Unsymmetrically Substituted Dimethyldiaminosilanes as Ligands towards Zirconium(IV)

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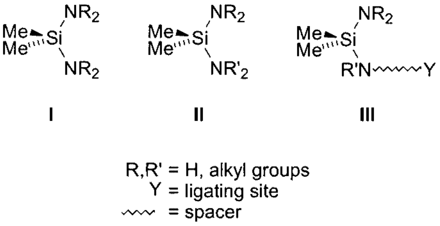
Keywords: Zirconium / N ligands / Chelates / Silicon

Unsymmetrically substituted dimethyldiaminosilanes of the general formula $SiMe_2(NR_2)(NR'_2)$ have been prepared by treating $LiNR_2$ with $SiMe_2Cl(NR'_2)$ (NR_2, NR'_2 = NMe_2, NC_4H_8, NH*i*Pr, NH*t*Bu, $NHCH_2CH_2NMe_2$ or $NHCH_2CH_2OMe$). Their ligating properties towards zirconium(IV) have been investigated as a function of the nitrogen substituents and the syntheses of the binary compound $Zr[SiMe_2(NiPr)(NtBu)]_2$ and of the zirconium derivatives $ZrX_3(L)$ [X = Cl, NMe_2; L = $SiMe(NR)(NR'_2)$, NR = N*i*Pr, N*t*Bu, $NCH_2CH_2NMe_2$, NCH_2CH_2OMe; NR'_2 = NMe_2, NC_4H_8, NH*i*Pr, NH*t*Bu] are also reported. The solution structures and dynamics of the compounds have been elucidated by 1D/2D multinuclear NMR spectroscopy.

Introduction

The discovery of novel nonmetallocene polymerisation catalysts[1] has raised new interest in amido metal chemistry. As far as silylamides are concerned, a large number of data exist on SiR_3 *N*-substituted amido ligands (see refs.[1a−1c] for examples) but only a few papers[2−8] describe the synthesis, starting from diaminosilanes, of coordination compounds (Scheme 1, **I−II**).



Scheme 1

Nevertheless diaminosilanes appear to be flexible ligands, their coordination mode strongly depending on the nature of the nitrogen substituents. Examples of the zirconium systems include, i) $Zr(NMe_2)_4$ reacts with $SiMe_2(NHR)_2$ yielding $Zr(NMe_2)_3(NHMe_2)[SiMe_2(NtBu)(NHtBu)]$[3] or $Zr(NMe_2)_2(NHMe_2)[SiMe_2(NPh)_2]$ (Ph = 2,6-$Me_2C_6H_3$);[4] ii) the binary amido derivative $Zr[SiMe_2(NR)_2]_2$ is a dimer when R = *i*Pr[3] and a monomer when R = *t*Bu.[5]

Moreover, as a consequence of the different structures, different physical and/or chemical properties are observed and expected for the metal derivatives. For instance, the above mentioned *tert*-butyl derivative $Zr[SiMe_2(NtBu)_2]_2$ is volatile,[5] while the isopropyl analogue decomposes at about 430 K without subliming.[3]

Based on this background, it seemed interesting to enlarge the class of dimethyldiaminosilanes and their metal complexes and, since little[6−8] is known about the ligating ability of unsymmetrically substituted diaminosilanes, we have pursued a) the synthesis of novel compounds of this class (eventually containing additional ligating sites) (Scheme 1, **II−III**) and b) the investigation of their ligating properties towards zirconium(IV).

Results and Discussion

Synthesis of $SiMe_2XY$ (X = NR_2, Y = Cl, NR'_2)

According to the literature procedures,[7,9] the following general route to $SiMe_2(NR_2)(NR'_2)$ was followed (Scheme 2): a) ligand exchange reactions between $SiMe_2Cl_2$ and $SiMe_2(NR_2)_2$;[10] b) treatment of the resultant $SiMe_2Cl(NR_2)$ with $LiNR'_2$.

The ^1H and ^{13}C NMR spectra of **1−11** show high field resonances for $SiMe_2$, while the signals of the NR_2 moieties can be observed in the range δ = 1−4 ppm (^1H) and 20−80 ppm (^{13}C). In addition, note that the nature of the amido group and the degree of substitution of the $SiMe_2$ core affect δ_{Si} (cf. ESI).

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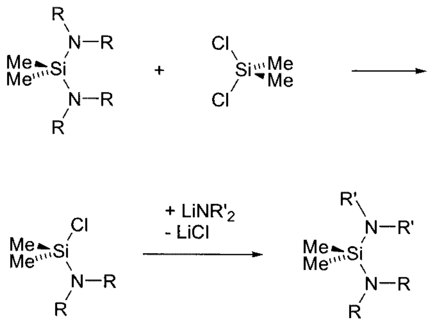


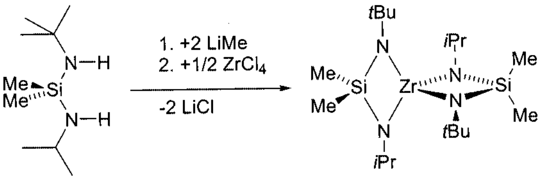
	NR_2
1	NMe_2
2	NC_4H_8
3	NH*i*Pr
4	NH*t*Bu

	NR_2	NR'_2
5	NMe_2	NH*t*Bu
6	NMe_2	NH*i*Pr
7	NMe_2	$NHCH_2CH_2NMe_2$
8	NMe_2	$NHCH_2CH_2OMe$
9	NH*i*Pr	NH*t*Bu
10	NC_4H_8	NH*t*Bu
11	NC_4H_8	$NHCH_2CH_2NMe_2$

Scheme 2

Synthesis of Zr[SiMe$_2$(N*t*Bu)(N*i*Pr)]$_2$

As alluded to in the introduction, the binary species Zr[SiMe$_2$(NR)$_2$]$_2$ adopts a different molecular structure (both in the solid state and in solution) depending on the identity of R (R = *i*Pr, dimer;[3] R = *t*Bu, monomer[5]) and elsewhere[3] we proposed that the different steric hindrances of *i*Pr and *t*Bu should be responsible for this observation. Therefore, elucidation of the molecular structure of Zr[SiMe$_2$(N*t*Bu)(N*i*Pr)]$_2$ (**12**) appeared interesting. Compound **12** was prepared by treating $ZrCl_4$ with Li$_2$[SiMe$_2$(N*i*Pr)(N*t*Bu)] (1:2 molar ratio) and it was obtained as a pure material after crystallisation from an Et_2O/pentane solution at 243 K, Equation (1).

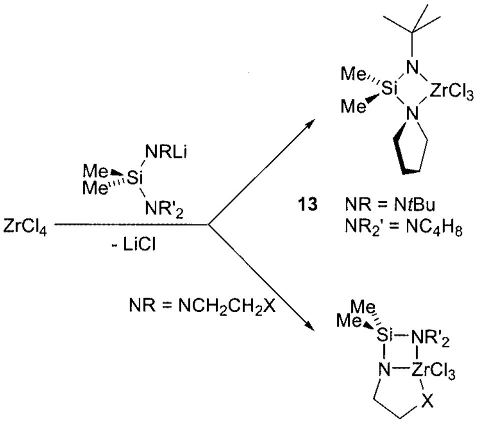


9 **12** (1)

Despite a large number of attempts, we were unable to obtain suitable crystals for a single-crystal X-ray diffraction study of the structure. Nevertheless, ^1H, ^{13}C and ^{29}Si NMR spectroscopy allowed at least the solution molecular structure to be elucidated. Provided that the ^{29}Si chemical shifts reported for ZrL_2 are −40.5 [L = SiMe$_2$(N*t*Bu)$_2$,[5] chelating], −38.0 [L = SiMe$_2$(N*i*Pr)$_2$,[3] chelating] and −12.2 ppm [L = SiMe$_2$(N*i*Pr)$_2$,[3] bidentate bridging], the only ^{29}Si resonance of **12** at −40.5 ppm indicates that two equivalent ligands are present and that they are both chelating. In addition, the ^1H and ^{13}C spectra show only one kind of *i*Pr and *t*Bu group even at 200 K, thus suggesting an approximately tetrahedral arrangement of the donor atoms around the zirconium centre. Finally, the two methyls of each $SiMe_2$ moiety are nonequivalent, i.e. two ^1H and two ^{13}C signals have been observed for the $SiMe_2$ group. Thus, the solution molecular structure of **12** should be similar to that of Zr[SiMe$_2$(N*t*Bu)$_2$]$_2$.

Synthesis of ZrCl$_3$(L)

Treatment of $ZrCl_4$ with LiL (prepared in situ by treating LiMe with HL, 1:1 molar ratio; HL = **7**, **8**, **10** and **11**) yielded the trichloro derivatives ZrCl$_3$(L) (Scheme 3).



	NR'_2	X
14	NC_4H_8	NMe_2
15	NMe_2	NMe_2
16	NMe_2	OMe

Scheme 3

For convenience, **13** will be discussed separately from the other compounds in order to illustrate in detail, the correlation between the spectroscopic data and the proposed molecular structure.

The ^1H and ^{13}C NMR spectra of **13** show high field resonances for $SiMe_2$ (^1H, δ = 0.18 ppm; ^{13}C, 1.4 ppm), the signals of the hydrocarbyl moieties being observed in the range 1−3.5 ppm (^1H) and 20−60 ppm (^{13}C). As far as the CH_2NCH_2 moiety (pyrrolidinide) is concerned, i) the ^{13}C and ^1H ^{13}C HMQC spectra show that the two carbons are equivalent (54.0 ppm) and that two nonequivalent methylene protons (δ_H = 3.49, 3.35 ppm) are bonded to each carbon; ii) a negative crosspeak was observed in the ^1H NOESY spectrum of **13** between the resonances at δ = 3.35 and 0.18 ppm ($SiMe_2$) and iii) the ^{13}C resonances of CH_2NCH_2 are shifted with respect to the uncomplexed ligand (Table 1), thus suggesting that **13** contains SiMe$_2$(N*t*Bu)(NC$_4$H$_8$) as a bidentate ligand.

Table 1. Shifts of the ^{13}C resonances of the $\mathit{CH_x}$N$\mathit{CH_x}$ moiety in ZrX$_3$(SiMe$_2$YZ) (X = Cl, NMe$_2$) ($\Delta\delta_C = \delta_C^{ZrX3(L)} - \delta_C^{HL}$), cf. Schemes 3 and 4

Compound	Y	Z	$\Delta\delta_C$ X = Cl
13	N*t*Bu	N($\mathit{CH_2}$CH$_2$)$_2$	7.3
14	N(CH$_2$)$_2$NMe$_2$	N($\mathit{CH_2}$CH$_2$)$_2$	3.0
15	N(CH$_2$)$_2$NMe$_2$	N*Me*$_2$	7.4
16	N(CH$_2$)$_2$OMe	N*Me*$_2$	6.6
			X = NMe$_2$
17	N(CH$_2$)$_2$NMe$_2$	N($\mathit{CH_2}$CH$_2$)$_2$	0.7
18	N(CH$_2$)$_2$OMe	N*Me*$_2$	0.8
19	N(CH$_2$)$_2$NMe$_2$	N*Me*$_2$	0.7
20	N*t*Bu	N($\mathit{CH_2}$CH$_2$)$_2$	4.8
21	N*i*Pr	N*Me*$_2$	4.8
22	N*t*Bu	N*Me*$_2$	5.2

Similar to **13**, the ^{1}H and ^{13}C spectra of **14−16** show high field resonances for the SiMe$_2$ moiety (^{1}H, about δ = 0.3 ppm; ^{13}C, about −2.2 ppm) and signals of the hydrocarbyl groups in the range 2−4.5 ppm (^{1}H) and 20−80 ppm (^{13}C). In addition, i) the downfield shift of the ^{1}H and ^{13}C resonances of the amino NMe$_2$ moieties in **14** and **15** and of the ethereal OMe group in **16** with respect to the uncomplexed ligands, and ii) the equivalent methylene protons of the ethylene chain, even at 190 K, indicate that the NMe$_2$ and the OMe groups coordinate to the metal centre and that a mirror plane containing the ZrNC$_2$X moiety should exist in the molecule (X = OMe, NMe$_2$).

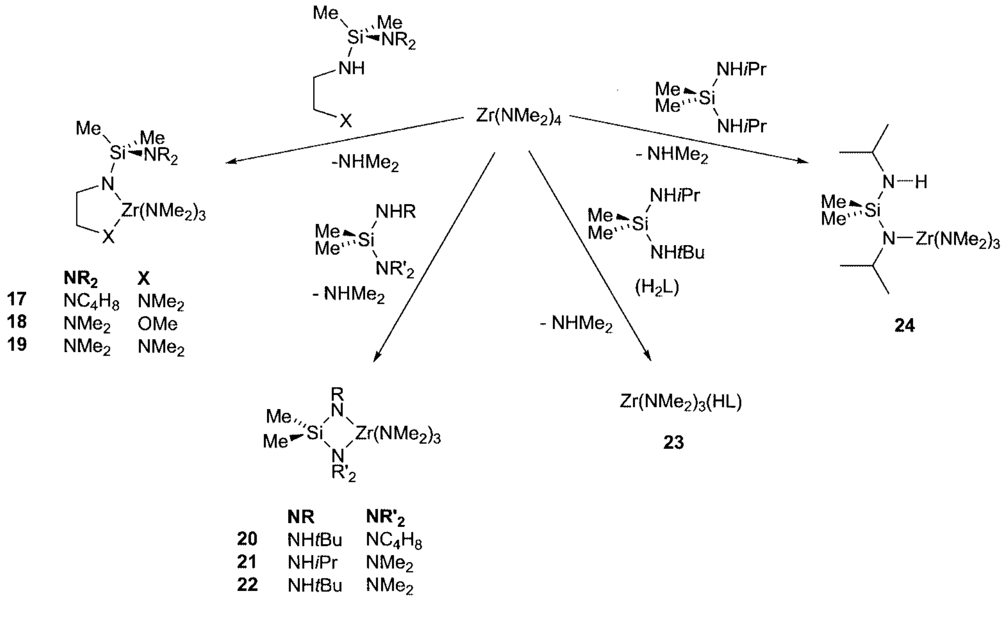
Moreover, similar to **13**, the observed ^{13}C shifts for the pyrrolidinide CH$_2$N(Si)CH$_2$ moiety in **14** and for the SiNMe$_2$ group in **15** and **16** (Table 1) suggest that the SiNR$_2$ moiety is also coordinated to the metal centre, making the silane ligands tridentate.[3]

As far as **14** is concerned, further comments are appropriate. In contrast with the proposed coordination of the SiNC$_4$H$_8$, the two faces of the pyrrolidinide ring appear equivalent at room temperature, i.e. one ^{1}H resonance is observed for each N$\mathit{CH_2}$ and NCH$_2$$\mathit{CH_2}$ proton set. In order to further elucidate this feature, we undertook a variable temperature NMR investigation and we observed that at 213 K i) the ^{1}H N$\mathit{CH_2}$ (pyrrolidinide) signal broadened and appeared unresolved and the NCH$_2$$\mathit{CH_2}$ (pyrrolidinide) resonance split into two signals at δ = 1.86 and 1.54 ppm (1:1 molar ratio) ii) in the ^{1}H NOESY spectrum a negative crosspeak was observed only between the NCH$_2$$\mathit{CH_2}$ resonance at 1.54 and the signal at δ = 0.39 ppm (SiMe$_2$) and iii) the carbon responsible for the resonance at δ = 25.1 ppm is bonded to the protons which yield the resonances at δ = 1.86 and 1.54 ppm (^{1}H ^{13}C HMQC). Therefore, the proposed coordination of the SiNC$_4$H$_8$ moiety is confirmed and it appears that the two faces of the pyrrolidinide ring are nonequivalent at 213 K and exchange at room temperature.

Synthesis of Zr(NMe$_2$)$_3$(L)

Compounds **5−11** readily react with Zr(NMe$_2$)$_4$ displacing one NMe$_2$ group as NHMe$_2$ and yielding the mixed amido derivatives Zr(NMe$_2$)$_3$(L) (**17−24**) (Scheme 4).

The NMR spectra of **17−19** show i) ^{13}C chemical shifts of the CH$_x$N(Si)CH$_x$ (x = 2, 3) moiety similar to the uncomplexed ligands (Table 1) and ii) downfield shifted $\mathit{CH_2}$N($\mathit{CH_3}$)$_2$ and $\mathit{CH_2OCH_3}$ resonances (^{1}H and ^{13}C), thus suggesting that **17−19** should contain the diaminosilane as a bidentate ligand coordinating to the metal centre through the amido SiNCH$_2$ nitrogen atom and the amino NMe$_2$ or the ethereal OMe moieties, while the SiNR$_2$ group is un-

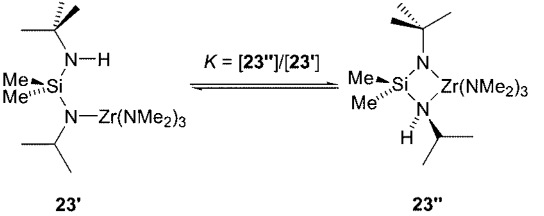


Scheme 4

complexed. As confirmation, the ^{1}H methylene NC_4H_8 resonances of **17** appear as unique multiplets even at 190 K (cf. **13** and **14**).

As far as **20–22** are concerned, since the ^{13}C $CH_xN(Si)CH_x$ resonances are noticeably shifted with respect to those of the uncomplexed ligand (Table 1) and the two faces of the pyrrolidinide ring of **20** appear nonequivalent at 200 K (^{1}H NMR), the mixed amido derivatives **20–22** should contain the SiN_2 core coordinated to the metal centre.

The microcrystalline powder obtained from the reaction of $Zr(NMe_2)_4$ with $SiMe_2(NH\textit{i}Pr)(NH\textit{t}Bu)$ (H_2L) was identified as $Zr(NMe_2)_3(HL)$ (**23**) and the NMR spectra of a C_6D_6 solution indicated that two isomers were present in solution, namely $Zr(NMe_2)_3[SiMe_2(N\textit{i}Pr)(NH\textit{t}Bu)]$ (**23′**) and $Zr(NMe_2)_3[SiMe_2(N\textit{t}Bu)(NH\textit{i}Pr)]$ (**23′′**) [Eqn. (2)]. In fact, the ^{29}Si NMR spectrum shows two signals (−2.8, −5.9 ppm) and the ^{1}H COSY and ^{1}H ^{13}C HMQC spectra indicate two nonequivalent $SiMe_2$, *i*Pr and *t*Bu moieties (vide infra, cf. Exp. Sect.).

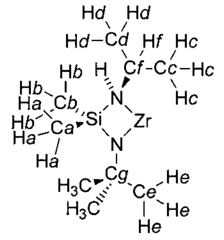


(2)

As far as **23′** is concerned, the ^{1}H and ^{13}C NMR resonances are little affected by the temperature (188–298 K) and the signal of the *tert*-butyl quaternary ^{13}C nucleus is slightly shifted with respect to the uncomplexed ligand, thus indicating that the NH*t*Bu moiety is probably not complexed and that we are dealing with the mono-hapto $SiMe_2(N\textit{i}Pr)(NH\textit{t}Bu)$ ligand [Equation (2)].

On the other hand the ^{1}H and ^{13}C signals of **23′′** are strongly affected by the temperature. At 188 K, one ^{29}Si resonance and two nonequivalent methyls both in the $SiMe_2$ and the *i*Pr moiety (^{1}H, ^{13}C) suggest that the SiNH*i*Pr unit is coordinated. For confirmation, and relevant to the molecular structure elucidation, the following comments can be made i) the ^{1}H COSY spectrum shows correlation peaks between the two isopropyl methyl groups (δ = 0.86, 0.72 ppm) and the methyne resonance (δ = 2.79 ppm), confirming that we are dealing with one isopropyl group containing two nonequivalent methyls; ii) both the $SiCH_3$ resonances are correlated (^{1}H NOESY) with the *tert*-butyl CH_3, confirming that only one $SiMe_2$ moiety is present with the methyls in different chemical environments; iii) a strong correlation (^{1}H NOESY) exists between the $SiMe_2$ methyl at δ = 0.29 ppm and the isopropyl methyl groups, suggesting that this methyl and the *i*Pr group are in a *syn* configuration with respect to the SiN_2Zr ring (Table 2). Finally, at 188 K, three nonequivalent $ZrNMe_2$ groups (δ_H, δ_C = 3.36, 45.97; 3.12, 46.00; 3.04, 45.2 ppm) were observed for **23′′** as a consequence of the asymmetric zirconium coordination sphere.

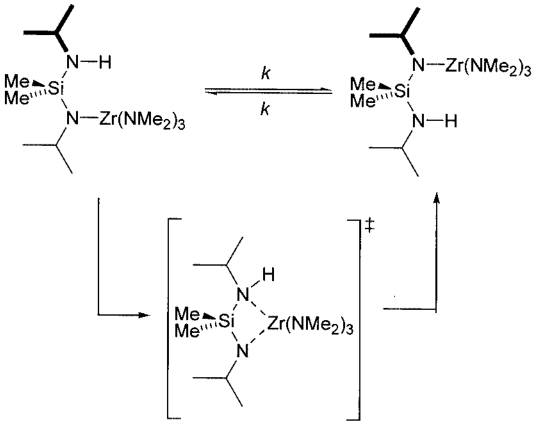
Table 2. Proposed assignment of ^{1}H and ^{13}C signals of $Zr(NMe_2)_3[SiMe_2(N\textit{t}Bu)(NH\textit{i}Pr)]$ (**23′′**)



δ_H (188 K)	δ_C (188 K)
0.29 (H*a*)	7.20 (C*a*)
0.33 (H*b*)	1.29 (C*b*)
0.72 (H*c*)	27.3 (C*c*)
0.86 (H*d*)	25.0 (C*d*)
1.40 (H*e*)	35.3 (C*e*)
2.79 (H*f*)	45.7 (C*f*)
–	54.7 (C*g*)

The equilibrium constants K = [**23′′**]/[**23′**] [Equation (2)] at different temperatures [198–293 K] were calculated from the integrals of the $SiCH_3$ ^{1}H NMR resonances and the van't Hoff plot yielded ΔH_r = −3.4±0.4 kJ·mol^{-1} and ΔS_r = −7.3±1.8 J·mol^{-1}·K^{-1}. Reasonably, the negative ΔS_r results from the loss of entropy due to the chelation of the SiN_2 system and the negative ΔH_r should be related to a) the different basicities of the SiN*i*Pr and SiN*t*Bu moieties, b) the formation of a novel Zr–N bond and c) the reorganisation of the zirconium coordination sphere. Reasonably, the difference between the two Brønsted sites is negligible and the enthalpy contribution of Zr–N bond formation (esothermic) is higher with respect to that of the reorganisation of the donor atoms set on increasing the zirconium coordination number (endothermic). Nevertheless, the small absolute value of ΔH_r clearly indicates that the above mentioned effects are comparable.

For comparison (vide infra), the mixed amido derivative $Zr(NMe_2)_3[SiMe_2(N\textit{i}Pr)(NH\textit{i}Pr)]$ (**24**) was prepared (Scheme 4) and its solution molecular structure elucidated. Only one ^{29}Si resonance was observed and the ^{1}H and ^{13}C NMR spectra show one resonance for the $SiMe_2$ and two nonequivalent *i*Pr moieties (i.e. two nonequivalent CH_3 and two nonequivalent CH proton sets). Moreover, the ^{1}H and ^{13}C signals of the $SiMe_2$ and *i*Pr moieties are little affected by the temperature and appear as single well-shaped resonances even at 188 K. Finally, at room temperature, *positive* crosspeaks between both the CH_3 and the CH resonances of the two nonequivalent *i*Pr groups were observed in the ^{1}H NOESY spectrum and the coalescences of the CH and CH_3 ^{1}H resonances occur above 370 K. Therefore, the SiNH*i*Pr group is not coordinated and the chemical exchange between the two halves of $SiMe_2(NH\textit{i}Pr)(N\textit{i}Pr)$ operates with the consequent 1,3-shift of the NH proton (Scheme 5).



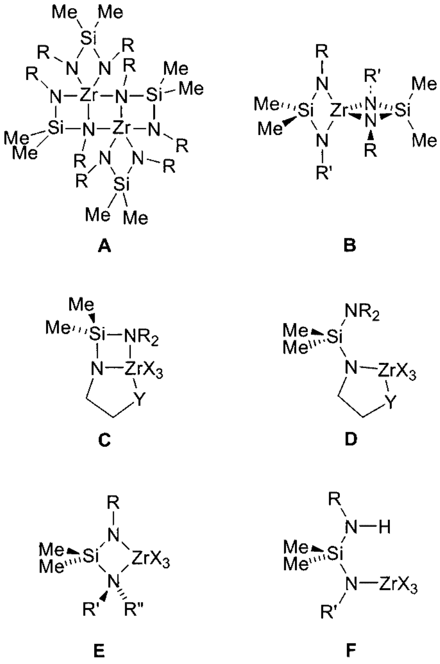
Scheme 5

This phenomenon has been investigated by variable temperature ^{13}C NMR spectroscopy in the range of 298−358 K and a line shape analysis of the isopropyl methyl resonances enabled us to calculate the kinetic constant *k* (Scheme 5) at different temperatures and to determine the activation parameters using the Eyring plot (ΔH_{act} = 47.1±1.2 kJ·mol^{-1}; ΔS_{act} = −73.8±3.8 J·mol^{-1}·K^{-1}). The negative value of ΔS_{act} suggests that the mechanism should be concerted, the 1,3-shift of the Zr(NMe$_2$)$_3$ fragment being reasonably the rate determining step (Scheme 5), yielding a **23′′**-type transition state. In this respect, the positive ΔH_{act} is reasonably indicative of the kinetic influence of the proposed rate-determining labilisation of the amido Zr−N(Si)*i*Pr bond.

Finally, a comparison among compounds **20−24** throws light on the influence of the nitrogen substituents on the coordination mode of L in Zr(NMe$_2$)$_3$(L) [HL = **5**, **6**, **9**, **10**, SiMe$_2$(NH*i*Pr)$_2$]. Provided that the coordination of the SiNHR moiety (R = *i*Pr, *t*Bu) is observed only in **23′′** and not in **23′** or in **24**, we propose that the steric hindrance of SiNHR is hardly relevant in determining its ligating ability and that the steric interactions within the SiN(R)Zr group should be decisive, i.e. the more sterically demanding *t*Bu group in **23′′** encourages the chelation. This could reasonably be due to the consequent reduction of unfavourable steric interactions within the SiN(*t*Bu)Zr fragment itself. Conversely, compounds **20−22** contain SiMe$_2$(NR)(NR′$_2$) as a chelating ligand, regardless of the nature of R (R = *i*Pr, *t*Bu), thus suggesting that the SiNR′$_2$ moieties, namely SiNMe$_2$ and SiNC$_4$H$_8$, have better ligating abilities with respect to SiNH*i*Pr and SiNH*t*Bu (in **23′** and **24**).

Conclusions

The ligating ability of SiMe$_2$(NR$_2$)(NR′$_2$) towards zirconium(IV) is affected by the nitrogen substituents and eventually by the zirconium ancillary ligands. As far as the binary derivatives ZrL$_2$ are concerned, in contrast to {Zr[SiMe$_2$(N*i*Pr)$_2$]$_2$}$_2$ (Scheme 6, A) and similar to Zr[SiMe$_2$(N*t*Bu)$_2$]$_2$ (Scheme 6, B), Zr[SiMe$_2$(N*i*Pr)(N*t*Bu)]$_2$ is mononuclear indicating that the formal substitution of one methyne proton with CH$_3$ in each silane ligand of {Zr[SiMe$_2$(N*i*Pr)$_2$]$_2$}$_2$ makes the ligand itself too bulky to be accommodated in the dimer frame.



Scheme 6

The coordination mode of SiMe$_2$(NR′)(NR$_2$) (NR$_2$ = NMe$_2$ or NC$_4$H$_8$; NR′ = N*i*Pr, N*t*Bu, NCH$_2$CH$_2$NMe$_2$ or NCH$_2$CH$_2$OMe) to the ZrX$_3$ moiety (X = Cl, NMe$_2$) is strictly determined by the ancillary ligands. In fact, SiMe$_2$(NR$_2$)(NCH$_2$CH$_2$Y) (NR$_2$=NMe$_2$ or NC$_4$H$_8$; Y = NMe$_2$ or OMe) is tridentate when X = Cl (Scheme 6, C) and bidentate when X = NMe$_2$ (Scheme 6, D). This could reasonably be due to the higher steric hindrance of the amido NMe$_2$ with respect to Cl and to the ability of NMe$_2$ to act as a π-donor. In addition, when X = NMe$_2$, the formation of the more stable five membered ring ZrNC$_2$Y (Y = NMe$_2$, OMe) can be observed rather than the four membered SiN$_2$Zr one. On the other hand, SiMe$_2$(NR′)(NR$_2$) (R′ = *i*Pr or *t*Bu; NR$_2$ = NMe$_2$ or NC$_4$H$_8$) exhibit similar ligating properties towards ZrX$_3$ (X = Cl, NMe$_2$) regardless of the nature of X and the formation of chelates is always observed (Scheme 6, E).

Finally, the hapticity of the silane ligand in Zr(NMe$_2$)$_3$[SiMe$_2$(NR)(NHR′)] is related to the steric hindrance of the nitrogen substituent R. As a matter of fact, the chelation of SiMe$_2$(N*t*Bu)(NH*i*Pr) (Scheme 6, E) in Zr(NMe$_2$)$_3$[SiMe$_2$(N*t*Bu)(NH*i*Pr)] and the mono-hapto coordination of SiMe$_2$(N*i*Pr)(NHR) (Scheme 6, F) in Zr(NMe$_2$)$_3$[SiMe$_2$(N*i*Pr)(NHR)] (R = *i*Pr, *t*Bu) indicate that the release of some steric congestion within the amido moiety SiN(R)Zr is decisive.

Experimental Section

All operations were carried out in a glove-box under dinitrogen. Elemental analyses (C, H, N) were performed using a Fisons Instruments analyser (Mod. EA 1108). The chlorine content in the samples was determined by potentiometric titration using a standard solution of silver nitrate (Aldrich). NMR spectra were recorded with a BRUKER AMX 300 spectrometer (300 MHz for ^{1}H). ^{1}H, ^{13}C and ^{29}Si NMR spectra are referred to TMS. The multiplicity is indicated as s (singlet), d (doublet), t (triplet), dt (doublet of triplets), q (quadruplet), sp (septet), ds (doublet of septets), m (multiplet) and br. was used to indicate broad signals.

The mass spectra (100−800 amu) were recorded with a Thermo-Finnigan Trace GC-MS instrument equipped with an accessory for the direct introduction of the sample into the source. The probe temperature was initially maintained at 373 K for 10 min, then raised to 473 K (50 K/min) and finally maintained at 473 K for 10 min. The source temperature was 473 K.

Zirconium tetrachloride ($ZrCl_4$, Fluka) was washed with boiling toluene then with pentane, dried in vacuo and stored under dinitrogen. *tert*-Butylamine ($C_4H_{11}N$, Aldrich), isopropylamine (C_3H_9N, Aldrich) and *N,N*-dimethylethylenediamine ($C_4H_{12}N_2$, Aldrich) were refluxed over BaO for one day, then distilled and stored under dinitrogen. Dichlorodimethylsilane ($SiMe_2Cl_2$, Aldrich), 2-methoxyethyleneamine (C_3H_9NO, Aldrich), LiMe (Et_2O solution, 1.6 M, Aldrich) and dimethylamine (C_2H_7N, Aldrich) were used as received. $SiMe_2(NR_2)_2$ [3,9] (NR_2 = NH*i*Pr, NH*t*Bu, NMe_2 or NC_4H_8) and $Zr(NMe_2)_4$ [11] were prepared according to the published procedures. The lithium amides $LiNR_2$ (NR_2 = NH*i*Pr, NH*t*Bu, $NHCH_2CH_2NMe_2$ or $NHCH_2CH_2OMe$) were prepared by treating NHR_2 with LiMe in Et_2O (1:1 molar ratio) and the resultant mixture was used without isolating the product.

Synthesis of $SiMe_2Cl(NR_2)$ (NR_2 = NH*i*Pr, NH*t*Bu, NMe_2 or NC_4H_8)

Only the synthesis of $SiMe_2Cl(NMe_2)$ is described in detail, the others being similar except for the reaction time (vide infra).

A solution of $SiMe_2(NMe_2)_2$ (1.20 g, 8.20 mmol) in pentane (50 mL) was treated with $SiMe_2Cl_2$ (1.07 g, 8.29 mmol). After 10 min stirring volatiles were removed in vacuo yielding a colourless liquid material, identified as $SiMe_2Cl(NMe_2)$ (**1**).

$SiMe_2Cl(NMe_2)$ (1): 2.15 g, 95% yield. $C_4H_{12}ClNSi$ (137.68): calcd. C 34.9, H 8.8, Cl 25.7, N 10.2; found C 34.8, H 8.9, Cl 25.5, N 10.1. ^{1}H NMR (C_6D_6, 298 K): δ = 2.28 (s, 1 H, NCH_3), 0.28 (s, 1 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 37.1 (NCH_3), 1.32 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = 13.9 ppm.

$SiMe_2Cl(NC_4H_8)$ (2): Reaction time: 10 min, colourless liquid, 96% yield. $C_6H_{14}ClNSi$ (163.72): calcd. C 44.0, H 8.6, Cl 21.7, N 8.6; found C 44.2, H 8.8, Cl 21.7, N 8.4. ^{1}H NMR (C_6D_6, 298 K): δ = 2.85 (m, 2 H, NCH_2), 1.53 (m, 2 H, NCH_2CH_2), 0.33 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 46.5 (NCH_2), 26.9 (NCH_2CH_2), 1.82 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = 10.1 ppm.

$SiMe_2Cl$(NH*i*Pr) (3): Reaction time: 18 h, colourless liquid, 92% yield. $C_5H_{14}ClNSi$ (151.71): calcd. C 39.6, H 9.3, N 9.2; found C 39.7, H 9.1, N 9.0. ^{1}H NMR (C_6D_6, 298 K): δ = 3.00 (ds, $^{3}J_{H,H}$ = 10.7, 1 H, CH, 6.4 Hz), 0.95 (d, $^{3}J_{H,H}$ = 6.4 Hz, 6 H, $CHCH_3$), 0.74 (br., 1 H, NH), 0.27 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 43.3 (CH), 27.1 ($CHCH_3$), 2.07 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = 8.4. ppm

$SiMe_2Cl$(NH*t*Bu) (4): Reaction time: 80 h, colourless liquid, 91% yield. $C_6H_{16}ClNSi$ (165.74): calcd. C 43.5, H 9.7, Cl 21.4, N 8.5; found C 43.2, H 10.0, Cl 21.3, N 8.2. ^{1}H NMR (C_6D_6, 298 K): δ = 1.14 (s, 9 H, CCH_3), 0.55 (br., 1 H, NH), 0.34 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 50.3 (C), 33.2 (CCH_3), 4.52 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = 5.6 ppm.

Synthesis of $SiMe_2(NR_2)(NR'_2)$: Only the synthesis of $SiMe_2(NMe_2)$(NH*t*Bu) is reported in detail, the others being similar. A solution of $SiMe_2Cl(NMe_2)$ (**1**, 900 mg, 6.54 mmol) in Et_2O (30 mL) was treated with an Et_2O suspension of LiNH*t*Bu (4.1 mL of an Et_2O solution, 1.6 M, 6.6 mmol of LiMe +485 mg, 6.63 mmol of NH_2*t*Bu) and the resultant suspension stirred for 3 h. The colourless solid was filtered (270 mg) and the solvent was removed in vacuo from the filtrate yielding a pale yellow liquid identified as $SiMe_2(NMe_2)$(NH*t*Bu) (**5**).

$SiMe_2(NMe_2)$(NH*t*Bu) (5): 1.05 g, 92% yield. $C_8H_{22}N_2Si$ (174.36): calcd. C 55.1, H 12.7, N 16.1; found C 55.1, H 12.9, N 16.0. ^{1}H NMR (C_6D_6, 298 K): δ = 2.41 (s, 6 H, $SiNCH_3$), 1.12 (s, 9 H, CCH_3), 0.53 (br., 1 H, NH), 0.10 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 48.8 (C), 37.6 ($SiNCH_3$), 33.5 (CCH_3), −0.08 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −10.8 ppm.

$SiMe_2(NMe_2)$(NH*i*Pr) (6): Colourless liquid, 90% yield, from $SiMe_2Cl(NMe_2)$ (**1**) + LiNH*i*Pr. $C_7H_{20}N_2Si$ (160.33): calcd. C 52.4, H 12.6, N 17.5; found C 52.0, H 12.5, N 17.3. ^{1}H NMR (C_6D_6, 298 K): δ = 2.99 (ds, $^{3}J_{H,H}$ = 10.2, 6.3 Hz, 1 H, CH), 2.49 (s, 6 H, $SiNCH_3$), 1.00 (d, $^{3}J_{H,H}$ = 6.3 Hz, 6 H, $CHCH_3$), 0.29 (br., 1 H, NH), 0.07 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 42.6 (CH), 37.5 ($SiNCH_3$), 27.8 ($CHCH_3$), −1.96 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −7.5 ppm.

$SiMe_2(NMe_2)(NHCH_2CH_2NMe_2)$ (7): Colourless liquid, 91% yield, from $SiMe_2Cl(NMe_2)$ (**1**) + $LiNHCH_2CH_2NMe_2$. $C_8H_{23}N_3Si$ (189.37): calcd. C 50.7, H 12.2, N 22.2; found C 51.0, H 11.9, N 22.1. ^{1}H NMR (C_6D_6, 298 K): δ = 2.74 (dt, $^{3}J_{H,H}$ = 6.9, 6.2 Hz, 2 H, $SiNCH_2$), 2.48 (s, 6 H, $SiNCH_3$), 2.18 (t, $^{3}J_{H,H}$ = 6.2 Hz, 2 H, CH_2NCH_3), 2.08 (s, 6 H, CH_2NCH_3), 1.15 (br., 1 H, NH), 0.04 ($SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 63.2 (CH_2NCH_3), 45.5 (CH_2NCH_3), 39.2 ($SiNCH_2$), 37.7 ($SiNCH_3$), −2.38 ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −5.3 ppm.

$SiMe_2(NMe_2)(NHCH_2CH_2OMe)$ (8): Colourless liquid, 95% yield, from $SiMe_2Cl(NMe_2)$ (**1**) + $LiNHCH_2CH_2OMe$. $C_7H_{20}N_2OSi$ (176.33): calcd. C 47.7, H 11.4, N 15.9; found C 47.7, H 11.0, N 15.8. ^{1}H NMR (C_6D_6, 298 K): δ = 3.19 (t, $^{3}J_{H,H}$ = 5.6 Hz, 2 H, OCH_2), 3.13 (s, 3 H, OCH_3), 2.87 (dt, $^{3}J_{H,H}$ = 7.7, 5.6 Hz, 2 H, $SiNCH_2$), 2.48 (s, 6 H, $SiNCH_3$), 0.99 (br., 1 H, NH), 0.06 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 76.0 (OCH_2), 58.4 (OCH_3), 41.3 ($SiNCH_2$), 37.6 ($SiNCH_3$), −2.38 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −5.0 ppm.

$SiMe_2$(NH*i*Pr)(NH*t*Bu) (9): Colourless liquid, 88% yield, from $SiMe_2Cl$(NH*i*Pr) (**3**) + LiNH*t*Bu. $C_9H_{24}N_2Si$ (188.39): calcd. C 57.4, H 12.8, N 14.9; found C 57.3, H 12.8, N 14.7. ^{1}H NMR (C_6D_6, 298 K): δ = 3.13 (ds, $^{3}J_{H,H}$ = 10.4, 6.3 Hz, 1 H, CH), 1.19 (s, 9 H, CCH_3), 1.04 (d, $^{3}J_{H,H}$ = 6.3 Hz, 6 H, $CHCH_3$), 0.56 (br., 1 H, NH), 0.24 (br., 1 H, NH), 0.12 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 49.1 (C), 42.6 (CH), 33.8 (CCH_3), 28.0 ($CHCH_3$), 1.74 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −15.0 ppm.

$SiMe_2(NC_4H_8)(NH\textit{t}Bu)$ (10): Colourless liquid, 92% yield, from $SiMe_2Cl(NC_4H_8)$ (**2**) + $LiNH\textit{t}Bu$. $C_{10}H_{24}N_2Si$ (200.40): calcd. C 59.9, H 12.1, N 14.0; found C 60.0, H 12.0, N 14.1. ^1H NMR (C_6D_6, 298 K): δ = 2.97 (m, 4 H, NCH_2), 1.61 (m, 4 H, NCH_2CH_2), 1.14 (s, 9 H, CCH_3), 0.58 (br., 1 H, NH), 0.12 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 48.9 (C), 46.7 (NCH_2), 33.7 (CCH_3), 27.2 (NCH_2CH_2), 0.14 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −14.4 ppm.

$SiMe_2(NC_4H_8)(NHCH_2CH_2NMe_2)$ (11): Colourless liquid, 90% yield, from $SiMe_2Cl(NC_4H_8)$ (**2**) + $LiNHCH_2CH_2NMe_2$. $C_{10}H_{25}N_3Si$ (215.41): calcd. C 55.8, H 11.7, N 19.5; found C 55.6, H 11.5, N 19.5. ^1H NMR (C_6D_6, 298 K): δ = 2.99 (m, 4 H, NCH_2CH_2), 2.81 (dt, $^3J_{H,H}$ = 7.0, 6.2 Hz, 2 H, $SiNHCH_2$), 2.21 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, CH_2NCH_3) 2.09 (s, 6 H, NCH_3), 1.61 (m, 4 H, NCH_2CH_2), 1.18 (br., 1 H, NH), 0.13 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 63.4 (CH_2NCH_3), 46.8 (NCH_2CH_2), 45.5 (NCH_3), 39.4 ($SiNHCH_2$), 27.3 (NCH_2CH_2), −2.05 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −8.9 ppm.

Synthesis of $Zr[SiMe_2(N\textit{i}Pr)(N\textit{t}Bu)]_2$: An Et_2O solution of $SiMe(NH\textit{i}Pr)(NH\textit{t}Bu)$ (**9**, 1.25 g, 6.64 mmol) was treated with LiMe (Et_2O solution, 1.6 M, 8.3 mL, 13.3 mmol), stirred for 1.5 h and then cooled to 243 K. $ZrCl_4$ (780 mg, 3.35 mmol) was added and after 2 h stirring at 243 K the mixture was warmed to the room temperature and the solid was filtered (540 mg). The pale yellow solution was partially evaporated, pentane was added and $Zr[SiMe_2(N\textit{i}Pr)(N\textit{t}Bu)]_2$ (**12**) was finally obtained as a microcrystalline powder on cooling the resultant solution to 240 K overnight (985 mg, 64% yield). $C_{18}H_{44}N_4Si_2Zr$ (463.96): calcd. C 46.6, H 9.6, N 12.1; found C 46.4, H 9.4, N 12.0. ^1H NMR (C_6D_6, 298 K): δ = 3.35 (sp, $^3J_{H,H}$ = 6.2 Hz, 1 H, CH), 1.32 (s, 9 H, CCH_3), 1.24 (d, $^3J_{H,H}$ = 6.2 Hz, 6 H, $CHCH_3$), 0.44 (s, 3 H, $SiCH_3$), 0.43 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 55.6 (C), 50.6 (CH), 36.2 (CCH_3), 31.2 ($CHCH_3$), 4.3 ($SiCH_3$), 4.1 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −40.5 ppm.

Synthesis of $ZrCl_3(L)$: Only the procedure for L = $SiMe_2(NMe_2)(NCH_2CH_2NMe_2)$ is described in detail, the others being similar. A solution of $SiMe_2(NMe_2)(NHCH_2CH_2NMe_2)$ (**7**, 780 mg, 4.12 mmol) in Et_2O (40 mL) was treated with LiMe (Et_2O solution, 1.6 M, 2.6 mL, 4.2 mmol). After gas evolution ceased, the solution was cooled to 243 K and $ZrCl_4$ (960 mg, 4.12 mmol) was added. The suspension was stirred at 243 K for 3 h and was then warmed to the room temperature and stirred overnight. The resultant suspension was filtered (165 mg of colourless solid) and the filtrate was evaporated yielding a sticky material which was recrystallized from Et_2O/pentane yielding a microcrystalline powder, identified as **$ZrCl_3[SiMe_2(NMe_2)(NCH_2CH_2NMe_2)]$ (15):** Colourless solid, 1.35 mg, 85% yield. MS: m/z (%) = 368 (9) [$M^{+\bullet}$ − CH_3], 332 (100) [$M^{+\bullet}$ − CH_3 − H − Cl]. $C_8H_{22}Cl_3N_3SiZr$ (385.95): calcd. C 24.9, H 5.7, Cl 27.6, N 10.9; found C 25.0, H 5.5, Cl 27.5, N 11.0. ^1H NMR ($CDCl_3$, 298 K): δ = 3.51 (t, $^3J_{H,H}$ = 5.6 Hz, 1 H, $SiNCH_2$), 3.00 (t, $^3J_{H,H}$ = 5.6 Hz, 1 H, CH_2NMe_2), 2.71 (s, 3 H, $SiNCH_3$), 2.70 (s, 3 H, CH_2NCH_3), 0.35 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 298 K): δ = 67.1 (CH_2NMe_2), 50.5 (CH_2NCH_3), 47.8 ($SiNCH_2$), 45.1 ($SiNCH_3$), −2.5 ($SiCH_3$) ppm.

$ZrCl_3[SiMe_2(NC_4H_8)(N\textit{t}Bu)]$ (13): Colourless solid, 70% yield. $C_{10}H_{23}Cl_3N_2SiZr$ (396.97): calcd. C 30.3, H 5.8, Cl 26.8, N 7.1; found C 30.0, H 5.6, Cl 27.2, N 7.2. ^1H NMR ($CDCl_3$, 298 K): δ = 3.49 (br., 2 H, NCH_2), 3.35 (br., 2 H, NCH_2), 1.48 (s, 9 H, CCH_3), 1.01 (br., 4 H, NCH_2CH_2), 0.18 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 298 K): δ = 58.2 (C), 54.0 (NCH_2), 34.1 (CCH_3), 24.9 (NCH_2CH_2), 1.4 ($SiCH_3$) ppm.

$ZrCl_3[SiMe_2(NC_4H_8)(NCH_2CH_2NMe_2)]$ (14): Colourless solid, 91% yield. MS: m/z (%) = 339 (17.8) [$M^{+\bullet}$ − $NCH_2CH_2CH_2CH_2$], 332 (75.3) [$M^{+\bullet}$ − $CH_2CH_2CH_2$ − Cl]. $C_{10}H_{24}Cl_3N_3SiZr$ (411.98): calcd. C 29.2, H 5.9, N 10.2; found C 29.3, H 5.8, N 10.1. ^1H NMR ($CDCl_3$, 298 K): δ = 3.48 (t, $^3J_{H,H}$ = 5.5 Hz, 1 H, $SiNCH_2$), 3.36 (m, 2 H, NCH_2 pyrrolidinide), 2.98 (t, $^3J_{H,H}$ = 5.5 Hz, 1 H, CH_2NMe_2), 2.72 (s, 3 H, NCH_3), 1.61 (m, 2 H, NCH_2CH_2 pyrrolidinide), 0.31 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 298 K): δ = 66.6 (CH_2NMe_2), 53.3 (NCH_3), 49.8 (NCH_2 pyrrolidinide), 47.5 ($SiNCH_2$), 25.1 (NCH_2CH_2 pyrrolidinide), −2.14 ($SiCH_3$) ppm.

$ZrCl_3[SiMe_2(NMe_2)(NCH_2CH_2OMe)]$ (16): Colourless solid, 88% yield. MS: m/z (%) = 355 (15.9) [$M^{+\bullet}$ − CH_3], 319 (29.4) [$M^{+\bullet}$ − CH_3 − H − Cl]. $C_7H_{19}Cl_3N_2OSiZr$ (372.91): calcd. C 22.5, H 5.1, Cl 28.5, N 7.5; found C 22.3, H 5.0, Cl 28.8, N 7.6. ^1H NMR ($CDCl_3$, 298 K): δ = 4.24 (t, $^3J_{H,H}$ = 5.3 Hz, 2 H, OCH_2), 3.94 (s, 3 H, OCH_3), 3.56 (t, $^3J_{H,H}$ = 5.3 Hz, 2 H, NCH_2), 2.74 (s, 6 H, NCH_3), 0.32 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 298 K): δ = 81.5 (OCH_2), 65.4 (OCH_3), 47.5 (NCH_2), 44.2 (NCH_3), −2.16 ($SiCH_3$) ppm.

Synthesis of $Zr(NMe_2)_3(L)$: Only the procedure for L = $SiMe_2(N\textit{i}Pr)(NMe_2)$ is reported in detail, the others being similar except for the reaction time (vide infra). A solution of $SiMe_2(NH\textit{i}Pr)(NMe_2)$ (**6**, 540 mg, 3.37 mmol) in toluene (20 mL) was treated with $Zr(NMe_2)_4$ (900 mg, 3.36 mmol). After 3 h stirring, the solution was evaporated yielding a pale yellow solid which was identified as $Zr(NMe_2)_3[SiMe_2(N\textit{i}Pr)(NMe_2)]$ (**21**).

$Zr(NMe_2)_3[SiMe_2(N\textit{i}Pr)(NMe_2)]$ (21): Colourless solid, 1.20 g, 93% yield. $C_{13}H_{37}N_5SiZr$ (382.78): calcd. C 40.8, H 9.7, N 18.3; found C 40.5, H 9.9, N 18.5. ^1H NMR (C_6D_6, 298 K): δ = 3.53 (sp, $^3J_{H,H}$ = 6.4 Hz, 1 H, CH), 3.04 (s, 18 H, $ZrNCH_3$), 2.24 (s, 6 H, $SiNCH_3$), 1.23 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, $CHCH_3$), 0.14 ($SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 50.2 (CH), 43.2 ($ZrNCH_3$), 42.3 ($SiNCH_3$), 28.9 ($CHCH_3$), 0.67 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = 3.2 ppm.

$Zr(NMe_2)_3[SiMe_2(NC_4H_8)(NCH_2CH_2NMe_2)]$ (17): Reaction time: 3 h, colourless solid, 90% yield. $C_{16}H_{42}N_6SiZr$ (437.86): calcd. C 43.9, H 9.7, N 19.2; found C 44.0, H 9.5, N 19.0. ^1H NMR (C_6D_6, 298 K): δ = 3.26 (t, $^3J_{H,H}$ = 5.6 Hz, 1 H, $SiNCH_2$), 3.07 (m, 2 H, NCH_2 pyrrolidinide), 2.99 (s, 9 H, $ZrNCH_3$), 2.42 (t, $^3J_{H,H}$ = 5.6 Hz, 1 H, CH_2NMe_2), 1.96 (s, 3 H, NCH_3), 1.68 (m, 2 H, NCH_2CH_2 pyrrolidinide), 0.28 (s, 3 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 61.0 (CH_2NMe_2), 47.5 (NCH_2 pyrrolidinide), 46.4 ($SiNCH_2$), 46.2 (CH_2NCH_3), 43.4 ($ZrNCH_3$), 27.3 (NCH_2CH_2 pyrrolidinide), −0.7 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −5.9 ppm.

$Zr(NMe_2)_3[SiMe_2(NMe_2)(NCH_2CH_2OMe)]$ (18): Reaction time: 3 h, colourless solid, 92% yield. $C_{13}H_{37}N_5OsiZr$ (398.78): calcd. C 39.2, H 9.4, N 17.6; found C 39.0, H 9.4, N 17.5. ^1H NMR (C_6D_6, 298 K): δ = 3.31 (t, $^3J_{H,H}$ = 5.4 Hz, 2 H, CH_2O), 3.19 (t, $^3J_{H,H}$ = 5.4 Hz, 2 H, $SiNCH_2$), 3.05 (s, 18 H, $ZrNCH_3$), 2.98 (s, 3 H, OCH_3), 2.56 (s, 6 H, $SiNCH_3$), 0.24 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 79.2 ($SiNCH_2$), 59.2 (OCH_3), 46.5 (CH_2O), 43.2 ($ZrNCH_3$), 38.4 ($SiNCH_3$), −1.0 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −3.9 ppm.

$Zr(NMe_2)_3[SiMe_2(NMe_2)(NCH_2CH_2NMe_2)]$ (19): Reaction time: 3 h, colourless solid, 87% yield. $C_{14}H_{40}N_6SiZr$ (411.82): calcd. C 40.8, H 9.8, N 20.4; found C 41.0, H 10.0, N 20.0. ^1H NMR (C_6D_6, 298 K): δ = 3.21 (t, 1 H, $SiNCH_2$, $^3J_{H,H}$ = 5.9 Hz), 3.02 (s, 18 H, $ZrNCH_3$), 2.62 (s, 3 H, $SiNCH_3$), 2.36 (t, $^3J_{H,H}$ = 5.9 Hz, 1 H, CH_2NMe_2), 1.90 (s, 3 H, CH_2NCH_3), 0.32 (s, 3 H, $SiCH_3$) ppm.

^{13}C NMR (C_6D_6, 298 K): δ = 60.7 (CH_2NMe_2), 46.5 ($SiNCH_2$), 46.0 (CH_2NCH_3), 43.3 ($ZrNCH_3$), 38.4 ($SiNCH_3$), −0.93 ($SiCH_3$) ppm.

$Zr(NMe_2)_3[SiMe_2(N\mathit{t}Bu)(NC_4H_8)]$ (20): Reaction time: 30 h, colourless solid, 85% yield. $C_{16}H_{41}N_5SiZr$ (422.84): calcd. C 45.5, H 9.8, N 16.6; found C 45.7, H 9.5, N 16.5. ^{1}H NMR (C_6D_6, 298 K): δ = 3.04 (s, 18 H, $ZrNCH_3$), 2.74 (m, 4 H, NCH_2), 1.37 (m, 4 H, NCH_2CH_2), 1.33 (s, 9 H, CCH_3), 0.23 ($SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 55.1 (C), 51.5 (NCH_2), 43.9 ($ZrNCH_3$), 35.5 (CCH_3), 24.7 (NCH_2CH_2), 3.5 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −2.7 ppm.

$Zr(NMe_2)_3[SiMe_2(N\mathit{t}Bu)(NMe_2)]$ (22): Reaction time: 28 h, colourless solid, 88% yield. $C_{14}H_{39}N_5SiZr$ (396.80): calcd. C 42.4, H 9.9, N 17.6; found C 42.3, H 10.0, N 17.8. ^{1}H NMR (C_6D_6, 298 K): δ = 3.04 (s, 18 H, $ZrNCH_3$), 2.19 (s, 6 H, $SiNCH_3$), 1.33 (s, 9 H, CCH_3), 0.20 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 54.8 (C), 43.8 ($ZrNCH_3$), 42.8 ($SiNCH_3$), 35.4 (CCH_3), 3.4 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = 1.0 ppm.

When $Zr(NMe_2)_4$ was reacted with $SiMe_2(NH\mathit{i}Pr)(NH\mathit{t}Bu)$ (**9**, H_2L) (1:1 molar ratio) a microcrystalline powder was obtained which was analytically identified as $Zr(NMe_2)_3(HL)$ (**23**).

$Zr(NMe_2)_3(HL)$ (23): Colourless sticky material, 95% yield. $C_{15}H_{41}N_5SiZr$ (410.83): calcd. C 43.9, H 10.1, N 17.1; found C 44.0, H 10.2, N 17.4. The ^{1}H, ^{13}C and ^{29}Si NMR spectra (298 K, C_6D_6) indicated the presence of two isomers, namely $Zr(NMe_2)_3[SiMe_2(N\mathit{i}Pr)(NH\mathit{t}Bu)]$ (**23′**) and $Zr(NMe_2)_3[SiMe_2(NH\mathit{i}Pr)(N\mathit{t}Bu)]$ (**23′′**) (**23′**/**23′′** molar ratio about 0.7). **$Zr(NMe_2)_3[SiMe_2(N\mathit{i}Pr)(NH\mathit{t}Bu)]$ (23′):** ^{1}H NMR (C_6D_6, 298 K): δ = 3.38 (sp, $^3J_{H,H}$ = 6.4 Hz, 1 H, CH), 3.07 (s, 18 H, $ZrNCH_3$), 1.23 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, $CHCH_3$), 1.05 (s, 9 H, CCH_3), 0.25 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 52.0 (C), 50.3 (CH), 43.7 ($ZrNCH_3$), 32.1 (CCH_3), 29.0 ($CHCH_3$), 3.6 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −4.6 ppm.

$Zr(NMe_2)_3[SiMe_2(NH\mathit{i}Pr)(N\mathit{t}Bu)]$ (23′′): ^{1}H NMR (C_6D_6, 298 K): δ = 2.93 (sp, $^3J_{H,H}$ = 6.1 Hz, 1 H, CH), 3.06 (s, 18 H, $ZrNCH_3$), 1.32 (s, 9 H, CCH_3), 0.88 (d, $^3J_{H,H}$ = 6.1 Hz, 6 H, $CHCH_3$), 0.32 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 54.9 (C), 45.9 (CH), 43.3 ($ZrNCH_3$), 35.5 (CCH_3), 26.6 ($CHCH_3$), 4.6 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −5.9 ppm.

$Zr(NMe_2)_3[SiMe_2(N\mathit{i}Pr)(NH\mathit{i}Pr)]$ (24): Colourless solid, 95% yield. $C_{14}H_{39}N_5SiZr$ (396.80): calcd. C 42.4, H 9.9, N 17.6; found C 42.7, H 9.8, N 18.0. ^{1}H NMR (C_6D_6, 298 K): δ = 3.45 (sp, $^3J_{H,H}$ = 6.4 Hz, 1 H, CH), 3.08 (s, 18 H, $ZrNCH_3$), 2.92 (sp, $^3J_{H,H}$ = 6.4 Hz, 1 H, CH), 2.0 (br., 1 H, NH), 1.23 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, $CHCH_3$), 0.89 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, $CHCH_3$), 0.22 (s, 6 H, $SiCH_3$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 50.2 (CH), 45.6 (CH), 43.4 ($ZrNCH_3$), 29.0 ($CHCH_3$), 26.6 ($CHCH_3$), 1.7 ($SiCH_3$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −2.8 ppm.

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[10] The rate of the reaction is strongly affected by the nature of R. In fact Cl/NR_2 exchange occurs within the mixing time when NR_2 = NMe_2, NC_4H_8, whereas the reaction is markedly slower when NR_2 = Nh*i*Pr or NH*t*Bu, the conversion being complete after 12 h for NR_2 = NH*i*Pr and 70 h for NR_2=NH*t*Bu.

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