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Zirconium Chelates of a Bulky Ferrocene-Based Diamido Ligand

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Summary: The arylamino-substituted ferrocene derivative $\{Fe[C_5H_4(NH\text{-}2,4,6\text{-}iPr_3\text{-}C_6H_2)]_2\}$ *(**1b**) reacts with* $Zr(CH_2Ph)_4$ *and* $Zr(NMe_2)_4$ *to afford the respective zirconium chelates* $[(PhCH_2)_2Zr\{Fe[C_5H_4(N\text{-}2,4,6\text{-}iPr_3\text{-}C_6H_2)]_2\}]$ *(**2**) and* $[(Me_2N)_2Zr\{Fe[C_5H_4(N\text{-}iPr_3\text{-}2,4,6\text{-}C_6H_2)]_2\}]$ *(**3**), which exhibit unexpectedly low catalytic activity in the polymerization of ethylene after activation with MAO and* $[Ph_3C][B(C_6F_5)_4]$*, respectively. In order to elucidate stereoelectronic effects of the bulky aryl substituents, the structures of **2** and **3** and of their parent ferrocene derivative **1b** have been determined as well as that of the phenylamino analogue* $\{Fe[C_5H_4(NHPh)]_2\}$ *(**1a**), for which an improved synthesis has been developed.*

Introduction

Transition metal chelates containing the ferrocene-based diamido ligand framework $Fe[C_5H_4(NR)]_2^{2-}$ are of great current interest.[1] This is in part due to the relevance of diamido chelates for α-olefin polymerization.[2] Compounds containing aryl groups (R = Ph,[3] 2,6-Me_2-C_6H_3,[3a] 2,6-Cl_2-C_6H_3,[4] 2,4,6-Me_3-C_6H_2,[4] 2,4,6-*i*Pr_3-C_6H_2[3a]) have received particular attention in this context. In fact, Shafir and Arnold have published encouraging results concerning α-olefin polymerization utilizing the zirconium chelate $[(CH_2Ph)_2Zr\{Fe[C_5H_4(N\text{-}2,4,6\text{-}C_6H_2Me_3)]_2\}]$ as precatalyst.[4] Activation of this complex with $[Ph_3C][B(C_6F_5)_4]$ afforded an active catalyst for the polymerization of 1-hexene. We have previously described[3b] zirconium chelates based on the phenylamido system $Fe[C_5H_4(NR)]_2^{2-}$ and here report on related compounds containing bulkier aryl groups.

Results and Discussion

The parent di(arylamino)ferrocenes $\{Fe[C_5H_4(NHPh)]_2\}$ (**1a**) and $\{Fe[C_5H_4(NH\text{-}2,4,6\text{-}iPr_3\text{-}C_6H_2)]_2\}$ (**1b**) served as starting materials in our study.[3] **1a** had previously been synthesized in 50% overall yield by a two-step sequence involving an Ullmann reaction of 1,1′-dibromoferrocene with *N*-phenylacetamide and subsequent saponification of the amide.[3a] We have now utilized the less tedious one-step procedure based on a Hartwig-Buchwald type cross-coupling reaction of 1,1′-diaminoferrocene with phenyl bromide, which affords **1a** in 74% yield. The crystal structures of **1a** (Figure 1) and **1b** (Figure 2) have been determined by single-crystal X-ray diffraction.

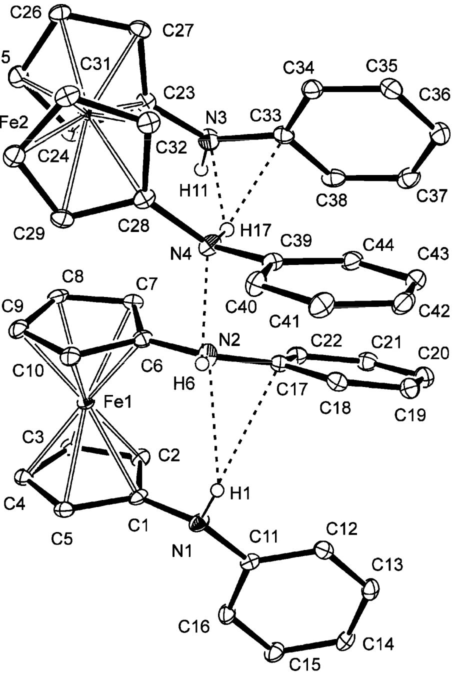

Figure 1. View of the asymmetric unit of **1a** in the crystal (bottom: species A, top: species B; ORTEP diagram with 30% probability ellipsoids and atom-numbering scheme). H atoms not involved in hydrogen bonding are omitted for clarity.

In the case of the phenylamino-substituted derivative **1a** two independent molecules are present in the unit cell, which both exhibit an intramolecular hydrogen bond, which is most likely responsible for the eclipsed orientation of the cyclopentadienyl rings. This hydrogen bond involves hydrogen atom H1 in species A and hydrogen atom H17 in species B. Since both species exhibit very similar bond parameters, only species A will be discussed here. The experimentally determined distance of 0.80 Å between H1 and N1 is considerably shorter than the sum of the covalent radii (1.01 Å), which indicates that a detailed discussion of this hydrogen bond is fraught with problems. These limitations notwithstanding, it is quite evident that the amine moiety which acts as the hydrogen bond donor is pyramidal (sum of angles around N1 342°), whereas that containing N2 is trigonal planar (sum of angles 360°). For comparison, we note that the sum of bond angles around the N atom of diphenylamine is close to 359° in the single crystal[5] and 353° in the gas phase.[6] The hybridization of N2 is sp^2, whereas that of N1 is intermediate between sp^2 (sum of angles 360°) and sp^3 (sum of angles 328.5°). The p-type lone pair of N2 is in conjugation with the π-system of the phenyl group attached to this atom, the C6−

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[1] Reviews: (a) Siemeling, U.; Auch, T.-C. *Chem. Soc. Rev.* **2005**, *34*, 584−594. (b) Herberhold, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 956−958.

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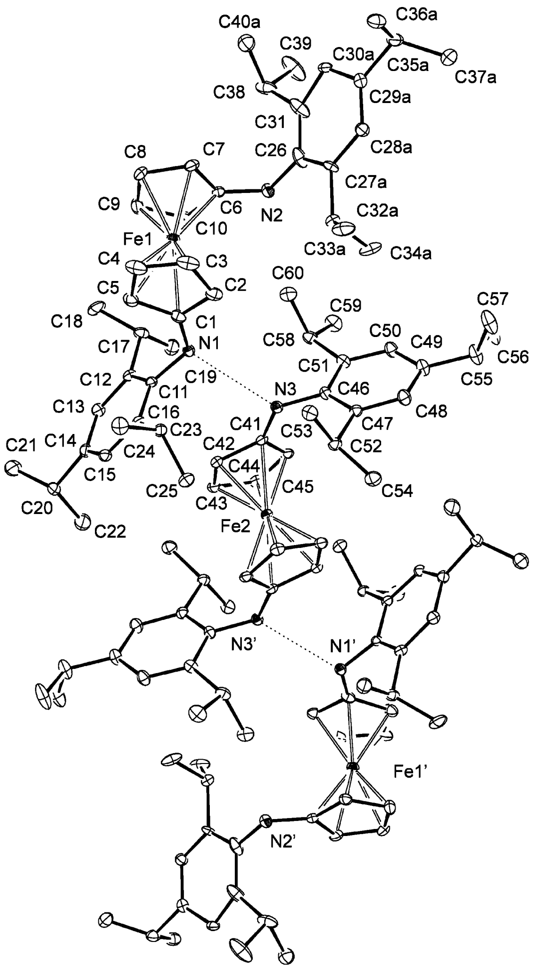
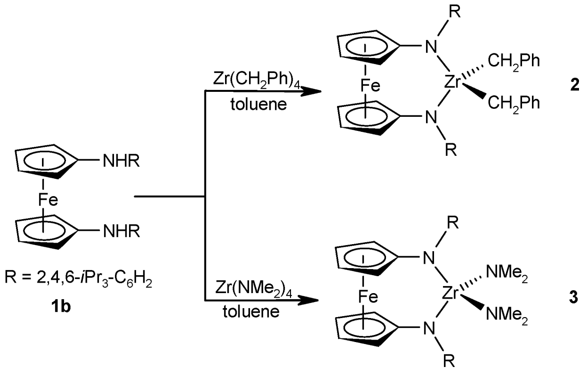


Figure 2. View of a trimeric unit of **1b** in the crystal (ORTEP diagram with 30% probability ellipsoids and atom-numbering scheme). H atoms are omitted for clarity. Atoms labeled with "a" represent one of two possible split positions.

N2−C17−C18 torsion angle being 179.9°. The N2−C17 bond length is 1.398(2) Å, which is shorter than the value of 1.412(2) Å observed for N1−C11. This small but significant difference can be explained by the n−π interaction just described. The intramolecular hydrogen bond can be classified as weak by applying commonly accepted criteria.[7] The distance between N1 and the hydrogen bond acceptor atom is 3.382 Å for N2 and 3.402 Å for C17, the hydrogen bond angle at H1 being 149.2° and 158.9°, respectively. The distance between H1 and the acceptor atom, as determined from X-ray crystallographic data, is 2.65 Å for N2 and 2.62 Å for C17. These values are most likely systematically overestimated by the experimental method (vide supra). The sum of the estimated van der Waals radii is 2.8 Å for H and N and 2.9 Å for H and C.[8] In view of the two acceptor atoms the hydrogen bond can in principle be classified as bifurcated. However, a more suitable description is that of an N−H π-hydrogen bond,[9] since the acceptor electron density resides in a delocalized π-orbital.[10] Such interactions are well documented for organometallic crystals.[11] The structural role of the hydrogen bond acceptor atom N2 is not unequivocal. It seems to drag H1 away from the acceptor atom C17. However, this H atom is still pointing toward this C atom, although its projection on the C_6 ring plane lies outside the C_6 ring. According to a recent database analysis, such a structural arrangement generally is the most common one for N−H···phenyl interactions and therefore need not be due to the H1···N2 interaction.[12]

Scheme 1



In addition to the intramolecular hydrogen bond present in species A and B, these molecules are linked together through intermolecular hydrogen bonds, giving rise to $(AB)_\infty$ chains. The intermolecular hydrogen bond present within the asymmetric unit (Figure 1) is slightly shorter than the intramolecular ones (N2···N4 3.312 Å vs N1···N2 3.382 Å and N3···N4 3.446 Å), whereas the hydrogen bond that interconnects the asymmetric units is the longest one (N1···N3 3.521 Å).

The unit cell of **1b** contains two crystallographically independent molecules (species A and B). Owing to the steric bulk of the arylamino substituents, intramolecular hydrogen bonding does not occur. Instead, aggregation through intermolecular hydrogen bridges is observed, leading to the formation of a trimolecular ABA assembly. The hydrogen bonds show an N···N separation of 3.243 Å. Species A exhibits essentially eclipsed cyclopentadienyl ligands with a synclinal arrangement of the two arylamino substituents. Species B is centrosymmetric and has a crystallographically imposed staggered orientation of the cyclopentadienyl rings with diametrically opposed substituents. Species A can be viewed as being an integral part of the substituent attached to each cyclopentadienyl ring of species B, which thus contains two extremely bulky substituents. Consequently, the fully staggered conformation observed for B is the most favorable one. This has been observed before for very bulky 1,1′-disubstituted ferrocene derivatives,[13] including, inter alia, the trinuclear compound $[\{[CpFe(C_5H_4SiMe_2)]C_5H_4\}_2Fe]$.[13a]

Metathesis of **1b** with $Zr(CH_2Ph)_4$ and $Zr(NMe_2)_4$ afforded the respective zirconium chelates $[(PhCH_2)_2Zr\{Fe[C_5H_4(N\text{-}2,4,6\text{-}i\text{Pr}_3\text{-}C_6H_2)]_2\}]$ (**2**) and $[(Me_2N)_2Zr\{Fe[C_5H_4(N\text{-}i\text{Pr}_3\text{-}2,4,6\text{-}C_6H_2)]_2\}]$ (**3**) (Scheme 1). When the reactions were performed in a sealed NMR tube in C_6D_6, they both proved to be sluggish at room temperature, affording **2** and **3** in essentially quantitative yield only after two and three weeks, respectively. At higher temperatures, some decomposition occurred, leading to para-

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[7] See, for example: (a) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: Sausalito, CA, 2006; pp 168−180. (b) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, 1997.

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[9] Seminal paper: Drew, M. G. B.; Willey, G. R. *J. Chem. Soc., Perkin Trans. 2* **1986**, 215−220.

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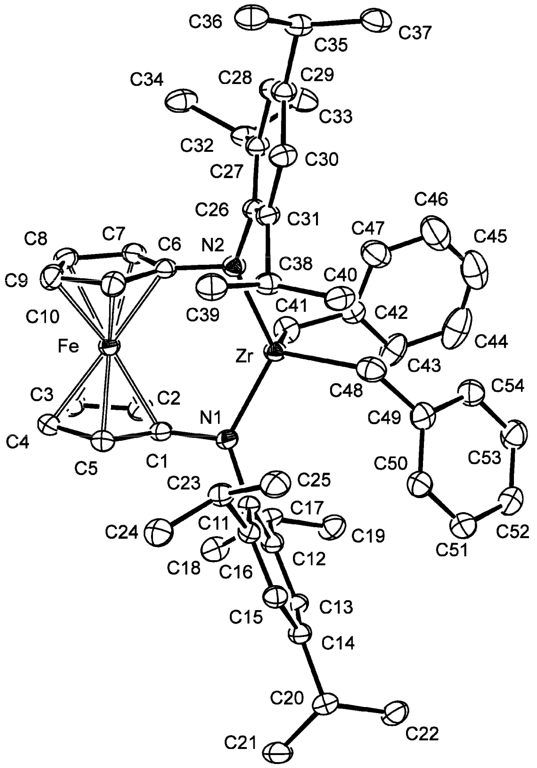

Figure 3. Molecular structure of **2** in the crystal (ORTEP diagram with 30% probability ellipsoids and atom-numbering scheme). H atoms are omitted for clarity.

magnetic broadening of ^{1}H NMR resonance signals. Preparative-scale reactions were therefore exclusively performed at room temperature. Owing to its high solubility, the benzyl derivative **2** could be isolated only in 55% yield, whereas an isolated yield of 85% was achieved in the case of **3**. Both compounds were obtained as yellow solids.

We have determined the crystal structures of **2** (Figure 3) and **3** (Figure 4) by single-crystal X-ray diffraction. Pertinent bond parameters are collected in Table 1 for both compounds.

Both compounds contain a relatively unstrained six-membered chelate ring, the two chelating nitrogen atoms being connected by a C−Fe−C bridge. Alternatively, **2** and **3** can be viewed as [3]ferrocenophanes. Their cyclopentadienyl rings are in an eclipsed orientation in each case, and their ring planes are slightly tilted (Table 1), with the ferrocene unit opening up toward the Zr atom. The iron−zirconium distance is well above the sum of the estimated van der Waals radii in each case, precluding any bonding interaction between these atoms. The coordination of the zirconium atom can be described as distorted tetrahedral in each case. The chelating N atoms are sp^2 hybridized (sum of angles between 359.5° and 360.0°). The same holds true for the NMe$_2$ nitrogen atoms present in **3**, whose bonding environment is trigonal planar, too (sum of angles 359.9°). The NMe$_2$ groups exhibit an essentially perpendicular orientation to one another, which minimizes steric repulsions between them. The best planes of the aryl groups present in **2** and **3** are in a perpendicular orientation with respect to the bonding plane of the N atoms of the chelate ring. This arrangement is certainly due to the steric bulk of these aryl groups, which do not show rotation around the N−C$_{\text{ipso}}$ bond in solution according to NMR spectroscopic results. The methyl groups of the *ortho*-*i*Pr units are diastereotopic and give rise to two resonance signals in the ^{13}C{^{1}H} NMR spectrum. This is similar to the behavior observed for the related [(Me$_2$N)$_2$Zr{C$_3$H$_6$(N-*i*Pr$_2$-2,6-C$_6$H$_3$)$_2$}],[14] which also contains a three-atom bridge connecting the chelating nitrogen atoms.

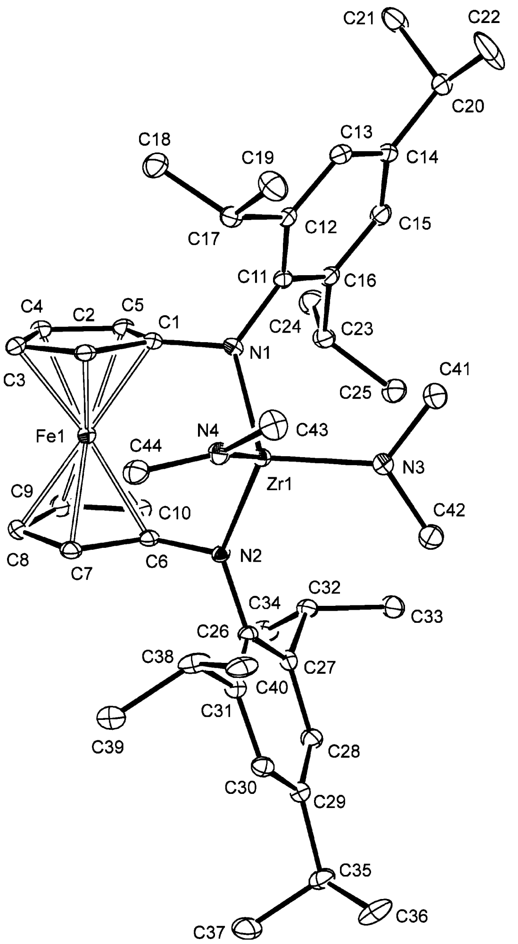

Figure 4. Molecular structure of **3** in the crystal (ORTEP diagram with 30% probability ellipsoids and atom-numbering scheme). H atoms are omitted for clarity. Atoms C39 and C40 represent one of two possible split positions.

Table 1. Selected Bond Parameters for 2 and 3

compound	chelate bite angle at Zr	Zr−N (chelate)	X−Zr−X	Zr−X	cyclo-pentadienyl ring tilt angle
2	121.78(8)°	2.0523(19) Å	112.94(11)°	2.292(3) Å	5.9(2)°
(X = *C*H$_2$Ph)		2.063(2) Å		2.224(3) Å	
3	116.02(14)°	2.081(3) Å	104.68(15)°	2.030(4) Å	6.4(3)°
(X = *N*Me$_2$)		2.066(3) Å		2.082(4) Å	

A close relative of **2** is the silylamido complex [(PhCH$_2$)$_2$-Zr{Fe[C$_5$H$_4$(NSiMe$_3$)]$_2$}].[15] Both compounds differ noticeably in their bond angles around the zirconium atom. The chelate bite angle of **2** is 121.78(8)°, whereas that of its silylamido counterpart is 138.6(1)°. The C−Zr−C angle of **2** is 112.94(11)°, whereas that of the silylamido complex is 97.3(2)°.

It is instructive to compare the products of the reaction of Zr(NMe$_2$)$_4$ with **1b** and the less bulky **1a**. The latter reaction affords [(HNMe$_2$)(Me$_2$N)$_2$Zr{Fe[C$_5$H$_4$(NPh)]$_2$}] (**4**).[3b] In contrast to **3**, chelate **4** contains a pentacoordinate Zr atom, whose coordination is best described as distorted trigonal bipyramidal.[3b] This is due to coordination of a molecule of dimethylamine, which is liberated as the second product in the metathesis reaction. A similar result has been reported for the reaction of Zr(NMe$_2$)$_4$ with the N,N′-disilylated 1,8-diaminonaphthalene 1,8-(Me$_3$SiHN)$_2$C$_{10}$H$_6$,[16] which also contains a three-atom bridge connecting the chelating nitrogen atoms. The fact that coordina-

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tion of $HNMe_2$ is not observed in the case of the analogous reaction of **1b** most likely reflects a stereoelectronic effect due to the bulky arylamido ligands present in the product. Owing to the perpendicular orientation of the aryl ring planes with respect to the bonding plane of the N atoms of the chelate ring (vide supra), each aryl π-system is decoupled from the respective p-type nitrogen lone pair. Just the opposite is the case for the less bulky phenylamido chelate **4**, whose phenyl rings are positioned in the bonding plane of the N atoms of the chelate ring, leading to perfect conjugation of each phenyl π-system with the respective nitrogen lone pair.[3b] Consequently, the zirconium atom of **4** competes with the phenyl rings for nitrogen lone pair electron density. This competition is absent in **3**, leading to a higher π-loading of its zirconium atom.

We have utilized **2**−**4** as precatalysts in the polymerization of ethylene. According to results of a computational study by Ziegler and co-workers, the π-loading of the metal center described above is expected to be beneficial for α-olefin polymerization.[17] The activity was poor when MAO was used as activator for the tetraamides (Zr/Al 1:500, 10 bar ethylene, 70 °C; **3** 0.8 g/mmol•h•bar, **4** 3.3 g/mmol•h•bar). In the case of the dibenzyl derivative **2**, the use of $B(C_6F_5)_3$ as cocatalyst did not lead to any noticeable activity. This is compatible with results reported by Shafir and Arnold with $B(C_6F_5)_3$-activated $[(PhCH_2)_2Zr\{Fe[C_5H_4(N\text{-}2,4,6\text{-}Me_3\text{-}C_6H_2)]_2\}]$.[4] With $[Ph_3C][B(C_6F_5)_4]$ as cocatalyst a rather low activity was observed for **2** in chlorobenzene solvent (1 bar ethylene, 40 °C; 4.0 g/mmol•h•bar). Shafir and Arnold have reported an ethylene polymerization activity of 102 g/mmol•h•bar for $[Ph_3C][B(C_6F_5)_4]$-activated $[(PhCH_2)_2Zr\{Fe[C_5H_4(NSiMe_3)]_2\}]$ under very similar reaction conditions.[18] The reasons for this large difference in polymerization activity remain unclear and are unexpected, especially in view of the work performed by Ziegler's group.

Experimental Section

All reactions were performed in an inert atmosphere (dinitrogen) by using standard Schlenk techniques or a conventional glovebox. 1,1′-Diaminoferrocene was prepared according to a published procedure.[15] Solvents and reagents were procured from standard commercial sources. NMR spectra were recorded with a Varian Unity INOVA 500 spectrometer operating at 500.13 MHz for ^1H. Elemental analyses were performed by the microanalytical laboratory of the University of Halle and by Mikroanalytisches Laboratorium H. Kolbe (Mülheim an der Ruhr).

Improved Synthesis of 1a. This compound was prepared in analogy with **1b**.[3a] $Pd_2(dba)_3$ (0.42 g, 0.45 mmol) and dppf (0.42 g, 0.75 mmol) were placed in a thick-walled Rotaflo ampule. Toluene (50 mL) was added and the resulting red solution stirred for 5 min. Sodium *tert*-butoxide (1.76 g, 18.3 mmol) and bromobenzene (2.87 g, 18.3 mmol) were added, followed after 10 min by 1,1′-diaminoferrocene (1.95 g, 9.15 mmol) in THF (100 mL). The mixture was stirred at 90 °C for 70 h. It was subsequently allowed to cool to room temperature, poured into degassed water (300 mL), and extracted with diethyl ether (5 × 100 mL). The combined organic layers were dried with sodium sulfate. Volatile components were removed in vacuo. The solid residue was extracted with a mixture of diethyl ether and *n*-hexane (2:3, 100 mL) and the extract filtered through a pad of Florisil (ca. 5 cm). The volume of the filtrate was reduced to ca. 20 mL, affording the crude product as a light orange, microcrystalline solid, which was purified by recrystallization from toluene. Yield: 2.47 g (74%). NMR spectroscopic data were identical to those of an authentic sample.[3a]

2. 1b (766 mg, 1.24 mmol), $Zr(CH_2Ph)_4$ (630 mg, 1.39 mmol), and a small amount of sodium *tert*-butoxide[4] (ca. 5 mg, ca. 0.05 mmol) were placed in a thick-walled Rotaflo ampule. Toluene (15 mL) was added and the mixture stirred for 14 days. Volatile components were removed in vacuo, and *n*-hexane (5 mL) was added. Storing of the mixture at −40 °C afforded the product as a yellow, microcrystalline solid, which was isolated by cannula filtration. Yield: 604 mg (55%). ^1H NMR (C_6D_6): δ 1.28 (d, $J = 6.8$ Hz, 24 H, $CHMe_2$); 1.48 (d, $J = 6.4$ Hz, 12 H, $CHMe_2$); 2.43 (s, 4 H, CH_2); 2.84 (sept, $J = 6.4$ Hz, 2 H, $CHMe_2$); 3.75 (s, 4 H, cyclopentadienyl); 3.84 (sept, $J = 6.8$ Hz, 4 H, $CHMe_2$); 4.00 (s, 4 H, cyclopentadienyl); 6.79 (d, $J = 7.3$ Hz, 4 H, Ph); 6.88 (t, $J = 6.8$ Hz, 2 H, Ph); 7.10 ("t", apparent $J = 7.3$ Hz, 4 H, Ph); 7.21 (s, 4 H, 2,4,6-*i*Pr-C_6H_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 25.0, 26.0, 27.5 ($CHMe_2$); 29.8, 35.5 ($CHMe_2$); 70.0, 70.1 (cyclopentadienyl); 73.0 (CH_2); 94.0 (cyclopentadienyl); 123.0, 126.5, 127.9, 129.9, 145.2, 146.8, 147.1, 147.8 (Ph and 2,4,6-*i*Pr-C_6H_2). Anal. Calcd for $C_{54}H_{68}N_2FeZr$ (892.2): C, 72.69; H, 7.68; N, 3.14. Found: C, 72.30; H, 7.67; N, 3.09.

3. 1b (621 mg, 1.00 mmol) and $Zr(NMe_2)_4$ (268 mg, 1.00 mmol) were placed in a thick-walled Rotaflo ampule. Toluene (15 mL) was added and the mixture stirred for 21 days. The volume of the solution was reduced to ca. 5 mL in vacuo. Crystallization at −40 °C afforded the product as a yellow, microcrystalline solid, which was isolated by cannula filtration. Yield: 679 mg (85%). ^1H NMR (C_6D_6): δ 1.23, 1.37 (2 d, $J = 6.8$ Hz, 2 × 12 H, $CHMe_2$); 1.43 (d, $J = 6.6$ Hz, 12 H, $CHMe_2$); 2.83 (sept, $J = 6.6$ Hz, 2 H, $CHMe_2$); 2.84 (s, 12 H, NMe_2); 3.91 (s, 4 H, cyclopentadienyl); 3.96 (sept, $J = 6.8$ Hz, 4 H, $CHMe_2$); 4.29 (s, 4 H, cyclopentadienyl); 7.18 (s, 4 H, aryl). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 25.1, 26.0, 26.6 ($CHMe_2$); 29.1, 35.1 ($CHMe_2$); 43.9 (NMe_2); 68.8, 70.0, 99.8 (cyclopentadienyl); 122.6, 146.0, 146.3, 147.2 (aryl). Anal. Calcd for $C_{44}H_{66}N_4FeZr$ (798.1): C, 66.22; H, 8.34; N, 7.02. Found: C, 66.07; H, 8.30; N, 6.88.

Polymerization of Ethene with 3 and 4 as Precatalyst. An autoclave was charged with *n*-heptane (400 mL) and heated to 70 °C. The precatalyst (**3** 20 mg; **4** 15 mg) was added, followed by MAO (30% in toluene, 2.5 mL). The autoclave was pressurized with ethene (10 bar). After 60 min the reaction was quenched and the polymer precipitated by addition of a mixture of methanol (300 mL) and concentrated hydrochloric acid (10 mL). The polymer was filtered off, washed with methanol (3 × 50 mL), and dried in vacuo at 80 °C.

Polymerization of Ethene with 2 as Precatalyst. A two-necked flask was charged with **2** (40 mg, 50 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (46 mg, 50 μmol). Chlorobenzene (5 mL) was added and the mixture stirred for 5 min. A stream of ethene was passed through the stirred solution for 60 min. The mixture was subsequently purged with argon. The polymer was precipitated by addition of a mixture of methanol (30 mL) and concentrated hydrochloric acid (1 mL). The polymer was filtered off, washed with methanol (3 × 20 mL), and dried in vacuo at 80 °C.

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Supporting Information Available: CIF files for the structures of **1a**, **1b**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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