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Synthesis of chelating, C_2-symmetric bis(silylamido) complexes of zirconium, and their activities as olefin polymerization catalysts

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Dedicated to Dick Schrock, in recognition of his many seminal contributions to inorganic chemistry

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Abstract

The zirconium bis(silylamido) complexes {[DADMB]$ZrCl_2$}$_2$ (**3**; DADMB = 2,2′-bis(*tert*-butyldimethylsilylamido)-6,6′-dimethylbiphenyl), and [DMBN]$ZrCl_2$·THF (**4**; DMBN = 2,2′-bis(*tert*-butyldimethylsilylamido)-1,1′-binaphthyl) were prepared from the corresponding lithiated silylamines. The structure of **3** was determined by X-ray crystallography. The benzyl and methyl derivatives of **4**, [DBMN]$Zr(CH_2Ph)_2$ (**5**) and [DMBN]$ZrMe_2$·THF (**6**), were prepared by treatment of **4** with $PhCH_2K$ and MeLi, respectively. Reaction of **5** with $B(C_6F_5)_3$ produces the crystallographically characterized zwitterionic complex [DMBN]$Zr(CH_2Ph)[\eta^6\text{-}PhCH_2B(C_6F_5)_3]$ (**7**), in which the benzyl group of the anion is coordinated in an η^6-fashion to zirconium. Compounds **3** and **4** are moderately active as ethylene polymerization catalysts when activated with excess MAO. Activation of **5** with 1 equiv. of $[Ph_3C][B(C_6F_5)_4]$ resulted in formation of a catalyst which polymerizes neat 1-hexene to give low molecular weight polyhexene.

Keywords: Crystal structures; Olefin polymerization; Zirconium complexes; Silylamido complexes

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1. Introduction

Chelating and multidentate amido ligands [1–20] have recently emerged as a viable alternative to the traditionally used cyclopentadienide ligands [21–23] in the chemistry of early transition metals. Complexes of d^0 metals can be used as catalysts for olefin polymerization [3–23], silane dehydropolymerization [24–28], olefin hydrosilylation [29–38] and related transformations. It has been recognized that modifying the electronic and steric environment at the metal center significantly affects the reactivity of the complex, and coordinative unsaturation and electrophilicity are believed to contribute to high reactivity in d^0 systems.

We recently reported studies on the structure and reactivity of silylamido yttrium complexes containing the $[DADMB]^{2-}$ ligand (DADMB = 2,2′-bis(*tert*-butyldimethylsilylamido)-6,6′-dimethylbiphenyl) [1], and their application as olefin hydrosilylation catalysts [38]. In a continuing effort to explore the properties of C_2-symmetric chelating silylamides as ancillary ligands for early transition metals, we have investigated a number of zirconium complexes of these ligands, which are based on biphenyl or binaphthyl backbones.

2. Results and discussion

The lithiated silylamine Li_2[DADMB]·2THF (**1**) was prepared as previously described [1]. The analogous binaphthyl compound, Li_2[DMBN]·2THF (**2**), was obtained using the same procedure (Eq. (1)), starting from diaminobinaphthyl.

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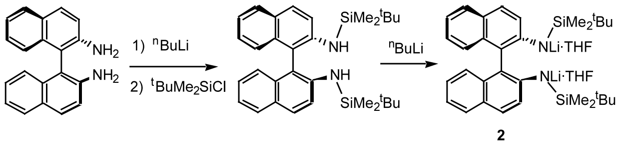
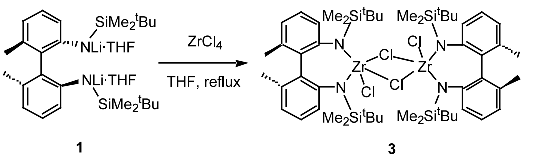


(1)

Reaction of **1** with $ZrCl_4$ in refluxing THF (Eq. (2)) produced the zirconium complex $\{[DADMB]ZrCl_2\}_2$ (**3**), isolated in 82% yield from pentane solution. The solid state structure of **3** (Fig. 1) was determined by X-ray crystallography. Relevant bond lengths and angles are listed in Table 1. Compound **3** crystallizes as a centrosymmetric dimer, with two bridging chloride ligands and one terminal chloride per zirconium. The zirconium centers adopt a distorted trigonal bipyramidal geometry. The two μ-Cl ligands asymmetrically bridge the zirconium centers, resulting in inequivalent $Zr-Cl_\mu$ bond lengths of 2.575(1) and 2.733(1) Å. For comparison, the terminal $Zr-Cl_t$ bond length is 2.412(1) Å. The close $Zr-C_{ipso}$ distance (2.529(4) Å) and the small $Zr-N-C_{ipso}$ angle (93.4(2)°) suggest the presence of Zr–carbon bonding interactions with one of the biphenyl rings, as is often found in complexes of this type [3–39]. Similar dimeric chloride-bridged structures have often been determined or suggested for zirconium dichloride derivatives [11,40,41].



(2)

The binaphthyl analogue, $[DMBN]ZrCl_2\cdot THF$ (**4**; DMBN = 2,2′-bis(*tert*-butyldimethylsilylamido)-1,1′-binaphthyl) was prepared in 95% yield from **1** and $ZrCl_4$ under the same reaction conditions. A notable difference in the properties of **3** and **4** is the tendency of **4** to coordinate 1 equiv. of THF, which could not be fully removed even after repeated recrystallization.

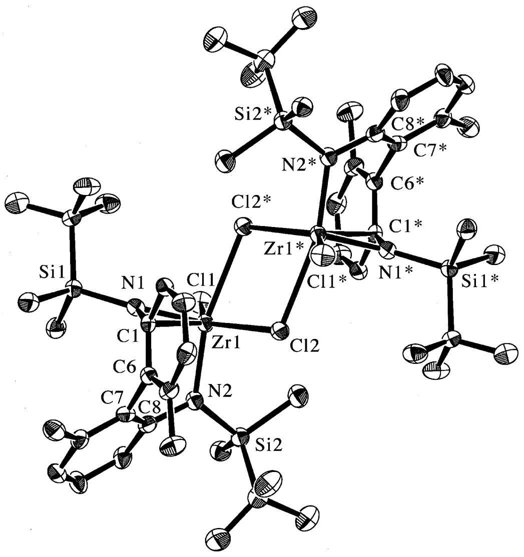


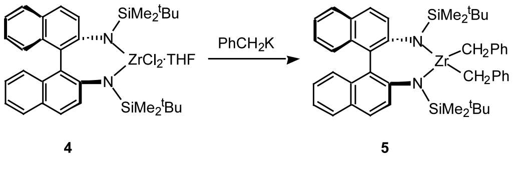
Fig. 1. ORTEP diagram of $([DADMB]ZrCl_2)_2$ (**3**).

Table 1
Selected bond lengths (Å) and angles (°) for compound **3**

Bond lengths			
Zr(1)–Cl(1)	2.412(1)	Zr(1)–Cl(2)	2.575(1)
Zr(1)–Cl(2*)	2.733(1)	Zr(1)–N(1)	1.996(3)
Zr(1)–N(2)	2.063(3)	Zr(1)–C(1)	2.529(4)
Bond angles			
Cl(1)–Zr(1)–Cl(2)	132.85(4)	Cl(1)–Zr(1)–Cl(2*)	84.17(4)
Cl(2)–Zr(1)–Cl(2*)	74.59(3)	Cl(1)–Zr(1)–N(1)	104.51(9)
Cl(1)–Zr(1)–N(2)	96.56(9)	Cl(2)–Zr(1)–N(1)	119.18(9)
Cl(2)–Zr(1)–N(2)	95.14(9)	N(1)–Zr(1)–N(2)	96.8(1)
Zr(1)–N(1)–C(1)	93.4(2)		

The reactivity of **3** and **4** as olefin polymerization catalysts when activated with MAO (500 equiv.) was investigated. Both complexes were active towards ethylene polymerization (at 40–50 psi C_2H_4, toluene solution, room temperature), with activities of 4.59 kg mol^{-1} h^{-1} atm^{-1} for **3** and 4.17 kg mol^{-1} h^{-1} atm^{-1} for **4**, but no measurable polymer formation was observed with other olefins (1,3-butadiene, propylene) under the same conditions. This rather low reactivity is comparable to that observed for other MAO-activated amido complexes (cf. 64 kg mol^{-1} h^{-1} for $\{Me_2Si(NCMe_3)_2\}ZrCl_2(THF)_2$ [11], 13 kg mol^{-1} h^{-1} atm^{-1} for $\{(C_6H_3)_2\text{-}2,2'\text{-}(NCH_2C_6H_4{}^tBu\text{-}4)_2\text{-}6,6'\text{-}Me_2\}Zr(CH_2Ph)_2$ [8], and 2.9 kg mol^{-1} h^{-1} atm^{-1} for $[Ti(Me_3SiNCH_2CH_2NSiMe_3)Cl_2]$ [16]) but is much lower than those for the best Group 4 metallocene/MAO polymerization catalysts, which often exhibit activities exceeding 1×10^5 kg mol^{-1} h^{-1}) [22,23], and lower than many catalysts with amido or alkoxide ligands (cf. $\{Zr[RN(Me_2SiCH_2CH_2SiMe_2)NR](NMe_2)_2\}$ (R = 2,6-$Me_2C_6H_3$) 990 kg mol^{-1} h^{-1} atm^{-1} [17], 2,2′-S(4-Me,6-$^tBuC_6H_2O)_2TiCl_2$ 4740 kg mol^{-1} h^{-1}) [42].

Attempts to isolate alkyl derivatives of **3** by reaction with MeMgBr, MeLi or $PhCH_2MgBr$ resulted in the formation of yellow oils that were difficult to handle and characterize due to the very high solubility of these alkyl derivatives. The analogous complexes of **4**, however, were found to be less soluble and thus easier to isolate and characterize. The benzyl derivative $[DMBN]Zr(CH_2Ph)_2$ (**5**) was obtained as a yellow foamy solid by reaction of **4** with 2 equiv. of $PhCH_2K$ (Eq. (3)).



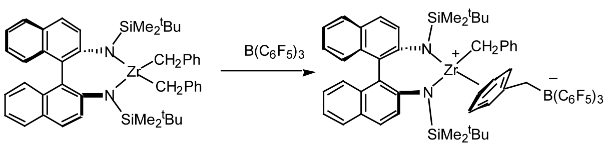
(3)

The benzyllic protons in **5** give rise to two doublets in the ^{1}H NMR spectrum at 2.24 and 2.09 ppm ($^{2}J_{HH} = 10$ Hz), with the ZrCH$_2$Ph carbon appearing at 72.1 ppm in the ^{13}C NMR spectrum ($^{1}J_{CH} = 110$ Hz). These NMR shifts are consistent with η^{1}-coordination of the benzyl group and are within the typical ranges reported for Zr benzyl complexes [11,12,17,19,42–44].

The methyl derivative [DMBN]ZrMe$_2$·THF (**6**), prepared by reaction of **4** with 2 equiv. of MeLi, was isolated as a brown foamy solid. Attempts to purify this compound via recrystallization were prohibited by its reluctance to crystallize from solution. The sample presumably contains small amounts of impurities (as suggested by its color), but these were not detected by NMR spectroscopy. The methyl groups in **6** give rise to a singlet at 0.55 ppm in the ^{1}H NMR spectrum, with the carbon atom appearing at 47.0 ppm ($^{1}J_{CH} = 105$ Hz) in the ^{13}C NMR spectrum, consistent with the values typically reported for ZrMe species [12,17,42,43].

No reaction was observed between **5** or **6** and ethylene (in benzene-d$_6$) after 3 h at room temperature, and heating the reaction mixtures at 80 °C resulted in decomposition with no evidence for polymer formation. Similarly, no reaction was observed between **5** and PhSiH$_3$ or H$_2$ (in benzene-d$_6$) after 2 days at room temperature, and heating at 80 °C resulted in decomposition of **5** in both systems.

While the reaction of **6** with B(C$_6$F$_5$)$_3$ gave an intractable mixture of products, the reaction of **5** with B(C$_6$F$_5$)$_3$ resulted in clean benzyl abstraction (Eq. (4)) and formation of the zirconium complex [DMBN]Zr(CH$_2$Ph)[η^{6}-PhCH$_2$B(C$_6$F$_5$)$_3$] (**7**), isolated in 71% yield. The ^{1}H NMR spectrum of **7** reveals the presence of two inequivalent ^{t}Bu groups, which suggests anion coordination leading to a non-C_2 symmetric structure in solution. Such coordination has often been observed in analogous zwitterionic zirconium species [11,12,19,42,44–47]. The ZrCH$_2$Ph group gives rise to two doublets at 2.14 and 1.58 ppm ($^{2}J_{HH} = 11$ Hz) in the ^{1}H NMR spectrum, and a signal at 73.6 ppm ($^{1}J_{CH} = 121$ Hz) in the ^{13}C NMR spectrum of **7** (cf. 1.95, 52.5 ppm, $^{1}J_{CH} = 122.5$ Hz for the ZrCH$_2$Ph group in {Me$_2$Si(NCMe$_3$)$_2$}Zr(CH$_2$Ph)[η^{6}-PhCH$_2$B(C$_6$F$_5$)$_3$] [11]). The BCH$_2$Ph methylene group appears at 2.8–3.2 ppm (br m) in the ^{1}H NMR spectrum, and the ^{13}C NMR shift for the BCH$_2$Ph carbon is at 38.5 ppm (cf. 3.36 and 36.2 ppm in {Me$_2$Si(NCMe$_3$)$_2$}Zr(CH$_2$Ph)[η^{6}-PhCH$_2$B(C$_6$F$_5$)$_3$]). A variable temperature NMR study of **7** in toluene-d$_8$ showed that coalescence of the signals from the ^{t}Bu groups occurs at 300 K, which corresponds to an activation energy barrier of 63 kJ mol^{-1} (15 kcal mol^{-1}) for anion dissociation. This value is very similar to that of 13.8 kcal mol^{-1} reported for [(1,2-Me$_2$Cp)$_2$ZrR][CH$_3$B(C$_6$F$_5$)$_3$] (R = CH$_2$CMe$_3$, CH$_2$SiMe$_3$) [48].



5 **7**

(4)

The solid state structure of **7** was determined by X-ray diffraction (Fig. 2). Relevant bond lengths and angles are listed in Table 2. As usually found in such cationic complexes, the borane anion is closely associated with the metal cation, the PhCH$_2$B group being coordinated to the Zr atom in a η^{6} fashion. The distance between the plane of the C$_6$ ring and the Zr atom is 2.325(6) Å; similar to that in other related complexes [44,49]. All Zr–C distances are similar (ranging from 2.675(7) to 2.773(6) Å), which is consistent with an η^{6} rather than an η^{4} or lower coordination mode. The remaining η^{1}-benzyl group (Zr–C–C angle of 132.7(4)°), is not associated with agostic or Zr-aromatic ring interactions. There are close contacts, however, between the Zr atom and the *ipso* carbons of both binaphthyl rings, with an average Zr–C distance of 2.567(6) Å and a Zr–N–C$_{ipso}$ angle of 91.5(3)°.

Reaction of **7** with ethylene (room temperature, 5–10 psi) resulted in rapid formation of a new complex within 15 min, presumably an ethylene insertion product, as observed by ^{1}H NMR (δ 0.84, 0.62 (s, 9H each, ^{t}Bu), −0.24, −0.26, −0.54, −0.76 (s, 3H each, Me$_2$Si), other peaks obscured). The formation of ethylene oligomers was also detected after 3 h (by ^{1}H NMR spectroscopy). However, unlike compounds **3** and **4**, complex **7** produced no measurable amount of polyethylene when tested under the same conditions (without MAO cocatalyst). Similar rapid single insertion of α-olefins, but limited polymerization activity has been reported for the analogous complex {Me$_2$Si(NCMe$_3$)$_2$}Zr(CH$_2$Ph)[η^{6}-

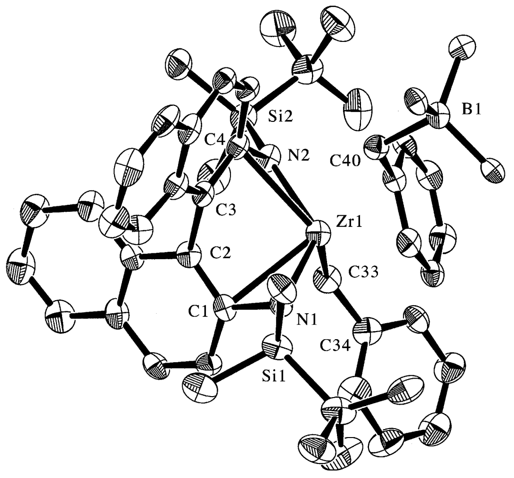


Fig. 2. ORTEP diagram of [DMBN]Zr(CH$_2$Ph)[η^{6}-PhCH$_2$B(C$_6$F$_5$)$_3$]·3.5C$_6$H$_6$ (**7**). The C$_6$F$_5$ groups of the borane anion have been omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for compound **7**

Bond lengths			
Zr(1)–N(1)	2.083(5)	Zr(1)–N(2)	2.094(5)
Zr(1)–C(33)	2.250(6)	Zr(1)–C(1)	2.576(6)
Zr(1)–C(4)	2.558(6)		
Bond angles			
N(1)–Zr(1)–N(2)	126.1(2)	Zr(1)–C(33)–C(34)	132.7(4)
Zr(1)–N(1)–C(1)	92.0(3)	Zr(1)–N(2)–C(4)	91.0(3)
B(1)–C(40)–C(41)	113.5(5)		

$PhCH_2B(C_6F_5)_3]$ [11]. This may be contrasted to the high polymerization activity reported for $(Me_2C_5H_3)_2ZrMe[MeB(C_6F_5)_3]$ 6800 kg mol^{-1} h^{-1} atm^{-1} [46,47], $\{Me_3SiN(CH_2CH_2NSiMe_3)_2\}Zr(CH_2Ph)[\eta^6\text{-}PhCH_2B(C_6F_5)_3]$ 330 kg mol^{-1} h^{-1}) [12], $Cp^*Zr(CH_2Ph)_2[\eta^6\text{-}PhCH_2B(C_6F_5)_3]$ 88 kg mol^{-1} h^{-1}) [44], and other catalysts [4,49,50].

Compound **7** was also observed to react rapidly with 1-hexene (by ^{1}H NMR spectroscopy), presumably forming an insertion product (δ 0.37, 0.78 (s, ^{t}Bu, 9H each), −0.22, −0.26, −0.40, −0.70 (s, Me_2Si, 3H each), other peaks obscured), but only a small amount of hexene oligomers was observed after 1 day. When the reaction occurred in neat 1-hexene (in presence of approximately 10% toluene), at room temperature, no measurable amount of polymer could be isolated after standard workup (see Section 4). No reaction occurred between **7** and $PhMeC{=}CH_2$ (benzene-d$_6$, room temperature, 24 h).

An attempt to abstract a methyl group from **6** using $[Ph_3C][B(C_6F_5)_4]$ in dichloromethane-d$_2$ solution resulted in a new set of ^{1}H NMR peaks, assigned to a cationic zirconium species (δ 0.99, 0.96 (s, 9H each, ^{t}*Bu*), 0.25, 0.22, 0.14 (m, 12H total, *Me*$_2$Si), −0.37 (s, 3H, Zr*Me*); other peaks obscured). This new species, however, is also inactive as an olefin polymerization catalyst, as no polymer was formed when an excess of 1-hexene was added to the reaction mixture (24 h, room temperature). In addition, no polymer formation occurred on exposure of neat 1-hexene to a mixture of **6** and $[Ph_3C][B(C_6F_5)_4]$.

The reaction of **5** with $[Ph_3C][B(C_6F_5)_4]$ in benzene-d$_6$ or dichloromethane-d$_2$ resulted in a mixture of products, as observed by ^{1}H NMR spectroscopy. Addition of an excess 1-hexene to this solution did not result in polymer formation (2 h, room temperature). However, a catalyst generated in situ from **5** and $[Ph_3C][B(C_6F_5)_4]$ (1:1 molar ratio) was found to polymerize hexene when exposed to neat olefin (in the presence of approximately 10% toluene, to improve catalyst solubility). The polymer formed was shown by gel permeation chromatography (GPC) to have an M_w value of 2384 ($M_n = 1720$) and a polydispersity of 1.39. This molecular weight is much lower than those obtained with other recently reported chelating diamide- and alkoxide-based catalysts. For comparison, $(MeN(CH_2)_3NMe)Ti(2,6\text{-}{}^iPr_2C_6H_3)_2 + [Ph_3C][B(C_6F_5)_4]$ and related systems produce molecular weights up to $M_w = 239{,}100$ [9,43,51], $[(^tBu\text{-}d_6)N\text{-}o\text{-}C_6H_4)_2O]ZrMe(PhNMe_2)[B(C_6F_5)_4]$ gives $M_n = 45{,}000$ [4], and $\{1,1'\text{-}(2,2',3,3'\text{-}OC_{10}H_5SiMePh_2)\}ZrCl_2/MAO$ results in $M_w = 674{,}000$ [42]. The activity of the **5**/$[Ph_3C][B(C_6F_5)_4]$ catalyst mixture for ethylene polymerization, 5.10 kg mol^{-1} h^{-1} atm^{-1}, was not significantly different from those observed for the MAO-activated dichlorides **3** and **4**.

3. Conclusions

A series of zirconium chloride and alkyl complexes with chelating silylamido ligands have been synthesized and studied. The polymerization activity of the MAO-activated dichlorides towards ethylene was found to be moderately low, as compared to both Cp and non-Cp based catalytic systems. Reaction of the benzyl and methyl derivatives with Lewis acids results in alkyl abstraction and formation of zwitterionic species. Anion coordination has been shown to occur both in the solid state and in solution for the zwitterionic complex **7**. The activity of non-Cp olefin polymerization catalysts has already been seen to depend on a number of factors, including ligand steric bulk and electrophilicity, type of cocatalyst, coordination affinity of the counter-anion in case of cationic species, solvent polarity, etc. [13,23,42,44,46–48]. It has been observed that MAO-activated catalysts are usually more active than the borane-activated species, in which anion coordination can significantly inhibit polymerization activity [11,20,43,51,52]. While the silylamido complexes presented in this chapter exhibit reactivity in agreement with these general trends, they are not among the most active olefin polymerization catalysts. The wide range of activities so far observed for chelating diamide catalysts of the type $(R'N\text{–}L\text{–}NR')MR^+$ ($L =$ linking group; $M =$ Ti or Zr) is quite remarkable, and it would appear that much is yet to be learned concerning the major factors that influence activity in such systems.

Further studies of the zirconium complexes reported here will focus on other catalytic reactions. In particular, our recent discovery that resolved yttrium catalysts of the type $[DADMB]YH(L)_n$ are effective in enantioselective hydrosilations [38] suggests that the zirconium complexes may be useful as catalysts for a number of enantioselective transformations.

4. Experimental

4.1. General

All reactions with air-sensitive compounds were performed under dry nitrogen, using standard Schlenk and glove box techniques. Reagents were obtained from commercial suppliers and used without further purification, unless otherwise noted. Olefin-free C_5H_{12}, C_6H_6, and $C_6H_5CH_3$ were prepared by pretreating with concd. H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, $NaHCO_3$ and finally anhydrous $MgSO_4$. Solvents (C_5H_{12}, Et_2O, C_6H_6, $C_6H_5CH_3$, THF) were distilled under nitrogen from sodium benzophenone ketyl. Benzene-d_6 was distilled from Na/K alloy. ^{n}BuLi was used as a 1.6 M solution in hexanes, as supplied by Aldrich, and MeLi as a 1.6 M solution in Et_2O, as supplied by Alpha Aesar. Li_2[DADMB]·2THF (**1**) [1], diaminobinaphthyl [53,54], $B(C_6F_5)_3$ [55], and $[Ph_3C][B(C_6F_5)_4]$ [56] were prepared according to published literature procedures. NMR spectra were recorded at 300 or 500 MHz (^{1}H) with Bruker AMX-300 and DRX-500 spectrometers, or at 100 MHz ($^{13}C\{^1H\}$) with an AMX-400 spectrometer, at ambient temperature and in C_6H_6-d_6, unless otherwise noted. Signal multiplicities are reported as follows: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; m, multiplet. Elemental analyses were performed by the Microanalytical Laboratory at UC Berkeley or by Desert Analytics. For Zr complexes containing the binaphthyl group (**4**–**7**), we consistently obtained combustion analyses which were in agreement with the proposed elemental compositions, except for the percentage of carbon. Since for these complexes the spectroscopic data supports the presence of pure compounds, we assume that the low carbon analyses result from the Zr-promoted formation of carbides during the combustion analysis. IR spectra were recorded with a Mattson Infinity 60 MI FTIR spectrometer, as KBr pellets. The molecular weight distributions (vs. polystyrene standards) for polyhexene were measured with a Waters Associates chromatograph equipped with a refractive index detector and a PLgel 5μ mixed-D column using THF as the mobile phase.

4.2. *Li_2[DMBN]·2THF* (**2**)

DABN (6.90 g, 24.3 mmol) was dissolved in 250 ml of THF and the solution was cooled in an ice/water bath. Two equivalents of ^{n}BuLi (32 ml, 51 mmol) were added dropwise with a syringe, with vigorous stirring. The solution turned cloudy and gradually changed from almost colorless through reddish yellow, to bright yellow–orange, with formation of an orange precipitate. After the mixture was stirred at room temperature (r.t.) overnight, a solution of ^{t}BuMe$_2$SiCl (8.31 g, 53.5 mmol) in 70 ml of C_5H_{12} was added. The solution was heated at reflux for 6 h, which resulted in formation of a white precipitate, and was then left to cool slowly overnight. Removal of the volatiles in vacuo yielded brown foamy oil, which was extracted twice with C_5H_{12} (200 and 50 ml). After filtration, the C_5H_{12} extracts were concentrated to about 50 ml, and 40 ml of THF was added. ^{n}BuLi (32 ml, 51 mmol) was added at r.t., resulting in the formation of a bright yellow–greenish crystalline precipitate. The volatile material was removed and the solid product was washed with C_5H_{12} (2 × 50 ml) and dried in vacuo to give 15.0 g (92% yield) of **2**. ^{1}H NMR: δ 7.53 (m, 6H), 6.91 (m, 4H), 6.79 (m, 2H, binaphthyl H), 2.86 (m, 8H, THF), 1.11 (s, 18H, ^{t}*Bu*Me$_2$Si), 1.09 (m, 8H, THF), 0.54 (s, 6H, ^{t}Bu*Me*$_2$Si), 0.13 (s, 6H, ^{t}Bu*Me*$_2$Si). $^{13}C\{^1H\}$ NMR: δ 155.8, 138.7, 128.6, 128.5, 128.1, 127.7, 127.4, 126.5, 122.0, 120.9 (binaphthyl C), 68.5 (THF), 28.7 ($(CH_3)_3C$), 25.1 (THF), 21.3 ($(CH_3)_3C$), 1.1 ($(CH_3)_2Si$), −0.4 ($(CH_3)_2Si$). IR (cm^{-1}): 3056 (w), 2952 (s), 2927 (s), 2857 (s), 1618 (s), 1596 (s), 1510 (m), 1469 (s), 1403 (s), 1343 (s), 1285 (s), 1250 (s), 1148 (w), 990 (m), 941 (w), 830 (s), 775 (m), 746 (m). *Anal*. Calc. for $C_{40}H_{58}Li_2N_2O_2Si_2$: C, 71.82; H, 8.74; N, 4.19. Found: C, 71.52; H, 8.76; N, 4.03%.

4.3. *{[DADMB]ZrCl$_2$}$_2$* (**3**)

To a mixture of Li_2[DADMB]·2THF (**1**) (3.42 g, 5.72 mmol) and $ZrCl_4$ (1.40 g, 6.01 mmol) was added 200 ml of THF. The clear, yellow solution was heated at reflux for 20 h. The solvent was removed in vacuo and the resulting oily solid was extracted with C_5H_{12} (3 × 80 ml). Concentration of the C_5H_{12} extracts and cooling to −78 °C produced a yellow crystalline precipitate, which was isolated and dried in vacuo to give 3.16 g (82%) of **3**, containing about 1 equiv. of residual THF (by ^{1}H NMR integration). Recrystallization of 2.88 g of the product from C_5H_{12} gave 1.35 g of the THF-free complex. ^{1}H NMR: δ 7.17 (d, 2H), 7.05 (t, 2H), 6.80 (d, 2H, aromatic H), 1.87 (s, 6H, *Me*Ar), 0.96 (s, 18H, ^{t}*Bu*Me$_2$Si), 0.04 (s, 6H, ^{t}Bu*Me*$_2$Si), 0.03 (s, 6H, ^{t}Bu*Me*$_2$Si). $^{13}C\{^1H\}$ NMR: δ 139.4, 138.2, 137.0, 130.4, 129.6, 128.1 (aromatic C), 27.6 ($(CH_3)_3C$), 21.1 ($(CH_3)_3C$), −1.6 ($(CH_3)_2Si$), −3.5 ($(CH_3)_2Si$). IR (cm^{-1}): 3052 (w), 2952 (s), 2927 (s), 2856 (s), 1580 (s), 1465 (s), 1305 (s), 1236 (s), 1036 (m), 960 (m), 830 (s). *Anal*. Calc. for $C_{26}H_{42}Cl_2N_2Si_2Zr$: C, 51.97; H, 7.05; N, 4.66. Found: C, 51.78; H, 7.24; N, 4.43%.

4.4. *[DMBN]ZrCl$_2$(THF)* (**4**)

A mixture of **2** (2.51 g, 3.75 mmol) and $ZrCl_4$ (0.92 g, 3.95 mmol) in 80 ml of THF was heated at reflux for 6 h. The volatiles were removed in vacuo and the yellow solid residue was extracted with Et_2O (2 × 50 ml). The filtrate was concentrated to 15 ml and cooled to −78 °C. The resulting crystalline precipitate was washed with C_5H_{12} and dried in vacuo, to obtain 2.57

g of product in two crops (95% yield). The NMR spectra contained no evidence for the presence of impurities. ^{1}H NMR: δ 7.62 (m, 2H), 7.51 (m, 2H), 7.43 (m, 2H), 7.08 (m, 2H), 7.01 (m, 2H), 6.91 (m, 2H, binaphthyl H), 3.61 (m, 4H, THF), 1.39 (m, 4H, THF), 0.994 (s, 18H, ^{t}*Bu*Me$_2$Si), 0.15 (s, 6H, ^{t}Bu*Me*$_2$Si), −0.25 (s, 6H, ^{t}Bu*Me*$_2$Si). ^{13}C{^{1}H} NMR: δ 138.9, 134.4, 132.8, 131.8, 129.6, 129.0, 128.9, 128.1, 127.6, 126.3 (binaphthyl C), 70.1 (THF), 27.7 ((*C*H$_3$)$_3$C), 25.8 (THF), 19.9 ((CH$_3$)$_3$*C*), −1.6 ((C*H*$_3$)$_2$Si), −2.4 ((C*H*$_3$)$_2$Si). IR (cm^{-1}): 3056 (w), 2953 (s), 2927 (s), 2882 (m), 2855 (s), 1618 (s), 1596 (s), 1509 (m), 1469 (s), 1404 (s), 1391 (s), 1344 (s), 1285 (s), 1250 (s), 1211 (m), 1148 (m), 993 (s), 938 (s), 831 (s), 812 (s), 776 (s), 746 (s), 672 (m). *Anal*. Calc. for $C_{36}H_{50}Cl_2N_2OSi_2Zr$: C, 58.03; H, 6.76; N, 3.76. Found: C, 56.45; H, 6.69; N, 3.50%.

*4.5. [DBMN]Zr(CH$_2$Ph)$_2$ (**5**)*

A mixture of **4** (0.60 g, 0.80 mmol) and KCH$_2$Ph (0.22 g, 1.68 mmol) was dissolved in 25 ml of C_6H_6 at r.t. The red insoluble KCH$_2$Ph was consumed within 20 min resulting in the formation of a cloudy yellow solution. After 45 min the C_6H_6 was removed in vacuo and the solid residue was extracted with hexanes (2 × 30 ml). The filtrate was concentrated to 10 ml and cooled to −78 °C to give a voluminous oily yellow precipitate. The product was isolated by filtration at −78 °C and dried in vacuo to give 0.31 g of a yellow foamy solid (50% yield). The NMR spectra contained no evidence for the presence of impurities. ^{1}H NMR: δ 7.61 (m, 4H), 7.32 (m, 2H), 7.22 (m, 3H), 7.06 (m, 4H), 6.99 (m, 2H), 6.89 (m, 2H, aromatic H), 2.24 (d, 2H, $^{2}J_{HH} = 10$ Hz, ZrC*H*$_2$Ph), 2.09 (d, 2H, $^{2}J_{HH} = 10$ Hz, ZrC*H*$_2$Ph), 0.68 (s, 18H, ^{t}*Bu*Me$_2$Si), −0.06 (s, 6H, ^{t}Bu*Me*$_2$Si), −0.19 (s, 6H, ^{t}Bu*Me*$_2$Si). ^{13}C{^{1}H} NMR: δ 144.8, 140.1, 134.7, 131.5, 131.1, 130.2, 130.0, 129.2, 128.7, 128.7, 127.9, 127.0, 125.6, 123.4 (aromatic C), 72.1 (Zr*C*H$_2$Ph, $^{1}J_{CH} = 110$ Hz), 27.3 ((*C*H$_3$)$_3$C), 19.9 ((CH$_3$)$_3$*C*), −1.2 ((*C*H$_3$)$_2$Si), −2.3 ((*C*H$_3$)$_2$Si). IR (cm^{-1}): 3055 (w), 3016 (w), 2951 (s), 2927 (s), 2881 (m), 2854 (s), 1617 (w), 1593 (s), 1470 (m), 1389 (w), 1343 (m), 1249 (s), 1207 (s), 1146 (m), 1030 (m), 991 (s), 938 (m), 865 (m), 834 (s), 810 (s), 744 (s), 697 (m), 670 (m). *Anal*. Calc. for $C_{46}H_{56}N_2Si_2Zr$: C, 70.44; H, 7.20; N, 3.57. Found: C, 67.70; H, 7.16; N 3.78%.

*4.6. [DMBN]ZrMe$_2$(THF) (**6**)*

To a solution of **4** (0.60 g, 0.80 mmol) in 30 ml of Et$_2$O was added 1.1 ml of MeLi (1.7 mmol) at r.t. The mixture turned dark brown within 30 min. After stirring for 1 h, the volatiles were removed in vacuo and the resulting black solid was extracted with a 1:1 hexanes/C_6H_6 mixture (75 ml). The filtrate was dried in vacuo to obtain 0.41 g of dark brown foamy solid. The lack of crystallinity prevented purification of the product by recrystallization. ^{1}H NMR: δ 7.6 (m, 6H), 7.0 (m, 4H, binaphthyl H), 3.56 (m, 4H, THF), 1.24 (m, 4H, THF), 0.98 (s, 18H, ^{t}*Bu*Me$_2$Si), 0.55 (s, 6H, Zr*Me*$_2$), 0.22 (s, 6H, ^{t}Bu*Me*$_2$Si), −0.30 (s, 6H, ^{t}Bu*Me*$_2$Si). ^{13}C{^{1}H} NMR: δ 138.6, 134.6, 131.9, 131.1, 129.7, 128.9, 128.7, 128.5, 128.3, 127.9, 127.6, 127.4, 125.6, 124.5 (binaphthyl C), 69.3 (THF), 47.0 (Zr(*C*H$_3$)$_2$, $^{1}J_{CH} = 105$ Hz), 27.6 ((*C*H$_3$)$_3$C), 25.6 (THF), 19.6 ((CH$_3$)$_3$*C*), −1.4 ((*C*H$_3$)$_2$Si), −2.8 ((*C*H$_3$)$_2$Si). IR (cm^{-1}): 3056 (w), 2951 (s), 2928 (s), 2880 (s), 2853 (s), 1616 (w), 1590 (w), 1500 (w), 1470 (m), 1422 (m), 1345 (m), 1261 (s), 1249 (s), 1224 (s), 1148 (m), 1034 (m), 998 (s), 939 (m), 834 (s), 775 (s), 748 (s), 677 (m).

4.7. [DMBN]Zr(CH$_2$Ph)[η^6-PhCH$_2$B(C$_6$F$_5$)$_3$]·3.5C$_6$H$_6$ (7)

A mixture of **5** (0.169 g, 0.215 mmol) and $B(C_6F_5)_3$ (0.11 g, 0.215 mmol) was dissolved in 15 ml of C_6H_6. The solution immediately turned bright orange. After the mixture was stirred for 30 min at r.t., the solvent was removed in vacuo and the remaining orange powder was washed with hexanes and dried to obtain 0.24 g of product (71% yield). ^{1}H NMR: δ 8.05 (m, 1H), 7.70 (m, 2H), 7.19–7.41 (m, 5H), 7.02 (m, 4H), 6.90 (m, 3H), 6.80 (m, 2H, aromatic H), 2.8–3.2 (br m, 2H, BC*H*$_2$Ph), 2.14 (d, 1H, $^{2}J_{HH} = 11$ Hz, ZrC*H*$_2$Ph), 1.58 (d, 1H, $^{2}J_{HH} = 11$ Hz, ZrC*H*$_2$Ph), 0.83 (br s, 9H, ^{t}*Bu*Me$_2$Si), 0.76 (br s, 9H, ^{t}*Bu*Me$_2$Si), −0.27 (s, 6H, ^{t}Bu*Me*$_2$Si), −0.54 (s, 6H, ^{t}Bu*Me*$_2$Si). ^{13}C{^{1}H} NMR: δ 150.1, 150.0, 150.0, 148.2, 148.1, 140.4, 138.8, 136.9, 129.3, 128.9, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 128.0, 128.0, 127.9, 127.2, 124.2 (aromatic C), 73.6 (Zr*C*H$_2$Ph, $^{1}J_{CH} = 121$ Hz), 28.0 ((*C*H$_3$)$_3$C), 27.5 ((*C*H$_3$)$_3$C), 20.0 ((CH$_3$)$_3$*C*), 38.5 (B*C*H$_2$Ph), 0.24 ((*C*H$_3$)$_2$Si), −0.72 ((*C*H$_3$)$_2$Si). IR (cm^{-1}): 3050 (w), 2956 (s), 2932 (s), 2898 (m), 2859 (s), 1640 (w), 1598 (s), 1458 (s), 1382 (w), 1263 (s), 1208 (m), 1151 (m), 1084 (s), 981 (s), 935 (m), 835 (s), 814 (s), 776 (m), 750 (m), 677 (m). *Anal*. Calc. for $C_{85}H_{77}BF_{15}N_2Si_2Zr$: C, 65.04; H, 4.94; N, 1.78. Found: C, 58.93; H, 4.46; N, 2.16%. For this compound, loss of solvent of crystallization probably influenced the observed elemental analysis data.

4.8. Ethylene polymerization

A sample of the Zr complex (approximately 0.03 mmol) and a 500-fold excess of MAO (approximately 15 mmol) were dissolved in 20 ml of $C_6H_5CH_3$ and the solution was transferred to a high-pressure glass reaction vessel. The mixture was pressurized with ethylene at 40–50 psi for 1 h at r.t. The reaction was stopped by venting the ethylene gas and pouring the solution into a mixture of 100 ml CH$_3$OH, 100 ml H$_2$O and 50 ml concd. HCl. The precipitated polyethylene was separated by filtration, washed several times with CH_3OH, H_2O and C_3H_6O, and dried under vacuum overnight.

4.9. 1-Hexene polymerization

A sample of **5** (7.0 mg, 0.01 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (10 mg, 0.01 mmol) was dissolved in 0.2 ml of $C_6H_5CH_3$. To the resulting bright orange solution was added 1.0 g of 1-hexene. The mixture spontaneously heated up. The reaction was stopped after 90 min by addition of 5 ml of THF containing a few drops of concd. HCl. The polymer formed was washed twice with 30 ml of H_2O and dried in vacuo for 24 h at r.t. to give 0.78 g of polyhexene (78% isolated yield) as a viscous colorless oil. ^1H NMR ($CHCl_3$-d_3): δ 1.26 (m), 1.07 (m), 1.01 (m), 0.90 (m), olefinic signals at 5.36, 4.70. $^{13}C\{^1H\}$ NMR ($CHCl_3$-d_3): δ 40.46, 34.81, 32.60, 28.93, 23.46, 14.41, olefinic signals at 125.5, 128.4, 129.2.

4.10. X-ray structure determinations

X-ray diffraction measurements were made on a Siemens SMART diffractometer with a CCD area detector, using graphite monochromated Mo Kα radiation. The crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. A hemisphere of data was collected using ω scans of 0.3°. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range $4 < 2\theta < 45°$. The frame data were integrated using the program SAINT (SAX Area-Detector Integration Program; V4.024; Siemens Industrial Automation, Inc., Madison, WI, 1995). An empirical absorption correction based on measurements of multiply redundant data was performed using the programs XPREP (part of the SHELXTL Crystal Structure Determination Package; Siemens Industrial Automation, Inc., Madison, WI, 1995) or SADABS. Equivalent reflections were merged. The data were corrected for Lp effects. A secondary extinction correction was applied if appropriate. The structures were solved using the TEXSAN crystallographic software package of the Molecular Structure Corporation, using direct methods, and expanded with Fourier techniques. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in calculated positions but not refined unless otherwise noted. The function minimized in the full-matrix least-squares refinement was $\Sigma\, w(|F_o|-|F_c|)^2$. The weighting scheme was based on counting statistics and included a p-factor to downweight the intense reflections (Table 3).

Table 3
Crystallographic data for compounds **3** and **7**

Compound	**3**	**7**
Crystal parameters		
Empirical formula	$C_{26}H_{42}Cl_2N_2Si_2Zr$	$C_{85}H_{77}BF_{15}N_2Si_2Zr$
Formula weight	600.93	1569.73
Temperature (°C)	−136	−130
Crystal system	monoclinic	triclinic
Space group	$C2/c$ (#15)	$P\bar{1}$ (#2)
a (Å)	30.6339(4)	15.023(1)
b (Å)	11.2771(2)	16.254(1)
c (Å)	21.7039(3)	18.377(1)
α (°)	90	73.647(1)
β (°)	128.042(1)	73.426(1)
γ (°)	90	63.245(1)
V (Å^3)	5905.0(2)	3778.4(4)
Z	8	2
Dcalc (g cm^{-3})	1.352	1.380
μ(Mo Kα) (cm^{-1})	6.51	2.61
F(000)	2512	1618.00
Size (mm)	0.10 × 0.04 × 0.06	0.17 × 0.26 × 0.10
Data collection		
Unique/total reflection	4466/12 111	12 772/18 308
R_{int}	0.045	0.049
Empirical absorption correction	0.06	0.025
μR, T_{min}–T_{max}	0.884–0.986	0.732–0.978
Refinement		
Observations [$I > 3\sigma(I)$]	3330	5948
Variables	299	955
Reflection/parameters ratio	11.14	6.23
$R = \Sigma\, \|\|F_o\|-\|F_c\|\|/\Sigma\, \|F_o\|$	0.036	0.053
$Rw = [(\Sigma\, \omega(\|F_o\|-\|F_c\|)^2/\Sigma\, \omega F_o^2)]^{1/2}$	0.046	0.050
Goodness-of-fit $([\Sigma\, w(\|F_o\|-\|F_c\|)^2/(N_o-N_v)]^{1/2})$	1.65	1.49
Max. and min. peaks in final difference map (e Å^{-3})	0.38/−0.43	0.54/−0.75

5. Supplementary material

The material is available from the authors on request.

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