Mixed Amide Thiolate Complexes of Zinc with Low Coordination Number at the Metal Atom

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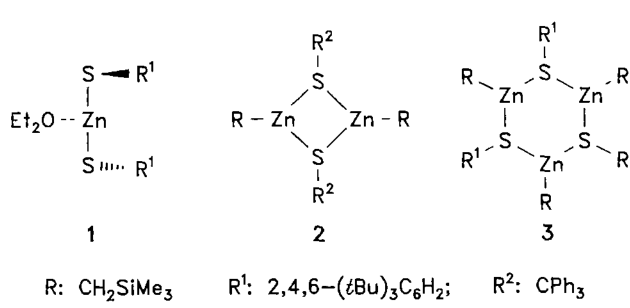
Three different thiophenoles 2,4,6-$(CF_3)_3C_6H_2SH$ (**4**), 2,4,6-$(i\mathrm{Pr})_3C_6H_2SH$ (**5**), and 2,6-$(Me_3Si)_2C_6H_3SH$ (**6**) with bulky substituents in *ortho* position were treated with $Zn[N(SiMe_3)_2]_2$ (**7**) in a non-coordinating solvent like CH_2Cl_2 or toluene to yield mixed amide thiolate zinc complexes $Zn_2[N(SiMe_3)_2]\{S[2,4,6\text{-}(CF)_3C_6H_2]\}_3$ (**8**), $Zn_3[N(SiMe_3)_2]_2\{S[2,4,6\text{-}(i\mathrm{Pr})_3C_6H_2]\}_4$ (**9**), and $Zn_2\{S[2,6\text{-}(Me_3Si)_2C_6H_3]\}_4$ (**10**), respectively. These compounds comprise low-coordinated zinc atoms. Initially, the reactions were performed in a 1:1 ratio of the reactants. However, in no reaction the expected $\{Zn[N(SiMe_3)_2](SR)\}_x$ ($x = 1,2,3...$) species were obtained but compounds which are richer in thiolate substituents ($SR/NR_2 > 1$) even if a large excess of amide **7** was used. Distinct from these, the reaction between **7** and 2,6-$(i\mathrm{Pr})_2C_6H_3OH$ (**14**) in a 1:1 ratio afforded indeed dimer $Zn_2[N(SiMe_3)_2]_2\{O[2,6\text{-}(i\mathrm{Pr})_2C_6H_3]\}_2$ (**15**). The molecular structures of **8**, **9**, **10**, and **15** in the crystal are elucidated by X-ray structural analyses and compared with proposed structures in solution based on multinuclear NMR experiments.

Apart from the biological significiance of zinc[1], recently the interest of various research groups focused on zinc compounds with low coordination numbers at the metal atoms[2]. On the one hand these compounds are of interest due to the bonding between the metal atom and the ligands attached to it. On the other hand the reactivity of such compounds with "unusual" coordination numbers at the zinc atoms might be elucidatory for the biochemistry and catalytic activity of zinc. Three species prepared recently in Powers laboratory[2a,b] are presented in Scheme 1 because they are relevant to this work.

Scheme 1



Pseudoaromaticity has been proposed for **3** by Power and his coworkers deduced from the flattened geometry of the heterocycle and the almost planar coordination of the sulfur atoms[2b].

We originally wanted to prepare "simple" sterically hindered $Zn[N(SiMe_3)_2](SR)$ compounds (or oligomers thereof) to use these as starting materials for the introduction of highly coordinatively unsaturated and Lewis-acidic reaction sites. In this paper we report on the failure of these efforts and the outcome of the performed experiments.

Preparation

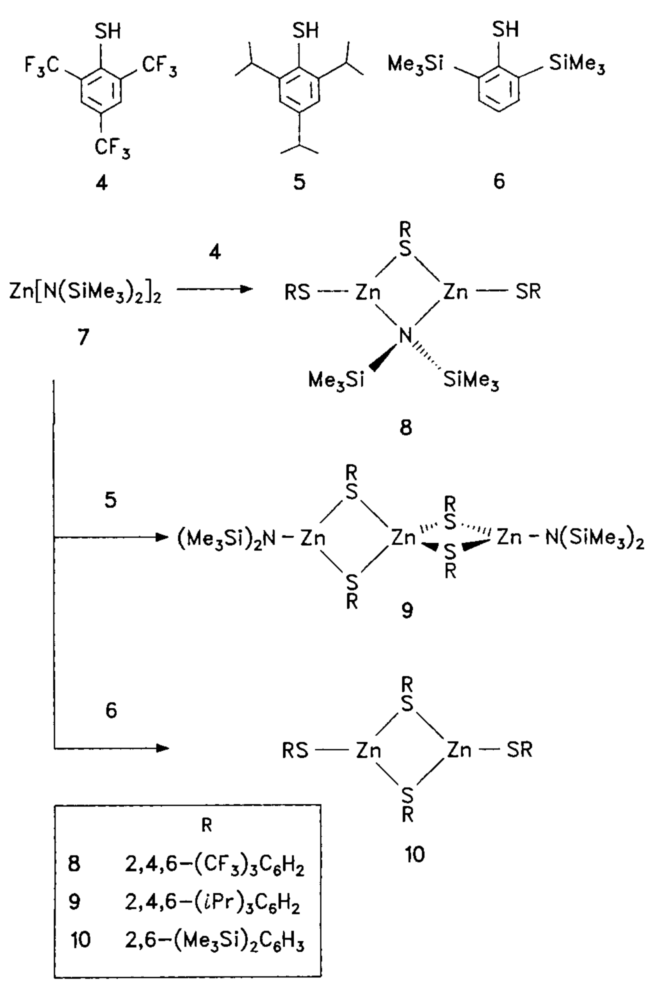
Three thiols **4**–**6**[3–5] with bulky substituents in *ortho* position were employed for our attempts to prepare a mixed amide thiolate zinc complex. Initially, they were treated with zinc bis[bis(trimethylsilyl)amide] (**7**)[6] in a non-coordinating solvent like dichloromethane or toluene at room temperature in a 1:1 ratio (Scheme 2).

Volatile components were pumped off, and the residue was crystallized from *n*-hexane. The ^1H-NMR spectra of the recrystallized materials showed signals which were already present in the curde reaction mixture. Thus, it is ascertained that no transformation of the products during the workup procedures occurred. In every experiment a signal in the ^1H-NMR spectrum of the reaction mixture at $\delta = 0.08$ was detected which corresponds to unreacted **7**. Thus it was clear that in no reaction the product contained the used and desired 1:1 ratio of the amide **7** and thiolate ligands from **4**–**6**. X-ray crystal structure determinations were performed in order to determine the structures of the obtained products **8**, **9**, and **10**. These may be prepared in good yields by using a stoichiometric ratio of the reactants and are moisture-sensitive colorless compounds.

Finally, we investigated the reaction of **7** with sterically congested 2,6-diisopropylphenol (**14**) (Scheme 3). In the obtained simple mixed amide aryloxide zinc complex **15** the employed ligand ratio 1:1 is found. The product again forms colorless highly moisture-sensitive crystals.

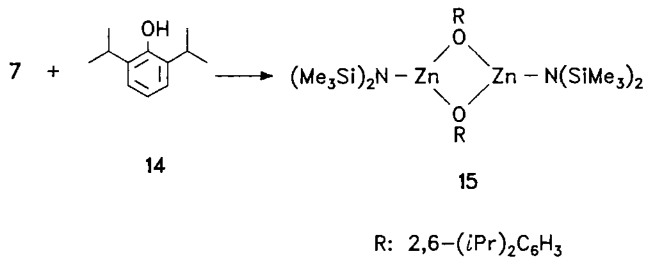
0009–2940/92/1010–2199 $ 3.50+.25/0

Scheme 2



	R
8	$2,4,6\text{-}(CF_3)_3C_6H_2$
9	$2,4,6\text{-}(iPr)_3C_6H_2$
10	$2,6\text{-}(Me_3Si)_2C_6H_3$

Scheme 3



Molecular Structures in the Crystal

The molecular structure of the product **8** obtained by the reaction of zinc amide **7** with thiol **4** is shown in Figure 1; selected bond lengths and angles are given in the figure caption.

Formally, the structure might be described as an adduct between $Zn[N(SiMe_3)_2](SR)$ and the thiolate $Zn(SR)_2$ [R = $2,4,6\text{-}(CF_3)_3C_6H_2$]. The central four-membered ring is not planar but folded by 31.5° about the Zn–Zn axis. In the solid state two of the thiolate groups are bound terminally while one thiolate and the amide group occupy bridging positions between the threefold coordinated zinc atoms. The Zn–N bonds are 2.005(7) Å long and correspond to Zn–N distances previously found in threefold coordinated zinc compounds[7]. The Zn–S distances within the heterocycle [Zn1–S1 2.349(3), Zn2–S1 2.413(3) Å] differ by 0.064 Å and are longer than the terminal Zn–S bonds. These are short [2.193(3) Å], likely caused by electrostatic attractions, and are comparable to the Zn–S bond length in the low-coordinated zinc thiolate **1**[2a]. From the bond angles C15–S2–Zn1 [103.0(2)°] and C24–S3–Zn2 [109.8(2)°] it is clear that the sulfur atoms of the terminal thiolate ligands have to be regarded as 2 e donors. A very acute Zn1–S1–Zn2 angle [75.2(1)°] is responsible for a relatively short Zn–Zn distance [2.907(2) Å].

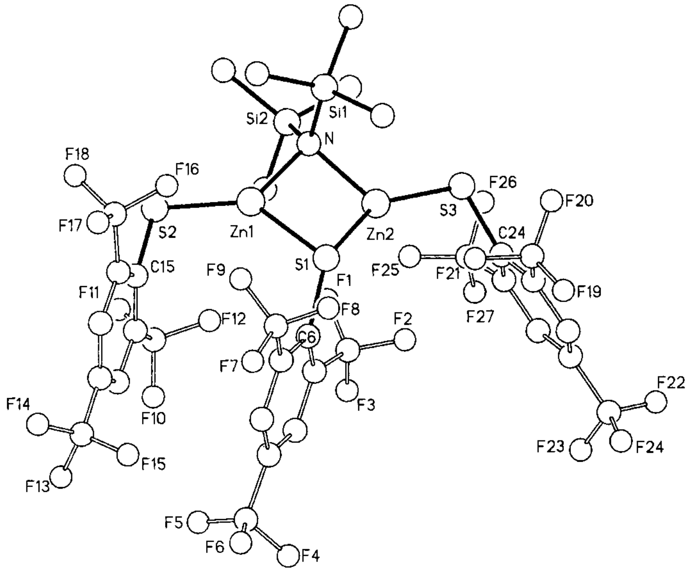


Figure 1. Molecular structure of **8**. Selected bond lengths [Å] and angles [°]: Zn1–Zn2 2.907(2), Zn1–S1 2.349(3), Zn1–S2 2.196(3), Zn1–N 1.993(7), Zn2–S1 2.413(3), Zn2–S3 2.191(3), Zn2–N 2.018(7), S1–C6 1.798(6), S2–C15 1.799(6), S3–C24 1.788(6), N–Si1 1.789(8), N–Si2 1.778(8); S1–Zn1–N 92.6(2), S2–Zn1–N 130.2(2), S2–Zn1–S1 137.0(1), Zn1–S1–Zn2 75.2(1), Zn1–S1–C6 110.5(2), Zn2–S1–C6 125.7(2), S3–Zn2–S1 144.6(1), S3–Zn2–N 122.3(2), N–Zn2–S1 90.1(2), Zn2–N–Zn1 92.9(3), Si2–N–S1 119.9(4), Si1–N–Zn2 107.4(4), Si1–N–Zn1 108.9(4), Si2–N–Zn1 110.1(4), Si2–N–Zn2 114.1(4), C15–S2–Zn1 103.0(2), C24–S3–Zn2 109.8(2)

An *intra*molecular van der Waals arene stacking[2a,2g] of the rings attached to S1 and S2 causes a considerable distortion of the bond angles at S1 [Zn–S1–C6 110.5(2) vs. Zn2–S1–C6 125.7(2)°]. The interplane angle between the almost congruent arranged aromatic rings is 8.5°. The distance d_1 between the centers of the rings at S2 and S1 is 4.142(2) Å and far beyond any electronic interaction of the disturbed aromatic systems[8]. Additionally, *inter*molecular stacking of arene ligands is observed in the crystal aligning molecules of **8** along the crystallographic z axis [d_2 = 4.234(2) Å] and y axis [d_3 = 4.245(2) Å].

The result of the X-ray analysis of the product **9** obtained in the reaction of zinc amide **7** with 2,4,6-tri(isopropyl)thiophenol **5** is shown in Figure 2; selected bond lengths and angles are listed in the figure caption.

In the solid state molecules of **9** possess a crystallographic twofold axis. They are built up by two $Zn[N(SiMe_3)_2](SR)$ units and one $Zn(SR)_2$ molecule [R = $2,4,6\text{-}(iPr)_3C_6H_2$]. Two almost planar Zn_2S_2 four-membered rings (max. deviation

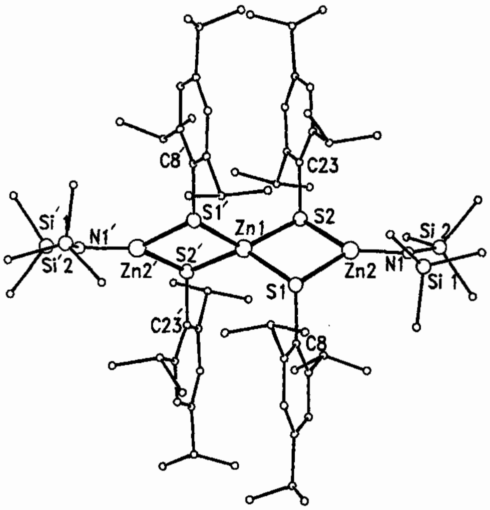


Figure 2. Molecular structure of **9**. Selected bond lengths [Å] and angles [°]: Zn1–Zn2 3.394(1), Zn1–Zn2′ 3.394(1), Zn1–S1 2.346(2), Zn1–S1′ 2.346(3), Zn1–S2 2.352(2), Zn1–S2′ 2.351(2), Zn2–S1 2.318(2), Zn2–S2 2.313(3), Zn2–N1 1.863(7), S1–C8 1.802(6), S2–C23 1.788(6), Si1–N1 1.717(8), Si2–N1 1.706(8); Zn2–Zn1–Zn2′ 172.0(1), Zn2–S1–Zn1 93.4(1), Zn2–S2–Zn1 93.4(1), S2–Zn1–S1 85.7(1), S2–Zn2–S1 87.3(1), S1′–Zn1–S2′ 85.7(1), Si1–N1–Zn2 114.2(4), Si2–N1–Zn2 118.7(4), Si2–N1–Si1 126.7(4), C8–S1–Zn1 124.4(2), C8–S1–Zn2 121.2(2), C23–S2–Zn1 119.8(2), C23–S2–Zn2 122.2(3), S1′–Zn1–S1 107.7(1), S2′–Zn1–S1 133.6(1), S2′–Zn1–S2 117.1(1), S1′–Zn1–S2 133.6(1)

0.036 Å) are interconnected by one common zinc atom. The central zinc atom adopts a severely distorted tetrahedral coordination geometry (interplane angle S1–Zn1–S2/S2′–Zn1–S1′ 69.8°). The $N(SiMe_3)_2$ substituents occupy terminal positions, the Zn–N bond distance being short as expected [Zn2–N1 1.863(3) Å][9]. The nearly planar bis(silyl)amide group [Σ °(N) 359.6°] is twisted by 28.8° against the S2–Zn2–S1 plane. All thiolates have bridging positions between the trigonal-planar zinc atoms Zn2, Zn2′ and tetrahedral Zn1 with an averaged Zn–S bond length [2.315(2) Å] a little shorter than the corresponding distances in **8**. The Zn2–Zn1–Zn2′ array deviates only slightly from linearity [172.0(1)°]; the Zn–Zn distance of 3.394(1) is considerably longer than in **8**. A comparable zinc complex with phenolate instead of thiophenolate ligands was recently described by Power et al.[2b] It is noteworthy that the aryl groups at the sulfur atoms S1, S1′, S2, S2′ are orientated towards each other and not – as one might expect for steric reasons – in a right- or left-handed propeller-like fashion (inversion at the sulfur atoms S1, S2 or S1′, S2′). Although speculative in character it might be assumed that again attractive van der Waals contacts contribute to the stability of **9** in the solid stated which dissociates in solution (vide infra). To some extent, the complexes **8** and **9** have characteristics of liver alcohol dehydrogenase (LADH)[1b,1c,10]. In this metallo enzyme two zinc atoms are located per subunit of which one is coordinated to four sulfur atoms of cysteine residues and has a structural function. The other metal atom – 20 Å away from the other one – is the catalytical active site and binds two sulfur atoms (cysteinate) and one nitrogen atom (histidine). The coordination sphere of this zinc atom is completed by a further loosely bound water molecule.

Independently of the used stoichiometry of reactants the sterically demanding thiophenol **6** reacts with zinc diamide **7** to yield the dimer **10** of $Zn(SR)_2$ exclusively [R = 2,6-$(Me_2Si)_2C_6H_3$]. The molecular structure of **10** is shown in Figure 3; selected bond lengths and angles are given in the figure caption.

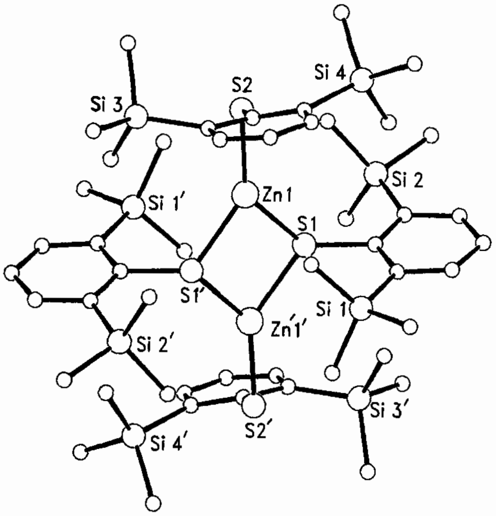


Figure 3. Molecular structure of **10**. Selected bond lengths [Å] and angles [°]: Zn1–Zn1′ 3.539(2), Zn1–S1 2.338(2), Zn1–S1′ 2.344(2), Zn1–S2 2.202(2), S1–C1 1.800(6), S2–C13 1.810(7); S1–Zn1–S1′ 81.8(1), S2–Zn1–S1 135.7(19, S2–Zn1–S1′ 141.4(1), Zn1–S1–Zn1′ 98.2(1), Zn1–S1–C1 123.4(2), Zn1′–S1–C1 126.8(2), Zn1–S2–C13 103.5(2)

The central four-membered Zn_2S_2 ring is centrosymmetric. The Zn–S distances in the heterocycle are 2.341(2) Å long on an average while the exocyclic bonds are shorter [Zn1–S2 2.202(2) Å] and comparable to the terminal Zn–S bonds in **1** and **8**. The Zn–Zn distance equals 3.539(2) Å and is the longest transannular distance reported in this work. Steric repulsions cause a distortion of the aromatic ring systems towards a boat conformation (Figure 4). This twist is strongest in the ring attached to the sulfur atom S2.

A comparison of **10** with the structure of the zinc alkanethiolate **2** is instructive. Because the difference in the steric demand of the substituents at the sulfur atoms (Ph_3C) and

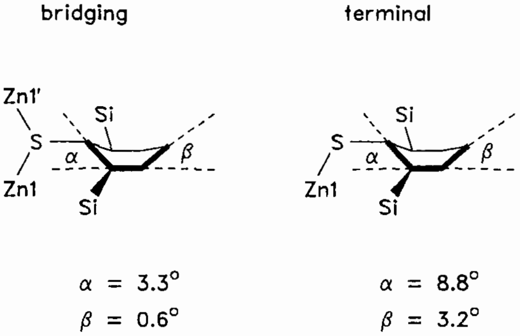


Figure 4. Deformation of the bridging and terminal arene ligands in **10**

the zinc atoms (CH_2SiMe_3) in **2** is very large (Ph_3C > CH_2SiMe_3) the Zn–S–Zn bond angle [83.2(1)°][2b] becomes smaller than the S–Zn–S angle [96.8(1)°]. The substituents at the sulfur atoms are identical in **10**. However, interference of the Me_3Si groups leads to a compression of the Zn_2S_2 cycle in **10** in a way that now the S–Zn–S angle [81.8(1)°] is more acute than the Zn–S–Zn angles [98.2(1)°]. Another consequence of the steric congestions is a much larger sum of bond angles at the bridging sulfur atoms in **10** [Σ°(S) 348.4°] – compared to **2** [Σ°(S) 285.6°] – which lie in the range of angle sums observed in the "pseudoaromatic" zinc sulfur heterocycles **3** [Σ°(S) 343.7 ± 5.2° to 356.3 ± 2.8°]. Thus, we suspect that the observed geometries in these "pseudoaromatics"[2b] are mainly caused by delicate steric effects and have no electronic origin leading to an extra stability of these six-membered heterocycles[11]. Zinc complex **15** was characterized by an X-ray diffraction analysis as well (Figure 5).

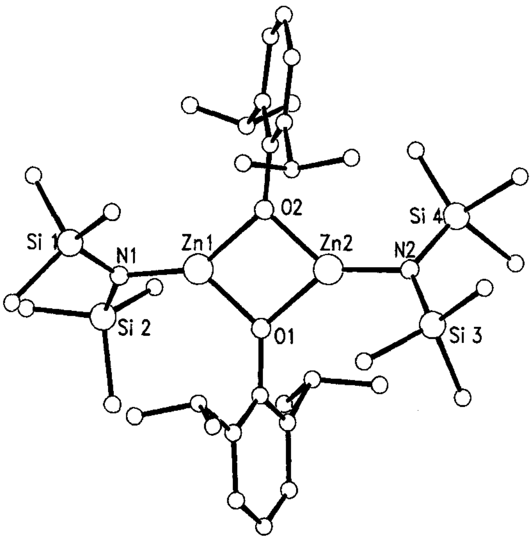


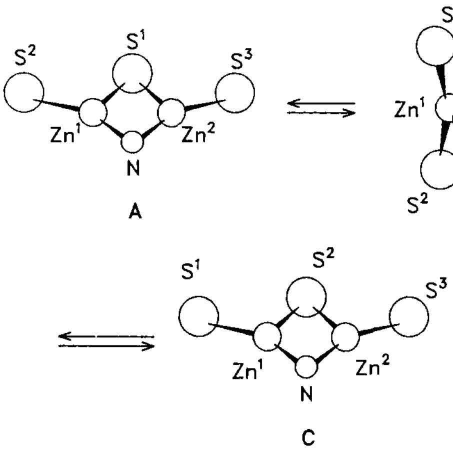
Figure 5. Molecular structure of **15**. Selected bond lengths [Å] and angles [°]: Zn1–Zn2 2.990(1), Zn1–O1 1.951(5), Zn1–O2 1.951(5), Zn1–N1 1.854(6), Zn2–O1 1.944(5), Zn2–O2 1.962(4), Zn2–N2 1.856(6), N1–Si1 1.717(7), N1–Si2 1.713(7), N2–Si3 1.720(7), N2–Si4 1.716(7), O1–C1 1.389(10), O2–C13 1.385(10); O1–Zn1–O2 80.0(2), O2–Zn1–N1 145.0(2), O1–Zn1–N1 134.9(2), O2–Zn2–O1 79.9(2), O1–Zn2–N2 139.6(2), O2–Zn2–N2 140.4(2), Zn1–O1–Zn2 100.3(2), Zn1–O2–Zn2 99.6(2), Zn1–O1–C1 132.6(4), Zn1–O2–C13 132.9(4), Zn2–O1–C1 126.9(4), Zn2–O2–C13 127.3(4), Zn1–N1–Si1 115.1(3), Zn1–N1–Si2 117.5(3), Si1–N1–Si2 127.3(3), Zn2–N2–Si3 117.4(3), Zn2–N2–Si4 117.2(4), Si3–N2–Si4 125.4(3)

It is a dimer of $Zn[N(SiMe_3)_2](OR)$ [R = 2,6-(iPr)$_2C_6H_3$] in the crystal with an almost planar four-membered Zn_2O_2 ring (fold angle 3.4° about the Zn–Zn axis). The Zn–N and Zn–O distances lie in the expected range for threefold coordinated zinc complexes [Zn–N 1.855(6), Zn–O 1.952(5) Å][2b,f,9].

NMR Investigations

Often the structure of metal thiolates in solution does not correspond to the structure observed in the crystal[1c,2a,12]. Indeed, the NMR spectra of **8** at ambient temperature do not correspond with the structure in the solid state but are temperature-dependent. In $CDCl_3$ solution at a temperature of 297 K only one signal is observed in the ^1H- or ^{19}F-NMR spectrum for the aryl groups in **8**. Lowering the temperature to 243 K leads to splitting of the signals, and the expeceted spectrum of **8** with different aryl protons in a 2:1 ratio is obtained. Coalescence is observed at about 278 K; from a line-shape analysis and an evaluation of data[13] according to the arrhenius equation an activation barrier E_A of 39(4.9) kJ mol^{-1} [ΔH^{+}(298) = 37(4.9) kJ mol^{-1}] is calculated. A relatively large and negative activation entropy points to solvation effects[14]. Taken the derived value ΔS^{+}(298) = −87(26) J mol^{-1} K^{-1} the entropy term $-T\Delta S^{+}$ comprises 41% [26(8) kJ mol^{-1}] of the calculated free energy of activation ΔG^{+} [63(12) kJ mol^{-1}] at 298 K. Interestingly, in CD_2Cl_2 in which **8** is less soluble the described temperature-dependent NMR phenomena cannot be observed. In the temperature range of 243–297 K only the signals of one aryl group are observed. Obviously, the dynamic process responsible for the equilibration of the thiolate substituents is not frozen out on the NMR time scale in this solvent which supports the argument that solvation plays an important role. In principle, two mechanisms are possible to explain this fluxional process: a) fragmention of **8** into $Zn(SR)_2$ and $Zn(SR)[N(SiMe_3)_2]$ which then recombine or b) cleavage of on Zn–S bond and intramolecular rotation around the Zn–N bond in intermediate **B** followed by ring closure (Scheme 4).

Scheme 4

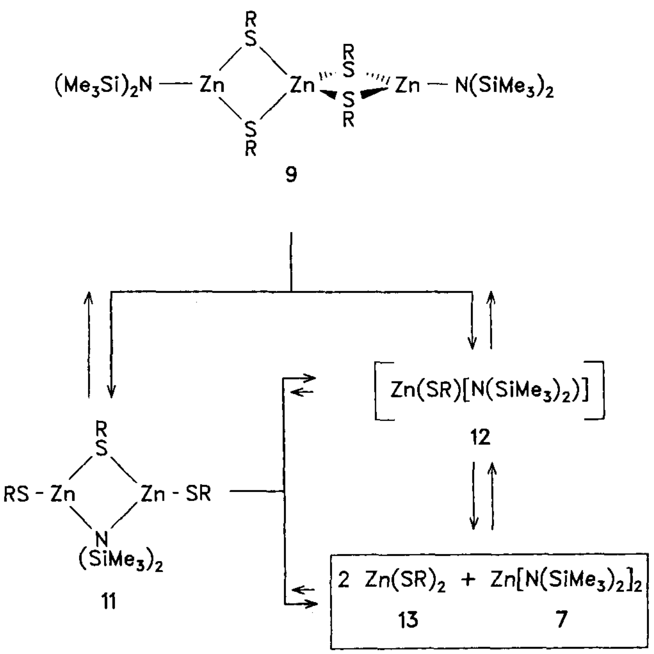


The phenomena observed are independent of the concentration of **8** in $CDCl_3$ (4.0 × 10^{-2} – 0.2 mol/l) and therefore we favor in accordance with the observed negative activation entropy the *intra*molecular equilibration path b. Cleavage of one Zn–S instead of one Zn–N bond – which cannot be excluded – is more likely because of the asymmetric Zn–S–Zn bridge with one longer and hence weakened Zn–S bond. Of diagnostic value are the signals of the Me_3Si protons in **8** (δ = 0.46; $CDCl_3$) which are significantly deshielded compared to the resonances of the ^1H nuclei in $Zn[N(SiMe_3)_2]_2$ (**7**) (δ = 0.08; $CDCl_3$). In an INEPT experiment the signal of the ^{29}Si nuclei of the bridging $(Me_3Si)_2N$

group (δ = 11.3; $CDCl_3$) is shifted to lower field as well (**7**: −0.06; $CDCl_3$).

The spirocyclic zinc complex **8** dissociates into various products in solution as indicated by NMR spectra recorded at variable temperatures. Plausible products of this dissociation process are shown in Scheme 5. On cooling the solution the complex **9** begins to crystallize again proving that the dissociation of **9** is a reversible process.

Scheme 5



In Figure 6 a ^{29}Si INEPT spectrum of **9** recorded at a temperature of 238 K is shown along with a solid-state ^{29}Si CP/MAS spectrum of **9** (Figure 6, insertion above). In the solid-state spectrum two peaks at δ = −0.5 and −2.1 are observed in the range expected for terminal $N(SiMe_3)_2$ groups which correspond to the rigid and inequivalent $SiMe_3$ groups of **9** in the crystal (Figure 2). Furthermore, it undoubtedly proves the homogeneity of the sample in the solid state. The averaged value of δ = −1.3 is in reasonable accord with the value of the signal at δ = −1.1 in the solution NMR spectrum which therefore is attributed to **9** (marked with a triangle ▲, Figure 6). The signal at δ = 0.2 belongs to **7** ascertained by adding a small portion of **7** to the reaction mixture (marked with a square ■, Figure 6). The third signal at δ = 7.7 (marked with a circle ○) is typical of a bridging $N(SiMe_3)_2$ and is tentatively assigned to **11** based on a comparison with spectral data of **8**. A small invariant peak at δ = 3.1 (ref.[15] δ = 2.2) can be assigned to $HN(SiMe_3)_2$ which is an inevitable impurity due to hydrolysis of **9**. A plot of the relative intensity ratios N of **9**, **7** and **11** (calculated from the integral intensities) versus temperature is shown at the bottom frame of Figure 6.

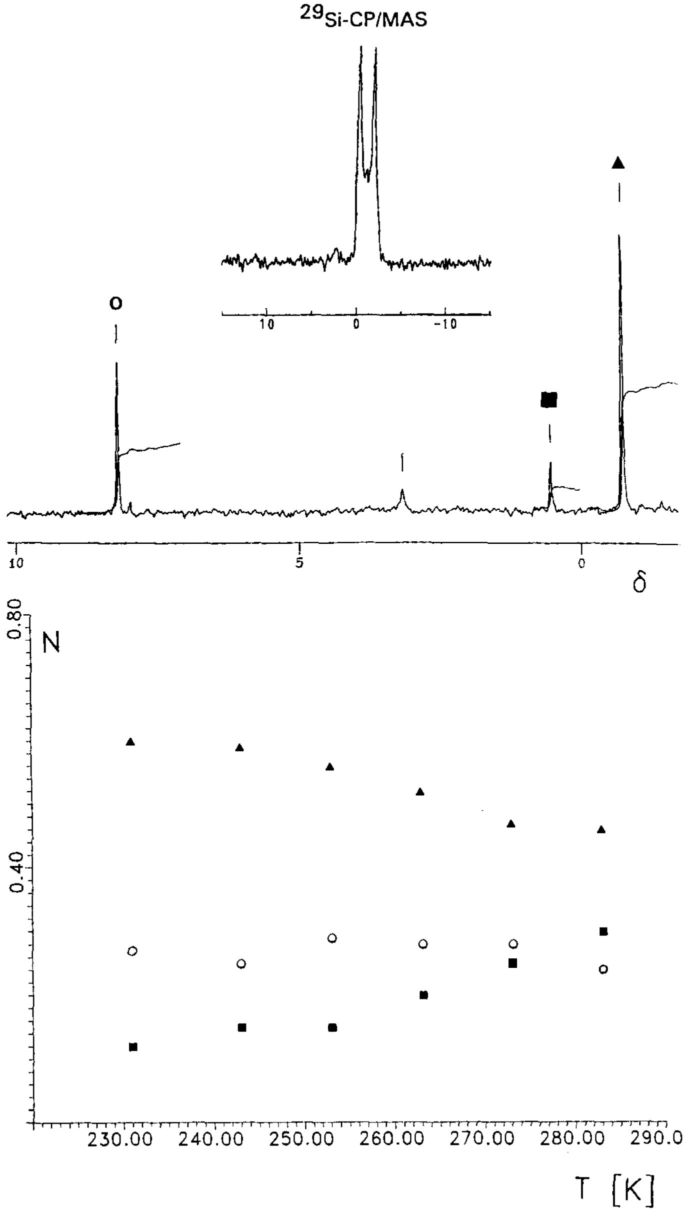


Figure 6. Insertion above: ^{29}Si-CP/MAS spectrum of **9**; δ = −0.52, −2.15. top frame: ^{29}Si-NMR (INEPT) spectrum of **9** in CD_2Cl_2 solution at 238 K. ▲ (**9**): δ = −1.11; ■ (**7**): δ = 0.21; ○ (**11**): δ = 7.73. bottom frame: Intensity $N_i = I_i/\Sigma I$ (I = integral; i = **9**, **7**, **11**) versus temperature (K). The small signal at δ = 3.14 corresponds to $HN(SiMe_3)_2$ and is due to hydrolysis of **9**. It is constant in intensity over the temperature range

The intensity of the signal at δ = −1.1 (▲) assigned to non-dissociated **9** decreases as expected with increasing temperature. At the same time the intensity of the signal (■) belonging to zinc bis(silylamide) **7** increases. Over the temperature range (238−300 K) studied the signal at δ = 7.7 attributed to **11** (○) remains relatively constant in intensity. Note that the same information can be drawn from the signals of the Me_3Si groups in the temperature-dependent ^{1}H-NMR spectra[16]. Above 300 K no signal in the ^{29}Si-INEPT spectrum can be recorded but a very simple ^{1}H spectrum is obtained showing only singnals for one 2,4,6-$(i\text{Pr})_3C_6H_2$ group. Obviously, apart from dissociation and intramolecular fluxionality additional *intermolecular exchange* processes have to be taken into account which become rapid on the NMR time scale. Unfortunately, we could not prepare pure $Zn(SR)_2$ (**13**) [R = 2,4,6-$(i\text{Pr})_3C_6H_2$]. In the ^1H-NMR spectrum complex **10** shows only signals for one aryl ligand in the temperature range between 203 – 293 K. In accordance with previous reports[2a,12a] monomeric $Zn(SR)_2$ species are highly likely to exist in solution.

Concluding Remarks

Bulky thiols were treated with zinc bis[bis(trimethylsilyl)-amide] (**7**) in a 1:1 ratio in a non-coordinating solvent to obtain simple compounds of the $\{Zn[N(SiMe_3)_2](SR)\}_x$ (x = 1,2,3..) with low coordination number at the metal atom. In no reaction described here we could observe a zinc complex in which the used amide/thiolate ratio is reflected in the product. Even if a large excess of **7** was used only the described products **8**, **9**, and **10** formed in which the $(Me_3Si)_2N$/SR ratio is smaller than one. In solution these thiolate-enriched zinc complexes are obviously the thermodynamically more favored products (self-organization[17]). The exact composition and the structure of the obtained products **8** – **10** in the solid state is determined by the group occupying the *ortho* position of the thiophenolate substituent. In contrast to the observations described in this paper Power et al. could isolate mixed zinc alkanethiolate compounds from the reaction of $Zn(CH_2SiMe_3)_2$ with HSR in which the found ratio agreed with the used ratio of ligands[2a,b].

One possible (speculative) explanation for the failure to prepare $\{Zn[N(SiMe_3)_2](SR)\}_x$ (x = 1,2,3..) compounds could be the difference in the ability of the used ligands to occupy bridging postions in mixed oligomeric aggregates of ZnR′(XR) [R′ = alkyl, amide; XR = alkoxide or phenolate (X = O), thiolate (X = S)]. This difference is large in the case R = CH_2SiMe_3 < SR or R = $N(SiMe_3)_2$ < OR but is – according to the presented experiments – much less pronounced in the case R = $N(SiMe_3)_2 \approx$ SR. When medium-sized thiophenols are employed in reactions with **7**, aggregates of $\{Zn[N(SiMe_3)_2](SR)\}_x$ – most likely dimers (x = 2) – may form first in solution. These are probably more fluxional (compare **8**) than zinc alkanethiolates (e.g. **1** – **3**) or zinc amide phenolates (e.g. **15**). In the course of a dynamic process intermediates like **B** in Scheme 4 with low-coordinated zinc centers will emerge. Alternatively, a high content of monomers like $Zn[N(SiMe_3)_2](SR)$ with coordinatively highly unsaturated zinc centers will be formed first in solution when **7** is treated with bulky thiols like **6**. In both cases it is reasonable to assume that further substitution of amide for thiolate groups is kinetically favored. This hypothesis would explain the formation of **8** and **9** via $\{Zn[N(SiMe_3)_2](SR)\}_2$ and the exclusive formation of **10** from $Zn[N(SiMe_3)_2](SR)$ [R = 2,4,6-$(CF_3)_3C_6H_2$, 2,4,6-$(i\text{Pr})_3C_6H_2$, 2,6-$(Me_3Si)_2C_6H_3$, respectively].

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Experimental

The thiophenols **4**, **5**, **6**[3–5] and zinc bis[bis(trimethylsilyl)amide] (**7**)[6] were prepared according to literature methods, 2,6-diisopropylphenol (**14**) was purchased by ALDRICH-Chemie GmbH & Co. KG. All solvents were carefully dried and freshly distilled under nitrogen. All operations were carried out in flame-dried glassware under dry nitrogen or argon by using a modified Schlenk technique. – Equipment: ^{19}F, ^1H, ^{13}C, ^{29}Si NMR: Jeol FX-90 Q, Bruker AC 200 with $CFCl_3$ and Me_4Si as internal standards. – Melting points: sealed capillaries, uncorrected.

General Procedure for the Preparation of Zinc Complexes **8**, **9**, **10**, *and* **15**: **8**, **9**, and **10** are formed in CH_2Cl_2 or toluene solution when **7** is treated with the thiophenolates **4** – **6** in a 1:1 ratio or

Table 1. Crystallographic data for compounds **8**, **9**, **10**, and **15** and data collection procedures

	8	**9**	**10**	**15**
Formula	$C_{33}H_{24}F_{27}NS_3Si_2Zn_2$	$C_{72}H_{128}N_2S_4Si_4Zn_3$	$C_{48}H_{84}S_4Si_8Zn_2$	$C_{36}H_{70}N_2O_2Si_4Zn_2$
Formula weight	1230.5	1458.5	1144.9	806.1
Crystal system	triclinic	monoclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$Pbca$
a [Å]	9.150(4)	18.782(19)	10.843(10)	16.988(9)
b [Å]	13.443(6)	41.71(4)	13.259(13)	21.389(11)
c [Å]	20.467(8)	14.335(16)	13.429(13)	25.792(13)
α [°]	86.52(3)	90.0	106.67(8)	90.0
β [°]	81.58(3)	128.28(6)	113.06(7)	90.0
γ [°]	79.89(3)	90.0	97.06(8)	90.0
Volume [$Å^3$]	2450	8815	1640	9372
Z	2	4	1	8
d_{calc} [g cm^{-3}]	1.67	1.10	1.16	1.14
μ(Mo-K_α) [cm^{-1}]	12.1	9.4	9.8	11.0
Crystal size [mm]	0.2 · 0.3 · 0.5	0.3 · 0.4 · 0.6	0.2 · 0.4 · 0.4	0.4 · 0.5 · 0.6
Transmission	0.77 – 1.00	0.81 – 1.00	0.68 – 1.00	0.93 – 1.00
$2\Theta_{max}$ [°]	45	46	50	50
hkl range	±9, ±14, 21	±16, 39, 15	±12, ±16, 16	20, 25, 30
Reflections measured	6011	5825	5974	9029
observed ($I > 2\sigma_I$)	4533	2639	3127	4218
No. of variables	470	368	321	434
R	0.066	0.057	0.064	0.066
R_w	0.062	0.060	0.055	0.062
Residual electron density [e $Å^{-3}$]	–0.9, 1.0	–0.3, 0.3	–0.4, 0.5	–0.3, 0.5

Table 2. Atomic coordinates and equivalent isotropic displacement factors $\bar{U}$ [Å^2] for compound **8**. $\bar{U}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$\bar{U}$
Zn1	0.60781(14)	0.21610(8)	0.34095(5)	0.043
Zn2	0.73560(13)	0.12585(8)	0.21530(5)	0.039
S1	0.5183(3)	0.25529(17)	0.23901(12)	0.039
S2	0.6016(4)	0.2934(2)	0.43302(13)	0.063
S3	0.8742(3)	0.0322(2)	0.13782(13)	0.052
Si1	0.5928(4)	-0.0080(2)	0.32464(15)	0.054
Si2	0.8929(4)	0.0542(2)	0.34318(15)	0.055
N	0.7186(8)	0.0814(5)	0.3117(3)	0.037
C1	0.6361(5)	0.4300(4)	0.1929(3)	0.039
C2	0.6241(5)	0.5345(4)	0.1827(3)	0.046
C3	0.4855(5)	0.5968(4)	0.1974(3)	0.044
C4	0.3589(5)	0.5546(4)	0.2224(3)	0.047
C5	0.3709(5)	0.4502(4)	0.2327(3)	0.037
C6	0.5095(5)	0.3878(4)	0.2179(3)	0.036
C7	0.7840(12)	0.3671(8)	0.1700(6)	0.051
C8	0.4770(14)	0.7123(9)	0.1878(6)	0.065
C9	0.2274(12)	0.4093(9)	0.2556(6)	0.056
C10	0.5586(5)	0.4958(5)	0.3914(3)	0.051
C11	0.4724(5)	0.5912(5)	0.3840(3)	0.051
C12	0.3179(5)	0.6057(5)	0.4039(3)	0.048
C13	0.2497(5)	0.5248(5)	0.4311(3)	0.055
C14	0.3359(5)	0.4294(5)	0.4385(3)	0.052
C15	0.4904(5)	0.4149(5)	0.4186(3)	0.046
C16	0.7222(14)	0.4886(10)	0.3679(6)	0.067
C17	0.2207(15)	0.7089(9)	0.3942(7)	0.075
C18	0.2531(17)	0.3482(9)	0.4718(7)	0.072
C19	0.8045(5)	0.1304(5)	0.0201(3)	0.038
C20	0.8399(5)	0.1821(5)	-0.0397(3)	0.051
C21	0.9801(5)	0.2115(5)	-0.0553(3)	0.049
C22	1.0849(5)	0.1891(5)	-0.0112(3)	0.053
C23	1.0495(5)	0.1374(5)	0.0486(3)	0.048
C24	0.9093(5)	0.1080(5)	0.0642(3)	0.040
C25	0.6494(12)	0.1025(11)	0.0343(6)	0.061
C26	1.0178(17)	0.2688(11)	-0.1218(7)	0.085
C27	1.1632(14)	0.1212(12)	0.0958(7)	0.079
C28	0.4557(16)	0.0246(11)	0.3990(6)	0.124
C29	0.4859(13)	0.0004(8)	0.2534(6)	0.068
C30	0.6879(14)	-0.1389(8)	0.3335(6)	0.085
C31	0.8607(15)	0.0211(10)	0.4324(6)	0.092
C32	1.0257(13)	-0.0486(8)	0.2973(6)	0.084
C33	0.9854(12)	0.1674(8)	0.3317(6)	0.070
C34	0.187	0.442	0.036	0.099
C35	0.343	0.436	0.028	0.106
C36	0.434	0.499	0.008	0.096
F1	0.8390(6)	0.3016(4)	0.2156(3)	0.059
F2	0.7751(7)	0.3121(4)	0.1184(3)	0.069
F3	0.8901(7)	0.4236(5)	0.1502(4)	0.082
F4	0.5596(14)	0.7337(9)	0.1278(6)	0.076
F5	0.5320(14)	0.7464(9)	0.2336(6)	0.071
F6	0.3399(14)	0.7582(9)	0.1822(6)	0.076
F4X	0.472(2)	0.7400(12)	0.1304(9)	0.066
F5X	0.593(2)	0.7411(13)	0.2110(9)	0.066
F6X	0.3425(19)	0.7595(12)	0.2228(9)	0.066
F7	0.1076(7)	0.4855(5)	0.2617(4)	0.092
F8	0.1995(7)	0.3473(5)	0.2131(3)	0.069
F9	0.2276(7)	0.3618(5)	0.3144(3)	0.069
F10	0.7579(8)	0.5742(5)	0.3398(4)	0.087
F11	0.8052(7)	0.4614(5)	0.4169(3)	0.079
F12	0.7707(7)	0.4179(5)	0.3219(3)	0.077
F13	0.3013(13)	0.7838(9)	0.3932(6)	0.072
F14	0.1108(15)	0.7301(11)	0.4431(7)	0.092
F15	0.1630(17)	0.7113(10)	0.3391(7)	0.097
F13X	0.291(2)	0.7669(14)	0.3545(11)	0.083
F14X	0.166(2)	0.7459(16)	0.4536(11)	0.083
F15X	0.098(2)	0.6976(14)	0.3655(10)	0.083
F16	0.2701(8)	0.2679(5)	0.4341(3)	0.086
F17	0.1071(9)	0.3800(5)	0.4847(4)	0.101
F18	0.3023(9)	0.3136(5)	0.5297(3)	0.085
F19	0.5682(7)	0.1379(6)	-0.0136(3)	0.080
F20	0.6508(7)	0.0046(5)	0.0422(3)	0.075
F21	0.5759(6)	0.1497(5)	0.0901(3)	0.066
F22	1.1000(18)	0.2162(11)	-0.1635(7)	0.108
F23	1.0904(16)	0.3418(10)	-0.1126(7)	0.108
F24	0.8970(16)	0.3107(12)	-0.1473(7)	0.108
F22X	0.962(3)	0.2318(17)	-0.1709(10)	0.108
F23X	1.179(2)	0.2369(16)	-0.1417(10)	0.108
F24X	0.941(2)	0.3631(16)	-0.1199(10)	0.108
F25	1.1111(7)	0.1633(5)	0.1538(3)	0.082
F26	1.2133(7)	0.0240(7)	0.1071(3)	0.091
F27	1.2836(8)	0.1638(7)	0.0705(4)	0.109

even when a large excess of **7** is employed. However, for a rational synthesis of **8**–**10** an almost stoichiometric ratio of the reactants is used. Because of convenience CH_2Cl_2 was used as solvent in all reactions described in the following. Generally, to $Zn[N(SiMe_3)_2]_2$ (**7**) in 20 ml of CH_2Cl_2 the calculated quantity of thiophenols **4**–**6** or phenol **14** was added slowly at room temp. by using a syringe. The solvent was removed in vacuo and the residue crystallized from small quantities of *n*-hexane at the temperatures given below.

Table 3. Atomic coordinates and equivalent isotropic displacement factors $\bar{U}$ [Å^2] for compound **9**. $\bar{U}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$\bar{U}$
Zn1	0.500	0.36624(4)	0.250	0.059
Zn2	0.30793(7)	0.37188(3)	0.22358(9)	0.064
S1	0.37161(16)	0.39941(6)	0.1510(2)	0.064
S2	0.42908(16)	0.33682(6)	0.3118(2)	0.064
Si1	0.1708(2)	0.42003(8)	0.1796(3)	0.087
Si2	0.1438(2)	0.34908(9)	0.2044(3)	0.099
N1	0.2031(5)	0.38046(18)	0.2067(6)	0.071
C2	0.1173(7)	0.4313(2)	0.0232(9)	0.114
C3	0.2716(7)	0.4461(2)	0.2788(10)	0.123
C4	0.0880(8)	0.4303(3)	0.2076(10)	0.139
C5	0.0267(7)	0.3465(3)	0.0602(9)	0.143
C6	0.1330(8)	0.3513(3)	0.3260(10)	0.152
C7	0.2035(8)	0.3118(3)	0.2270(11)	0.152
C8	0.3047(4)	0.4103(2)	-0.0037(5)	0.062
C9	0.3157(4)	0.4410(2)	-0.0318(5)	0.070
C10	0.2671(4)	0.4501(2)	-0.1504(5)	0.090
C11	0.2076(4)	0.4286(2)	-0.2409(5)	0.095
C12	0.1966(4)	0.3979(2)	-0.2128(5)	0.090
C13	0.2452(4)	0.3887(2)	-0.0942(5)	0.074
C14	0.3795(9)	0.4650(3)	0.0659(11)	0.103
C15	0.4523(9)	0.4766(3)	0.0619(11)	0.176
C16	0.3264(10)	0.4937(3)	0.0585(13)	0.196
C17	0.1559(11)	0.4377(4)	-0.3727(11)	0.140
C18	0.2107(11)	0.4275(4)	-0.4091(11)	0.197
C19	0.1264(10)	0.4705(3)	-0.4006(10)	0.221
C20	0.2279(9)	0.3553(3)	-0.0699(10)	0.100
C21	0.1321(9)	0.3497(3)	-0.1226(14)	0.184
C22	0.2553(11)	0.3301(3)	-0.1103(19)	0.288
C23	0.4928(4)	0.3248(2)	0.4637(5)	0.070
C24	0.5272(4)	0.2937(2)	0.4931(5)	0.085
C25	0.5813(4)	0.2836(2)	0.6112(5)	0.115
C26	0.6010(4)	0.3047(2)	0.7000(5)	0.124
C27	0.5667(4)	0.3358(2)	0.6707(5)	0.107
C28	0.5126(4)	0.3459(2)	0.5525(5)	0.075
C29	0.5055(10)	0.2689(3)	0.3992(10)	0.111
C30	0.5894(10)	0.2523(3)	0.4331(11)	0.188
C31	0.4374(12)	0.2454(4)	0.3758(13)	0.236
C32	0.6674(12)	0.2944(6)	0.8359(17)	0.194
C33	0.6281(14)	0.2794(5)	0.8734(16)	0.316
C34	0.7569(13)	0.2971(5)	0.8824(14)	0.295
C35	0.4753(8)	0.3799(3)	0.5285(9)	0.090
C36	0.3999(7)	0.3821(3)	0.5377(9)	0.128
C37	0.5503(9)	0.4045(3)	0.6149(12)	0.155

$Zn_2[N(SiMe_3)_2]\{S[2,4,6\text{-}(CF)_3C_6H_2]\}_3$ (**8**): Addition of 1.22 g of **4** (3.9 mmol) to 1 g of **7** (2.6 mmol) and stirring of the clear solution for 10 min afforded **8** (1.34 g, 84%) as colorless crystals after recrystallization at 0°C. M.p. 153–157°C (*n*-hexane). – ^1H NMR ($CDCl_3$, 297 K): δ = 0.46 [s, 3H, $Si(CH_3)_3$], 7.84 (s, 1H, aromat. H). – ^{13}C NMR ($CDCl_3$, 297 K): δ = 4.74 [$Si(CH_3)_3$], 122.5 [q, $^1J(^{13}C^{19}F)$ = 271.7 Hz, CF_3], 126.61 (aromat. C-3/5), 128.05 [very broad ($\nu_{1/2} \approx$ 880 Hz), aromat. C-4], 136.93 (broad, aromat. C-2/6), 142.14 (broad, aromat. C1–S), the signal for 4-CF_3 was not detected. – ^{29}Si NMR (INEPT, $CDCl_3$, 297 K): δ = 11.33 [Si-

$(CH_3)_3]$. – ^{19}F NMR ($CDCl_3$, 297 K): δ = −63.94 (s, 9F, 4-CF_3), −61.28 (s, 18F, 2-CF_3).

$C_{33}H_{24}F_{27}NS_3Si_2Zn_2$ (1230.5) Calcd. C 32.21 H 1.96 N 1.14
Found C 32.28 H 2.01 N 0.98

$Zn_3[N(SiMe_3)_2]_2\{S[2,4,6-(iPr)_3C_6H_2]\}_4$ (**9**): Addition of 0.82 g of **5** (3.47 mmol) to 1 g of **7** (2.6 mmol) and stirring of the clear solution for 2 h afforded **9** (1.08 g, 91%) as colorless crystals after recrystallization at −30°C. M.p. 166–171°C (*n*-hexane). – ^1H NMR ($CDCl_3$, 297 K): δ = −0.22 [s, broad, $Si(CH_3)_3$], 0.08 [s, broad, $Si(CH_3)_3$], 0.32 [s, broad, $Si(CH_3)_3$], 0.97 [d, broad, 4-$CH(CH_3)_2$], 1.11 [d, broad, 2-$CH(CH_3)_2$], 2.56–2.99 [m, 4-$CH(CH_3)_2$], 3.43–3.92 [m, 2-$CH(CH_3)_2$], 6.75 (s, aromat. H). – ^{13}C NMR ($CDCl_3$, 297 K): δ = 2.49 [$Si(CH_3)_3$], 4.69 [$Si(CH_3)_3$], 23.54 [$CH(CH_3)_2$], 23.98 [$CH(CH_3)_2$], 32.56 [$CH(CH_3)_2$], 34.09 ($CH(CH_3)_2$), 121.62 (broad, aromat. C-1/3), 147.68 (aromat. C-4), 150.37 (aromat. C-2). – ^{29}Si NMR (INEPT, $CDCl_3$, 231 K): δ = −1.11 [$Si(CH_3)_3$, 60.2%], 0.21 [$Si(CH_3)_3$, 12.3%], 7.73 [$Si(CH_3)_3$, 27.5%].

$C_{72}H_{128}N_2S_4Si_4Zn_3$ (1458.5)
Calcd. C 59.29 H 8.85 N 1.92 S 8.79
Found C 59.13 H 8.74 N 1.99 S 8.70

$Zn_2\{S[2,6-(Me_3Si)_2C_6H_3]\}_4$ (**10**): Addition of 1.32 g of **6** (5.20 mmol) to 1 g of **7** (2.6 mmol) and stirring of the clear solution for 2 h afforded **10** as colorless crystals (0.89 g, 60%) after recrystallization at −30°C. M.p. 169–174°C (*n*-hexane). – ^1H NMR ($CDCl_3$, 297 K): δ = 0.24 [s, 18H, $Si(CH_3)_3$], 7.17 [t, ^3J = 7.32 Hz, 1H, aromat. 4-H), 7.37 (d, ^3J = 7.32 Hz, 2H, aromat. 3/5-H). – ^{13}C NMR ($CDCl_3$, 297 K): δ = 1.28 [$Si(CH_3)_3$], 125.62 (aromat. C-4), 136.45 (aromat. C-3/5), 144.92 (aromat. C-2/6), 145.55 (aromat. C-1). – ^{29}Si NMR (INEPT, $CDCl_3$, 297 K): δ = −4.46 [$Si(CH_3)_3$].

$C_{48}H_{84}S_4Si_8Zn_2$ (1144.9) Calcd. C 50.35 H 7.39
Found C 50.38 H 7.41

Table 4. Atomic coordinates and equivalent isotropic displacement factors $\bar{U}$ [Å²] for compond **10**. $\bar{U}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$\bar{U}$
Zn1	0.40137(9)	0.91697(7)	0.03961(7)	0.053
S1	0.37010(17)	0.97836(14)	-0.11317(15)	0.052
S2	0.26396(19)	0.83176(14)	0.09189(16)	0.057
Si1	0.4437(2)	0.75505(18)	-0.26729(19)	0.067
Si2	0.0741(2)	1.04046(19)	-0.22813(19)	0.067
Si3	0.4972(2)	0.77685(19)	0.3121(2)	0.072
Si4	0.0280(3)	0.61680(19)	-0.1463(2)	0.080
C1	0.2533(7)	0.8972(6)	-0.2631(5)	0.048
C2	0.2874(7)	0.8081(6)	-0.3245(6)	0.052
C3	0.1905(9)	0.7525(6)	-0.4405(7)	0.071
C4	0.0710(9)	0.7818(7)	-0.4908(7)	0.078
C5	0.0404(8)	0.8673(7)	-0.4272(7)	0.069
C6	0.1287(7)	0.9279(6)	-0.3096(6)	0.053
C7	0.4186(11)	0.6244(7)	-0.3807(8)	0.114
C8	0.4625(10)	0.7247(8)	-0.1365(8)	0.100
C9	0.6047(9)	0.8487(7)	-0.2390(9)	0.104
C10	-0.1074(9)	1.0305(9)	-0.3253(8)	0.117
C11	0.0681(11)	1.0226(9)	-0.0984(8)	0.110
C12	0.1842(10)	1.1784(6)	-0.1888(9)	0.106
C13	0.2950(8)	0.6977(5)	0.0660(7)	0.054
C14	0.4056(8)	0.6841(6)	0.1553(7)	0.062
C15	0.4322(9)	0.5799(8)	0.1250(9)	0.088
C16	0.3521(11)	0.4996(8)	0.0195(11)	0.100
C17	0.2371(10)	0.5132(7)	-0.0604(8)	0.087
C18	0.2002(8)	0.6129(6)	-0.0405(7)	0.063
C19	0.5931(10)	0.9162(7)	0.3437(7)	0.105
C20	0.6263(11)	0.7140(9)	0.3958(9)	0.124
C21	0.3663(12)	0.7834(9)	0.3682(8)	0.110
C22	-0.0703(13)	0.4761(9)	-0.2488(12)	0.218
C23	-0.0780(11)	0.6605(12)	-0.0690(10)	0.159
C24	0.0366(12)	0.7047(11)	-0.2272(9)	0.153

$Zn_2[N(SiMe_3)_2]_2\{O[2,6-(iPr)_2C_6H_3]\}_2$ (**15**): Addition of 0.46 g of **14** (2.6 mmol) to 1 g of **7** (2.6 mmol) and stirring of the solution for 24 h afforded **12** as colorless crystals (0.42 g, 40%) after recrystallization at −80°C. M.p. 131–137°C (dec.). – ^1H NMR ($CDCl_3$, 297 K): δ = −0.13 [s, 9H, $Si(CH_3)_3$], 1.37 [d, ^3J = 6.82 Hz, 12H, $CH(CH_3)_2$], 3.45 [sept., ^3J = 6.82 Hz, 2H, $CH(CH_3)_2$], 7.01 [t, ^3J = 8.53 Hz, 1H, aromat. 4-H], 7.13 [d, ^3J = 8.53 Hz, 2H, aromat. 3/5-H]. – ^{13}C NMR ($CDCl_3$, 297 K): δ = 4.74 [$Si(CH_3)_3$], 24.16 [$CH(CH_3)_2$], 27.25 [$CH(CH_3)_2$], 122.09 (aromat. C-4), 123.99 (aro-

Table 5. Atomic coordinates and equivalent isotropic displacement factors $\bar{U}$ [Å²] for compound **15**. $\bar{U}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$\bar{U}$
Zn1	0.55324(5)	0.20863(4)	0.60356(4)	0.061
Si1	0.63931(16)	0.08545(12)	0.60755(12)	0.083
Si2	0.58136(17)	0.13695(13)	0.50306(11)	0.084
O1	0.5581(3)	0.2987(2)	0.59230(18)	0.066
N1	0.5919(4)	0.1390(3)	0.5691(3)	0.064
Zn2	0.48922(5)	0.32755(4)	0.64752(4)	0.061
Si3	0.50824(19)	0.46214(12)	0.68525(11)	0.093
Si4	0.34456(18)	0.40408(15)	0.67728(14)	0.110
O2	0.4882(3)	0.2373(2)	0.66116(18)	0.060
N2	0.4452(4)	0.4013(3)	0.6720(2)	0.072
C1	0.6024(5)	0.3357(4)	0.5590(3)	0.059
C2	0.6827(6)	0.3415(4)	0.5677(4)	0.073
C3	0.7253(7)	0.3825(5)	0.5353(5)	0.097
C4	0.6894(8)	0.4141(5)	0.4975(5)	0.109
C5	0.6112(8)	0.4063(5)	0.4879(4)	0.099
C6	0.5648(6)	0.3660(4)	0.5181(4)	0.078
C7	0.7232(7)	0.3030(6)	0.6089(5)	0.113
C8	0.7739(8)	0.2534(6)	0.5894(5)	0.190
C9	0.7774(12)	0.3392(8)	0.6423(6)	0.371
C10	0.4769(7)	0.3539(6)	0.5068(4)	0.108
C11	0.4322(6)	0.4151(6)	0.5141(4)	0.142
C12	0.4662(7)	0.3327(5)	0.4494(5)	0.173
C25	0.5892(7)	0.0086(4)	0.6080(5)	0.131
C26	0.6407(6)	0.1166(4)	0.6745(3)	0.108
C27	0.7429(6)	0.0735(5)	0.5886(5)	0.133
C28	0.4789(6)	0.1541(6)	0.4850(4)	0.132
C29	0.6431(7)	0.1969(5)	0.4710(4)	0.137
C30	0.6073(7)	0.0600(4)	0.4748(5)	0.131
C13	0.4473(5)	0.2062(4)	0.6998(3)	0.062
C14	0.3850(6)	0.1664(4)	0.6852(4)	0.079
C15	0.3445(6)	0.1383(5)	0.7259(5)	0.104
C16	0.3633(8)	0.1481(6)	0.7763(5)	0.121
C17	0.4239(7)	0.1870(5)	0.7894(4)	0.100
C18	0.4671(6)	0.2161(4)	0.7517(4)	0.074
C19	0.3642(7)	0.1550(5)	0.6287(5)	0.101
C20	0.3716(7)	0.0900(5)	0.6138(4)	0.161
C21	0.2822(10)	0.1738(6)	0.6164(5)	0.264
C22	0.5349(7)	0.2589(6)	0.7667(4)	0.105
C23	0.5100(7)	0.3095(5)	0.8038(5)	0.158
C24	0.6004(7)	0.2214(6)	0.7927(5)	0.179
C31	0.6124(10)	0.4303(8)	0.6851(7)	0.124
C32	0.4930(12)	0.4970(9)	0.7524(8)	0.132
C33	0.5130(13)	0.5242(10)	0.6350(8)	0.156
C34	0.3114(10)	0.4453(8)	0.7408(7)	0.121
C35	0.3026(15)	0.3276(12)	0.6754(11)	0.186
C36	0.3031(13)	0.4749(10)	0.6363(8)	0.152
C31a	0.4500(15)	0.5435(11)	0.6670(10)	0.107
C32a	0.5787(16)	0.4763(12)	0.6295(11)	0.115
C33a	0.5427(19)	0.4664(14)	0.7549(12)	0.141
C34a	0.3053(17)	0.3318(13)	0.7210(12)	0.130
C35a	0.3060(16)	0.3386(13)	0.6259(11)	0.123
C36a	0.2836(17)	0.4299(14)	0.6195(11)	0.136

mat. C-3/5), 137.46 (aromat. C-2), 151.77 (aromat. C-1). – ^{29}Si NMR (INEPT, $CDCl_3$, 297 K): $\delta = -0.41$ ($SiMe_3$). – No satisfying C,H,N analysis could be obtained due to high sensitivity of **15** to hydrolysis.

NMR Experiments: 20 mg of **8** were dissolved in 0.4 ml of $CDCl_3$ (4.0×10^{-2} mol/l) in a 5-mm NMR tube. The solution was frozen in liquid nitrogen and the tube sealed under vacuum. The proton-NMR spectra were recorded in a temperature range between 243 and 323 K; every 5°C a spectrum was taken. The obtained spectra were simulated with the programm package described in ref.[13] on an IBM compatible computer with 80486 processor. Thus, estimated $\ln k$ values were plotted versus $1/T$ [K^{-1}] and according to the Arrhenius equation $\ln k = -(\Delta E_A/R)1/T + \ln A$ the activation energy E_A and $\ln A$ were obtained; from the relation $\Delta S^{+} = R[\ln(hA/k_bT) - 1]$ ($R = 8.314\ J\ K^{-1}\ mol^{-1}$, $h = 6.6265 \cdot 10^{-34}$ J s; $k_b = 1.3805 \cdot 10^{-23}\ J\ K^{-1}$) the activation entropy was calculated. ΔH^{+} and ΔG^{+} were calculated according to $\Delta H^{+} = E_A - RT$ and $\Delta G^{+} = \Delta H^{+} - T\Delta S^{+}$. For errors see ref.[14]

X-Ray Single-Crystal Structure Determination of **8**, **9**, **10**, and **15**: Crystal data and experimental details of the crystal structure determinations are summarized in Table 1, atom parameters are listed in Tables 2–5. Data were collected for **8** with a Synthex R3, for **9**, **10**, and **15** with a Siemens-Stoe four-cycle diffractometer (Mo-K_α radiation, ω scan). Structures were solved and refined by using the programs SHELX76 and SHELXS86[18].

Non-hydrogen atoms were refined anisotropically (exceptions see below), hydrogen atoms in calculated positions or as part of rigid groups (phenyl, methyl) with common isotropic thermal parameters. For **8** and **9** the phenyl rings were refined as rigid groups. In **8** the CF_3 groups in *para* positions are disordered and were refined each by two sets with occupancy factors of 0.6 and 0.4, respectively. The ring carbon and the disordered fluorine atoms were refined anisotropically. The difference Fourier map showed some additional peaks of a solvent hexane molecule which were inserted in the found positions but not refined (only the isotropic parameters). In **15** the Me_3Si groups show rotational disorder. For the groups at N2 two sets of methyl carbons were inserted (occupancy factors 0.6 and 0.4, respectively) and refined isotropically[19].

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