The Ligating Ability of Functionalised Diaminodimethylsilanes towards Zirconium(IV)

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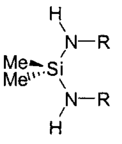
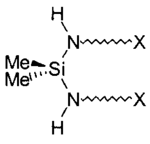
The functionalised diaminodimethylsilanes $SiMe_2[NH(CH_2)_nX]_2$ (X = NMe_2, n = 2, H_2L^1; n = 3, H_2L^2; X = OMe, n = 2, H_2L^3; n = 3, H_2L^4) have been synthesised by aminolysis of $SiMe_2Cl_2$ with $NH_2(CH_2)_nX$, and their ligating ability towards zirconium(IV) has been investigated. The syntheses of $[ZrY_2(L)]$ (Y = Cl, NMe_2, Me; L = L^1, L^2, L^3, L^4) are reported and the solid-state structures of some selected compounds determined by X-ray crystallography. In addition, the solution molecular structures of all the metal derivatives have been elucidated by variable-temperature multinuclear 1D/2D NMR spectroscopy, and the dynamics have been investigated in some selected cases.

Introduction

Due to the observed peculiar catalytic and structural properties of metal amide derivatives,[1] increasing attention has been devoted to the synthesis of novel compounds of this class. Silylamides of the type $NRSiR'_3$ are widely reported in the literature,[1a−1c] while only a limited number of papers are available[2] dealing with the ligating ability of diaminosilanes (**I**). Nevertheless, in the case of the zirconium derivatives, it appears that the substituents of the $SiMe_2N_2$ core, i.e. the hydrocarbyl groups on the nitrogen atoms, play a fundamental role in determining the nature of the product(s). For instance, the *tert*-butyl derivative $[Zr\{(NtBu)_2SiMe_2\}_2]$[2a] is mononuclear, while the isopropyl analogue is dinuclear,[2r] containing both bridging and terminal $SiMe_2(NiPr)_2$ amido ligands. In addition to the molecular structure of $[Zr\{(NiPr)_2SiMe_2\}_2]_2$,[2r] relevant to this paper are the crystallographically established pentacoordinate or hexacoordinate zirconium derivatives, namely $[Zr(NMe_2)_2(NHMe_2)\{(NAr)_2SiMe_2\}]$,[1d] $[ZrCl_2\{(NAr')_2SiMe_2\}(THF)_2]$[2p] and $[AlMe_2(THF)_2][Zr_2Cl_5\{(NAr')_2SiMe_2\}_2]$[2p] (Ar = 2,6-$Me_2C_6H_3$; Ar′ = 2,6-$iPr_2C_6H_3$). These results suggest that when the starting diaminosilane contains the $Si(NHR)_2$ moiety, the zirconium centre of the formally resulting $[ZrX_2\{(NR)_2SiMe_2\}]$ moiety is coordinatively unsaturated and therefore able to bond additional ligands, thus yielding mononuclear solvento species or ligand-bridged structures. In light of this, it appeared of interest to synthesise novel functionalised diaminodimethylsilanes (**II**), containing potential ligating sites besides the SiN_2 moiety, investigate their ligating ability towards zirconium, and elucidate the molecular structure of the complexes both in solution and in the solid state.



(I)



(II)

〰 = spacer
X = ligating site

Results and Discussion

Synthesis of $SiMe_2[NH(CH_2)_nX]_2$ (H_2L; n = 2, 3; X = NMe_2, OMe) and Li_2L

The aminolysis of $SiMe_2Cl_2$ by $NH_2(CH_2)_nX$ (n = 2, 3; X = NMe_2, OMe) yields the diaminodimethylsilanes $SiMe_2[NH(CH_2)_nX]_2$ (**1**, H_2L^1, n = 2, X = NMe_2; **2**, H_2L^2, n = 3, X = NMe_2; **3**, H_2L^3, n = 2, X = OMe; **4**, H_2L^4, n = 3, X = OMe), the chlorides being removed as the ammonium salt $NH_2(CH_2)_nX{\cdot}HCl$ (see Scheme 1). The resulting silanes H_2L are readily deprotonated by MeLi (1:2 molar ratio) yielding the lithium salts Li_2L (Scheme 1).

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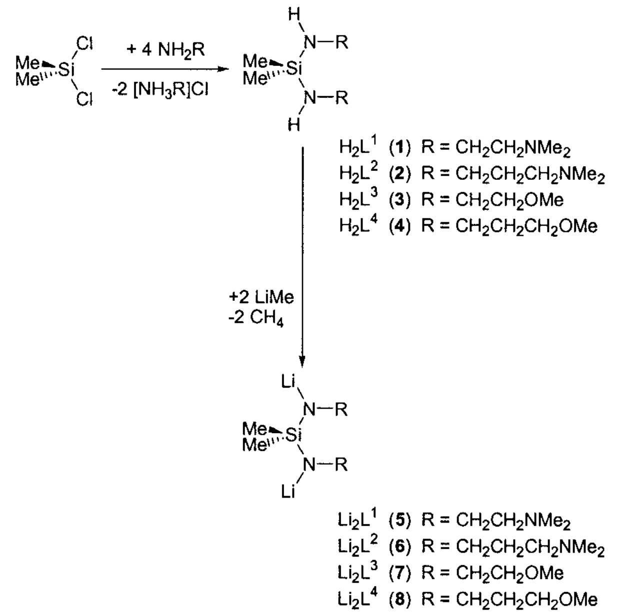
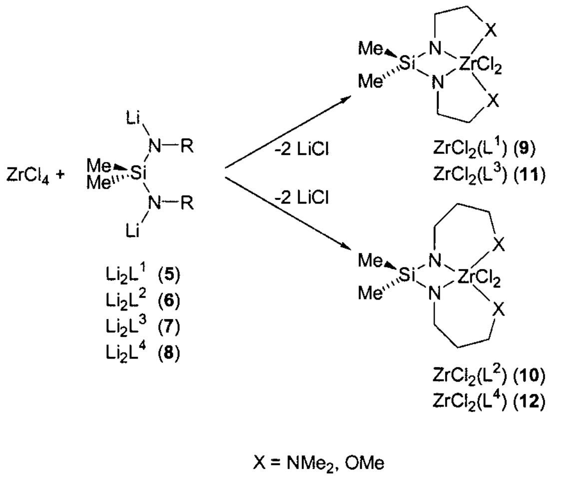


Scheme 1

The ^1H and ^{13}C NMR spectra of H_2L and Li_2L ($L = L^1$, L^2, L^3, L^4) show high-field resonances for the $SiMe_2$ group, while the peaks of the $NH(CH_2)_nX$ moiety are observed in the range $\delta = 1-4$ ppm (^1H) and $\delta = 30-80$ ppm (^{13}C). The ^{29}Si NMR resonances of the lithium salts Li_2L are high-field shifted with respect to H_2L due to the formal doubly negative charge on L in Li_2L.

Synthesis of [$ZrY_2(L)$] (Y = Cl, Me, NMe_2; $L = L^1$, L^2, L^3, L^4)

The reaction of $ZrCl_4$ with Li_2L yields the dichloro derivatives [$ZrCl_2(L)$] (**9**, $L = L^1$; **10**, $L = L^2$; **11**, $L = L^3$; **12**, $L = L^4$) as pure materials after recrystallisation from pentane at 249 K (Scheme 2).



Scheme 2

The solid-state molecular structures of compounds **10** and **12** were determined by single-crystal X-ray diffraction analysis, showing the $ZrCl_2$ moiety to be coordinated to the tetradentate ligand L (Figure 1A and 1B). The arrangement of the donor atoms in **10** is intermediate between the *cis*- and *trans*-octahedral isomers[3a] [Cl(1)−Zr−Cl(2): 109.0(1)°; N(3)−Zr−N(4): 160.1(1)°; the dihedral angle between the ZrCl(1)Cl(2) and ZrN(1)N(2) planes is 28.3(1)°]. Compound **12** shows a more symmetric coordination sphere in which the tetradentate ligand defines the equatorial plane (containing the metal centre) and the chlorine ligands occupy opposite sites with respect to it [Cl(1)−Zr−Cl(2): 140.7(1)°; O−Zr−O′: 122.4(2)°; the dihedral angle between the ZrCl(1)Cl(2) and ZrNN′ planes is 90.0°].

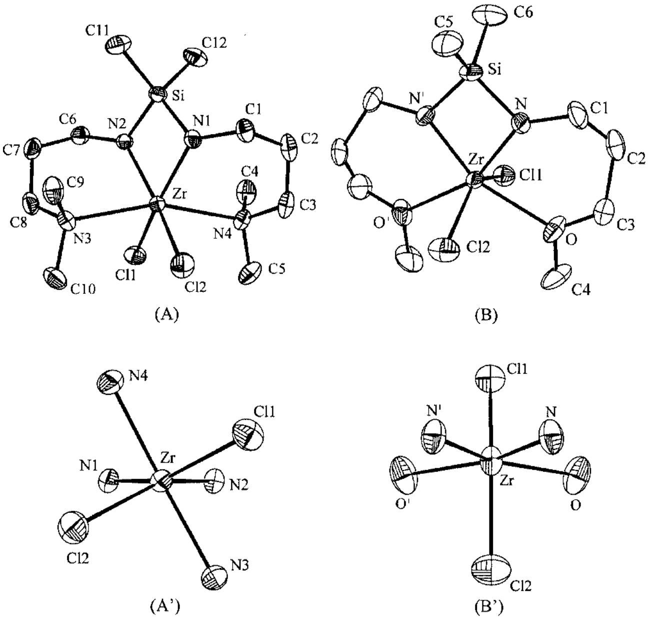


Figure 1. Molecular structures of (A) [$ZrCl_2(L^2)$] (**10**) and (B) [$ZrCl_2(L^4)$ (**12**)] with the numbering schemes adopted and the coordination polyhedra {[$ZrCl_2(L^2)$] (A′); [$ZrCl_2(L^4)$] (B′)}

As far as the SiN_2Zr moiety in **10** and **12** is concerned, similar bond lengths and angles (Table 1 and 2) have been observed in related compounds {e.g. Zr−N: 2.052 Å (av.); Si−N: 1.753 Å (av.) in [$Zr\{(NtBu)_2SiMe_2\}_2$][2a]}and it is important to note that the shorter the Zr−N [**10**, Zr−N(1); Zr−N(2); **12**, Zr−N] and Si−N [**10**, Si−N(1); Si−N(2); **12**, Si−N] bond lengths, the wider the N−Zr−N [**10**, N(1)−Zr−N(2); **12**, N−Zr−N′] and N−Si−N angles [**10**, N(1)−Si−N(2); **12**, N−Si−N′; cf. Table 1, 2].

Concerning the neutral ligating sites NMe_2 and OMe, it should be noted that in agreement with the trends in zirconium(IV) compounds, the Zr−N distance is longer than the Zr−O one [**10**, Zr−N(3), 2.427(2) Å, 2.438(2) Å; **12**, Zr−O, 2.330(4) Å].[4]

Coordination polyhedra similar to **10** and **12** have already been observed for zirconium complexes[2p,5] but, to the best of our knowledge, **10** is the first structurally charac-

Table 1. Selected bond lengths (Å) and angles (°) for [$ZrCl_2(L^2)$] (**10**)

Zr−Cl(1)	2.507(1)	Zr−Cl(2)	2.510(1)
Zr−N(1)	2.059(2)	Zr−N(2)	2.059(2)
Zr−N(3)	2.427(2)	Zr−N(4)	2.438(2)
Si−N(1)	1.729(2)	Si−N(2)	1.728(2)
Si−C(11)	1.871(3)	Si−C(12)	1.866(3)
Cl(1)−Zr−Cl(2)	109.0(1)	Cl(1)−Zr−N(1)	153.9(1)
Cl(1)−Zr−N(2)	92.5(1)	Cl(1)−Zr−N(4)	83.4(1)
Cl(1)−Zr−N(3)	83.8(1)	Cl(2)−Zr−N(1)	91.3(1)
Cl(2)−Zr−N(2)	153.0(1)	Cl(2)−Zr−N(3)	84.6(1)
Cl(2)−Zr−N(4)	85.3(1)	N(1)−Zr−N(2)	73.9(1)
N(1)−Zr−N(3)	115.1(1)	N(1)−Zr−N(4)	82.2(1)
N(2)−Zr−N(3)	81.7(1)	N(2)−Zr−N(4)	114.0(1)
N(3)−Zr−N(4)	160.1(1)	N(1)−Si−N(2)	91.4(2)
N(1)−Si−C(11)	113.1(2)	N(1)−Si−C(12)	115.9(2)
N(2)−Si−C(11)	116.5(2)	N(2)−Si−C(12)	113.4(2)
C(11)−Si−C(12)	106.4(2)		

Table 2. Selected bond lengths (Å) and angles (°) for [$ZrCl_2(L^4)$] (**12**)

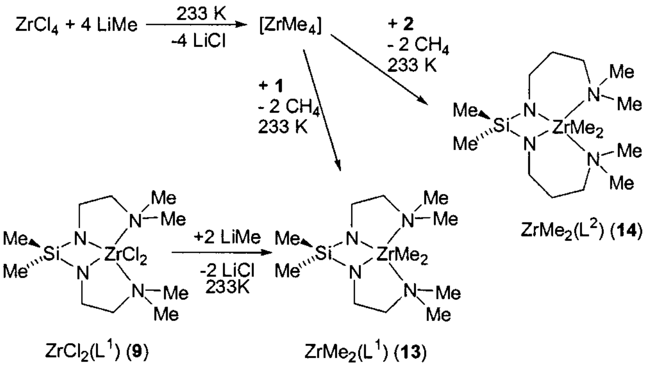
Zr−Cl(1)	2.465(2)	Zr−Cl(2)	2.463(2)
Zr−N	2.024(4)	Zr−O	2.330(4)
Si−N	1.719(4)	Si−C(5)	1.858(9)
Si−C(6)	1.865(9)	N(1)−C(1)	1.450(3)
O−C(3)	1.354(3)	O−C(4)	1.424(8)
Cl(1)−Zr−Cl(2)	140.7(1)	Cl(1)−Zr−N	104.7(1)
Cl(2)−Zr−N	106.1(1)	Cl(1)−Zr−O	80.7(1)
Cl(2)−Zr−O	80.7(1)	O−Zr−N	80.9(2)
N−Zr−N′[a]	75.6(2)	O−Zr−O′[a]	122.4(2)
N−Si−C(5)	113.7(1)	N−Si−C(6)	113.6(1)
N−Si−N′[a]	92.4(3)	C(5)−Si−C(6)	109.3(5)

[a] Equivalent atom generated by $-x$, y, z.

terised hexacoordinate derivative containing a linear open-chain N_4 ligand bonded to the $ZrCl_2$ moiety. With regards to **12**, the molecular structure of the solvento zirconium derivative [$ZrCl_2\{(NAr)_2SiMe_2\}(THF)_2$][2p] (Ar = 2,6-$i$$Pr_2C_6H_3$) is to be considered because of the strictly similar arrangement of the donor atoms, i.e. the zirconium, the oxygen and the nitrogen atoms define the equatorial plane, while the chlorides occupy the apical sites.

The solution molecular structures of **9**−**12** were investigated by NMR spectroscopy. The ^1H and ^{13}C NMR spectra show the expected patterns (see Exp. Sect.) and, relevant to the structure elucidation, the ^1H NMR resonances of the CH_2NMe_2 (**9**, **10**) and the CH_2OMe (**11**, **12**) moieties are shifted with respect to the uncomplexed ligands, thus indicating their coordination to the metal centre, and the two halves of the silane ligands, namely $SiN(CH_2)_nNMe_2$ and $SiN(CH_2)_nOMe$ are equivalent[3b] even at 188 K (^1H and ^{13}C NMR), suggesting the symmetric coordination[3a] of the ligand to the metal centre. The solution molecular structures of **9**−**12** should therefore be essentially similar to the solid-state structures of **10** and **12**.

In order to extend the class of the zirconium derivatives containing L^1 and L^2 the synthesis of complexes containing ancillary ligands other than Cl, namely Me and NMe_2, was investigated. The dimethyl derivatives [$ZrMe_2(L)$] (**13**, L = L^1; **14**, L = L^2) were prepared by reacting $ZrMe_4$ (generated in situ by treating $ZrCl_4$ with MeLi, 1:4 molar ratio, 233 K) with H_2L (L = L^1, L^2, Scheme 3). Alternatively, **13** could be obtained from the reaction of **9** with MeLi (1:2 molar ratio, 233 K; Scheme 3). The products are extremely air and moisture sensitive and thermally unstable (samples of both **13** and **14** were found to decompose within one week, even if stored under dinitrogen at 249 K).

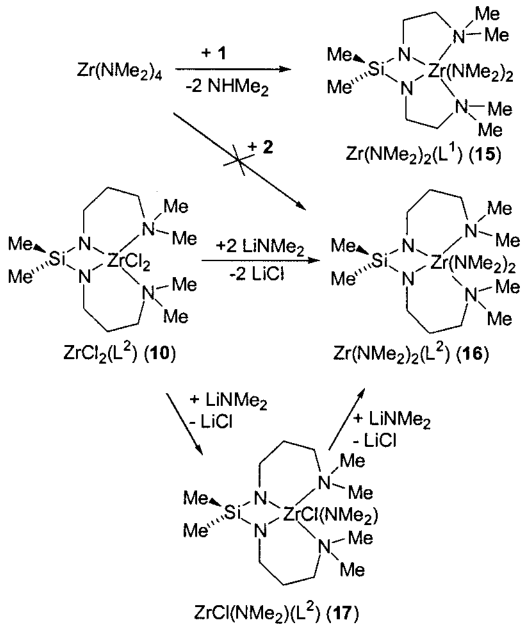


Scheme 3

Similar to [$ZrCl_2(L)$], the ^1H and/or ^{13}C NMR resonances of the $CH_2N(CH_3)_2$ group of [$ZrMe_2(L)$] (L = L^1, L^2) are shifted with respect to the uncomplexed ligands, thus proving the coordination of the neutral NMe_2 units to the zirconium centre. In addition, the equivalence of the two arms of the diaminosilane ligands (^1H, ^{13}C) indicates a symmetric coordination of the ligand.[3b]

The reaction of [$Zr(NMe_2)_4$] with **1** yields the mixed amido derivative [$Zr(NMe_2)_2(L^1)$] (**15**) as a microcrystalline solid, after removing all the volatiles from the reaction mixture (Scheme 4). Unfortunately, H_2L^2 reacts with [$Zr(NMe_2)_4$] to give a mixture of products that we were unable to separate and characterise. However, [$Zr(NMe_2)_2(L^2)$] (**16**) could be obtained as a pure material from the reaction of **10** with $LiNMe_2$ (1:2 molar ratio, Scheme 4); formation of the chloroamido derivative [$ZrCl(NMe_2)(L^2)$] (**17**) was also observed in the course of the reaction. As a matter of fact, when **10** was treated with $LiNMe_2$ (1:1 molar ratio), **17** was isolated as a pure material in high yield, and the treatment of **17** with $LiNMe_2$ (1:1 molar ratio) yielded **16**.

The solid-state molecular structure of **15** was determined by X-ray diffraction analysis, showing the zirconium centre to be coordinated to the tetradentate dianionic ligand L^1 and to the dimethylamido ligands (Figure 2). To the best of our knowledge, [$Zr(NMe_2)_2(L^1)$] (**15**) is the first structurally characterised hexacoordinate zirconium complex containing a linear open-chain N_4 ligand coordinated to the $Zr(NMe_2)_2$ moiety. The coordination polyhedron can be described as a distorted octahedron or a bicapped tetrahedron (amino NMe_2 groups capping two faces). In any case, the four donor atoms from the silane ligand define the equa-



Scheme 4

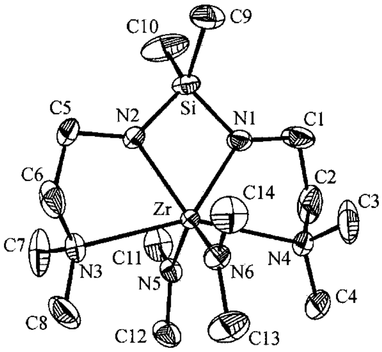


Figure 2. Molecular structure of [$Zr(NMe_2)_2(L^1)$] (**15**) with the numbering scheme adopted

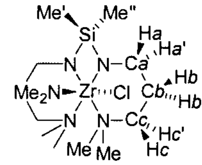
torial plane of the molecule and the dimethylamido groups occupy opposite coordination sites with respect to it. Concerning bond lengths and angles (Table 3), the Si−N(1), Si−N(2), Zr−N(1) and Zr−N(2) distances and the N(1)−Si−N(2) and N(1)−Zr−N(2) angles of the SiN_2Zr core are similar to those observed in **10**, **12** and related compounds (vide supra). The Zr−N(3) and Zr−N(4) distances [2.566(6), 2.580(7) Å, respectively] in **15** are longer than those in **10** [2.427(2), 2.438(2) Å, respectively], and we propose that the different hydrocarbon chains (the shorter ethylene one in **15** vs. the longer propylene one in **10**), the different arrangement of the tetradentate ligand (Figure 1 and 2), and the presence of the more sterically demanding dimethylamido ligand (with respect to Cl) might be responsible for this.

Table 3. Selected bond lengths (Å) and angles (°) for [$Zr(NMe_2)_2(L^1)$ (**15**)]

Zr−N(1)	2.103(6)	Zr−N(2)	2.117(6)
Zr−N(3)	2.566(6)	Zr−N(4)	2.580(7)
Zr−N(5)	2.075(6)	Zr−N(6)	2.084(6)
Si−N(1)	1.683(7)	Si−N(2)	1.684(7)
Si−C(9)	1.87(1)	Si−C(10)	1.85(1)
N(4)−Zr−N(1)	67.9(3)	N(4)−Zr−N(2)	136.7(2)
N(4)−Zr−N(3)	154.4(2)	N(4)−Zr−N(5)	84.2(2)
N(4)−Zr−N(6)	83.5(3)	N(1)−Zr−N(2)	69.1(3)
N(1)−Zr−N(5)	110.6(3)	N(1)−Zr−N(3)	137.7(3)
N(1)−Zr−N(6)	113.7(3)	N(2)−Zr−N(3)	68.8(3)
N(2)−Zr−N(5)	115.4(3)	N(2)−Zr−N(6)	110.1(3)
N(3)−Zr−N(5)	84.4(3)	N(3)−Zr−N(6)	84.5(3)
N(5)−Zr−N(6)	124.8(3)	N(1)−Si−N(2)	90.6(3)
N(1)−Si−C(9)	115.9(5)	N(1)−Si−C(10)	114.7(6)
N(2)−Si−C(9)	114.6(5)	N(2)−Si−C(10)	116.0(7)
C(9)−Si−C(10)	105.2(6)		

The ^1H and ^{13}C NMR spectra of [$Zr(NMe_2)_2(L)$] (**15**, **16**) show only two (**15**) and three (**16**) methylene resonances, suggesting a symmetrical coordination[3b] of L to the $Zr(NMe_2)_2$ moiety, and, consequently, that the solid-state molecular structure of **15** is preserved in solution. A similar arrangement of the donor atoms can be proposed for **16** (vide infra).

As far as the chloroamido derivative [$ZrCl(NMe_2)(L^2)$] (**17**) is concerned, only one ^{29}Si NMR signal ($\delta = -22.1$ ppm) is observed, while the ^{13}C NMR spectrum shows three resonances for the methylene carbons atoms (even at 188 K), thus indicating that the ligand should be symmetrically coordinated to the metal centre.[3b] In addition: i) the $SiMe_2$ moiety yields two ^1H and two ^{13}C resonances, ii) non-equivalent methylene protons of both the CH_2NMe_2 and the $CH_2CH_2CH_2$ units are observed, and iii) the $SiNCH_2$ signal is broad and unresolved (Scheme 5), suggesting that the coordinated L^2 should approximately define a plane and the Cl and dimethylamido groups should occupy opposite coordination sites with respect to it (Scheme 5). This would make the two faces of the molecular plane nonequivalent. This is confirmed by the *negative* cross-peaks observed in the ^1H NOESY spectrum of **17** (298 K) between the resonances of the dimethylamido ligand ($\delta = 2.99$ ppm) and the H*b* ($\delta = 1.56$ ppm), H*c* ($\delta = 2.05$ ppm) and Me′ ($\delta = 0.28$ ppm) resonances, thus leading to the assignment given in Scheme 5.[6]



δ_H (298 K)	δ_C (298 K)
3.57 [H*a*, H*a*′]	48.1 [C*a*]
1.56 [H*b*], 1.40 [H*b*′]	30.3 [C*b*]
2.05 [H*c*], 2.82 [H*c*′]	64.0 [C*c*]
0.28 [Me′]	1.1 [Me′]
0.31 [Me″]	1.4 [Me″]

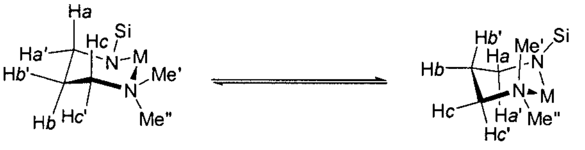
Scheme 5

Dynamics

Variable-temperature 1D/2D NMR spectra of selected compounds, namely LiL^2 (**6**), [$ZrCl_2(L^2)$] (**10**), [$Zr(NMe_2)_2(L^1)$] (**15**) and [$ZrCl(NMe_2)(L^2)$] (**17**) showed that dynamic processes occur in solution, i.e. the inversion of the six-membered [MN_2C_3] ring (**6**, **10**) and rotation of the amido ligand NMe_2 around the Zr−N bond (**15**, **17**).

Six-Membered [MN_2C_3] Ring Inversion

Despite the different nature of Li_2L^2 (**6**) and [$ZrCl_2(L^2)$] (**10**), the L^2 ligand exhibits similar dynamics in both compounds, i.e. the inversion of the six-membered [MN_2C_3] ring. As far as **10** is concerned, its ^1H NMR spectrum is strongly affected by the temperature: at 188 K each methylene resonance in the ^1H NMR spectrum splits into two signals (Scheme 6, cf. ESI) and the two NMe_2 methyls are nonequivalent. As both the solid-state and the proposed solution structure of **10** indicate the presence of a six-membered ZrN_2C_3 ring, we are dealing here with the slowing down of its inversion — on lowering the temperature the exchange between the equatorial and axial positions of the ring slows down, thus making both the geminal methylene protons and the NMe_2 groups nonequivalent (Scheme 6). The correlation peaks in the COSY spectrum at 188 K are indicative of both the geminal and the vicinal couplings of the methylene protons, and the observed pattern of the resonances in the 1D ^1H NMR spectrum (188 K) indicates that both the geminal and vicinal (axial-axial) couplings are responsible for the structure of the signals (as estimated from the spectrum, the geminal and the vicinal coupling constants are similar, i.e. about 12 Hz, cf. ESI). Likewise, the ^{13}C NMR spectrum at 188 K shows six signals (δ = 68.6, 56.9, 55.2, 49.0, 35.0, 5.6 ppm) and the ^1H-^{13}C HMQC spectrum indicates that the methylene carbons (δ = 68.6, 55.2 and 35.0 ppm) bear two nonequivalent protons (δ = 3.27, 1.52; 4.06, 3.18; 1.20, 1.10 ppm, respectively; cf. Scheme 6).



	δ_H (188 K)	
	M = Zr	M = Li
Ha, Ha'	4.06, 3.18	3.28 (broad)
Hb, Hb'	1.20, 1.10	1.36, 1.61
Hc, Hc'	3.27, 1.52	2.01, 2.30
Me', Me"	2.04, 2.68	1.99 (broad)

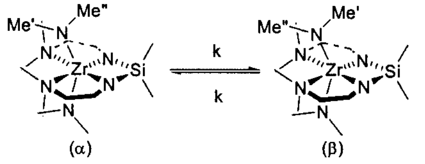
Scheme 6

A line-shape analysis[7] of the NMe_2 resonances has been carried out at different temperatures in order to obtain the kinetic constants of the ring inversion (cf. ESI) and the activation parameters [ΔH_{act} = (32.5 ± 0.7) kJ·mol^{-1}; ΔS_{act} = (−44 ± 3) J·mol^{-1}·K^{-1}]. The observed negative ΔS_{act} suggests that the ring inversion does not occur through a dissociative pathway, and that we are dealing with a cyclohexane-like ring inversion.

Despite the observation of one ^7Li peak and one ^{29}Si signal even at 188 K for **6**, the ^1H resonances of the $SiNCH_2$ and NCH_3 groups broaden and appear unresolved at 188 K; moreover, the ^1H resonances of both the CH_2NMe_2 and $CH_2CH_2CH_2$ groups split into two signals (Scheme 6), thus indicating that, independent of the coordination sphere around lithium, **6** should contain a six-membered LiN_2C_3 ring (Scheme 6), and that, as a consequence, the slowing down of ring inversion is responsible for the nonequivalence of the CH_2NMe_2 and $CH_2CH_2CH_2$ geminal protons and for the broadening of the $SiNCH_2$ and NCH_3 resonances (cf. Scheme 6 for assignment).

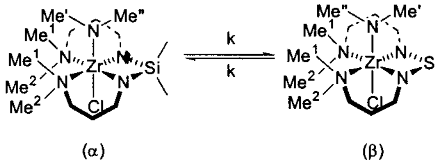
Zr−NMe_2 Rotation

The ^1H and ^{13}C NMR spectra of [$Zr(NMe_2)_2(L^1)$] (**15**) and [$ZrCl(NMe_2)(L^2)$] (**17**) at about 200 K show two resonances for the amido NMe_2 groups (Scheme 7), indicating that the two methyl groups experience different chemical environments at that temperature. As a matter of fact, the ^1H NOESY spectra of the compounds (**15**, 203 K; **17**, 193 K) show negative cross-peaks between the resonances of the $SiMe_2$ group and one of the amido NMe_2 methyl groups (**15**, δ = 3.03 ppm; **17**, δ = 2.94 ppm), and between the other amido NMe_2 methyl group (**15**, δ = 2.68 ppm; **17**, δ = 3.00 ppm) and the amino NMe_2 moiety, thus indicating that: i) one methyl group of the amido NMe_2 moiety points towards the $SiMe_2$ group, ii) the other one faces the coordinated NMe_2 unit (Scheme 7), similar to the solid-state structure of **15** (Figure 2), and iii) at these temperatures the rotation of the amido NMe_2 group is slow enough to prevent the exchange of the two methyl groups.



	δ_H (203 K)	δ_C (203 K)
Me' (α)	2.68	43.8
Me" (α)	3.03	44.5

(A)



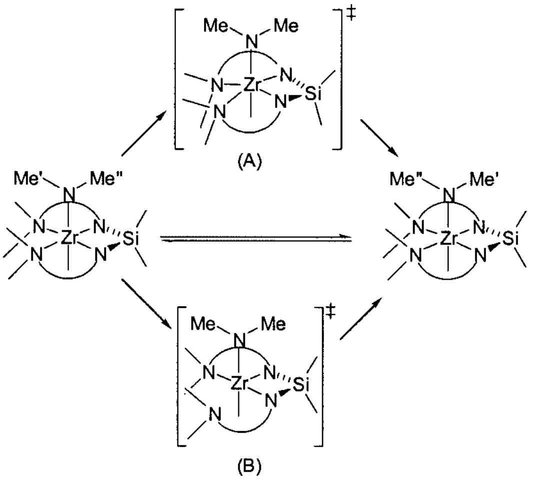
	δ_H (193 K)	δ_C (193 K)
Me' (α)	3.00	43.8
Me" (α)	2.94	46.0
Me^1	2.20	45.8
Me^2	2.15	45.6

(B)

Scheme 7

In order to further elucidate the dynamics, a line-shape analysis of the methyl resonances was undertaken, and the kinetic constants and the activation parameters were calculated [**15**, ΔH_{act} = (61.5 ± 0.8) kJ·mol^{-1}; ΔS_{act} = (55 ± 3) J·mol^{-1}·K^{-1}; **17**, ΔH_{act} = (27 ± 1) kJ·mol^{-1}; ΔS_{act} = (−73 ± 7) J·mol^{-1}·K^{-1}].

As far as the exchange between the two methyls of the amido NMe_2 group in **15** and **17** is concerned, two mechanisms could be proposed: i) a distortion of the [ZrL] framework, allowing free rotation of the amido NMe_2 group (A in Scheme 8), or ii) dissociation of one amino NMe_2 moiety, yielding a pentacoordinate derivative in which the rotation of the amido NMe_2 group should be no longer restricted (B in Scheme 8).

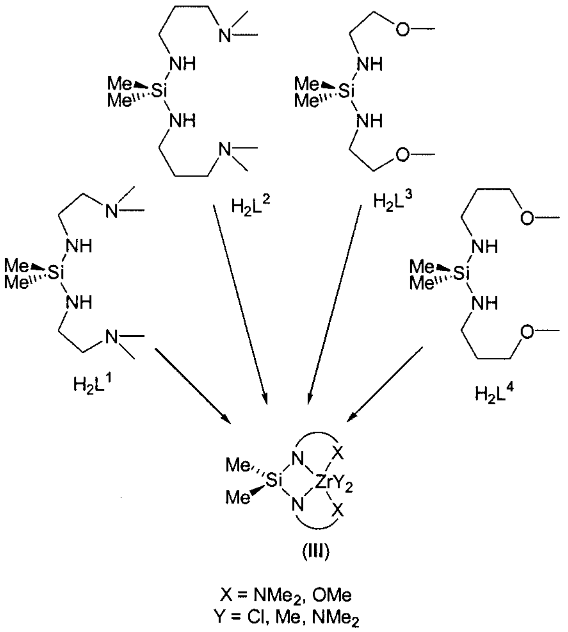


Scheme 8

Provided the activation entropy is negative for **17** and positive for **15** (vide supra), we propose that the exchange mechanisms are different for the two compounds and that the dissociative pathway (B in Scheme 8) is operative in **15**, while in **17** a distortion of the coordinated ligand should allow the exchange to occur (A in Scheme 8). In light of this, it is relevant that the activation enthalpy of **15** is about twice that of **17**, in agreement with the proposed dissociation of the Zr−N (amino) bond in **15** and the distortion in **17**. Moreover, L^2 is expected to be more flexible than L^1, due to the longer hydrocarbon chain between NMe_2 and SiN, and Cl is less sterically demanding than NMe_2, thus making the distortion of L in **17**, rather than in **15**, possible.[8]

Conclusions

The aminolysis of $SiMe_2Cl_2$ with the appropriate amine yields the functionalised diaminodimethylsilanes $SiMe_2[NH(CH_2)_nX]_2$ (H_2L, n = 2, 3; X = NMe_2, OMe, Scheme 9), which are able to coordinate to a ZrY_2 moiety, the zirconium derivatives of general formula $ZrY_2(L)$ (Scheme 9, **III**; Y = Cl, Me, NMe_2; L = L^1, L^2, L^3, L^4) being readily prepared according to the appropriate procedures.



Scheme 9

The solid-state structures of selected compounds, namely $[ZrCl_2(L)]$ (L = L^2, L^4) and $[Zr(NMe_2)_2(L^1)]$, show that L is tetradentate, coordinating to the metal centre through both the $Si(NR)_2$ and the neutral X moieties (X = OMe, NMe_2; Scheme 9). The coordination polyhedra are strongly affected by the nature of the diaminosilane ligand and by the zirconium ancillary ligands. To the best of our knowledge, $[ZrCl_2(L^2)]$ and $[Zr(NMe_2)_2(L^1)]$ are the first examples of hexacoordinate zirconium complexes containing a linear open-chain N_4 tetradentate ligand coordinated to the ZrY_2 moiety (Y = Cl, NMe_2).

1D/2D multinuclear NMR spectroscopic investigations on the compounds $[ZrY_2(L)]$ have shown that L is tetradentate and symmetrically coordinated to the metal centre, similar to the solid-state structures. In addition, variable-temperature 1D/2D multinuclear NMR measurements have allowed the dynamics of some selected compounds to be investigated, the kinetics of the six-membered $[MN_2C_3]$ ring inversion in $[Li_2L^2]$ and $[ZrCl_2(L^2)]$, and the rotation of the dimethylamido ligand around the Zr−N bond in $[Zr(NMe_2)(L^1)]$ and $[ZrCl(NMe_2)(L^2)]$ being elucidated.

Experimental Section

General: All operations were carried out in a glove-box under an atmosphere of 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 referenced to TMS; LiCl (1 M, D_2O) was used as reference for the ^{7}Li NMR spectra. Multiplicity is indicated as s (singlet), t (triplet), q (quadruplet), quint (quintuplet), m (multiplet). Variable-temperature NMR measurements were carried out on [D$_8$]toluene solutions.

Zirconium tetrachloride ($ZrCl_4$, Fluka) was washed with boiling toluene, then with pentane, dried in vacuo and stored under an atmosphere of dinitrogen. *N*,*N*-dimethylethylenediamine ($C_4H_{12}N_2$, Aldrich) was refluxed over BaO for one day, then distilled and stored under dinitrogen. *N*,*N*-dimethylpropanediamine ($C_5H_{14}N_2$, Aldrich), 3-methoxypropylamine ($C_4H_{11}NO$, Aldrich), 2-methoxyethylamine (C_3H_9NO, Aldrich), MeLi (Et_2O solution, 1.6 M, Aldrich) and dichlorodimethylsilane ($SiCl_2Me_2$, Aldrich) were used as received. $Zr(NMe_2)_4$ was prepared according to the published procedure.[9] $LiNMe_2$ was obtained as a colourless solid by bubbling $NHMe_2$ (Fluka) into an Et_2O solution of MeLi.

Synthesis of $SiMe_2[NH(CH_2)_nX_2]_2$ (H_2L; X = NMe_2, OMe; *n* = 2, 3): Only the synthesis of $SiMe_2(NHCH_2CH_2NMe_2)_2$ is reported in detail, the other reactions being carried out similarly. A pentane solution (50 mL) of $SiMe_2Cl_2$ (2.00 g, 15.5 mmol) was added dropwise to a pentane solution (50 mL) of $NH_2CH_2CH_2NMe_2$ (5.46 g, 61.9 mmol) and the prompt precipitation of a colourless solid was observed. After 12 h stirring, the suspension was filtered and the solid identified (vide infra) as $NH_2CH_2CH_2NMe_2\cdot HCl$ (3.77 g, 98% yield). The filtrate was evaporated to dryness and the residual liquid identified as $SiMe_2(NHCH_2CH_2NMe_2)_2$ (**1**, H_2L^1, colourless, 3.46 g, 96% yield). $C_{10}H_{28}N_4Si$ (232.44): calcd. C 51.7, H 12.1, N 24.1; found 52.0, H 12.0, N 24.0. ^{1}H NMR (C_6D_6, 298 K): δ = 0.17 (s, 3 H, $SiCH_3$), 1.22 (br., 1 H, NH), 2.18 (s, 6 H, NCH_3), 2.31 (t, $^3J_{H,H}$ = 6.1 Hz, 2 H, $C\mathit{H_2}NMe_2$), 2.94 (t, $^3J_{H,H}$ = 6.1 Hz, 2 H, $SiNCH_2$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = −1.20 ($SiCH_3$), 39.2 ($SiNCH_2$), 45.5 (NCH_3), 63.5 ($\mathit{C}H_2NMe_2$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −8.7 ppm.

$NH_2CH_2CH_2NMe_2\cdot HCl$: $C_4H_{13}ClN_2$ (124.61): calcd. C 38.6, H 10.5, Cl 28.5, N 22.5; found C 38.5, H 10.3, Cl 28.7, N 22.5. ^{1}H NMR ($CDCl_3$, 298 K): δ = 2.20 (s, 6 H, NCH_3), 2.52 (t, $^3J_{H,H}$ = 6 Hz, 2 H, CH_2), 2.96 (t, $^3J_{H,H}$ = 6 Hz, 2 H, CH_2), 7.2 (br., 3 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 298 K): δ = 37.7 (CH_2), 45.4 (CH_3), 57.1 (CH_2) ppm.

$SiMe_2(NHCH_2CH_2CH_2NMe_2)_2$ (2, H_2L^2): Colourless liquid (4.2 g, 92% yield). $C_{12}H_{32}N_4Si$ (260.50): calcd. C 55.3, H 12.4, N 21.5; found 55.0, H 12.5, N 21.3. ^{1}H NMR (C_6D_6, 298 K): δ = 0.10 (s, 3 H, $SiCH_3$), 0.63 (br., 1 H, NH), 1.52 (quint, $^3J_{H,H}$ = 6.2 Hz, 2 H, $CH_2C\mathit{H_2}CH_2$), 2.11 (s, 6 H, NCH_3), 2.23 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, $C\mathit{H_2}NMe_2$), 2.84 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, $SiNCH_2$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = −1.02 ($SiCH_3$), 33.0 ($CH_2\mathit{C}H_2CH_2$), 39.8 ($SiNCH_2$), 45.7 (NCH_3), 57.9 ($\mathit{C}H_2NMe_2$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −9.3 ppm.

$NH_2CH_2CH_2CH_2NMe_2\cdot HCl$: $C_5H_{15}ClN_2$ (138.64): calcd. C 43.3, H 10.9, Cl 25.6, N 20.2; found C 42.9, H 11.0, Cl 21.0, N 20.5. ^{1}H NMR ($CDCl_3$, 298 K): δ = 1.81 (quint, $^3J_{H,H}$ = 6.0 Hz, 2 H, CH_2), 2.27 (s, 6 H, NCH_3), 2.52 (t, $^3J_{H,H}$ = 6.0 Hz, 2 H, NCH_2), 3.09 (t, 2 H, NCH_2, $^3J_{H,H}$ = 6.0 Hz), 6.1 (br., 3 H, NH) ppm.

$SiMe_2(NHCH_2CH_2OMe)_2$ (3, H_2L^3): Colourless liquid (2.5 g 90% yield). $C_8H_{22}N_2O_2Si$ (206.36): calcd. C 46.6, H 10.7, N 13.6; found 46.5, H 10.5, N 13.8. ^{1}H NMR (C_6D_6, 298 K): δ = 1.10 (br., 1 H, NH), 1.28 (s, 3 H, $SiCH_3$), 2.88 (q, $^3J_{H,H}$ = 5.40 Hz, 2 H, NCH_2), 3.14 (s, 3 H, OCH_3), 3.18 (t, $^3J_{H,H}$ = 5.4 Hz, 2 H, OCH_2) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = −1.24 ($SiCH_3$), 41.1 (NCH_2), 58.4 (OCH_3), 76.1 (OCH_2) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −8.0 ppm.

$NH_2CH_2CH_2OMe\cdot HCl$: $C_3H_{10}ClNO$ (111.57): calcd. C 32.3, H 9.0, Cl 31.8, N 12.6; found C 32.2, H 9.2, Cl 31.7, N 12.4. ^{1}H NMR ($CDCl_3$, 298 K): δ = 3.16 (t, 2 H, OCH_2, $^3J_{H,H}$ = 5.1 Hz), 3.29 (s, 3 H, OCH_3), 3.62 (t, $^3J_{H,H}$ = 5.1 Hz, 2 H, NCH_2), 8.02 (br., 3 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 298 K): δ = 39.3 (OCH_2), 58.8 (OCH_3). 68.0 (NCH_2) ppm.

$SiMe_2(NHCH_2CH_2CH_2OMe)_2$ (4, H_2L^4): Colourless liquid (3.7 g, 94% yield). $C_{10}H_{26}N_2O_2Si$ (234.41): calcd. C 51.2, H 11.2, N 12.0; found 51.5, H 11.0, N 11.9. ^{1}H NMR (C_6D_6, 298 K): δ = −0.04 (s, 3 H, $SiCH_3$), 0.56 (br., 1 H, NH), 1.54 (m, 2 H, CH_2), 2.76 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, NCH_2), 3.11 (s, 3 H, OCH_3), 3.24 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, OCH_2) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = −1.23 ($SiCH_3$), 34.1 (CH_2), 38.6 (NCH_2), 58.3 (OCH_3), 70.7 (OCH_2) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −8.9 ppm.

$NH_2CH_2CH_2CH_2OMe\cdot HCl$: $C_4H_{12}ClNO$ (125.60): calcd. C 38.3, H 9.6, Cl 28.2, N 11.2; found C 38.4, H 10.0, Cl 28.0, N 11.0. ^{1}H NMR ($CDCl_3$, 298 K): δ = 2.02 (m, 2 H, CH_2), 3.15 (t, 2 H, NCH_2, $^3J_{H,H}$ = 6.5 Hz), 3.30 (s, 3 H, OCH_3), 3.52 (t, 2 H, OCH_2, 5.7 Hz), 8.2 (br., 3 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 298 K): δ = 38.4 (CH_2), 58.8 (NCH_2), 61.6 (OCH_3), 70.3 (OCH_2) ppm.

Synthesis of $Li_2\{SiMe_2[N(CH_2)_nX]_2\}$ (Li_2L, X = NMe_2, OMe; *n* = 2, 3): Only the synthesis of $Li_2[SiMe_2(NCH_2CH_2NMe_2)_2]$ is reported in detail, the other reactions being similar. A solution of $SiMe_2(NHCH_2CH_2NMe_2)_2$ (1.50 g, 6.45 mmol) in Et_2O (25 mL) was treated with MeLi (1.6 M, in Et_2O, 8.1 mL, 13.0 mmol) at room temperature. Prompt gas evolution was observed and after 2 h stirring the solution was evaporated to dryness yielding a colourless solid identified as $Li_2[SiMe_2(NCH_2CH_2NMe_2)_2]$ (**5**, Li_2L^1, 1.45 g, 92% yield). $C_{10}H_{26}Li_2N_4Si$ (244.31): calcd. C 49.2, H 10.7, N 22.9; found C 49.0, H 11.0, N 23.0. ^{1}H NMR (C_6D_6, 298 K): δ = 0.33 (s, 3 H, $SiCH_3$), 2.06 (s, 6 H, NCH_3), 2.29 (t, $^3J_{H,H}$ = 5.4 Hz, 2 H, $C\mathit{H_2}NMe_2$), 3.32 (t, $^3J_{H,H}$ = 5.4, 2 H, $SiNCH_2$) ppm. ^{7}Li NMR (C_6D_6, 298 K): δ = 9.9 ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 0.57 ($SiCH_3$), 44.4 ($SiNCH_2$), 44.8 (NCH_3), 68.3 ($\mathit{C}H_2NMe_2$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −9.5 ppm.

$Li_2[SiMe_2(NCH_2CH_2CH_2NMe_2)_2]$ (6, Li_2L^2): Colourless solid (1.2 g, 95% yield). $C_{12}H_{30}Li_2N_4Si$ (272.36): calcd. C 52.9, H 11.1, N 20.6; found C 53.0, H 11.0, N 20.8. ^{1}H NMR (C_6D_6, 298 K): δ = 0.27 (s, 3 H, $SiC\mathit{H_3}$), 1.51 (m, 2 H, $CH_2C\mathit{H_2}CH_2$), 2.06 (s, 6 H, NCH_3), 2.24 (m, 2 H, $C\mathit{H_2}NMe_2$), 3.37 (m, 2 H, $SiNCH_2$) ppm. ^{7}Li NMR (C_6D_6, 298 K): δ = 10.5 ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 1.76 ($SiCH_3$), 34.7 ($CH_2\mathit{C}H_2CH_2$), 45.7 (NCH_3), 50.7 ($SiNCH_2$), 63.7 ($\mathit{C}H_2NMe_2$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −11.6 ppm.

$Li_2[SiMe_2(NCH_2CH_2OMe)_2]$ (7, Li_2L^3): Colourless solid (1.7 g, 90% yield). $C_8H_{20}Li_2N_2O_2Si$ (218.22): calcd. C 44.0, H 9.2, N 12.8; found C 44.2, H 9.1, N 12.7. ^{1}H NMR (C_6D_6, 298 K): δ = 0.28 (s, 3 H, $SiCH_3$), 3.15 (s, 3 H, OCH_3), 3.37 (t, $^3J_{H,H}$ = 4.5 Hz, 2 H, NCH_2), 3.44 (t, $^3J_{H,H}$ = 4.5 Hz, 2 H, OCH_2) ppm. ^{7}Li NMR (C_6D_6, 298 K): δ = 9.6 ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 2.19 ($SiCH_3$), 47.6 (NCH_2), 58.5 (OCH_3), 80.5 (OCH_2) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −11.1 ppm.

$Li_2[SiMe_2(NCH_2CH_2CH_2OMe)_2]$ (8, Li_2L^4): Colourless solid (1.0 g, 93% yield). $C_{10}H_{24}Li_2N_2O_2Si$ (246.28): calcd. C 48.8, H 9.8, N 11.4; found C 48.9, H 9.7, N 11.3. ^{1}H NMR (C_6D_6, 298 K): δ = 0.29 (s, 3 H, $SiCH_3$), 1.68 (m, 2 H, CH_2), 3.12 (s, 3 H, OCH_3), 3.27 (t, $^3J_{H,H}$ = 4.8 Hz, 2 H, NCH_2), 3.46 (m, 2 H, OCH_2) ppm. ^{7}Li NMR (C_6D_6, 298 K): δ = 10.2 ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 1.01 ($SiCH_3$), 39.0 (CH_2), 48.9 (NCH_2), 59.6 (OCH_3), 77.4 (OCH_2) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −11.0 ppm.

Synthesis of $[ZrCl_2\{SiMe[N(CH_2)_nX]\}]$ $[ZrCl_2(L)$; X = NMe_2, OMe; *n* = 2, 3]: Only the synthesis of $[ZrCl_2(L^1)]$ is reported in detail, the other ones being similar. A solution of Li_2L^1 (800 mg, 3.27 mmol) in Et_2O (30 mL) was cooled to 243 K and then $ZrCl_4$ (762 mg, 3.27 mmol) was added. After 3 h stirring at 243 K, the suspension was allowed to warm up to room temperature and then filtered (260 mg of colourless solid). The filtrate was evaporated to dryness and $[ZrCl_2\{SiMe_2(NCH_2CH_2NMe_2)_2\}]$ (**9**, 770 mg g, 60% yield) was obtained as a colourless solid after recrystallisation from pentane at 249 K. $C_{10}H_{26}Cl_2N_4SiZr$ (392.56): calcd. C 30.6, H 6.7, Cl 18.1, N 14.3; found C 31.0, H 6.5, Cl 18.0, N 14.0. ^1H NMR (C_6D_6, 298 K): δ = 0.23 (s, 3 H, $SiCH_3$), 2.35 (s, 6 H, NCH_3), 2.81 (t, $^3J_{H,H}$ = 5.4 Hz, 2 H, $C\mathit{H}_2NMe_2$), 3.37 (t, $^3J_{H,H}$ = 5.4 Hz, 2 H, $SiNCH_2$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 0.11 ($SiCH_3$), 46.3 (NCH_3), 46.8 ($SiNCH_2$), 63.9 ($\mathit{C}H_2NMe_2$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −23.3 ppm.

$[ZrCl_2\{SiMe_2(NCH_2CH_2CH_2NMe_2)_2\}]$ [10, $ZrCl_2(L^2)$]: Colourless solid, recrystallised from pentane at 249 K (560 mg, 70% yield). $C_{12}H_{30}Cl_2N_4SiZr$ (420.61): calcd. C 34.3, H 7.2, Cl 16.9, N 13.3; found C 34.0, H 7.0, Cl 17.0, N 13.5. ^1H NMR (C_6D_6, 298 K): δ = 0.17 (s, 3 H, $SiCH_3$), 1.34 (m, 2 H, $CH_2C\mathit{H}_2CH_2$), 2.41 (s, 6 H, NCH_3), 2.59 (m, 2 H, $C\mathit{H}_2NMe_2$), 3.62 (m, 2 H, $SiNCH_2$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 0.33 ($SiCH_3$), 29.9 ($CH_2\mathit{C}H_2CH_2$), 48.2 (NCH_3), 49.6 ($SiNCH_2$), 63.8 ($\mathit{C}H_2NMe_2$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −28.8 ppm.

$[ZrCl_2\{SiMe_2(NCH_2CH_2OMe)_2\}]$ [11, $ZrCl_2(L^3)$]: Colourless solid, recrystallised from pentane at 249 K (612 mg, 70% yield). $C_8H_{20}Cl_2N_2O_2SiZr$ (366.47): calcd. C 26.2, H 5.5, Cl 19.3, N 7.6; found C 26.0, H 5.5, Cl 19.5, N 7.6. ^1H NMR (C_6D_6, 298 K): δ = 0.41 (s, 3 H, $SiCH_3$), 3.48 (t, $^3J_{H,H}$ = 5.7 Hz, 2 H, NCH_2), 3.56 (s, 3 H, OCH_3), 3.58 (t, $^3J_{H,H}$ = 5.7 Hz, 2 H, OCH_2) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 1.24 ($SiCH_3$), 47.2 (OCH_3), 61.1 (NCH_2), 78.4 (OCH_2) ppm.

$[ZrCl_2\{SiMe_2(NCH_2CH_2CH_2OMe)_2\}]$ [12, $ZrCl_2(L^4)$]: Colourless solid, recrystallised from pentane at 249 K, 850 mg, 70% yield]. $C_{10}H_{24}Cl_2N_2O_2SiZr$ (394.52): calcd. C 30.4, H 6.1, Cl 18.0, N 7.1; found C 30.3, H 6.2, Cl 17.9, N 7.0. ^1H NMR (C_6D_6, 298 K): δ = 0.44 ($SiCH_3$), 1.77 (m, 2 H, CH_2), 3.23 (s, 3 H, OCH_3), 3.24 (t, $^3J_{H,H}$ = 5.6 Hz, 2 H, NCH_2), 3.55 (m, 2 H, OCH_2) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = −1.02 ($SiCH_3$), 32.7 (CH_2), 48.1 (NCH_2), 60.5 (OCH_3), 76.9 (OCH_2) ppm.

Synthesis of $ZrMe_2\{SiMe_2[N(CH_2)_nNMe_2]_2\}$ [$ZrMe_2(L^1)$, *n* = 2; $ZrMe_2(L^2)$, *n* = 3] From $ZrMe_4$ and H_2L (L = L^1, L^2): Only the procedure yielding $[ZrMe_2(L^1)]$ is reported in detail, the other reaction being similar. A solution of MeLi in Et_2O (1.6 M, 12.9 mL, 20.6 mmol) was added to 20 mL of Et_2O, cooled to 243 K and treated with $ZrCl_4$ (1.20 g, 5.15 mmol). After 1 h stirring at 243 K, H_2L^1 (1.20 g, 5.16 mmol) was added dropwise. After a further 2 h stirring at 243 K, the suspension was allowed to warm to room temperature and then filtered (820 mg of a colourless solid). The solution was evaporated to dryness yielding a pale-orange sticky material identified as $[ZrMe_2\{SiMe_2(NCH_2CH_2NMe_2)_2\}]$ (**13**, 1.72 g, 95% yield). $C_{12}H_{32}N_4SiZr$ (351.72): calcd. C 41.0, H 9.2, N 15.9; found C 41.2, H 9.0, N 16.0. ^1H NMR (C_6D_6, 298 K): δ = −0.12 (s, 3 H, $ZrCH_3$), 0.40 (s, 3 H, $SiCH_3$), 2.23 (s, 6 H, NCH_3), 2.61 (t, $^3J_{H,H}$ = 5.5 Hz, 2 H, $C\mathit{H}_2NMe_2$), 3.54 (t, $^3J_{H,H}$ = 5.5 Hz, 2 H, $SiNCH_2$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 1.55 ($SiCH_3$), 33.2 ($ZrCH_3$), 46.3 (NCH_3), 46.4 ($SiNCH_2$), 65.3 ($\mathit{C}H_2NMe_2$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −22.4 ppm.

$[ZrMe_2\{SiMe_2(NCH_2CH_2CH_2NMe_2)_2\}]$ [14, $ZrMe_2(L^2)$]: Pale-yellow solid (950 mg, 90% yield). $C_{14}H_{36}N_4SiZr$ (379.77): calcd. C 44.3, H 9.6, N 14.8; found C 44.2, H 9.8, N 14.8. ^1H NMR (C_6D_6, 298 K): δ = −0.07 (s, 3 H, $ZrCH_3$), 0.41 (s, 3 H, $SiCH_3$), 1.62 (q, $^3J_{H,H}$ = 6.4 Hz, 2 H, $CH_2C\mathit{H}_2CH_2$), 2.01 (s, 6 H, NCH_3), 2.27 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, $C\mathit{H}_2NMe_2$), 3.58 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, $SiNCH_2$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 59.3 ($\mathit{C}H_2NMe_2$), 47.3 ($SiNCH_2$), 45.7 (NCH_3), 34.0 ($CH_2\mathit{C}H_2CH_2$), 15.4 ($ZrCH_3$), 2.87 ($SiCH_3$) ppm.

From $[ZrCl_2(L^1)]$ and MeLi: A solution of $[ZrCl_2(L^1)]$ (212 mg, 0.54 mmol) in Et_2O was cooled to 243 K and treated with a solution of MeLi in Et_2O (1.6 M, 0.68 mL, 1.09 mmol), yielding a pale-yellow solution, which was allowed to slowly warm up to room temperature (about 30 min). The precipitation of a colourless solid was observed and the suspension was stirred at room temperature for 1 h. The solid was filtered off (42 mg) and the solvents were evaporated from the pale-yellow filtrate, yielding a pale-orange sticky material analytically and spectroscopically identified as $[ZrMe_2(L^1)]$ (175 mg, 350 mg, 92% yield).

Synthesis of $[Zr(NMe_2)_2\{SiMe_2(NCH_2CH_2NMe_2)_2\}]$: A toluene solution (25 mL) of $Zr(NMe_2)_4$ (452 mg, 1.69 mmol) was treated with H_2L^1 (395 mg, 1.70 mmol). After 2 h stirring, the solution was evaporated to dryness and the colourless residue identified as $Zr(NMe_2)_2[SiMe_2(NCH_2CH_2NMe_2)_2]$ [**15**, $Zr(NMe_2)_2(L^1)$, 630 mg, 91% yield]. $C_{14}H_{38}N_6SiZr$ (409.80): calcd. C 41.0, H 9.3, N 20.5; found C 41.2, H 9.5, N 20.3. ^1H NMR (C_6D_6, 298 K): δ = 0.35 (s, 3 H, $SiCH_3$), 2.04 (s, 6 H, $CH_2NC\mathit{H}_3$), 2.39 (t, $^3J_{H,H}$ = 5.7 Hz, 2 H, $C\mathit{H}_2NMe_2$), 2.81 (s, 6 H, $ZrNCH_3$), 3.51 (t, $^3J_{H,H}$ = 5.7 Hz, 2 H, $SiNCH_2$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 1.09 ($SiCH_3$), 44.2 ($ZrNCH_3$), 46.0 ($SiNCH_2$), 46.1 ($CH_2N\mathit{C}H_3$), 64.3 ($\mathit{C}H_2NMe_2$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −20.3.

Synthesis of $[ZrCl_{2-x}(NMe_2)_x\{SiMe_2(NCH_2CH_2CH_2NMe_2)_2\}]$ (*x* = 1, 2). Only the procedure yielding $[Zr(NMe_2)_2(L^2)]$ is described, the other one being similar. A solution of $[ZrCl_2(L^2)]$ (324 mg, 0.77 mmol) in Et_2O (25 mL) was treated with $LiNMe_2$ (79 mg, 1.55 mmol) and the prompt precipitation of a colourless solid was observed. After 30 min stirring, the suspension was filtered and the filtrate evaporated in vacuo to dryness yielding a colourless solid identified as $[Zr(NMe_2)_2\{SiMe_2(NCH_2CH_2CH_2NMe_2)_2\}]$ (**16**, 296 mg, 88% yield). $C_{16}H_{42}N_6SiZr$ (437.86): calcd. C 43.9, H 9.7, N 19.2; found C 44.0, H 10.0, N 19.0. ^1H NMR (C_6D_6, 298 K): δ = 0.46 (s, 3 H, $SiCH_3$), 1.69 (quint, $^3J_{H,H}$ = 6.4 Hz, 2 H, $CH_2C\mathit{H}_2CH_2$), 2.05 (s, 6 H, $CH_2NC\mathit{H}_3$), 2.32 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, $C\mathit{H}_2NMe_2$), 2.95 (s, 6 H, $ZrNCH_3$), 3.51 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, $SiNCH_2$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 1.06 ($SiCH_3$), 32.7 (CH_2), 42.4 ($ZrNCH_3$), 46.8 ($CH_2N\mathit{C}H_3$), 47.8 ($SiNCH_2$), 61.0 ($\mathit{C}H_2NMe_2$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −24.7 ppm.

$[ZrCl(NMe_2)\{SiMe_2(NCH_2CH_2CH_2NMe_2)_2\}]$ [17, $ZrCl(NMe_2)(L^2)$]: Colourless solid (512 mg, 85% yield). $C_{14}H_{36}ClN_5SiZr$ (429.23): calcd. C 39.2, H 8.5, Cl 8.3, N 16.3; found C 39.0, H 8.4, Cl 8.0, N, 16.2. ^1H NMR (C_6D_6, 298 K): δ = 0.28 (s, 3 H, $SiCH_3$), 0.31 (s, 3 H, $SiCH_3$), 1.40 (br., 2 H, $CH_2C\mathit{H}_2CH_2$), 1.56 (br., 2 H, $CH_2C\mathit{H}_2CH_2$), 2.05 (m, 2 H, $C\mathit{H}_2NMe_2$), 2.28 (s, 12 H, $CH_2NC\mathit{H}_3$), 2.82 (m, 2 H, $C\mathit{H}_2NMe_2$), 2.99 (s, 6 H, $ZrNCH_3$), 3.57 (br., 4 H, $SiNCH_2$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 1.1 ($SiCH_3$), 1.4 ($SiCH_3$), 30.3 (CH_2), 45.1 ($ZrNCH_3$), 48.1 ($SiNCH_2$), 48.2 ($CH_2N\mathit{C}H_3$), 64.0 ($\mathit{C}H_2NMe_2$) ppm. ^{29}Si NMR (C_6D_6, 298 K): δ = −22.1 ppm.

Crystal Structure determination of $[ZrCl_2(L^2)]$ (10), $[ZrCl_2(L^4)]$ (12) and $[Zr(NMe_2)_2(L^1)]$ (15): Crystals of **10**, **12** and **15** were grown by slowly evaporating pentane (**10**, **15**) or Et_2O (**12**) from solutions of the compounds. The crystals were placed in Lindemann glass

Table 4. Crystallographic data for [$ZrCl_2(L^2)$] (**10**), [$ZrCl_2(L^4)$] (**12**) and [$Zr(NMe_2)_2(L^1)$] (**15**)

Compound	**10**	**12**	**15**
Chemical formula	$C_{12}H_{30}N_4Cl_2SiZr$	$C_{10}H_{24}N_2O_2Cl_2SiZr$	$C_{14}H_{38}N_6SiZr$
Molecular weight	420.61	394.52	409.80
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	*Cmca*	$P2_1/n$
a (Å)	10.349(2)	11.393(3)	16.121(3)
b (Å)	15.037(3)	17.033(3)	9.128(2)
c (Å)	13.110(3)	18.209(3)	16.308(3)
β (°)	106.41(4)		111.57(3)
V (Å^3)	1957.0(7)	3534(1)	2231.7(9)
Z	4	8	4
$D_{calcd.}$ (g cm^{-3})	1.428	1.483	1.220
$F(000)$	872	1616	872
μ(Mo-K_α) (mm^{-1})	0.893	0.989	0.553
Reflections collected	4500	2920	4848
Reflections observed [$I \geq 2\sigma(I)$]	4434	1825	4333
Final $R1$, $wR2$[a]	0.035; 0.089	0.059; 0.155	0.086; 0.180

[a] $R1 = \|F_o\| - \|F_c\|/\|F_o\|$; $wR2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$.

capillaries and centred on a four-circle Philips PW1100 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), at room temperature, following standard procedures. The diffraction data were corrected for Lorentz polarisation effects and for absorption, as described by North et al.[10]

The structures were solved by standard direct methods[11] and subsequently completed by Fourier syntheses. Non-hydrogen atoms were refined anisotropically in all the structures. The hydrogen atoms were introduced at the calculated positions with fixed isotropic thermal parameters (1.2 U_{equiv} of the parent carbon atom), except for the hydrogens of the CH_2 moiety of $ZrCl_2(L^2)$ (**10**), which were located from Fourier maps and refined isotropically. The C(2) carbon of **12** is disordered in two positions with an occupation factor of 0.5. Figure 1B shows only one of the two positions of C(2).

Structure refinement and final geometrical calculations were carried out with the SHELXL-97[12] program, implemented with the WinGX package.[13] Drawings were produced by using the ORTEP II program.[14] Crystallographic data are listed in Table 4. CCDC-207384 (**10**), -220157 (**12**) and -207385 (**15**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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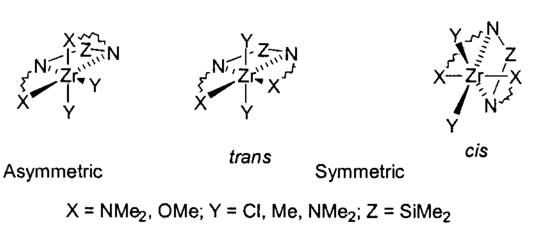

X = NMe_2, OMe; Y = Cl, Me, NMe_2; Z = $SiMe_2$

[4] As examples, Zr−N is 2.43 Å in [$ZrCl_4$(TMEDA)] (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) [cf. C. E. F. Rickard, M. W. Glenny, A. J. Nielson, *Acta Crystallogr., Sect. E (Struct. Rep. Online)*, **2003**, *59*, m183] and Zr−O(DME) is 2.33 Å in [$ZrCl_2(OSiPh_3)_2$(DME)] (DME = 1,2-dimethoxyethane) [cf. E. A. Babian, D. C. Hrnicr, S. G. Bott, J. L. Atwood, *Inorg. Chem.* **1986**, *25*, 4818].

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[8] In principle, also electronic factors should be taken into account, specifically the Zr−NMe_2 π-bonding. Nevertheless, due to the similar nature of **15** and **17**, this contribution is expected to be similar in the two complexes, thus making the abovementioned steric factors decisive in influencing the exchange mechanism.

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