göttingen: Germany, 1996. Sheldrick, G. M. *SHELX97*; University of Göttingen: Germany, 1997.

2 bar by further addition of propene. After 2 h, the autoclave was vented and the reaction mixture drained into 1 L of methanol acidified with 10 mL of concentrated aqueous HCl. The precipitated polymer was collected by filtration, washed with methanol, and dried at 50 °C to constant weight. Yield: 180 mg of a white powder, corresponding to an activity of 7.76 kg(polymer)/(mol(cat)·h·bar). Polymer ^{13}C NMR spectra were measured in $C_2D_2Cl_4$ (δ 74.1 ppm) at 120 °C on a 600 MHz spectrometer. Comparing the integral of the CH_3 resonance at δ 21.65 (365.5) to the sum of integrals of all CH_3 resonances at δ 19.59−21.65 (662.9) ppm gives 55% [mmmm] as a measure of isotacticity of the polymer.

Polymerization of Propene with 2-Zr(CH_2Ph)$_2$/[PhNMe$_2$H]-[B(C_6F_5)$_4$]. In a Büchi 1 L autoclave 500 mL of toluene was saturated with propene (2 bar) and 11.3 mL (11.3 mmol) of Al(*i*-Bu)$_3$ was added at 50 °C. In a Schlenk flask, complex **2**-Zr(CH_2Ph)$_2$ (7.5 mg, 11.3 μmol) in 15 mL of toluene was mixed with 3.75 mL (11.3 μmol) of a 4 mM solution of [PhNMe$_2$H]-[B(C_6F_5)$_4$] in toluene and transferred to the autoclave. The reaction then proceeded as described above to yield 20 mg of polypropene as a white powder, corresponding to an activity of 0.44 kg(polymer)/(mol(cat)·h·bar).

Polymerization of Ethene with 1-ZrCl$_2$(THF)/MAO. Complex **1**-ZrCl$_2$(THF)/MAO (11.1 mg, 21.07 μmol) and 6.5 mL (10.4 mmol) of methylaluminoxane MAO (1.6 M) were stirred in a Schlenk tube with 3.5 mL of toluene for 5 min and then added to a 100 mL autoclave which already contained 38 mL toluene and another 6.5 mL of MAO. The autoclave was preheated to 45 °C, charged with ethylene (20 bar), and stirred for 1 h. The autoclave was then vented and the reaction mixture quenched by pouring it into 150 mL of a MeOH/HCl solution. The white precipitate was filtered, washed with MeOH, and dried at 60 °C to yield 2.6 g of polyethylene, corresponding to an activity of 6.17 kg(polymer)/(mol(cat)·h·bar).

Acknowledgment. Financial support from the foundation of Fortum Oy (for M.K.) and from BASELL GMBH is gratefully acknowledged. We thank Ms. Anke Friemel for 2D NMR measurements.

Supporting Information Available: Details of the crystal structure determinations are available free of charge via the Internet at http://pubs.acs.org.

OM040011R