Synthesis, Characterization and Ethylene Polymerization Activity of Zirconium Complexes Containing Nonsymmetric Diamido Ligands Derived from 2-Aminobenzylamine

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Several *N*,*N'*-bis(trialkylsilyl)-substituted diamines of the general formula $[(SiR_3)_2\text{-ABA}]H_2$ [ABA = 2-amidobenzylamido, SiR_3 = $SiMe_3$ (**1a**), $SiMePh_2$ (**1b**), $SiMe_2tBu$ (**1c**) or $SiiPr_3$ (**1d**)], together with related compounds in which the substituents of the two nitrogen atoms are different, e.g. $[(SiMePh_2)(SiMe_3)\text{-ABA}]H_2$ (**1g**), have been synthesized. Their reaction with 2 equiv. of *n*BuLi afforded the dilithiated derivatives, which reacted with $ZrCl_4$ to yield metallaspirocyclic complexes of the type $Zr[(SiR_3)_2\text{-ABA}]_2$. Protonolysis of $Zr(NMe_2)_4$ with 1 equiv. of the parent diamines led to the monosubstituted complexes $Zr[(SiR_3)_2\text{-ABA}](NMe_2)_2$ [SiR_3 = $SiMe_3$ (**4a**), $SiMePh_2$ (**4b**) or $SiMe_2tBu$ (**4c**)] and $Zr[(SiMePh_2)(SiMe_3)\text{-ABA}](NMe_2)_2$ (**4g**) in high yield, and subsequent reaction with excess $SiMe_3Cl$ afforded the dichlorides $Zr[(SiMe_3)_2\text{-ABA}]Cl_2$ (**5a**), $Zr[(SiMe_2tBu)_2\text{-ABA}]Cl_2$ (**5c**), and $Zr[(SiMePh_2)(SiMe_3)\text{-ABA}]Cl_2$ (**5g**). The X-ray crystal structure of **5c** shows that it forms dimers via two Zr–Cl bridges; moreover, a bonding interaction between the zirconium centre and the aryl *ipso*-carbon atom linked to the anilinic nitrogen atom is evident. A hydrochlorinated derivative of **5c**, $Zr[(SiMe_2tBu)_2(H)\text{-ABA}]Cl_3$ (**6c**), was also analysed by X-ray diffraction and shown to exhibit analogous structural characteristics. Low-temperature NMR studies revealed all these complexes to be fluxional and permitted an insight into the molecular structures in solution. The ABA framework undergoes a rocking motion about the corresponding ZrN_2 plane, whose activation energy is between 37 and 43 kJ mol^{-1}. Compounds **3** and **5** exist as several stereoisomers that interconvert by this process. On activation with MAO, the dichloride complexes of type **5** polymerize ethylene at both room temperature and pressure to yield linear high molecular mass polyethylenes with a broad molecular mass distribution.

Introduction

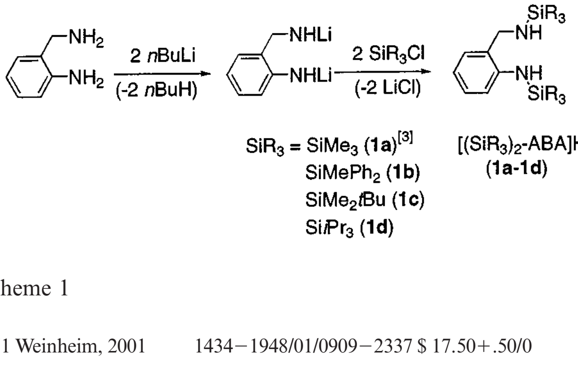
The search for new olefin polymerization catalysts based on chelating diamido ligands has concentrated mostly on Group 4 transition metal complexes of symmetric ligands containing two identical amide functions.[1] However, attempts to design catalysts for the stereoselective polymerization of α-olefins with the help of such ligands has met with limited success.[2] Nonsymmetric diamido ligands containing two different amido functions are potentially of great interest in this regard, particularly if the nitrogen substituents of each amido function can be modified independently. This would help us, if polymerization of α-olefins could be obtained, to better understand the influence of electronic and steric effects of the ligands on the stereoselectivity results.

Herein, we wish to describe the synthesis of several *N*,*N'*-disubstituted 2-aminobenzylamines. This fragment affords a suitable framework for the purpose outlined. Its application resulted in the generation of a series of bis(dimethylamido)- and dichlorozirconium complexes. The fluxional behaviour ot these new complexes and their ability to catalyse the polymerization of olefins have been analysed. One of these ligands has been reported recently, together with three titanium and two zirconium complexes containing the ligand.[3]

Results and Discussion

Ligands Precursors

The *N*,*N'*-bis(trialkylsilyl)-substituted diamines $[(SiR_3)_2\text{-ABA}]H_2$ (**1a**−**1d**) were synthesized as reported for **1a**[3] by treating the dilithio salt of 2-aminobenzylamine with 2



Scheme 1

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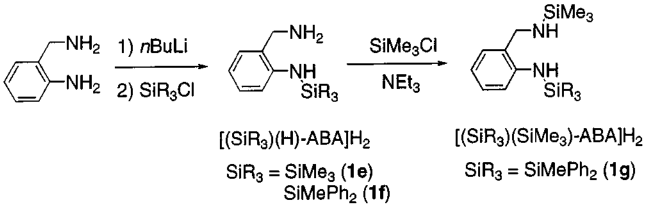
equiv. of trialkylchorosilanes in diethyl ether (or THF for **1d**)/hexane (Scheme 1), and isolated as viscous oils (or a cream solid for **1c**) in 80−90% yield. For **1d**, 18 h of heating in THF to reflux was necessary to complete the reaction. Compound **1a**, but not the others, could also be obtained by the reaction of 2-aminobenzylamine with 2 equiv. of Me_3SiCl in the presence of triethylamine (96% yield).

Initial attempts to synthesize $[(SiR_3)(SiR'_3)\text{-ABA}]H_2$ derivatives possessing two different nitrogen substituents led to the diamines $[(SiMe_3)(H)\text{-ABA}]H_2$ (**1e**) and $[(SiMePh_2)(H)\text{-ABA}]H_2$ (**1f**) being obtained as yellow-orange oils (93−95% yield, Scheme 2), which contain silyl substituents located solely on the anilino nitrogen atom. These compounds tend to disproportionate into **1a**−**b** and 2-aminobenzylamine. Compound **1e** was hence contaminated (7% total amount) with **1a**, and also with $[(H)(SiMe_3)\text{-ABA}]H_2$, of which neither could be properly separated. On the other hand, treatment of 2-aminobenzylamine with 1 equiv. of Me_3SiCl in the presence of triethylamine preferentially introduces the substituent on the benzylamino nitrogen atom, affording $[(H)(SiMe_3)\text{-ABA}]H_2$, but this reaction is also unselective and leads to the formation of **1a** in almost equal proportions. Only compound $[(SiMePh_2)(SiMe_3)\text{-ABA}]H_2$ (**1g**) could be generated as a viscous oil from **1f** (87% isolated yield, Scheme 2). The diamines were characterized by ^1H and ^{13}C NMR spectroscopy. It is of interest to note that the benzylic protons give rise to a doublet or a triplet, whether the adjacent nitrogen atom is substituted or not. This indicates that hydrogen exchange in the benzylamino groups is slower in these compounds than in the 2-aminobenzylamine precursor, for which the corresponding coupling is not observed.

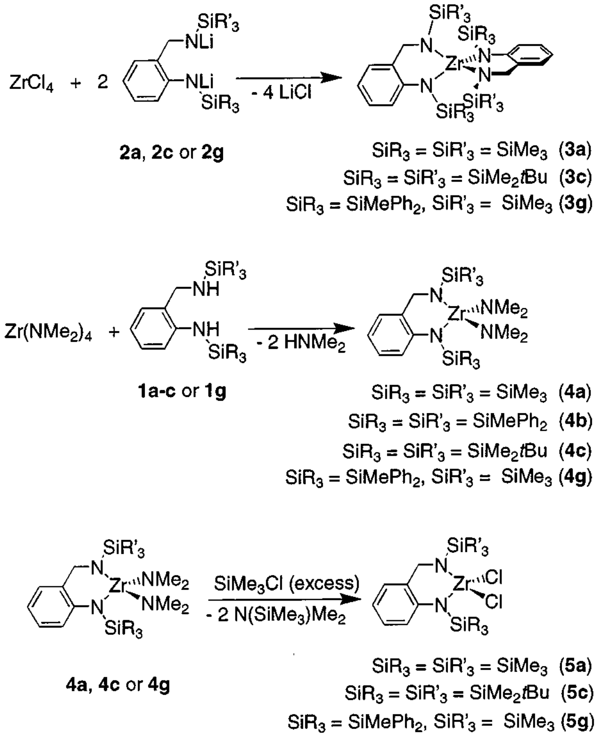


Scheme 2

The dilithiated derivatives $[(SiR_3)_2\text{-ABA}]Li_2$ [SiR_3 = $SiMe_3$ (**2a**), $SiMePh_2$ (**2b**), $SiMe_2\textit{t}Bu$ (**2c**)] or $Si\textit{i}Pr_3$ (**2d**)] and $[(SiMePh_2)(SiMe_3)\text{-ABA}]Li_2$ (**2g**) were obtained as white solids or a brown paste (**2d**) (34−95% yield) by double deprotonation of **1a**−**d** or **1g** with *n*BuLi in hexane. The observation of an AX pattern for the room-temperature ^1H NMR signal of the CH_2 groups of **2a** and **2g**, and of a broad singlet for the corresponding protons of **2b**−**d**, suggests that these compounds possess a disymmetrical aggregated structure in solution. This is confirmed by the dimeric ladder structure of **2a** in the solid state, established by X-ray diffraction.[4] The fluxional nature of these lithiated compounds was further characterized by the coalescence of the AX spectrum of **2a** into a singlet at 41 °C ($\Delta G^{\neq}$ = 61.6 kJ·mol^{-1}),[5] and by the splittting of the broad singlet of **2b** into a doublet of doublets at δ = 4.56 and 3.53 at −33 °C in [D$_8$]toluene.

Zirconium Complexes

Even when only low proportions of the dilithio reactants were used, transmetallation reactions between **2a**, **2c** or **2g** and $ZrCl_4$ led to the metallaspirocyclic complexes $Zr[(SiMe_3)_2\text{-ABA}]_2$ (**3a**), $Zr[(SiMe_2\textit{t}Bu)_2\text{-ABA}]_2$ (**3c**), and $Zr[(SiMePh_2)(SiMe_3)\text{-ABA}]_2$ (**3g**) (Scheme 3), as reported earlier for **3a**.[3] However, compounds **2b** and **2d** gave only mixtures that could not be separated. In particular, using 2 equiv. of **2g**, compound **3g** was synthesized in good yield in hot toluene and isolated as a yellow solid. Its ^1H NMR spectrum at room temperature is analogous to that of **3a**,[3] displaying an AX pattern at δ = 4.89 and 3.93 (CD_2Cl_2, ^2J = 13.4 Hz) for the two CH_2 groups, which is consistent with a tetrahedral structure of C_2 symmetry, of the type of that determined for **3a** by X-ray diffraction.[3]



Scheme 3

The dichloride derivatives were prepared from the bis(dimethylamido) precursors. These were synthesized by protonolysis of $Zr(NMe_2)_4$ [6] with 1 equiv. of the diamines **1** (Scheme 3). Complexes $Zr[(SiMe_3)_2\text{-ABA}](NMe_2)_2$ (**4a**), $Zr[(SiMePh_2)_2\text{-ABA}](NMe_2)_2$ (**4b**), $Zr[(SiMe_2\textit{t}Bu)_2\text{-ABA}](NMe_2)_2$ (**4c**), and $Zr[(SiMePh_2)(SiMe_3)\text{-ABA}](NMe_2)_2$ (**4g**) were obtained in high yield (96−99%) as pale yellow to orange, viscous oils. The diamine **1d**, however, did not react with $Zr(NMe_2)_4$. The ^1H and ^{13}C NMR spectra of the four complexes, at room temperature, reveal the presence of two apparently equivalent and symmetrical NMe_2 ligands for one coordinated ABA group, the two benzylic protons of which give rise to a singlet. The fluxional behaviour that lies at the root of these unexpected observations is specified below.

Complexes **4a**, **4c** and **4g** react with an excess of trimethylsilyl chloride to give the respective dichloride derivatives Zr[$(SiMe_3)_2$-ABA]Cl_2 (**5a**),[7] Zr[$(SiMe_2tBu)_2$-ABA]Cl_2 (**5c**), and Zr[$(SiMePh_2)(SiMe_3)$-ABA]Cl_2 (**5g**) in good yield (Scheme 3). However, the analogous reaction involving **4b** was unsuccessful. The solid pale yellow products are poorly soluble in hydrocarbons, and the singlets observed at δ = 4.72, 4.59 and 4.87 in their ^1H NMR spectra (C_6D_6, room temperature), which are assigned to their methylene groups, are indicative of a high apparent symmetry similar to that found for the amido complexes of type **4**.

Single crystals of **5c** were grown by cooling a saturated toluene/pentane solution to −20 °C and were analysed by X-ray diffraction. The molecular structure of **5c** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. The structure consists of discrete dimers that reside on an inversion centre of the space group, the association between the two monomeric units being realised via two weak zirconium−chlorine bridging interactions [Zr−Cl(2)′ = 2.706 Å]. Hence, each zirconium atom is pentacoordinate and possesses a distorted trigonal-bipyramidal coordination geometry. The benzylamido nitrogen atom and the bridging chloride ion occupy the axial sites [N(1)−Zr−Cl(2)′ = 163.7°]. The main distortion results from the acute Cl(2)−Zr−Cl(2)′ angle in the planar bridging Zr_2Cl_2 unit (75.5°), while the diamide ligand chelate angle [N(1)−Zr−N(2) = 93.1°], as well as the other bond angles around the zirconium centre, are within the usual ranges. Short Zr−N bond lengths [Zr−N(1) = 2.016 Å, Zr−N(2) = 2.012 Å] and sp^2-hybridized nitrogen atoms [the summation of bond angles is 359.0° at both N(1) and N(2)] indicate strong π-donation from the two nitrogen atoms to the electron-deficient zirconium centre. As expected, the zirconium−chlorine bond length of the bridging halide ion [Zr−Cl(2) = 2.554 Å] is longer than that of the terminal one [Zr−Cl(1) = 2.386 Å].

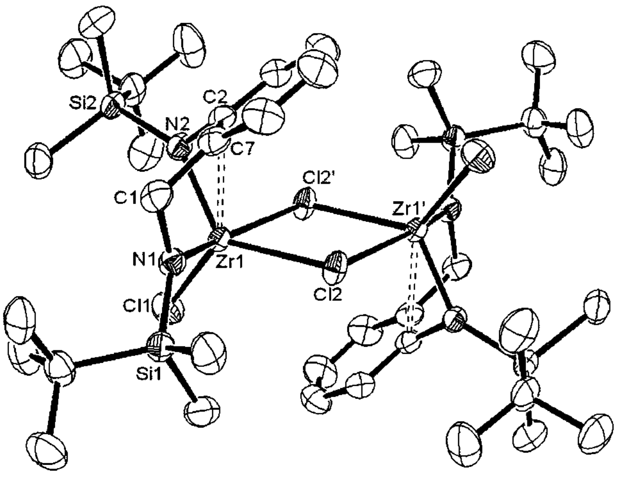


Figure 1. ORTEP view of the molecular structure of **5c** (50% probability thermal ellipsoids); hydrogen atoms are omitted for clarity; primed atoms refer to centrosymmetric equivalents

Table 1. Selected bond lengths [Å] and angles [°] for **5c**

Zr−N(1)	2.0163(17)	Zr−N(2)	2.0120(15)
Zr−C(2)	2.538(2)	Zr−Cl(1)	2.3864(8)
Zr−Cl(2)	2.5545(13)	Zr−Cl(2)′	2.7062(10)
Zr−C(1)	2.903(3)	Zr−C(7)	2.908(2)
N(1)−C(1)	1.489(2)	N(2)−C(2)	1.437(2)
C(1)−C(7)	1.510(3)	C(2)−C(7)	1.401(3)
N(2)−Zr−N(1)	93.09(7)	N(2)−Zr−Cl(1)	110.18(5)
N(2)−Zr−Cl(2)	124.92(5)	N(1)−Zr−Cl(2)	90.00(6)
Cl(1)−Zr−Cl(2)	122.18(3)	Cl(1)−Zr−Cl(2)′	90.08(3)
N(2)−Zr−Cl(2)′	89.30(6)	N(1)−Zr−Cl(2)′	163.71(5)
Cl(2)−Zr−Cl(2)′	75.51(3)	N(1)−Zr−Cl(1)	104.15(5)
N(2)−Zr−C(2)	34.43(6)	C(2)−N(2)−Zr	93.25(11)
Zr−Cl(2)−Zr′	104.49(3)		

The ligand chelate ring is severely puckered. Of particular relevance is its significant folding along the C(1)−N(2) axis (70.7°), and the correspondingly very short Zr−C(2) distance (2.537 Å). This effect, which is more pronounced than in compound **3a**,[3] and certainly contributes to an even shorter Zr−N(2) bond along with reduction of the C(2)−N(2)−Zr angle to 93.3°, is similar to that discussed for several *o*-phenylenediamido complexes.[8] It is ascribed to a bonding interaction between the zirconium centre and the aryl *ipso*-carbon atom linked to the anilinic nitrogen atom. This way of compensating electronic unsaturation at the metal centre is distinct from that found in the analogous titanium complex Ti[$(SiMe_3)_2$-ABA]Cl_2. In the latter case, an interaction between the metal centre and the benzylic methylene group, that gives rise to a significantly different ligand geometry, has been shown to occur.[3] It is similar, however, to that found in the lithium derivative **2a**.[4] The infrared spectra suggest that **5a** is also dimeric in the solid state, as revealed by the broad absorption observed at 254 cm^{-1}, assigned to zirconium−chloride bridges, but not **5g** for which an analogous band is totally absent.

By following the same crystallization procedure but, apparently, under slightly different and uncontrolled conditions, a further zirconium complex was unexpectedly crystallized in low yield from solutions of **5c**. An X-ray analysis of this compound revealed it to be Zr[$(SiMe_2tBu)_2$(H)-ABA]Cl_3 (**6c**) (i.e. the hydrochlorinated derivative of **5c**), in which the benzylamido nitrogen atom of **5c** has been protonated to afford a coordinated benzylamino function. This results in the sp^3 hybridization of this nitrogen atom [sum of angles formed by non-H atoms around N(2) = 343.2°] and in the substantial lengthening of the corresponding zirconium−nitrogen bond [Zr−N(2) = 2.388 Å]. The other structural characteristics of **6c** are similar to those of **5c**. Compound **6c** crystallizes in the same space group, and also consists of discrete centrosymmetric dimers that are associated via two chloride bridges (Figure 2, Table 2). The geometry of each monomeric unit is now a distorted octahedron, leading to somewhat different bond angles around the zirconium centre. However, the distinctive configuration of the ABA chelate ring is retained in this complex. The interaction between the zirconium centre and the anilinic *ipso*-carbon atom of the aryl ring is strengthened, as revealed by the shorter corresponding distance [Zr−C(1) = 2.513 Å] and the more acute C(1)−N(1)−Zr angle (91.2°), suggesting that the metal centre is slightly more electron-deficient than in **5c**. It may also be noted that the chloride bridges are *trans* to the anilido function and not to the benzylamido nitrogen atom as in **5c**. As a consequence, the aryl rings are perpendicular to the Zr_2Cl_2 plane, instead of overhanging it as in **5c**.

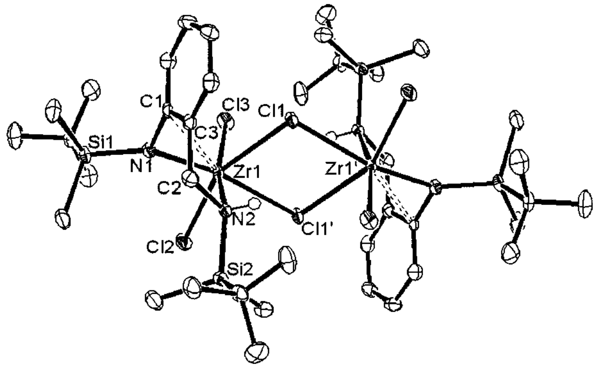


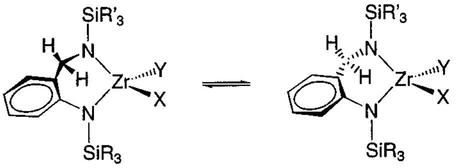
Figure 2. ORTEP view of the molecular structure of **6c** (50% probability thermal ellipsoids); hydrogen atoms are omitted for clarity, except those located on the benzylamino nitrogen atoms; primed atoms refer to centrosymmetric equivalents

Table 2. Selected bond lengths [Å] and angles [°] for **6c**

Zr−N(1)	2.030(3)	Zr−N(2)	2.388(3)
Zr−Cl(2)	2.4043(9)	Zr−Cl(3)	2.4181(10)
Zr−Cl(1)	2.6054(10)	Zr−Cl(1)′	2.6928(10)
Zr−C(2)	3.101(3)	Zr−C(3)	2.968(3)
Zr−C(1)	2.513(3)		
N(1)−Zr−N(2)	88.11(11)	Cl(2)−Zr−Cl(3)	99.05(3)
N(1)−Zr−Cl(2)	89.16(8)	N(2)−Zr−Cl(2)	95.21(7)
N(1)−Zr−Cl(3)	96.46(8)	N(2)−Zr−Cl(3)	165.07(8)
N(2)−Zr−Cl(1)	80.60(8)	Cl(2)−Zr−Cl(1)	153.00(3)
Cl(3)−Zr−Cl(1)	84.68(3)	N(1)−Zr−Cl(1)	117.15(8)
N(1)−Zr−Cl(1)′	168.84(8)	N(2)−Zr−Cl(1)′	91.16(8)
Cl(2)−Zr−Cl(1)′	79.81(3)	Cl(3)−Zr−Cl(1)′	87.05(3)
Cl(1)−Zr−Cl(1)′	73.65(3)	C(1)−N(1)−Zr	91.26(19)
Zr−Cl(1)−Zr′	106.35(3)		

Fluxionality

The apparent discrepancy between the twisted, nonplanar geometry of the ABA ligands in complexes **5c** and **6c** and the room-temperature NMR spectra of complexes **4**−**5** prompted us to examine the low-temperature ^1H NMR spectra of compounds **3**−**5**. Thus, it was possible to verify that the two benzylic hydrogen atoms are actually diastereotopic in all cases, but equilibrate rapidly at higher temperatures in **4**−**5** by a dynamic process that seems common to all members of the series. We suggest this process consists of the rocking motion of each ABA framework about the corresponding ZrN_2 plane, as illustrated in Scheme 4 for a monomeric tetrahedral structure. This process will interconvert the two enantiomeric configurations of the complexes if X = Y (complexes **4** and **5**, if monomeric), but not if X ≠ Y (complexes **3**).



Scheme 4

Figure 3 illustrates the coalescence of the broad AB quadruplet observed at 205 K for the benzylic protons of **4a** in $[D_8]$toluene (δ = 4.51/4.25, ^2J = 15.4 Hz) into the singlet already mentioned above. However, the two NMe_2 ligands give rise to a lone singlet over the whole temperature range, although up to four singlets may be expected in the limiting spectrum of this complex. Compound **4b** behaves similarly, revealing a doublet of doublets at δ = 4.30/4.08 at 185 K (CD_2Cl_2, ^2J = 15.1 Hz) that coalesce into a singlet at 202 K. Moreover, two distinct NMe_2 signals are observed, in this case, at 185 K (δ = 2.73 and 1.99), as well as two resonances at δ = 7.63 and 7.55 assigned to the *ortho*-protons of the $SiMePh_2$ substituent of the anilinic nitrogen atom, and these two pairs coalesce at 211 K and 194 K, respectively. This is in agreement with the proposed monomeric structure of this molecule and the fluxionality represented on Scheme 4. Compound **4g** affords less clear-cut observations because the limiting spectrum is not reached, even at 180 K in CD_2Cl_2. However, two broad $SiMePh_2$ resonances are distinguished again at δ = 7.60 and 7.49, that coalesce at 183 K. The activation energies determined[5] for these three complexes are reported in Table 3. Clearly, they depend on both the electronic and steric properties of the trialkylsilyl substituents of the two ABA nitrogen atoms, and on the strength of the Zr−aryl interaction discussed above for **5c** and **6c**.

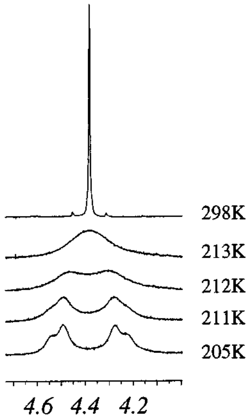


Figure 3. Variable-temperature ^1H NMR spectra of complex **4a** in the benzylic region ($[D_8]$toluene, 300 MHz)

Spirocyclic complexes of type **3** contain two ABA ligands and may therefore exist as three isomers differing in the respective configuration of these ligands. One of the isomers

Table 3. Activation energy for the ABA rocking process in complexes **4**

	4a ([D$_8$]toluene)	**4b** (CD$_2$Cl$_2$)	**4g** (CD$_2$Cl$_2$)
$\Delta G^{\neq}$ [kJ mol^{-1}]	42.4 (± 0.2)	40.3 (± 0.4)	37.5 (± 0.4)

would be nonsymmetric and the others ideally C_2-symmetric, so that the resonances of up to four nonequivalent ligands may be expected in the ^{1}H NMR limiting spectrum of each of the compounds. In full agreement with this assumption, complex **3g** at 185 K in CD$_2$Cl$_2$ exhibits four SiMe$_3$ singlets (δ = 0.06, −0.01, −0.09 and −0.20) and four Si*Me*Ph$_2$ singlets (δ = 1.03, 0.64, 0.46 and 0.22) of unequal intensity (Figure 4). The three isomers are therefore present in comparable amounts. The other regions of the spectrum are less well resolved but follow the same trend. On raising the temperature, all sets of resonances coalesce to yield the simple spectrum observed at room temperature. The complexity of the spectral changes makes the determination of the corresponding activation energies unsafe. Notwithstanding, these appear to be close to the values obtained for compounds **4** and it seems reasonable to conclude that the interconversion of the three stereoisomers occurs by the ligand rocking process of Scheme 4.

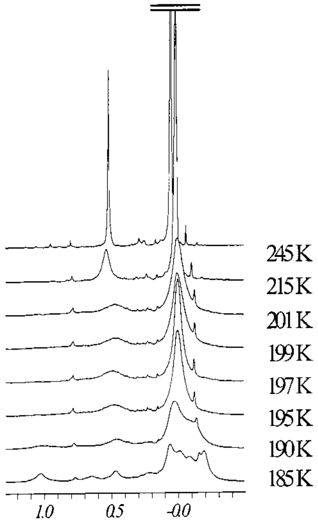


Figure 4. Variable-temperature ^{1}H NMR spectra of complex **3g** in the Si−Me region (CD$_2$Cl$_2$, 300 MHz)

Complex **3a** has been described as a single isomer in the solid state as well as in solution.[3] However, its ^{1}H NMR spectrum at 185 K in CD$_2$Cl$_2$ shows two broad singlets at δ = 0.42 and 0.07 for the SiMe$_3$ substituent of the anilinic nitrogen atom. The relative intensities of these signals, that coalesce at 195 K ($\Delta G^{\neq}$ = 38.2 ± 0.4 kJ mol^{-1}), are in the approximate ratio 3:1. Despite the fact that an analogous observation was not made for the benzylamido SiMe$_3$ substituent, nor for the benzylic protons (whose signals overlap at 185 K), this indicates that at least two of the three possible stereoisomers are present in solution, and that they interconvert at a rate which is close to that of **3g**.

The dichloride complexes **5** may remain dimeric in solution, as are **5a** and **5c** in the solid state, or they may dissociate into tetrahedral monomers. An ^{1}H NMR spectroscopic analysis of [D$_8$]toluene solutions of 5**a** and **5g** clearly favors the former, since very complicated spectra were obtained at 200 K (Figure 5). These coalesce again at a higher temperature. As for compounds **3**, the existence of the three stereoisomers expected for these dimers, and their interconversion by the ABA rocking process, are thus indicated. However, chemical exchange between the monomeric constituents of the dimers is also implied in this case, resulting in the singlet observed above 275 K for the benzylic protons, instead of the AB spin system shown by compounds **3**. The monomeric form could even be present in substantial amounts and be the origin of some of the resonances detected at 200 K. As illustrated in Figure 5, the coalescence phenomenon indeed seems to occur in two or three successive steps with slightly different rates.

On the other hand, the spectrum of **5a** in CD$_2$Cl$_2$ at 180 K is simpler and reveals only one doublet of doublets for the benzylic protons (δ = 5.42/4.33, ^2J = 16.2 Hz), that coalesces into a singlet on raising the temperature. This is analogous to the behavior of the bis(dimethylamido) derivatives **4** and may indicate the monomeric nature of **5a** in this solvent. However, it may also result from faster intermolecular exchange between the monomeric units of dimeric species, both assumptions are consistent with the more polar nature of dichloromethane with respect to toluene. From the temperature of coalescence (213 K), the activation energy of the ABA rocking motion that corresponds to this observation was calculated to be $\Delta G^{\neq}$ = 39.9 ± 0.4 kJ mol^{-1}, which is close to the values obtained for **3a** and **4a**, but markedly higher than that of the analogous titanium complex Ti[(SiMe$_3$)$_2$-ABA]Cl$_2$, for which the signal for the benzylic protons remains as a singlet at 183 K.[3] This latter observation may be correlated with the absence of any M−C$_{ipso}$ contact in the titanium complex. The importance of such interactions on the activation energies is further emphasized by the substantially higher value ($\Delta G^{\neq}$ = 51 kJ mol^{-1}) reported for a similar process involving compound [*o*-C$_6$H$_4$(NSi*i*Pr$_3$)$_2$Zr(O*t*Bu)$_2$], in which the Zr−aryl interaction in the 5-membered chelate ring is on the contrary stronger.[8]

Ethylene Polymerization

In the presence of MAO as cocatalyst, the dichloride complexes of type **5** polymerize ethylene at both room temperature and pressure, but remain inactive against α-olefins such as propylene and 1-hexene. As appears from Table 4, the ethylene polymerization activity of all compounds is low[1] and of a short life time. It is considerably inhibited at 0 °C for **5g**, but only slightly affected at 50 °C for **5a**. The resulting polyethylenes, which were separated by conventional methods, are linear (by ^{1}H NMR spectroscopy) and show a very broad molecular mass distribution, characteristic of multisite catalysts. Activation of the catalytic precursors with MAO thus appears more complicated than envisaged.[9] The molecular masses obtained with **5a** are high,

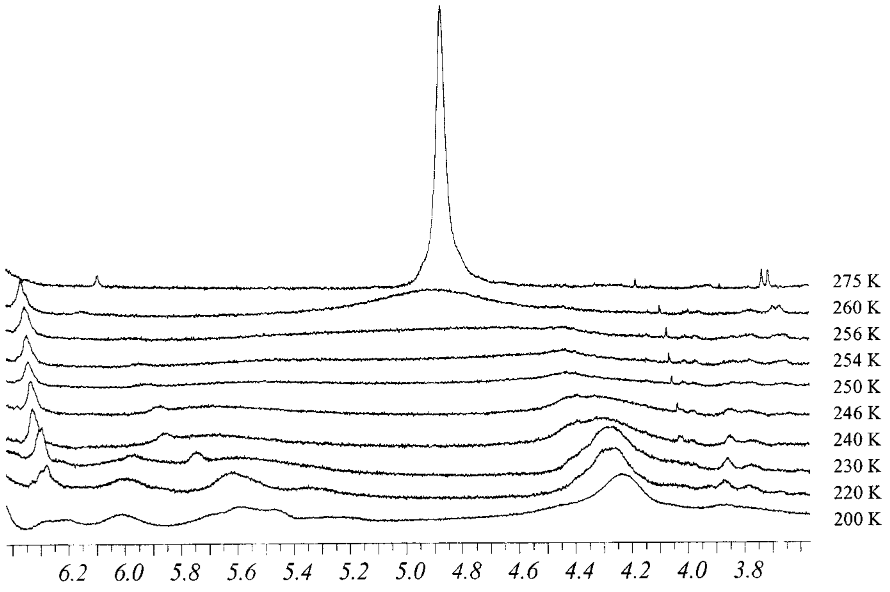


Figure 5. Variable-temperature ^1H NMR spectra of complex **5g** in the benzylic region ([D$_8$]toluene, 300 MHz)

Table 4. Ethylene polymerization results

Entry[a]	Cat. [μmol]	T [°C]	$p(C_2H_4)$ [bar]	t [h]	Yield [mg]	Activity [kg/mol bar h]	$10^{-3}M_w$[b] [g/mol]	$10^{-3}M_n$ [b] [g/mol]	M_w/M_n
1	**5a** (23.4)	25	6	3	1200	2.8	820	28.5	28.8
2	**5a** (2.34)	25	6	0.5	47	6.7			
3	**5a** (11.7)	50	6	0.25	132	7.5	insoluble		
4	**5c** (9.8)	25	1	0.17	21	13			
5	**5g** (18.1)	25	1	1	90	5.0	153	5.6	27.2
6	**5g** (18.1)	0	1	1	6	0.3			

[a] The reactions were run in toluene (10 mL) under constant ethylene pressure, using 1000 equiv. of MAO as cocatalyst (except for Entry 4: 500 equiv.). − [b] By SEC (140 °C, 1,2,4-trichlorobenzene) vs. polystyrene standards.

whereas **5g** leads to much lower values. If this difference does not result from the difference in ethylene pressure between experiments 1 and 5, it would indicate a ligand effect showing that ABA-based ligands remain bound to the zirconium centre in the catalytically active species. These catalytic systems were not further optimized.

Conclusion

We have shown that various trialkylsilyl substituents can be linked to the two nitrogen atoms of 2-aminobenzylamine, and that the chelating diamido ligands derived from these diamines can serve to stabilize a series of zirconium complexes and to modulate their properties. Structural investigations have shown that the chloride compounds form dimers, and that zirconium−aryl interactions are probably responsible for the restrained flexibility of the ligands. As expected from their low coordination numbers and high electron deficiency, these complexes catalyse the polymerization of ethylene, but unfortunately the activities remain low in all cases.

Experimental Section

General Procedures: All experiments were performed in a high-vacuum line using standard Schlenk techniques or in a dry box under N_2. Solvents were dried with Na/benzophenone ketyl (pentane, toluene, hexane, THF, ether) or P_2O_5 (dichloromethane) and distilled prior to use under nitrogen. Deuterated solvents were dried with activated 4-Å molecular sieves. Known compounds that were not commercial were prepared according to literature procedures. Methylaluminoxane (MAO) was purchased as a 10% toluene solution from Schering or Aldrich. − NMR spectra were recorded with a Bruker AC-300, AC-250 or SY-200 spectrometer at ambient probe temperature unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported in ppm versus $SiMe_4$ and were determined by reference to the residual solvent peaks. − Elemental analyses were performed by the Service Central d'Analyse du CNRS (Vernaison), the Service Commun de Microanalyse de l'ULP (Strasbourg), or the Service d'Analyse du LCC (Toulouse). − Infrared spectra were recorded with a Perkin−Elmer 1600 FT-IR spectrometer in the 4000−200 cm^{-1} range using KBr or CsI disks. − Size Exclusion Chromatography (SEC) analyses were carried out at BP−Grangemouth with a AT7 GPC Waters 150-CV instrument in 1,2,4-trichlorobenzene at 140 °C relative to polystyrene standards. − Activation energies were calculated using the Eyring equation.[5]

[(SiMe$_3$)$_2$-ABA]H$_2$ (1a): The synthesis of this compound has been reported in the literature.[3] In an alternative method, 13.8 mL of triethylamine (99.0 mmol) was added to a vigorously stirred solution of 2-aminobenzylamine (3 g, 24.6 mmol) in 130 mL of diethyl ether at 0 °C, and 6.90 mL of chlorotrimethylsilane (54.4 mmol) was then added dropwise. The reaction mixture containing a voluminous white precipitate was stirred for 48 h at room temperature and filtered, and the filtrate was concentrated to dryness. Extraction of the residue with 20 mL of pentane and removal of the volatiles in vacuo yielded the product as a yellow oil which could be used without further purification. Short-path distillation under high vacuum, however, led to an analytically pure colorless oil (6.281 g, 96%). − ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.17 (dt, 1 H, H^4 or H^5), 7.02, 6.92 (dd, 1 H, H^3 and H^6), 6.76 (dt, 1 H, H^4 or H^5), 5.30 (s, broad, 1 H, ArN*H*), 3.73 (d, ^3J = 6.8 Hz, 2 H, CH$_2$), 0.27 (s, 9 H, ArNHSi*Me*$_3$), 0.12 (t, broad, 1 H, CH$_2$N*H*), 0.00 (s, 9 H, CH$_2$NHSi*Me*$_3$). − ^{13}C NMR (C_6D_6, 75 MHz): δ = 147.83 (C^2), 129.98, 128.52, 117.66, 116.43 (C^3−C^6), 45.95 (CH$_2$), 0.43 (SiMe$_3$), −0.44 (SiMe$_3$). The C^1 signal could not be detected. − IR (neat): ṽ = 3342 (sh) and 3298 cm^{-1}, (ν_{N-H}). − $C_{13}H_{26}N_2Si_2$ (266.5): calcd. C 58.58, H 9.83, N 10.51; found C 58.24, H 9.68, N 10.37.

[(SiMePh$_2$)$_2$-ABA]H$_2$ (1b): 10.2 mL of a 1.6 M solution of *n*BuLi in hexane (16.4 mmol) was slowly added whilst stirring at −78 °C to a solution of 2-aminobenzylamine (1 g, 8.2 mmol) in 60 mL of diethyl ether. The yellow solution was allowed to warm to room temperature, stirred for 3 h, and cooled again to −20 °C; 3.81 g of chloro(methyl)diphenylsilane (16.4 mmol) in 20 mL of diethyl ether was then added dropwise. After stirring overnight at room temperature, the brown reaction mixture was centrifuged and the resulting orange solution was concentrated to dryness to yield 3.629 g of a yellow oil (86%) which can be recrystallized from cold pentane. − ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.72 (m, 4 H, H$_o$ ArNHSiMe*Ph*$_2$), 7.43 (m, 4 H, H$_o$ CH$_2$NHSiMe*Ph*$_2$), 7.18 (m, 12 H, H$_m$ + H$_p$ SiMe*Ph*$_2$), 6.92 (m, 3 H, Ar), 6.64 (m, 1 H, Ar), 5.70 (s, broad, 1 H, ArN*H*), 3.88 (d, ^3J = 6.4 Hz, 2 H, CH$_2$), 0.80 (t, broad, 1 H, CH$_2$N*H*), 0.78 (s, 3 H, ArNHSi*Me*Ph$_2$), 0.37 (s, 3 H, CH$_2$NHSi*Me*Ph$_2$). − ^{13}C NMR (C_6D_6, 75 MHz): δ = 146.67 (C^2), 137.10, 136.86 (C$_{ipso}$ SiMe*Ph*$_2$), 135.03, 134.88 (C$_{o/m}$ SiMe*Ph*$_2$), 130.13 (Ar), 130.08, 129.74 (C$_p$ SiMe*Ph*$_2$), 128.56 (Ar), 128.43, 128.18 (C$_{o/m}$ SiMe*Ph*$_2$), 118.31, 117.52 (Ar), 46.12 (CH$_2$), −2.22 (ArNHSi*Me*Ph$_2$), −3.39 (CH$_2$NHSi*Me*Ph$_2$). The C^1 signal could not be detected. − IR (nujol mull): ṽ = 3336 and 3256 cm^{-1}, (ν_{N-H}). − $C_{33}H_{34}N_2Si_2$ (514.8): calcd. C 76.99, H 6.66; found C 76.34, H 6.37.

[(SiMe$_2$*t*Bu)$_2$-ABA]H$_2$ (1c): This compound was prepared in THF according to the procedure described for **1b**. After removal of the volatiles under vacuum, the reaction residue was extracted with pentane. Concentration to dryness gave the product as a cream solid which was used without further purification (85% yield). − ^{1}H NMR (C_6D_6, 250 MHz): δ = 7.15 (t, 1 H, H^4 or H^5), 7.02, 6.98 (d, 1 H, H^3 and H^6), 6.79 (t, 1 H, H^4 or H^5), 5.21 (s, broad, 1 H, ArN*H*), 3.84 (d, 2 H, CH$_2$), 1.03 (s, 9 H, *t*Bu), 0.85 (s, 9 H, *t*Bu), 0.29 (s, 6 H, ArNHSi*Me*$_2$*t*Bu), 0.01 (s, 6 H, CH$_2$NHSi*Me*$_2$*t*Bu). The CH$_2$N*H* signal was not detected, but was found at δ = 1.44 in [D$_8$]THF. − $C_{19}H_{38}N_2Si_2$ (322.6): calcd. C 65.07, H 10.92, N 7.99; found C 64.9, H 10.8, N 7.9.

[(Si*i*Pr$_3$)$_2$-ABA]H$_2$ (1d): This compound was prepared in THF according to the procedure described for **1b**. The chlorotriisopropylsilane was added at room temperature, and the solution was refluxed for 18 h. After concentration to dryness, the product was extracted as a brown oil with pentane (82% yield). − ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.18 (dd, 1 H, H^3 or H^6), 7.12 (dt, 1 H, H^4 or H^5), 6.89 (dd, 1 H, H^3 or H^6), 6.77 (dt, 1 H, H^4 or H^5), 4.44 (s, broad, 1 H, ArN*H*), 3.92 (d, ^3J = 6.1 Hz, 2 H, CH$_2$), 1.15 (m, 42 H, Si*iPr*$_3$), 0.35 (t, broad, 1 H, CH$_2$N*H*). − ^{13}C NMR (C_6D_6, 75 MHz): δ = 147.04 (C^2), 129.47 (C^1), 129.58, 128.38, 118.10, 116.88 (C^3−C^6), 46.02 (CH$_2$), 18.72 (SiCH*Me*$_2$), 11.99 (SiC*H*Me$_2$), 11.64 (SiC*H*Me$_2$). − IR (neat): ṽ = 3361 (sh) and 3331 cm^{-1}, (ν_{N-H}). − $C_{25}H_{50}N_2Si_2$ (434.9): calcd. C 69.05, H 11.59, N 6.44; found C 68.66, H 11.47, N 6.35.

[(SiMe$_3$)(H)-ABA]H$_2$ (1e): To a solution of 250 mg of 2-aminobenzylamine (2.05 mmol) in 25 mL of diethyl ether at −80 °C, 1.3 mL of a 1.6 M solution of *n*BuLi in hexane (2.05 mmol) was added. A white precipitate built up rapidly. After 2 h at room temperature, the reaction mixture was cooled to −80 °C and 0.26 mL of chorotrimethylsilane (2.05 mmol) was added. The temperature was left to reach room temperature. After 12 h, filtration through Celite and concentration to dryness yielded an orange oil containing 93% of **1e** (by ^{1}H NMR). − ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.17 (dt, 1 H, H^4 or H^5), 6.92 (m, 2 H, H^3 and H^6), 6.75 (dt, 1 H, H^4 or H^5), 6.10 (s, broad, 1 H, ArN*H*), 3.51 (t, ^3J = 5.8 Hz, 2 H, CH$_2$), 0.45 (t, broad, 1 H, CH$_2$N*H*$_2$), 0.28 (s, 9 H, ArNHSi*Me*$_3$).

[(SiMePh$_2$)(H)-ABA]H$_2$ (1f): This compound was prepared as a yellow viscous oil according to the procedure described for **1e** (95% yield). − ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.76 (m, 4 H, H$_o$ SiMe*Ph*$_2$), 7.19 (m, 6 H, H$_m$ + H$_p$ SiMe*Ph*$_2$), 6.89 (m, 3 H, Ar), 6.83 (s, broad, 1 H, ArN*H*), 6.65 (m, 1 H, Ar), 3.53 (t, ^3J = 5.8 Hz, 2 H, CH$_2$), 0.80 (s, 3 H, ArNHSi*Me*Ph$_2$), 0.45 (t, broad, 2 H, CH$_2$N*H*$_2$). − ^{13}C NMR (C_6D_6, 75 MHz): δ = 147.97 (C^2), 137.39 (C$_{ipso}$ SiMe*Ph*$_2$), 134.96 (C$_{o/m}$ SiMe*Ph*$_2$), 129.93 (C$_p$ SiMe*Ph*$_2$), 129.82, 128.57 (Ar), 128.38 (C$_{o/m}$ SiMe*Ph*$_2$), 118.01, 117.82 (Ar), 46.73 (CH$_2$), −2.22 (ArNHSi*Me*Ph$_2$). The C^1 signal could not be detected. − $C_{20}H_{22}N_2Si_2$ (346.6): calcd. C 75.42, H 6.96; found C 75.77, H 7.07.

[(SiMePh$_2$)(SiMe$_3$)-ABA]H$_2$ (1g): 2.480 g of **1f** (7.8 mmol) was dissolved in 30 mL of diethyl ether at 0 °C; 1.26 mL of triethylamine (9 mmol) and 1.04 mL of chlorotrimethylsilane (9 mmol) were added successively, and the reaction mixture was left to reach room temperature. After 3 h, the white precipitate of triethylammonium chloride was filtered and the resulting solution was concentrated to dryness to yield 2.640 g of a pale yellow oil (87%). This can be used without further purification. − ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.72 (m, 4 H, H$_o$ SiMe*Ph*$_2$), 7.19 (m, 6 H, H$_m$ + H$_p$ SiMe*Ph*$_2$), 7.00 (dd, 1 H, H^3 or H^6), 6.91 (m, 2 H, H^4 or H^5 and H^3 or H^6), 6.69 (dt, 1 H, H^4 or H^5), 5.98 (s, broad, 1 H, ArN*H*), 3.79 (d, ^3J = 6.6 Hz, 2 H, CH$_2$), 0.78 (s, 3 H, ArNHSi*Me*Ph$_2$), 0.18 (t, broad, 1 H, CH$_2$N*H*), −0.12 (s, 9 H, CH$_2$NHSi*Me*$_3$). − ^{13}C NMR (C_6D_6, 75 MHz): δ = 147.45 (C^2), 137.00, (C$_{ipso}$ SiMe*Ph*$_2$), 135.00, (C$_{o/m}$ SiMe*Ph*$_2$), 130.04 (C$_p$ SiMe*Ph*$_2$), 129.89, 128.52 (Ar), 128.39 (C$_{o/m}$ SiMe*Ph*$_2$), 118.14, 117.53 (Ar), 46.21 (CH$_2$), −0.73 (CH$_2$NHSi*Me*$_3$), −2.47 (ArNHSi*Me*Ph$_2$). The C^1 signal could not be detected. − IR (neat): ṽ = 3372 (sh) and 3264 cm^{-1}, (ν_{N-H}).

[(SiMe$_3$)$_2$-ABA]Li$_2$ (2a): To a solution of 1.7 g of **1a** (6.38 mmol) in 50 mL of pentane at −70 °C, 8.4 mL of a 1.6 M solution of *n*BuLi in hexane (13.4 mmol) was slowly added. After leaving overnight at room temperature, the yellow solution was concentrated to ca. 15 mL and placed at −20 °C. Large crystals could be separated after one night, and a second crop was obtained on concentrating further (1.025 g, 58%). − ^{1}H NMR (C_6D_6, 300 MHz): δ = 6.94 (dt, 1 H, H^4 or H^5), 6.84 (dd, 1 H, H^3 or H^6), 6.58 (dt, 1 H, H^4 or H^5), 6.27 (d, 1 H, H^3 or H^6), 4.39 (d, ^2J = 10.3 Hz, 1 H, C*H*H′), 3.68 (d, ^2J = 10.3 Hz, 1 H, CH*H′*), 0.22 (s, 9 H, ArNSi*Me*$_3$), 0.05 (s, 9 H, CH$_2$NSi*Me*$_3$). On heating to 330 K, the two doublets at

$\delta = 4.39$ and 3.68 coalesce into a broad singlet at $\delta = 3.96$ (2 H); $T_c = 314$ K. − ^{13}C NMR (C_6D_6, 75 MHz): $\delta = 157.26$ (C^2), 136.53 (C^1), 131.60, 129.62, 125.83, 119.11 (C^3-C^6), 48.78 (CH_2), 2.96 ($SiMe_3$), 0.60 ($SiMe_3$). − IR (nujol mull): No absorptions above 3000 cm^{-1}.

[(SiMePh$_2$)$_2$-ABA]Li$_2$ (2b): This compound was prepared from **1b** according to the procedure described for **2a**. After 48 h of stirring at room temperature, the product was directly filtered as a white powder that was dried in vacuo (34% yield). − ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 7.46$ (m, broad, 20 H, $SiMe\mathit{Ph_2}$), 6.70 (m, 2 H, Ar), 6.67, 6.17 (m, 1 H, Ar), 4.02 (s, broad, 2 H, CH_2), 0.40 (s, 3 H, $ArNSi\mathit{Me}Ph_2$), 0.13 (s, 3 H, $CH_2NSi\mathit{Me}Ph_2$). − IR (nujol mull): No absorptions above 3000 cm^{-1}.

[(SiMe$_2$*t*Bu)$_2$-ABA]Li$_2$ (2c): This compound was prepared from **1c** according to the procedure described for **2a**. After 24 h of stirring at room temperature, the product was obtained as a thick brown oil after concentration to dryness, that eventually solidified as an off-white solid (80% yield). − ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.20$ (s, 1 H, H^4 or H^5), 7.05 (m, 2 H, H^3 and H^6), 6.56 (t, 1 H, H^4 or H^5), 4.37 (s, 2 H, CH_2), 1.16 (s, 9 H, *t*Bu), 1.15 (s, 9 H, *t*Bu), 0.33 (s, 6 H, $ArNSi\mathit{Me_2t}Bu$), 0.19 (s, 6 H, $CH_2NSi\mathit{Me_2t}Bu$).

[(Si*i*Pr$_3$)$_2$-ABA]Li$_2$ (2d): This compound was prepared as a viscous brown oil from **1d** according to the procedure described for **2c** (95% yield). − ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 7.10$ (m, 2 H, Ar), 6.97 (d, 1 H, H^3 or H^6), 6.70 (t, 1 H, H^4 or H^5), 4.23 (s, broad, 2 H, CH_2), 1.15 (m, 42 H, Si-iPr_3).

[(SiMePh$_2$)(SiMe$_3$)-ABA]Li$_2$ (2g): This compound was obtained as a white powder from **1g** according to the procedure described for **2b** (45% yield). − ^{1}H NMR (C_6D_6, 300 MHz, 286 K): $\delta = 7.69$ (d, 2 H, H_o $SiMe\mathit{Ph}Ph'$), 7.48 (d, 2 H, H_o $SiMePh\mathit{Ph'}$), 7.23 (m, 6 H, $H_m + H_p$ $SiMe\mathit{Ph_2}$), 6.77 (dt, 1 H, H^4 or H^5), 6.60 (dd, 1 H, H^3 or H^6), 6.50 (dt, 1 H, H^4 or H^5), 6.12 (d, 1 H, H^3 or H^6), 4.56 (d, $^2J = 11.9$ Hz, 1 H, $C\mathit{H}H'$), 3.60 (d, $^2J = 11.9$ Hz, 1 H, $CH\mathit{H'}$), 0.48 (s, 3 H, $ArNSi\mathit{Me}Ph_2$), 0.01 (s, 9 H, $CH_2NSi\mathit{Me_3}$). − IR (nujol mull): No absorptions above 3000 cm^{-1}.

Zr[(SiMe$_2$*t*Bu)$_2$-ABA]$_2$ (3c): This compound was obtained from **2c** according to the procedure described for **3g** (52% yield). − ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.16-7.00$ (m, 6 H, Ar), 6.88 (d, 2 H, H^3 or H^6), 4.80 (s, broad, 2 H, $C\mathit{H}H'$), 4.05 (s, broad, 2 H, $CH\mathit{H'}$), 1.08 (s, 18 H, *t*Bu), 0.82 (s, 18 H, *t*Bu), 0.44 (s, 12 H, $ArNSi\mathit{Me_2t}Bu$), 0.15 (s, 12 H, $CH_2NSi\mathit{Me_2t}Bu$).

Zr[(SiMePh$_2$)(SiMe$_3$)-ABA]$_2$ (3g): A mixture of 25 mg of $ZrCl_4$ (0.11 mmol) and 86 mg of **2g** (0.22 mmol) in 15 mL of toluene was stirred at 80 °C for 48 h. After cooling to room temperature, the mixture was centrifuged and the clear yellow solution was concentrated to dryness to yield 71 mg of a yellow solid (76%). − ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 7.25$ (m, 22 H, $SiMe\mathit{Ph_2}$ + Ar), 6.99 (m, 4 H, Ar), 6.55 (m, 2 H, Ar), 4.89 (d, $^2J = 13.4$ Hz, 2 H, $C\mathit{H}H'$), 3.93 (d, $^2J = 13.4$ Hz, 2 H, $CH\mathit{H'}$), 0.53 (s, 6 H, $ArNSi\mathit{Me}Ph_2$), 0.09 (s, 18 H, $CH_2NSi\mathit{Me_3}$).

Zr[(SiMe$_3$)$_2$-ABA](NMe$_2$)$_2$ (4a): To a solution of 497 mg of $Zr(NMe_2)_4$ (1.86 mmol) in 25 mL of pentane at −70 °C, a solution of 497 mg of **1a** (1.86 mmol) in 10 mL of pentane was added. After room temperature had been reached, the reaction mixture was stirred for one night. After evaporation of all volatiles under primary, and then secondary vacuum, 798 mg of a pale yellow oil (96%) was obtained. − ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 7.14$ (m, 2 H, Ar), 6.99 (d, 1 H, H^3 or H^6), 6.79 (dt, 2 H, H^4 or H^5), 4.42 (s, 2 H, CH_2), 2.84 (s, 12 H, NMe_2), 0.32 (s, 9 H, $ArNSi\mathit{Me_3}$), 0.13 (s, 9 H, $CH_2NSi\mathit{Me_3}$). − ^{13}C NMR (C_6D_6, 75 MHz): $\delta = 151.23$ (C^2), 137.8 (C^1), 129.10, 128.23, 123.53, 120.38 (C^3-C^6), 49.71 (CH_2), 41.92 (NMe_2), 1.43 ($SiMe_3$), 0.95 ($SiMe_3$).

Zr[(SiMePh$_2$)$_2$-ABA](NMe$_2$)$_2$ (4b): This compound was prepared from **1b** according to the procedure described for **4a**. It consists of a very viscous orange oil (96% yield). − ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 7.70$ (m, 4 H, H_o $SiMe\mathit{Ph_2}$), 7.62 (m, 4 H, H_o $SiMe\mathit{Ph_2}$), 7.20 (m, 12 H, $H_m + H_p$ $SiMe\mathit{Ph_2}$), 7.08, 6.97 (d, 1 H, H^3 and H^6), 6.95, (t, 1 H, H^4 or H^5), 6.70 (t, 1 H, H^4 or H^5), 4.61 (s, 2 H, CH_2), 2.45 (s, 12 H, NMe_2), 0.74 (s, 3 H, $Si\mathit{Me}Ph_2$), 0.65 (s, 3 H, $Si\mathit{Me}Ph_2$). − ^{13}C NMR (CD_2Cl_2, 75 MHz): $\delta = 151.56$ (C^2), 139.13, 137.16, 136.67 (C^2 and C_{ipso} $SiMe\mathit{Ph_2}$), 135.77, 135.13 (C_o $SiMe\mathit{Ph_2}$), 130.30, 129.46 (C_p $SiMe\mathit{Ph_2}$), 128.96 (Ar), 128.20, 128.04 (C_m $SiMe\mathit{Ph_2}$), 127.79, 124.01, 119.88 (Ar), 50.42 (CH_2), 41.60 (NMe_2), −1.12 ($Si\mathit{Me}Ph_2$), −1.61 ($Si\mathit{Me}Ph_2$). The C^1 signal could not be detected.

Zr[(SiMe$_2$*t*Bu)$_2$-ABA](NMe$_2$)$_2$ (4c): This compound was prepared from **1c** according to the procedure described for **4a**, along with 5 d of stirring at room temperature in pentane, or 4 h in refluxing toluene. The product was further purified by extraction with pentane (orange oil, 99% yield). − ^{1}H NMR (C_6D_6, 250 MHz): $\delta = 7.20-7.09$ (m, 3 H, Ar), 6.82 (t, 1 H, H^4 or H^5), 4.60 (s, broad, 2 H, CH_2), 2.80 (s, 12 H, NMe_2), 1.04 (s, 9 H, *t*Bu), 1.03 (s, 9 H, *t*Bu), 0.29 (s, 6 H, $ArNSi\mathit{Me_2t}Bu$), 0.16 (s, 6 H, $CH_2NSi\mathit{Me_2t}Bu$). − $C_{23}H_{48}N_4Si_2Zr$ (436.8): calcd. C 52.32, H 9.16, N 10.61; found C 52.29, H 9.77, N 10.73.

Zr[(SiMePh$_2$)(SiMe$_3$)-ABA](NMe$_2$)$_2$ (4g): This compound was prepared from **1g** according to the procedure described for **4a**. It consists of a yellow oil (98% yield). − ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 7.65$ (m, 4 H, H_o $SiMe\mathit{Ph_2}$), 7.14 (m, 7 H, $H_m + H_p$ $SiMe\mathit{Ph_2}$ and H^3 or H^6), 7.06 (d, 1 H, H^3 or H^6), 6.89, 6.73 (dt, 1 H, H^4 and H^5), 4.52 (s, 2 H, CH_2), 2.63 (s, 12 H, NMe_2), 0.79 (s, 3 H, $ArNSi\mathit{Me}Ph_2$), 0.14 (s, 9 H, $CH_2NSi\mathit{Me_3}$). − ^{13}C NMR (C_6D_6, 75 MHz): $\delta = 152.18$ (C^2), 136.96 (C_{ipso} $SiMe\mathit{Ph_2}$), 136.10, 135.96 (C^1 and C_o $SiMe\mathit{Ph_2}$), 130.27 (C_p $SiMe\mathit{Ph_2}$), 128.61 (Ar), 128.14 (C_m $SiMe\mathit{Ph_2}$), 127.85, 122.90, 119.74 (Ar), 49.14 (CH_2), 41.88 (NMe_2), 1.22 ($CH_2NSi\mathit{Me_3}$), −1.21 ($ArNSi\mathit{Me}Ph_2$). − ^{13}C NMR (CD_2Cl_2, 75 MHz): $\delta = 152.80$ (C^2), 136.59, 136.38 (C^1 and C_{ipso} $SiMe\mathit{Ph_2}$), 135.91 (C_o $SiMe\mathit{Ph_2}$), 130.48 (C_p $SiMe\mathit{Ph_2}$), 128.32 (Ar), 128.25 (C_m $SiMe\mathit{Ph_2}$), 127.30, 122.23, 119.98 (Ar), 48.67 (CH_2), 41.95 (NMe_2), 1.04 ($CH_2NSi\mathit{Me_3}$), −1.36 ($ArNSi\mathit{Me}Ph_2$).

Zr[(SiMe$_3$)$_2$-ABA]Cl$_2$ (5a): To a solution of 830 mg of **4a** (1.9 mmol) in 40 mL of pentane at −50 °C, 2.4 mL of chlorotrimethylsilane (19 mmol) was added. After room temperature had been reached, the reaction mixture was vigorously stirred overnight. After filtration, washing of the precipitate with cold pentane (20 mL) and drying in vacuo, one obtained 622 mg of a pale yellow solid (78%). − ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 7.00$ (m, 2 H, Ar), 6.77 (m, 2 H, Ar), 4.72 (s, 2 H, CH_2), 0.43 (s, 9 H, $ArNSi\mathit{Me_3}$), 0.15 (s, 9 H, $CH_2NSi\mathit{Me_3}$). − ^{13}C NMR (C_6D_6, 75 MHz): $\delta = 149.81$ (C^2), 132.22 (C^1), 128.72, 128.72, 122.47, 120.24 (C^3-C^6), 49.50 (CH_2), 0.56 ($SiMe_3$), 0.45 ($SiMe_3$). − IR (nujol mull): $\tilde{\nu} = 313$ (f), 289 (m) and 254 (F, broad) cm^{-1}, (ν_{Zr-Cl}).

Zr[(SiMe$_2$*t*Bu)$_2$-ABA]Cl$_2$ (5c): This compound was prepared from **4c** according to the procedure described for **5a** and a slightly different workup. The reaction mixture was first concentrated to dryness and the solid residue extracted with small amounts of toluene. Removal of toluene and other volatiles under vacuum afforded a solid that was washed again with 2×1 mL of cold pentane and dried under vacuum (55% yield). − ^{1}H NMR (C_6D_6, 250 MHz): $\delta = 7.20$ (m, 2 H, Ar), $7.00-6.96$ (m, 2 H, Ar), 4.59 (s, 2 H, CH_2), 1.02

(s, 9 H, *t*Bu), 0.95 (s, 9 H, *t*Bu), 0.40 (s, 6 H, ArNSi*Me*$_2$*t*Bu), 0.31 (s, 6 H, CH$_2$NSi*Me*$_2$*t*Bu). − $C_{19}H_{36}Cl_2N_2Si_2Zr$ (475.4): calcd. C 44.68, H 7.10, N 5.48; found C 44.45, H 6.71, N 5.24.

Zr[(SiMePh$_2$)(SiMe$_3$)-ABA]Cl$_2$ (5g): This compound was prepared from **4g** according to the procedure described for **5a**. It consists of a pale yellow solid (81% yield). − ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = 7.79 (m, 4 H, H$_o$ SiMe*Ph*$_2$), 7.15 (m, 6 H, H$_m$ + H$_p$ SiMe*Ph*$_2$), 6.93 (d, 2 H, H^3 and H^6), 6.75, 6.67 (dt, 1 H, H^4 and H^5), 4.87 (s, 2 H, CH$_2$), 0.92 (s, 3 H, ArNSi*Me*Ph$_2$), 0.19 (s, 9 H, CH$_2$NSi*Me*$_3$). − ^{13}C NMR (C$_6$D$_6$, 75 MHz): δ = 151.36 (C^2), 137.21 (C$_o$ SiMe*Ph*$_2$), 132.79 (C$_{ipso}$ SiMe*Ph*$_2$), 131.53 (C$_p$ SiMe*Ph*$_2$), 131.40 (C^1), 129.00 (C$_m$ SiMe*Ph*$_2$), 128.24, 121.87, 120.36 (Ar), 48.60 (CH$_2$), 0.89 (CH$_2$NSi*Me*$_3$), −1.52 (ArNSi*Me*Ph$_2$). − IR (nujol mull): 339 (m) and 294 (m) cm^{-1}, (ν_{Zr-Cl}).

X-ray Crystallographic Structure Determination and Refinements of 5c and 6c: Data for **5c** (and **6c**) were collected at low temperature (T = 160 K) with a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device and using graphite-monochromated Mo-K_α radiation (λ = 0.71073Å). The crystal-to-detector distance was 70 (80) mm, 179 (147) exposures were obtained with $0° < \varphi < 250°$ and with the crystal rotated through 1.4° (1.7°) in φ. The final unit cell parameters were obtained by means of a least-squares refinement of a set of 5000 well-measured reflections, and a crystal decay was monitored in the course of data collection by measuring 200 reflections by image. No significant fluctuations of intensities have been observed during measurements. Structures have been solved by direct methods using SIR92,[10] and refined by least-squares procedures on F^2 with the aid of SHELXL97.[11] The atomic scattering factors were taken from International Tables for X-ray Crystallography.[12] All non-hydrogen atoms were anisotropically refined and the last cycles of refinement weighting schemes[12] were applied. All hydrogen atoms were located on a difference Fourier map and refined with a riding model, except the hydrogen atom H(2) connected to the amine group of **6c** which has been isotropically refined. For **5c** a molecule of solvent (toluene) has been located, this molecule seems to be disordered around an inversion center and has been anisotropically refined with restraints on distances and angles. Drawings of molecules are performed with the program ZORTEP[13] with 50% probability displacement ellipsoids for non-hydrogen atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155993 (CCDC-155994). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Main data for **5c** and **6c** are reported in Table 5.

Ethylene Polymerization Procedures: Polymerization experiments were performed in a 50-mL glass reactor equipped with a mechanical stirrer or in standard Schlenk-type glassware with magnetic stirring, whether ethylene pressure was 6 bar or 1 bar, respectively. The catalyst precursor was first introduced into the reactor as a toluene solution of controlled volume and concentration. The MAO solution was added at the desired temperature, before the reactor was pressurized as rapidly as possible with ethylene and the pressure, as well as vigorous stirring, maintained constant during the polymerization time. The polymerization was then quenched by pouring the reaction mixture into a 10% solution of aqueous HCl in methanol. The polymer was collected by filtration, washed several times with methanol and then acetone, dried in vacuo at 80 °C, and weighed. ^{1}H NMR and SEC analyses were carried out at 140 °C in $C_2D_2Cl_4$ or 1,2,4-trichlorobenzene respectively.

Table 5. Crystallographic data for **5c** and **6c**

	5c	**6c**
Empirical formula	$C_{19}H_{36}Cl_2N_2Si_2Zr\cdot(C_7H_8)_{0.5}$	$C_{19}H_{37}Cl_3N_2Si_2Zr$
Formula mass	556.86	547.26
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	9.107(2)	8.5483(13)
b [Å]	12.019(2)	11.7137(18)
c [Å]	14.313(3)	14.916(2)
α [°]	69.26(3)	94.373(18)
β [°]	85.54(3)	106.485(17)
γ [°]	77.10(3)	110.619(17)
V [Å^3]	1428.2(5)	1314.4
Z	2	2
$D_{calcd.}$ [g cm^{-3}]	1.295	1.383
μ(Mo-K_α) [mm^{-1}]	0.668	0.822
F(000)	582	568
2θ range [°]	3.3−52.1	2.9−48.4
d(hkl) range [Å]	12.453−0.809	14.228−0.867
Measured reflections	10410	7738
Unique reflections	3818	3581
Parameters/ restraints	309/87	258/0
Final R1	0.0201	0.0306
Final wR2	0.0514	0.0673
Goodness of fit	1.025	0.939

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