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Synthesis and characterisation of novel zirconium(IV) derivatives containing the bis-amido ligand $SiMe_2(NRR')_2$

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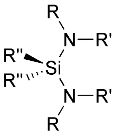
The silicon compounds $SiMe_2(NRR')_2$ [NRR′ = NMe_2 (**1**), NEt_2 (**2**), NC_4H_8 (**3**), NHEt (**4**), NH^{i}Pr (**5**), NH^{t}Bu (**6**), NMeBu (**7**)] have been synthesised *via* aminolysis of the dichloro species $SiMe_2Cl_2$ and their ligating ability has been investigated towards zirconium(IV). The dimer zirconium compound $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$ (**8**) has been synthesised by reacting $ZrCl_4$ with the lithium salt $Li_2[(N^iPr)_2SiMe_2]$ and its molecular structure has been determined in the solid state by X-ray diffraction analysis. The reaction of $ZrCl_4$ with $SiMe_2(NRR')_2$ yields the Lewis adducts $ZrCl_4[(NRR')_2SiMe_2]$ [NRR′ = NMe_2 (**10**), NC_4H_8 (**11**), NHEt (**12**), NH^{i}Pr (**13**), NH^{t}Bu (**14**), NMeBu (**15**)]. On the other hand, the mixed amido derivative $Zr(NMe_2)_3(NHMe)[(N^tBu)SiMe_2(NH^tBu)]$ (**9**) has been obtained from the reaction of $Zr(NMe_2)_4$ with $SiMe_2(NH^tBu)_2$. The solution molecular structure and dynamics of the zirconium derivatives have been elucidated by 1D and 2D multinuclear NMR spectroscopy.

Introduction

Amido or amino zirconium derivatives have been synthesised[1] and used in the deposition of zirconium nitride *via* CVD[2] or ceramic processes,[3] showing that the nature of the amino or amido ligands affects the composition and consequently the properties of the final materials. In this connection, the synthesis of novel volatile amido or amino zirconium derivatives is an attractive field. Moreover, a survey of the literature has shown that a few data are available concerning the ligating ability[4] of bis-amido–dialkylsilanes (**I**) towards zirconium(IV).



(**I**)

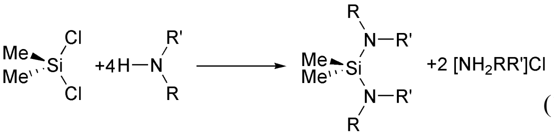
As a matter of fact, the spirocyclic species $Zr[(N^tBu)_2SiMe_2]_2$ has been synthesised from $SiMe_2(NH^tBu)_2$ and eventually structurally characterised,[5] and some data have appeared relating to the adduct $ZrCl_4[(NMe_2)_2SiMe_2]$.[6,7] In addition, recently Gibson *et al.*[8] have synthesised and structurally characterised the pentacoordinated zirconium derivative $Zr(NMe_2)_2(NHMe_2)[(NPh)_2SiMe_2)]$ (Ph = 2,6-$Me_2C_6H_3$).

In this connection, we report on the synthesis of novel bis-amido–dialkylsilanes and on the investigation of their ligating ability towards zirconium(IV).

Results and discussion

Synthesis of $SiMe_2(NRR')_2$

The silicon derivatives $SiMe_2(NRR')_2$ [NRR′ = NMe_2 (**1**), NEt_2 (**2**), NC_4H_8 (**3**), NMeBu (**4**), NHEt (**5**), NH^{i}Pr (**6**), NH^{t}Bu (**7**)] have been synthesised by aminolysis of $SiMe_2Cl_2$ with the appropriate amine (eqn. (1)), the chlorides being eliminated as the ammonium salt $[NH_2RR']Cl$.



(1)

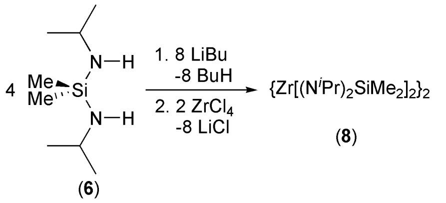
NRR' = NMe_2 (**1**), NEt_2 (**2**), NC_4H_8 (**3**),
NMeBu (**4**), NHEt (**5**), NH^{i}Pr (**6**), NH^{t}Bu (**7**)

The ^1H and ^{13}C NMR spectra of the compounds show the resonances of the $[SiMe_2]$ moiety and of the amido groups (Table 1).

As far as the isopropyl derivative **6** is concerned, additional comments are in order. Besides the ordinary coupling of the methyne proton with the methyl ones ($^3J_{HH}$ = 6.4 Hz), vicinal coupling with NH ($^3J_{HH}$ = 10.0 Hz) is also observed, the methyne resonance appearing as a double septet at 3.08 ppm. As a confirmation, the proton COSY spectrum shows a cross-peak between the resonance at 0.42 (NH) and 3.08 ppm (CH). Nevertheless, the ^1H NMR spectrum shows the NH resonance as a broad line reasonably due to the quadrupolar effect of the ^{14}N nucleus. A similar phenomenon has already been observed for Si(NH^{i}Pr)$_4$.[9]

Synthesis and characterisation of $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$

The reaction of $ZrCl_4$ with the lithium salt $Li_2[(N^iPr)_2SiMe_2]$ [obtained from the reaction of LiBu with $SiMe_2(NH^iPr)_2$] (eqn. (2)) yields the dimer zirconium derivative $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$ (**8**), obtained as a microcrystalline pure material after crystallisation from toluene–pentane at 243 K (58% yield).



(2)

The crystal structure of **8** shows that the compound is a dimer, containing a $[Zr_2N_2]$ core, formed by the coupling of two $Zr[(N^iPr)_2SiMe_2]_2$ units (Fig. 1(A)). The bridging ligands are asymmetrically coordinated to the zirconium centres, each containing one μ_2 nitrogen atom [N(2), N(3)] and an η^1 one [N(1), N(4)]. The coordination polyhedron of each zirconium centre is a distorted trigonal bipyramid (Fig. 1(B)), with N(3), N(4), N(8) and N(1), N(2), N(6) in the equatorial planes, and N(2), N(7) and N(3), N(5) in the apical positions, respectively. Selected bond distances and angles are reported in Table 2. Due to the different coordination modes of the $SiMe_2(N^iPr)_2$ ligands, different Zr–N bond distances are observed (Table 2). Moreover, also the N–Zr–N and N–Si–N angles vary as a function of the hapticity of the ligand: N(5)–Zr(1)–N(6), N(7)–Zr(2)–N(8), 76.5° av.; N(1)–Zr(1)–N(3), N(2)–Zr(2)–N(4), 69.1°, av.; N(5)–Si(3)–N(6), N(7)–Si(4)–N(8), 94.2°, av.; N(1)–Si(1)–N(3), N(2)–Si(2)–N(4), 98°, av. (Table 2).

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Table 1 Selected ^{1}H and ^{13}C NMR data for $SiMe_2(NRR')_2$

	δ_H		δ_C		
Compound	$SiCH_3$	R	$SiCH_3$	R	Ref.
$SiMe_2(NMe_2)_2$ (**1**)	−0.08	2.44 (CH_3)	−3.4	37.6 (CH_3)	7,[a]
$SiMe_2(NEt_2)_2$ (**2**)	0.14	2.82 (CH_2), 0.99 (CH_3)	−0.9	39.6 (CH_2), 15.8 (CH_3)	[a]
$SiMe_2(NC_4H_8)_2$ (**3**)	0.18	2.97 (NCH_2), 1.61 (NCH_2CH_2)	−2.9	46.9 (NCH_2), 27.2 (NCH_2CH_2)	[a]
$SiMe_2(NMeBu)_2$ (**4**)	0.12	2.73 (NCH_2), 2.45 (NCH_3), 1.43 (NCH_2CH_2), 1.26 (CH_2CH_3), 0.92 (CH_2CH_3)	−2.20	50.1 (NCH_2), 34.2 (NCH_2CH_2), 31.8 (NCH_3), 20.6 (CH_2CH_3), 14.4 (CH_2CH_3)	[a]
$SiMe_2(NHEt)_2$ (**5**)	0.01	2.77 (CH_2), 1.05 (CH_3), 0.42 (NH)	−1.33	36.0 (CH_2), 20.5 (CH_3)	[a]
$SiMe_2(NH^iPr)_2$ (**6**)	−0.01	3.08 (CH), 1.03 (CH_3), 0.42 (NH)	−0.38	42.3 (CH), 27.9 (CH_3)	[a]
$SiMe_2(NH^tBu)_2$ (**7**)	0.18	1.19 (CH_3), 0.52 (NH)	3.7	49.2 (C), 33.8 (CH_3)	5,[a]

[a] This work.

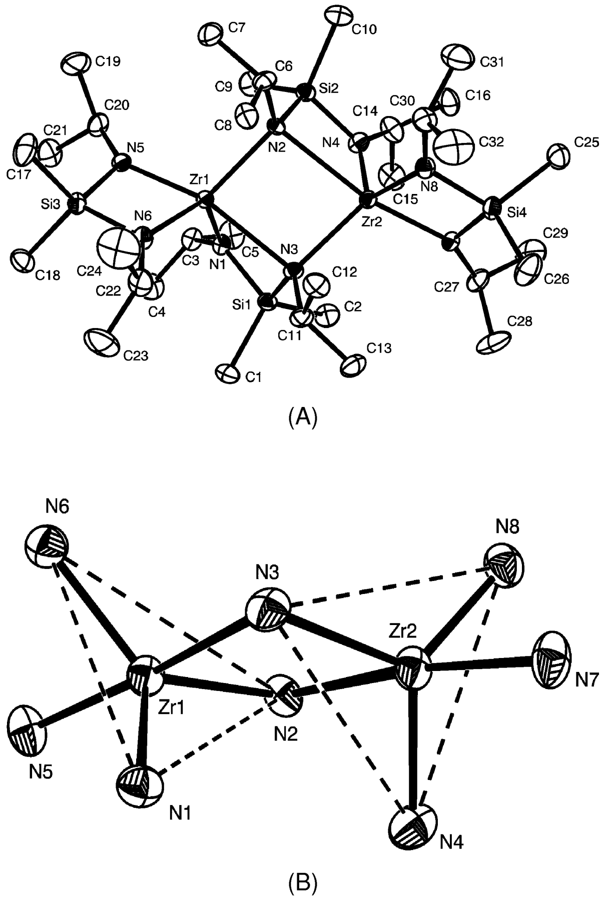

Fig. 1 (A) ORTEP view of the $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$ molecule (with the numbering scheme adopted). (B) Coordination polyhedrons of the zirconium centres in $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$ (**8**).

Interestingly, the titanium derivative $Ti[(N^iPr)_2SiMe_2]_2$ is a monomer[10] according to IR and multinuclear NMR spectroscopy, while for the *tert*-butyl derivative $Zr[(N^tBu)_2SiMe_2]_2$ a monomeric structure has been reported[5] (X-ray investigation), containing two $SiMe_2(N^tBu)_2$ groups, chelating the zirconium centre *via* monodentate nitrogens (defining a pseudo-tetrahedral coordination polyhedron).

In our opinion, the different molecular structures of ZrL_2 [L = $SiMe_2(NR)_2$, R = ^{i}Pr, ^{t}Bu] are reasonably related to the reduced steric hindrance of the isopropyl group with respect to the *tert*-butyl group. On the other hand, the lower coordination number in $Zr[(N^tBu)_2SiMe_2]_2$ with respect to $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$ causes a reduction of the Zr–N bond distances in $Zr[(N^tBu)_2SiMe_2]_2$ (2.05 Å[5]) compared with the corresponding bonds of the isopropyl derivative [Zr(1)–N(5), Zr(1)–N(6), Zr(2)–N(7), Zr(2)–N(8) 2.07 Å, av.], while similar N–Si–N angles are observed for the two compounds (*tert*-butyl derivative,[5] 94.8°; isopropyl derivative, terminal ligand, 94.2°, av.).

Table 2 Selected bond distances (Å) and angles (°) for $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$ (**8**)

Zr(1)–N(1)	2.075(6)	Zr(2)–N(2)	2.577(6)
Zr(1)–N(2)	2.240(6)	Zr(2)–N(3)	2.269(6)
Zr(1)–N(3)	2.496(6)	Zr(2)–N(4)	2.082(7)
Zr(1)–N(5)	2.075(6)	Zr(2)–N(7)	2.078(6)
Zr(1)–N(6)	2.082(6)	Zr(2)–N(8)	2.064(7)
Si(1)–N(1)	1.737(7)	Si(1)–N(3)	1.763(7)
Si(2)–N(2)	1.768(6)	Si(2)–N(4)	1.717(7)
Si(3)–N(5)	1.751(7)	Si(3)–N(6)	1.752(7)
Si(4)–N(7)	1.753(8)	Si(4)–N(8)	1.756(7)
N(1)–Zr(1)–N(2)	110.9(2)	N(1)–Zr(1)–N(3)	69.3(2)
N(1)–Zr(1)–N(5)	99.1(3)	N(1)–Zr(1)–N(6)	119.9(3)
N(2)–Zr(1)–N(3)	84.1(2)	N(2)–Zr(1)–N(5)	111.4(2)
N(2)–Zr(1)–N(6)	127.6(2)	N(3)–Zr(1)–N(5)	163.6(2)
N(5)–Zr(1)–N(6)	76.2(3)	N(3)–Zr(1)–N(6)	98.9(2)
N(2)–Zr(2)–N(4)	68.9(2)	N(2)–Zr(2)–N(3)	81.7(2)
N(2)–Zr(2)–N(8)	98.4(2)	N(2)–Zr(2)–N(7)	168.4(2)
N(3)–Zr(2)–N(7)	109.8(2)	N(3)–Zr(2)–N(4)	116.8(3)
N(4)–Zr(2)–N(7)	103.4(3)	N(3)–Zr(2)–N(8)	122.9(2)
N(7)–Zr(2)–N(8)	76.7(3)	N(4)–Zr(2)–N(8)	116.1(3)
N(2)–Si(2)–N(4)	99.9(3)	N(1)–Si(1)–N(3)	97.0(3)
N(5)–Si(3)–N(6)	94.1(3)	N(7)–Si(4)–N(8)	94.2(3)

As far as the solution molecular structure elucidation is concerned, the ^{29}Si NMR spectrum of **8** shows two resonances at −12.2 and −38.0 ppm, thus indicating the presence of two non-equivalent $[SiMe_2(N^iPr)_2]$ ligands. The monomer derivative $Zr[(N^tBu)_2SiMe_2]_2$† shows the ^{29}Si signal at −40.5 ppm, thus suggesting that the above mentioned resonance at −38.0 ppm is due to a chelating bidentate $(N^iPr)_2SiMe_2$ ligand.

On the other hand, as far as the isopropyl substituents are concerned, two sets of signals have been observed in the 1D (^{1}H, ^{13}C) and 2D (proton COSY, ^{1}H–^{13}C HMQC) NMR spectra (Table 3). Moreover, two resonances appear for the $[SiMe_2]$ moieties in the ^{1}H and ^{13}C NMR spectra (Table 3).

Furthermore, the proton NOESY spectrum shows negative crosspeaks between the resonances at 1.44 (CCH_3, *1*) and 4.36 ppm (CH, *2*), 1.32 (CCH_3, *2*) and 4.01 (CH, *1*) ppm, 1.44 (CCH_3, *1*) and 1.32 (CCH_3, *2*) ppm, and 4.01 (CH, *1*) and 4.36 (CH, *2*) ppm, indicating that a dipolar correlation exists between the two isopropyl groups (*i.e.* one "looks" at the other), and suggesting that the dimer structure is reasonably preserved in solution.

Moreover, the intense negative crosspeaks between the resonances at 0.63 ($SiCH_3$, *b*) and 1.32 ppm (CCH_3, *2*), and 0.56 ($SiCH_3$, *a*) and 1.44 ppm (CCH_3, *1*) indicate that the *a*-labelled

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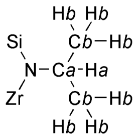
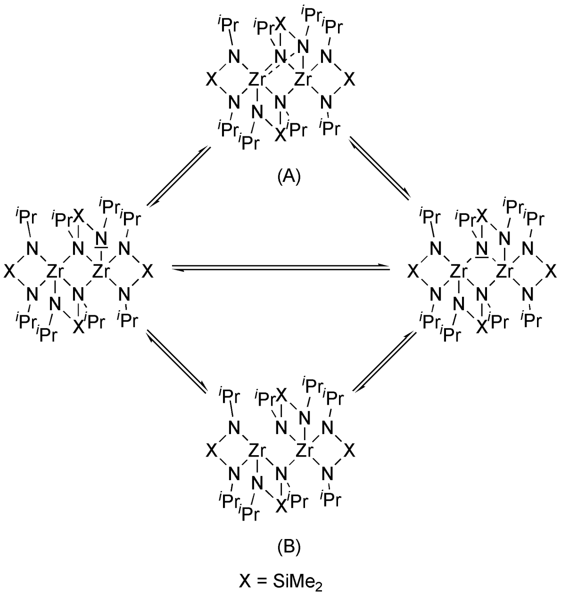
† The compound has been prepared according to the literature[5] and the ^{1}H, ^{13}C and ^{29}Si NMR spectra have been recorded (293 K, C_6D_6): δ_H, 1.33 (s, CCH_3, 9H), 0.51 (s, $SiCH_3$, 3H); δ_C, 56.2 (C), 36.3 (CCH_3), 6.7 ($SiCH_3$); δ_{Si}, 40.5.

Table 3 Selected ^{1}H and ^{13}C NMR data for $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$ (**8**)

		1	*2*
	δ_H	4.01 (H*a*) 1.44 (H*b*)	4.36 (H*a*) 1.32 (H*b*)
	δ_C	50.8 (C*a*) 29.1 (C*b*)	50.9 (C*a*) 28.3 (C*b*)
		a	*b*
[SiMe$_2$]	δ_H	0.56	0.63
	δ_C	6.02	9.13

[SiMe$_2$] moiety bears the *1*-type [N^{i}Pr] groups, and that the *b*-labelled [SiMe$_2$] moiety bears the *2*-type [N^{i}Pr] groups. In addition, on one hand, the presence of negative crosspeaks between the resonances at 0.56 ppm (SiCH$_3$, *a*) and those at 4.01 (CH, *1*) and 4.36 ppm (CH, *2*), and, on the other, the absence of crosspeaks between the resonances at 0.63 (SiCH$_3$, *b*) and 4.01 (CH, *1*) and 4.36 ppm (CH, *2*) indicates that (a) the *a*-labelled SiMe$_2$ moiety and the *1*-type isopropyl groups reasonably belong to the bridging ligand, (b) the *2*-labelled isopropyl groups (of the terminal ligand) are oriented so that the methyne hydrogen points far from the [SiMe$_2$] moiety, *i.e.* towards the [Zr$_2$N$_2$] core, similar to the solid state structure (Fig. 1(A)).

Provided that the solid state molecular structure is reasonably preserved in solution, one should expect *three* non-equivalent isopropyls, *i.e.* (a) the two *equivalent* isopropyl groups of the chelating ligands, and (b) the two *non-equivalent* isopropyls of the bridging ligands (Fig. 1(A)). As far as this point is concerned, we propose that a fast chemical exchange could occur between the [N^{i}Pr] groups of the bridging ligand (Scheme 1), thus making them equivalent at 293 K.



Scheme 1

In this connection, the ^{1}H NMR spectrum of the compound at 183 K (Fig. 2) shows three resonances for the methyne protons at 4.6, 4.3 and 3.8 ppm (integral ratio 1 : 2 : 1), the resonances at 4.6 and 3.8 ppm coalescing at 193 K,‡ thus confirming the proposed exchange (Scheme 1).

As far as the mechanism of this exchange is concerned, reasonably it occurs *via* a *concerted* attack/dissociation of the nitrogens of the bridging ligand (Scheme 1). The mechanism *should* be concerted (Scheme 1(A)), because the cleavage of the bond between zirconium and the nitrogen atom of the bridging ligand (Scheme 1(B)) should allow the terminal ligand to participate to the exchange mechanism, making the terminal and bridging ligands equivalent, and this can be reasonably excluded on the basis of the collected data, and by taking into account that the ^{1}H NMR spectrum is not affected by raising the temperature up to 343 K.

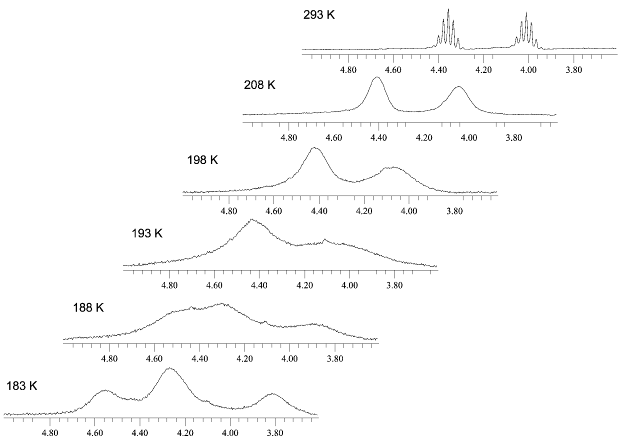
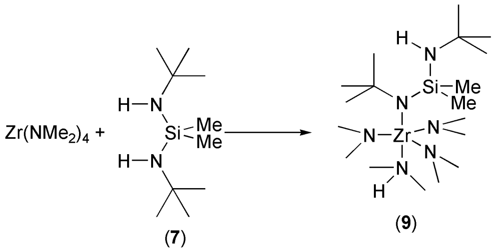


Fig. 2 ^{1}H NMR spectra of $\{Zr[(N^iPr)_2SiMe_2]_2\}_2$ (**8**) at different temperatures (toluene-d$_8$).

Reaction of $Zr(NMe_2)_4$ with $SiMe_2(NH^tBu)_2$

The binary amido derivative $Zr(NMe_2)_4$ reacts with $SiMe_2(NH^tBu)_2$ (molar ratio = 1 : 1) yielding $Zr(NMe_2)_3(NHMe)[(N^tBu)SiMe_2(NH^tBu)]$ (**9**) (eqn. (3)), no further reaction being observed even after 5 h stirring at 373 K.



(3)

The ^{1}H and ^{13}C NMR§ spectra of the compound show the characteristic resonance of the dimethylamido (^{1}H, 3.03 ppm; ^{13}C, 43.7 ppm) and the dimethylamino ligands (^{1}H, 2.13 ppm, ^{13}C, 39.0 ppm).¶ On the other hand, two non-equivalent *tert*-butyl groups have been observed (CH$_3$, ^{1}H: *a*, 1.31 ppm, *b*, 1.04 ppm; ^{13}C: *a*, 35.5 ppm; *b*, 31.7 ppm; C, ^{13}C: *a*, 55.2; *b*, 52.7 ppm). Interestingly, the *tert*-butyl groups in the zirconium derivative $Zr[(N^tBu)_2SiMe_2]_2$ yields the ^{1}H resonance at 1.33 ppm (CH$_3$) and the ^{13}C resonances at 56.2 and 36.3 ppm, thus suggesting that the *tert*-butylamido group is responsible for the *a*-labelled set of resonances and that the *b*-labelled set of signals is due to the uncomplexed *tert*-butylamino moiety. In addition, the resonances of the SiMe$_2$ moiety are observed at 0.36 ppm (^{1}H) and 6.86 ppm (^{13}C), and a broad signal at 0.85 ppm (^{1}H) is present due to the NH protons.

On heating the C$_6$D$_6$ solution of the compound at 343 K, the

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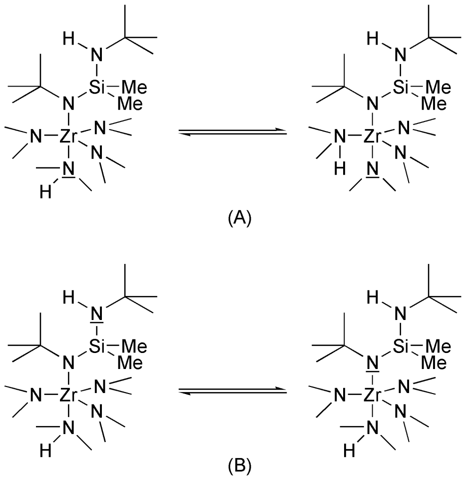
‡ As far as the methyl resonances of the isopropyl groups and the SiMe$_2$ moiety of the bridging ligand are concerned (*1* and *a* in Table 3), variations are observed as a function of the temperature. However, the ^{1}H resonances at 1.44 (CCH$_3$) and 0.56 ppm (SiCH$_3$) broaden and appear unresolved even at 183 K, thus preventing the assignment.

§ The ^{13}C NMR resonances have been assigned through the ^{1}H–^{13}C HMQC spectrum.

¶ Gibson *et al.* have reported[8] that $Zr(NMe_2)_4$ reacts with $SiMe_2(NHPh)_2$ (Ph = 2,6-Me$_2$C$_6$H$_3$) yielding the mixed amido derivative $Zr(NMe_2)_2(NHMe_2)[(NPh)_2SiMe_2]$ the NMR spectra of which show the resonances of the dimethylamido and dimethylamino ligands at 2.79 and 1.68 ppm (^{1}H) and 41.65 and 39.43 ppm (^{13}C), respectively.

coalescences of the signals at 3.03 and 2.14 ppm, on one hand, and those at 1.31 and 1.04 ppm, on the other, were observed,[‖] thus indicating that a chemical exchange occurs between (a) the two non-equivalent $[NMe_2]$ moieties of the dimethylamido ligand and of the coordinated dimethylamine (Scheme 2(A)) and (b) the two non-equivalent *tert*-butyl groups (of the coordinated and uncoordinated N^tBu moiety) with the consequent proton 1,3-shift from one nitrogen to the other (Scheme 2(B)).

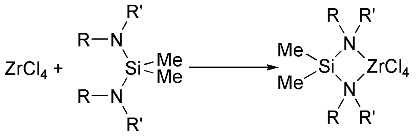


Scheme 2

The proton NOESY spectrum of the compound (298 K) shows *positive* crosspeaks between the resonances at 3.03 (NMe_2) and 2.14 ppm (NH*Me*), and those at 1.31 (*tert*-butylamido group) and 1.04 ppm (*tert*-butylamino group), confirming the above proposed chemical exchanges. Moreover, *negative* crosspeaks have been detected between the resonances of the *tert*-butyl groups and the dimethylamido ligand, and no correlation peaks have been observed between the resonance of the coordinated dimethylamine and the *tert*-butyl protons, thus suggesting that the coordination polyhedron of the zirconium could be a trigonal bipyramid, the equatorial positions being occupied by the dimethylamido ligand, and the apical positions by the coordinated dimethylamine and the $(N^tBu)SiMe_2(NH^tBu)$ group.

Synthesis of $ZrCl_4[(NRR')_2SiMe_2]$

The Lewis adducts $ZrCl_4[(NRR')_2SiMe_2]$ [NRR′ = NMe_2 (**10**), NC_4H_8 (**11**), NHEt (**12**), NH^iPr (**13**), NH^tBu (**14**), NMeBu (**15**)] have been prepared by reacting $ZrCl_4$ with the appropriate silicon compound in toluene (12 h, room temperature) (eqn. (4)).



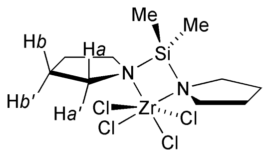
(4)

NRR′ = NMe_2 (**10**), NC_4H_8 (**11**), NHEt (**12**), NH^iPr (**13**), NH^tBu (**14**), NMeBu (**15**)

For convenience, the adducts will be discussed separately according to the kind of the nitrogen substitution, *i.e.* asymmetric (NRR′) or symmetric (NR_2).

NRR′ = NMe_2, NC_4H_8. The ^1H NMR spectrum of $ZrCl_4[(NMe_2)_2SiMe_2]$ (**10**) show two singlets at 2.43 and −0.28 ppm, indicative of the $[NMe_2]$ and $[SiMe_2]$ moieties, respectively.[**] Correspondingly, the ^{13}C NMR spectrum show two signals at 48.0 and −3.15 ppm, assigned to the dimethylamido and the dimethylsilylene groups, respectively.

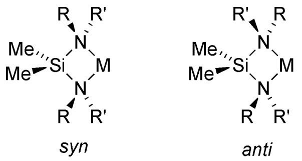
Table 4 Selection of ^1H NMR data of $ZrCl_4[(NC_4H_8)_2SiMe_2]$ (**11**)



	δ_H
H*a*	3.23
H*a′*	3.39
H*b*v	0.82
H*b′*	1.28
$SiMe_2$	−0.18

The ^{13}C NMR spectrum of $ZrCl_4[(NC_4H_8)_2SiMe_2]$ (**11**) shows two resonances at 57.3 (NCH_2CH_2) and 24.5 ppm (NCH_2CH_2), indicative of the pyrrolidinide group, and at −3.0 ppm, due to the dimethylsilylene moiety. On the other hand, in the ^1H NMR spectrum, two signals have been observed for each methylene (3.39, 3.23 ppm, NCH_2CH_2; 1.28, 0.82 ppm, NCH_2CH_2), thus indicating that the methylene protons experiment different chemical environments. As a matter of fact, due to the coordination of the ligand, the two faces of the C_4H_8N ring are non-equivalent, one facing zirconium and the other silicon (Table 4). This picture is fairly confirmed by the proton NOESY spectrum, (a) negative crosspeaks being observed between the resonance at −0.18 ppm ($SiCH_3$) and those at 3.23 (NCH_2CH_2) and 0.82 ppm (NCH_2CH_2); (b) no crosspeaks (*i.e.* dipolar correlation) being detected between the resonance of the dimethylsilylene group and those at 3.39 and 1.28 ppm. The proposed molecular structure and the assignment of the ^1H NMR resonances are reported in Table 4.

NRR′ = NHEt, NH^iPr, NH^tBu, NMeBu. Some preliminary considerations are in order. Due to the presence of two different groups in the [NRR′] moiety of $SiMe_2(NRR')_2$, the chelation of the ligand to a metal centre yields two different isomers, namely *syn* and *anti* (Scheme 3).



Scheme 3

The *anti* isomer has a C_2 rotational axis (passing through the silicon and zirconium centres), making the two methyls of $SiMe_2$ equivalent; on the other hand, a mirror plane (containing the $SiMe_2$ group) is present in the *syn* isomer, leaving the two methyl groups of $SiMe_2$ non-equivalent. Therefore, as far as ^1H and ^{13}C NMR spectra are concerned, one signal (*i.e.* one ^1H and one ^{13}C resonance) is expected for the dimethylsilylene moiety of the *anti* isomer, and two signals (*i.e.* two ^1H and two ^{13}C resonances) should appear for the *syn* isomer. Moreover, the tetra-substitution of the nitrogen atoms makes these centres stereogenic, and therefore non-equivalency is expected as far as the ^1H nuclei of the alkyl groups are concerned (*vide infra*).

The ethyl derivative $ZrCl_4[(NHEt)_2SiMe_2]$ (**12**) shows low solubility in C_6D_6; therefore, in order to record satisfactory ^1H and ^{13}C NMR spectra, the acquisitions were performed at

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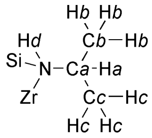
[‖] The ^{13}C NMR spectrum of the compound is also affected by the temperature. The resonances of the dimethylamido ligand and that of the coordinated dimethylamine coalesce at 343 K, yielding a broad signal at *ca.* 42.7 ppm ($\Delta\nu_{1/2} \approx 200$ Hz). On the other hand, the signals of both the *tert*-butyl CH_3 appear as partially merging broad lines ($\Delta\nu_{1/2} \approx 130$ Hz; $\Delta\delta = 2.6$ ppm.

[**] $ZrCl_4[(NMe_2)_2SiMe_2]$ (**10**) has already been described in the literature,[6,7] and the authors report that the dimethylamido group yields two resonances (2.15, 2.09 ppm), due to the proposed non-planar $[SiN_2Zr]$ core. This discrepancy with our data is mysterious, and there was no way for us to reproduce the published data.

Table 5 Selected ^1H and ^{13}C NMR[a] data for $ZrCl_4[(NH^iPr)_2SiMe_2]$ (**13**)

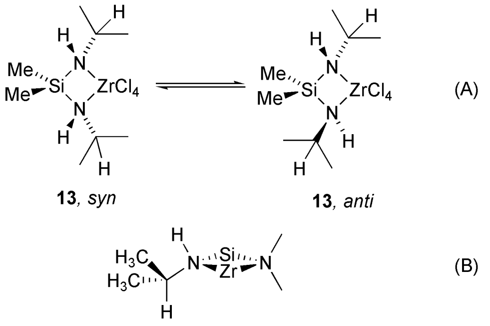
		1	*2*
	δ_H	2.96 (H*a*) 0.45 (H*b*) 1.21 (H*c*) 2.48 (H*d*)	3.05 (H*a*) 0.38 (H*b*) 1.23 (H*c*) 2.14 (H*d*)
	δ_C	49.6 (C*a*) 25.8 (C*b*) 25.7 (C*c*)	49.4 (C*a*) 25.8 (C*b*) 25.9 (C*c*)

[a] The ^{13}C resonances have been assigned through the ^1H–^{13}C HMQC spectrum.

343 K, the observed chemical shifts being reported in the following: ^1H, 2.92 (CH_2), 2.40 (NH), 0.49 (CH_2CH_3),†† 0.03 ($SiCH_3$) ppm; ^{13}C, 42.5 (CH_2), 17.5 (CH_2CH_3), 5.0 ($SiCH_3$) ppm. One ^1H and one ^{13}C NMR signals are observed for the $SiMe_2$ moiety, thus suggesting that the *anti* isomer is present. Nevertheless, two considerations are in order: (a) a mixture of the *syn* and *anti* isomers could be present, ready interconversion occurring and making the methyls of $SiMe_2$ equivalent; (b) it cannot be excluded that the two isomers have different solubility, the *anti* one being more soluble and therefore the only one detected.

The isopropyl derivative $ZrCl_4[(NH^iPr)_2SiMe_2]$ (**13**) is more soluble than the ethyl analogue, thus making possible a more accurate NMR investigation. In the ^1H and ^{13}C NMR spectra (Table 5), we have observed three resonances for the $SiMe_2$ moiety (^1H: 0.10, 0.06, 0.05 ppm, ^{13}C: 3.9, 0.09, −4.1 ppm), two resonances for the methyne protons (^1H: 2.96, 3.05 ppm; ^{13}C: 49.6, 49.4 ppm), four resonances for the methyls of the isopropyl group (^1H, 1.21, 1.23, 0.45, 0.38 ppm; ^{13}C: 25.7, 25.8,‡‡ 25.9 ppm), and two resonances for the amine proton (^1H: 2.48, 2.14 ppm).§§

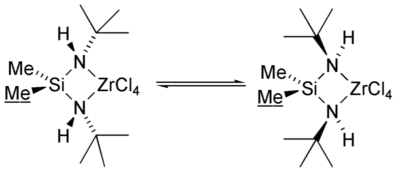
This set of experimental data suggests the presence of the two isomers, namely *syn* and *anti* (1 : 1 based on the integral ratios). As a matter of fact, the proton COSY spectrum indicates two non-equivalent isopropyl groups, each containing two *non-equivalent* methyls (Table 5), reasonably due to the presence of the two stereogenic nitrogens in each isomer (*vide supra*). In this connection, it is reported that the non-equivalency of the methyl groups in $[CH(CH_3)_2]$ is observed even if eight bonds are present between the isopropyl group and the stereogenic centre.[11] Finally, the NOESY spectrum of **13** shows *positive* crosspeaks between all the resonances of the methyls of the isopropyl groups, between the resonances of the methyls of $SiMe_2$, and between the NH signals, thus indicating that chemical exchanges exist between these groups (reasonably, *via* the *syn–anti* interconversion, Scheme 4(A)). On the other hand,



Scheme 4

(a) *negative* crosspeaks between the resonances at 1.21 (CCH_3, *1*) and 2.48 ppm (NH, *1*), 0.45 (CCH_3, *1*) and 2.48 ppm (NH, *1*), 0.38 (CCH_3, *2*) and 2.14 ppm (NH, *2*), 1.23 (CCH_3, *2*) and 2.14 ppm (NH, *2*), and (b) the absence of crosspeaks between the methyne resonances (2.96 ppm, *1*; 3.05 ppm, *2*) and the amine proton signals (2.48 ppn, *1*; 2.14 ppm, *2*) indicate that the methyne hydrogen points far from the $[SiN_2Zr]$ ring, and, on the other hand, both the methyls "look" at the NH proton (Scheme 4(B)).

The ^1H NMR spectrum of the adduct $ZrCl_4[(NH^tBu)_2SiMe_2]$ (**14**) shows a broad signal at 3.26 ppm (NH), a sharp singlet at 1.16 ppm (CCH_3) and two signals at 0.54 and −0.04 ppm due to the dimethylsilylene moiety, thus indicating that the *syn* isomer is present. The coalescence of the resonances at 0.54 and −0.04 ppm is observed at 333 K, and at 343 K a single broad signal is observed at 0.32 ppm ($\Delta\nu_{1/2}$ = 50 Hz). On this basis, we propose that a dynamic process occurs making the two methyls in $SiMe_2$ equivalent (Scheme 5). As a confirmation, the proton NOESY spectrum of **14** shows *positive* crosspeaks between the resonances of the dimethylsylilene moiety. As far as the mechanism is concerned, reasonably, the deprotonation/protonation of the coordinated nitrogen atoms could allow the interconversion to occur.¶¶



Scheme 5

On the other hand, a stronger dipolar correlation (*i.e.* more intense negative crosspeaks) of the $SiCH_3$ protons at −0.04 ppm and NH (with respect to the $SiCH_3$ protons at 0.54 ppm) has been observed in the proton NOESY spectrum, thus suggesting that the methyl protons at −0.04 and the NH proton are on the same side of the $[SiN_2Zr]$ core.

The ^{13}C resonances of **14** are reported in the following, the assignment being based on the ^1H–^{13}C HMQC spectrum: 0.3 and 7.9 ($SiCH_3$), 32.1 (CCH_3), and 57.1 ppm (C).

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†† Despite the observation of the triplet at 0.49 ppm for CH_3 of the ethyl group, the resonance of the methylene protons at 2.92 ppm appears broad and unresolved. In our opininion this is related to the presence of the stereogenic nitrogen atoms, making the methylene protons diastereotopic. Because of the low solubility of the compound, this point was not investigated further, but related insightful considerations have been drawn for the zirconium derivative $ZrCl_4[(NMeBu)_2SiMe_2]$ (**15**), *vide infra*.

‡‡ As reported in Table 5, two methyl groups are responsible for the ^{13}C resonance at 25.8 ppm. As a confirmation, the intensity of this signal is about double with respect to the others.

§§ The ^1H resonances of the NH protons appear as doublets, thus indicating that vicinal coupling occurs between NH and CH of the isopropyl groups ($^3J_{HH}$ = 10.0 Hz). On the other hand, the direct observation of the coupling in the CH pattern was prevented by the overlap of the resonances of the CH protons of the two isomers. Nevertheless, as a confirmation, the proton COSY spectrum shows crosspeaks between the resonances at 2.96 (CH) and 2.48 ppm (NH), and those at 3.05 (CH) and 2.14 ppm (NH).

¶¶ The step-by-step interconversion *via* the *anti* isomer could be proposed (see below), but reasonably the formation of the *anti* isomer should be observed, as a consequence. In this connection, we have observed no signals in the ^1H NMR spectrum attributable to the *anti* isomer, even after one week.

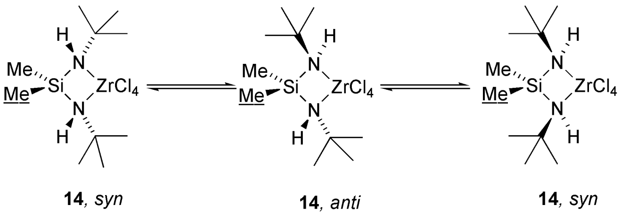

Table 6 Selected ^{1}H and ^{13}C NMR data for $ZrCl_4[(NMeBu)_2SiMe_2]$ (**15**)

	syn		*anti*	
	δ_C	δ_H	δ_C	δ_H
$Si(CH_3)_2$	−0.64	0.04	−1.01	0.16
	−1.19	0.32		
NCH_2	58.4	3.32, 3.28	59.1	3.33, 3.10
NCH_3	43.6	2.66	43.0	2.67
$NCH_2\mathit{CH_2}$	29.9 or 29.8[a]	1.65	29.9 or 29.8[a]	1.75
$\mathit{CH_2}CH_3$	20.8	1.01	20.7	1.05
$CH_2\mathit{CH_3}$	14.1	0.82	14.0	0.79

[a] Due to the broad correlation peaks observed for the ^{13}C signals at 29.9 and 29.8 ppm, we could not confidently assign the related proton resonances.

The ^{13}C NMR spectrum of $ZrCl_4[(NMeBu)_2SiMe_2]$ (**15**) shows three resonances for the $SiMe_2$ moiety, thus indicating the presence of both the *syn* and *anti* isomers (1 : 1 based on the integral ratios). Moreover, as a confirmation, two series of resonances have been observed for the NMeBu group (Table 6). The ^{1}H NMR spectrum is quite complicated, nevertheless, the ^{1}H–^{13}C HMQC spectrum allows full elucidation of the ^{1}H NMR spectrum through the correlation peaks, the observed ^{1}H chemical shifts being reported in Table 6, with the proposed assignment (*vide infra* for further details).

As far as the NCH_2 resonances are concerned, some comments are in order. As anticipated, the nitrogen atoms of **15** are stereogenic, thus making the methylene protons diasterotopic. The ^{1}H–^{13}C HMQC spectrum indicates that the methylene carbon atoms of both the *syn* and *anti* isomers bear two non-equivalent protons (Fig. 3(A)XX). Moreover, the ^{1}H NMR pattern of the methylene protons at 3.10 ppm (Fig. 3) allows the determination of both the geminal and vicinal ^{1}H–^{1}H coupling constants ($^{2}J_{HH}$ = 3.7 Hz; $^{3}J_{HH}$ = 12.3 Hz). In this connection, the proton COSY spectrum shows a characteristic system of crosspeaks between the methylene resonances (Fig. 3(B)) indicating the geminal coupling between the resonances at 3.10 and 3.33 ppm.

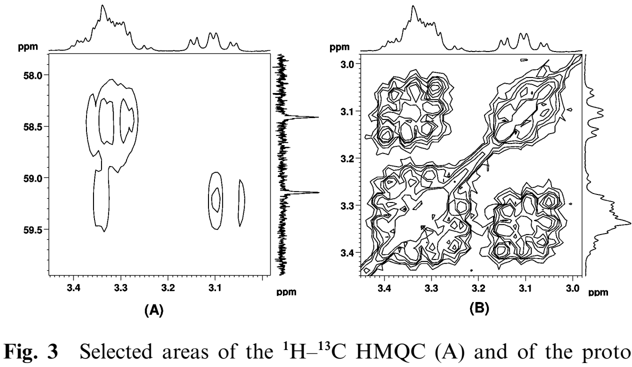

Fig. 3 Selected areas of the ^{1}H–^{13}C HMQC (A) and of the proton COSY (B) spectra of $ZrCl_4[(NMeBu)_2SiMe_2]$ (**15**).

Moreover, in the proton COSY and NOESY spectra, two sets of resonances have been recognised for the butyl groups (Table 6), and the assignment of the configuration have been done on the basis of the correlation peaks of the NOESY spectrum. Negative crosspeaks have been detected between the resonances at 2.66 (NCH_3, *syn*) and 0.04 ppm ($SiCH_3$, *syn*), and between the resonances at 2.67 (NCH_3, *anti*) and 0.16 ppm ($SiCH_3$, *anti*), thus indicating that: (a) the NCH_3 group yielding the signal at 2.66 ppm belongs to the *syn* isomer; (b) the methyl of the dimethylsilylene moiety of the *syn* isomer "looking" at the NCH_3 methyl is that responsible for the resonance at 0.04 ppm. On the other hand, the negative crosspeaks between the resonances at 2.66 (NCH_3, *syn*) and 3.32, 3.28 ppm (NCH_2, *syn*) and between the resonances at 2.67 (NCH_3, *anti*) and 3.33 and 3.10 ppm (NCH_2, *anti*) allow the assignment of the butyl resonances to the appropriate isomer (Table 6).

Conclusions

The aminolysis of the Si–Cl bond in $SiMe_2Cl_2$ readily affords the bis-amido derivatives $SiMe_2(NRR')_2$ [NRR′ = NMe_2 (**1**), NEt_2 (**2**), NC_4H_8 (**3**), NMeBu (**4**), NHEt (**5**), $NH^{i}Pr$ (**6**), $NH^{t}Bu$ (**7**)]. As far as their ligating ability towards the zirconium(IV) centre is concerned, this study has shown that coordination compounds containing the above mentioned species as neutral, monoanionic and dianionic ligand can be prepared.

The Lewis adducts $ZrCl_4[(NRR')_2SiMe_2]$ [NRR′ = NMe_2 (**10**), NC_4H_8 (**11**), NHEt (**12**), $NH^{i}Pr$ (**13**), $NH^{t}Bu$ (**14**), NMeBu (**15**)] result from the treatment of $SiMe_2(NRR')_2$ with $ZrCl_4$. If R ≠ R′, the $[ZrN_2Si]$ ring contains two stereogenic nitrogen atoms, and, as a consequence, the diasterotopicity of the NCH_2 protons in **15** and the non-equivalency of the methyls in the isopropyl groups of **13** have been observed.

The reaction of $SiMe_2(NH^{t}Bu)_2$ and $Zr(NMe_2)_4$ yields the mixed amido derivative $Zr(NMe_2)_3(NHMe_2)[(N^{t}Bu)SiMe_2(NH^{t}Bu)]$ (**9**), containing the monodentate monoanionic ligand $(N^{t}Bu)SiMe_2(NH^{t}Bu)$. Reasonably because of the bulky *tert*-butyl groups, the chelation of the ligand is not observed and correspondingly the transfer of only one proton from the silicon species to the coordinated NMe_2 groups occurs.

Finally, the dianionic ligand $SiMe_2(N^{i}Pr)_2$ coordinates zirconium(IV) yielding the binary dimer derivative $\{Zr[(N^{i}Pr)_2SiMe_2]_2\}_2$ (**8**), whose molecular structure has been elucidated both in the solid state (X-ray diffraction analysis) and in solution (1D and 2D multinuclear NMR spectroscopy).

Experimental

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 referred to TMS. Multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quartet), sp (septet), ds (double septet), m (multiplet).

Zirconium tetrachloride ($ZrCl_4$, Fluka) was washed with boiling toluene, then with pentane, dried *in vacuo* and stored under an atmosphere of dinitrogen. Isopropylamine ($NH_2{}^{i}Pr$, Aldrich), *tert*-butylamine ($NH_2{}^{t}Bu$, Aldrich), diethylamine ($NHEt_2$, Aldrich), pyrrolidine (C_4H_8NH, Aldrich) were refluxed over BaO for one day, then distilled and stored under dinitrogen. Dichlorodimethylsilane ($SiCl_2Me_2$, Aldrich), dimethylamine ($NHMe_2$, Fluka) and ethylamine (NH_2Et, Fluka) were used as received. $Zr(NMe_2)_4$ was prepared according to the published procedure.[12]

Synthesis of $SiMe_2(NRR')_2$ (NRR′ = NHEt, $NH^{i}Pr$, $NH^{t}Bu$, NMe_2, NEt_2, NC_4H_8)

Only the reaction for NRR′ = NMe_2 is described in detail, the others being similar.

The gaseous amine $NHMe_2$ was bubbled into a pentane (30 ml) solution of $SiMe_2Cl_2$ (1.3 g, 10.1 mmol). A colourless solid readily precipitated out. After 15 min bubbling, the suspension was filtered and the solid washed with pentane, dried *in vacuo* and spectroscopically (^{1}H NMR) and analytically (C, H, N, Cl) identified as $[NH_2Me_2]Cl$ (1.51 g, 92% yield). The filtrate was evaporated yielding a colourless liquid identified as $SiMe_2(NMe_2)_2$ (**1**, 1.40 g, 95% yield). Found: C, 49.0; H, 12.7; N, 19.0. $C_6H_{18}N_2Si$ requires C, 49.3; H, 12.4; N, 19.1%.

δ_{H} ($\mathrm{C_6D_6}$, 298 K): 2.44 (s, 2H, $\mathrm{NCH_3}$), −0.08 (s, 1H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 37.6 ($\mathrm{NCH_3}$), −3.4 ($\mathrm{SiCH_3}$).

$\mathrm{SiMe_2(NEt_2)_2}$ (**2**, 97% yield, colourless liquid). Found: C, 59.0; H, 12.5; N, 13.5. $\mathrm{C_{10}H_{26}N_2Si}$ requires C, 59.3; H, 12.9; N, 13.8%. δ_{H} ($\mathrm{C_6D_6}$, 298 K): 2.82 (q, 4H, $\mathrm{CH_2}$, $^3J_{\mathrm{CH}}$ = 7.0 Hz), 0.99 (t, 6H, $\mathrm{CH_2\mathit{CH_3}}$, $^3J_{\mathrm{CH}}$ = 7.0 Hz), 0.14 (s, 3H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 39.6 ($\mathrm{CH_2}$), 15.8 ($\mathrm{CH_2\mathit{C}H_3}$), −0.9 ($\mathrm{SiCH_3}$).

$\mathrm{SiMe_2(NC_4H_8)_2}$ (**3**, 95% yield, colourless liquid). Found: C, 61.0; H, 11.0; N, 14.0. $\mathrm{C_{10}H_{22}N_2Si}$ requires C, 60.5; H, 11.2; N, 14.1%. δ_{H} ($\mathrm{C_6D_6}$, 298 K): 2.97 (m, 4H, $\mathrm{N\mathit{CH_2}CH_2}$), 1.61 (m, 4H, $\mathrm{NCH_2\mathit{CH_2}}$), 0.18 (s, 3H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 46.9 ($\mathrm{N\mathit{C}H_2CH_2}$), 27.2 ($\mathrm{NCH_2\mathit{C}H_2}$), −2.9 ($\mathrm{SiCH_3}$).

$\mathrm{SiMe_2(NMeBu)_2}$ (**4**, 90% yield, colourless liquid). Found: C, 62.3; H, 13.3; N, 12.0. $\mathrm{C_{12}H_{30}N_2Si}$ requires C, 62.5; H, 13.1; N, 12.2%. δ_{H} ($\mathrm{C_6D_6}$, 298 K): 2.73 (t, 2H, $\mathrm{NCH_2}$, $^3J_{\mathrm{HH}}$ = 7.1 Hz), 2.45 (s, 3H, $\mathrm{NCH_3}$), 1.43 (tt, 2H, $\mathrm{NCH_2\mathit{CH_2}}$, $^3J_{\mathrm{HH}}$ = 7.1, 8.2 Hz), 1.26 (tq, 2H, $\mathrm{\mathit{CH_2}CH_3}$, $^3J_{\mathrm{HH}}$ = 7.1, 8.2 Hz), 0.92 (t, 3H, $\mathrm{CH_2\mathit{CH_3}}$, $^3J_{\mathrm{HH}}$ = 7.1 Hz), 0.12 (s, 3H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 50.1 ($\mathrm{NCH_2}$), 34.2 ($\mathrm{NCH_3}$), 31.8 ($\mathrm{NCH_2\mathit{C}H_2}$), 20.6 ($\mathrm{\mathit{C}H_2CH_3}$), 14.4 ($\mathrm{CH_2\mathit{C}H_3}$), −2.20 ($\mathrm{SiCH_3}$).

$\mathrm{SiMe_2(NHEt)_2}$ (**5**, 90% yield, colourless liquid). Found: C, 49.0; H, 12.4; N, 19.3. $\mathrm{C_6H_{18}N_2Si}$ requires C, 49.3; H, 12.4; N, 19.1%. δ_{H} ($\mathrm{CDCl_3}$, 298 K): 2.77 (q, 2H, $\mathrm{CH_2}$, $^3J_{\mathrm{HH}}$ = 7.0 Hz), 1.05 (t, 3H, $\mathrm{CH_2\mathit{CH_3}}$, $^3J_{\mathrm{HH}}$ = 7.0 Hz), 0.42 (br, 1H, NH), 0.01 (s, 3H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{CDCl_3}$, 298 K): 36.0 ($\mathrm{CH_2}$), 20.5 ($\mathrm{CH_2\mathit{C}H_3}$), −1.33 ($\mathrm{SiCH_3}$).

$\mathrm{SiMe_2(NH^{\mathit{i}}Pr)_2}$ (**6**, 92% yield, colourless liquid). Found: C, 55.0; H, 12.5; N, 16.0. $\mathrm{C_8H_{22}N_2Si}$ requires C, 55.1; H, 12.7; N, 16.1%. δ_{H} ($\mathrm{C_6D_6}$, 298 K): 3.08 (ds, 1H, CH, $^3J_{\mathrm{HH}}$ = 10.0, 6.4 Hz), 1.03 (d, 6H, $\mathrm{CH\mathit{CH_3}}$, $^3J_{\mathrm{HH}}$ = 6.4 Hz), 0.42 (br, 1H, NH), −0.01 (s, 3H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 42.3 (CH), 27.9 ($\mathrm{CH\mathit{C}H_3}$), −0.38 ($\mathrm{SiCH_3}$).

$\mathrm{SiMe_2(NH^{\mathit{t}}Bu)_2}$ (**7**, 95% yield, colourless liquid). Found: C, 59.5; H, 12.5; N, 13.8. $\mathrm{C_{10}H_{26}N_2Si}$ requires C, 59.3; H, 12.9; N, 13.8%. δ_{H} ($\mathrm{C_6D_6}$, 298 K): 1.19 (s, 9H, $\mathrm{CCH_3}$), 0.52 (br, 1H, NH), 0.18 (s, 3H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 49.2 (C), 33.8 ($\mathrm{C\mathit{C}H_3}$), 3.7 ($\mathrm{SiCH_3}$).

Synthesis of $\{\mathrm{Zr[(N^{\mathit{i}}Pr)_2SiMe_2]_2}\}_2$

A pentane (15 ml) solution of $\mathrm{Li_2[(N^{\mathit{i}}Pr)_2SiMe_2]}$ [obtained by reacting LiBu, 1.6 M, in hexane, 7.20 ml, 11.5 mmol, with $\mathrm{SiMe_2(NH^{\mathit{i}}Pr)_2}$, 1.00 g, 5.74 mmol, in pentane, 15 ml] was added dropwise to a toluene (25 ml) suspension of $\mathrm{ZrCl_4}$ (665 mg, 2.85 mmol). The ready precipitation of a colourless solid was observed. After 18 h stirring, the solid was filtered off and the solution was evaporated (residual 10 ml), pentane added (20 ml) and then cooled at 243 K for a week. The precipitated solid was filtered off, dried *in vacuo* and identified as $\{\mathrm{Zr[(N^{\mathit{i}}Pr)_2SiMe_2]_2}\}_2$ (**8**, 720 mg, 58% yield, colourless solid). Found: C, 44.2; H, 9.1; N, 13.0. $\mathrm{C_{16}H_{40}N_4Si_2Zr}$ requires: C, 44.1; H, 9.2; N, 12.9%. δ_{H} ($\mathrm{C_6D_6}$, 298 K): 4.36 (sp, 1H, CH, $^3J_{\mathrm{HH}}$ = 6.5 Hz), 4.01 (sp, 1H, CH, $^3J_{\mathrm{HH}}$ = 6.5 Hz), 1.44 (d, 6H, $\mathrm{CCH_3}$, $^3J_{\mathrm{HH}}$ = 6.5 Hz), 1.32 (d, 6H, $\mathrm{CCH_3}$, $^3J_{\mathrm{HH}}$ = 6.5 Hz), 0.63 (s, 3H, $\mathrm{SiCH_3}$), 0.56 (s, 3H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 50.9 (CH), 50.8 (CH), 29.1 ($\mathrm{C\mathit{C}H_3}$), 28.3 ($\mathrm{C\mathit{C}H_3}$), 9.13 ($\mathrm{SiCH_3}$), 6.02 ($\mathrm{SiCH_3}$). δ_{Si} ($\mathrm{C_6D_6}$, 298 K): −12.2, −38.0 ppm

Crystal structure determination of $\{\mathrm{Zr[(N^{\mathit{i}}Pr)_2SiMe_2]_2}\}_2$

Single crystals suitable for X-ray analysis were obtained by cooling at 243 K a pentane solution of the compound. The intensities data were collected at room temperature using a Philips PW1100 single-crystal diffractometer (FEBO system) using a graphite-monochromator (Mo-Kα radiation), following the standard procedures. There were no significant fluctuations of intensities other than those expected from Poisson statistics. All intensities were corrected for Lorentz polarization and absorption.[13] The structure was solved by direct methods using SIR-92.[14] Refinement was carried out by full-matrix least-squares procedures (based on F_o^2) using anisotropic temperature factors for all non-hydrogen atoms. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters ($1.2U_{\mathrm{equiv}}$ of the parent carbon atom). The calculations were performed with the SHELXL-97 program,[15] implemented in the WinGX package,[16] and drawings were produced using ORTEP3.[17] Crystallographic and experimental details for the structure are summarized in Table 7.

Table 7 Crystallographic data for $\{\mathrm{Zr[(N^{\mathit{i}}Pr)_2SiMe_2]_2}\}_2$ (**8**)

Chemical formula	$\mathrm{C_{32}H_{80}N_8Si_4Zr_2}$
Formula weight	871.84
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.033(3)
b/Å	46.986(5)
c/Å	10.498(3)
β/°	110.12(3)
V/Å^3	4647(2)
Z	4
D_c/g cm^{-3}	1.246
F(000)	1856
μ(Mo-Kα)/mm^{-1}	0.581
Reflections collected	7761
Reflections observed [$I \geq 2\sigma(I)$]	6971
Final $R1$, $wR2$	0.079, 0.180

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]]^{½}$.

CCDC reference number 200050.

See http://www.rsc.org/suppdata/dt/b2/b212705a/ for crystallographic data in CIF or other electronic format.

Reaction of $\mathrm{Zr(NMe_2)_4}$ with $\mathrm{SiMe_2(NH^{\mathit{t}}Bu)_2}$

A toluene solution (25 ml) of $\mathrm{Zr(NMe_2)_4}$ (870 mg, 3.25 mmol) was added dropwise to a toluene solution (10 ml) of $\mathrm{SiMe_2(NH^{\mathit{t}}Bu)_2}$ (660 mg, 3.26 mmol). After 12 h stirring the solution was evaporated yielding a colourless solid which was identified as $\mathrm{Zr(NMe_2)_3(NHMe_2)[(N^{\mathit{t}}Bu)SiMe_2(NH^{\mathit{t}}Bu)]}$ (**9**, 1.34 g, 88% yield, colourless solid). Found: C, 45.8; H, 10.5; N, 17.7. $\mathrm{C_{18}H_{50}N_6SiZr}$ requires: C, 46.0; H, 10.7; N, 17.9%. δ_{H} ($\mathrm{C_6D_6}$, 298 K): 3.03 (s, 18H, $\mathrm{NCH_3}$), 2.13 (br, 6H, $\mathrm{HN\mathit{CH_3}}$), 1.31 (s, 9H, $\mathrm{CCH_3}$), 1.04 (s, 9H, $\mathrm{CCH_3}$), 0.85 (br, 2H, NH), 0.36 (s, 6H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 55.2.(C), 52.8 (C), 43.7 ($\mathrm{NCH_3}$), 39.0 ($\mathrm{HNCH_3}$), 35.5 ($\mathrm{C\mathit{C}H_3}$), 31.7 ($\mathrm{C\mathit{C}H_3}$), 6.86 ($\mathrm{SiCH_3}$).

Reaction of $\mathrm{ZrCl_4}$ with $\mathrm{SiMe_2(NRR')_2}$ (NRR′ = NHEt, NH^{i}Pr, NH^{t}Bu, $\mathrm{NMe_2}$, $\mathrm{NC_4H_8}$, NMeBu)

Only the procedure for NRR′ = $\mathrm{NMe_2}$ is reported in details, the others being similar.

A toluene (25 ml) solution of $\mathrm{SiMe_2(NMe_2)_2}$ (510 mg, 3.49 mmol) was treated with $\mathrm{ZrCl_4}$ (800 mg, 3.43 mmol). After 18 h stirring, the suspension was filtered, the solid washed with toluene and pentane, dried *in vacuo* and finally identified as $\mathrm{ZrCl_4[(NMe_2)_2SiMe_2]}$ (**10**, 1.21 g, 93% yield, colourless solid). Found: C, 19.2; H, 5.0; Cl, 37.3; N, 7.0. $\mathrm{C_6H_{18}Cl_4N_2SiZr}$ requires C, 19.0; H, 4.8; Cl, 37.4; N, 7.4%. δ_{H} ($\mathrm{C_6D_6}$, 298 K): 2.43 (s, 2H, $\mathrm{NCH_3}$); −0.28 (s, 1H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 48.0 ($\mathrm{NCH_3}$), −3.15 ($\mathrm{SiCH_3}$).

$\mathrm{ZrCl_4[(NC_4H_8)_2SiMe_2]}$ (**11**, 90% yield, colourless solid). Found: C, 27.7; H, 5.0; Cl, 33.3; N, 6.8. $\mathrm{C_{10}H_{22}Cl_4N_2SiZr}$ requires C, 27.8; H, 5.1; Cl, 32.9; N, 6.5%. δ_{H} ($\mathrm{C_6D_6}$, 298 K): 3.39 (m, 2H, $\mathrm{N\mathit{CH_2}CH_2}$), 3.23 (m, 2H, $\mathrm{N\mathit{CH_2}CH_2}$), 1.28 (m, 2H, $\mathrm{NCH_2\mathit{CH_2}}$), 0.82 (m, 2H, $\mathrm{NCH_2\mathit{CH_2}}$), −0.18 (s, 3H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 57.3 ($\mathrm{N\mathit{C}H_2CH_2}$), 24.5 ($\mathrm{NCH_2\mathit{C}H_2}$), −3.0 ($\mathrm{SiCH_3}$).

$\mathrm{ZrCl_4[(NHEt)_2SiMe_2]}$ (**12**, 97% yield, colourless solid). Found: C, 19.1; H, 5.0; Cl, 37.2; N, 7.5. $\mathrm{C_6H_{18}Cl_4N_2SiZr}$ requires C, 19.0; H, 4.8; Cl, 37.4; N, 7.4%. δ_{H} ($\mathrm{C_6D_6}$, 298 K): 2.92 (br, 2H, $\mathrm{CH_2}$), 2.40 (br, 1H, NH), 0.49 (t, 3H, $\mathrm{CH_2\mathit{CH_3}}$, $^3J_{\mathrm{HH}}$ = 6.9 Hz), 0.03 (s, 3H, $\mathrm{SiCH_3}$). δ_{C} ($\mathrm{C_6D_6}$, 298 K): 42.5 ($\mathrm{CH_2}$), 17.5 ($\mathrm{CH_2\mathit{C}H_3}$), 5.0 ($\mathrm{SiCH_3}$).

ZrCl$_4$[(NH^{i}Pr)$_2$SiMe$_2$] (**13**, 90% yield, colourless solid). Found: C, 23.5; H, 5.4; Cl, 34.9; N, 7.2. $C_8H_{22}Cl_4N_2SiZr$ requires C, 23.6; H, 5.4; Cl, 34.8; N, 6.9%. δ_H (C_6D_6, 298 K): 3.05 (m, 2H, CH), 2.96 (m, 2H, CH), 2.48 (d, 2H, NH, $^3J_{HH}$ = 10.0 Hz), 2.14 (d, 2H, NH, $^3J_{HH}$ = 10.0 Hz), 1.23 (d, 12H, CH$_3$, $^3J_{HH}$ = 6.4 Hz), 1.21 (d, 12H, CH$_3$, $^3J_{HH}$ = 6.4 Hz), 0.45 (d, 12H, CH$_3$, $^3J_{HH}$ = 6.4 Hz), 0.38 (d, 12H, CH$_3$, $^3J_{HH}$ = 6.4 Hz), 0.10 (s, 3H, SiCH$_3$), 0.06 (s, 6H, SiCH$_3$), 0.05 (s, 3H, SiCH$_3$). δ_C (C_6D_6, 298 K): 49.6 (CH), 49.4 (CH), 25.9 (C*C*H$_3$), 25.8 (C*C*H$_3$), 25.7 (C*C*H$_3$), 3.9 (SiCH$_3$), 0.09 (SiCH$_3$), −4.1 (SiCH$_3$).

ZrCl$_4$[(NH^{t}Bu)$_2$SiMe$_2$] (**14**, 90% yield, colourless solid). Found: C, 27.5; H, 6.2; Cl, 32.8; N, 6.5. $C_{10}H_{26}Cl_4N_2SiZr$ requires C, 27.6; H, 6.0; Cl, 32.6; N, 6.4%. δ_H (C_6D_6, 298 K): 3.26 (br, 2H, NH), 1.16 (s, 18H, CCH$_3$), 0.54 (s, 3H, SiCH$_3$), −0.04 (s, 3H, SiCH$_3$). δ_C (C_6D_6, 298 K): 57.1 (C), 32.1 (C*C*H$_3$), 7.9 (SiCH$_3$), 0.3 (SiCH$_3$).

ZrCl$_4$[(NMeBu)$_2$SiMe$_2$] (**15**) (the solid is soluble in toluene, therefore the reaction mixture was evaporated and the residue suspended in pentane. Finally, the zirconium compound was filtered off and dried *in vacuo*; 72% yield, colourless solid). Found: C, 31.0; H, 6.4; Cl, 31.0; N, 6.1. $C_{12}H_{30}Cl_4N_2SiZr$ requires C, 31.1; H, 6.5; Cl, 30.6; N, 6.0%. δ_H (C_6D_6, 298 K): 3.33 (m, NCH$_2$), 3.32 (m, NCH$_2$), 3.28 (m, NCH$_2$), 3.10 (dt, NCH$_2$, $^3J_{HH}$ = 12.3 Hz, $^2J_{HH}$ = 3.7 Hz), 2.67 (s, NCH$_3$), 2.66 (s, NCH$_3$), 1.75 (m, NCH$_2$C*H*$_2$), 1.65 (m, NCH$_2$C*H*$_2$), 1.05 (m, C*H*$_2$CH$_3$), 1.01 (m, C*H*$_2$CH$_3$), 0.82 (t, CH$_2$C*H*$_3$, $^3J_{HH}$ = 7.3 Hz), 0.79 (t, CH$_2$C*H*$_3$ $^3J_{HH}$ = 7.3 Hz), 0.32 (s, SiCH$_3$), 0.16 (s, SiCH$_3$), 0.04 (s, SiCH$_3$). δ_C (C_6D_6, 298 K): 59.1 (NCH$_2$), 58.4 (NCH$_2$), 43.6 (NCH$_3$), 43.0 (NCH$_3$), 29.9 (NCH$_2$*C*H$_2$), 29.8 (NCH$_2$-*C*H$_2$), 20.8 (*C*H$_2$CH$_3$), 20.7 (*C*H$_2$CH$_3$), 14.1 (CH$_2$*C*H$_3$), 14.0 (CH$_2$*C*H$_3$), −0.64 (SiCH$_3$), −1.01 (SiCH$_3$), −1.19 (SiCH$_3$).

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