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PAPER

Preparation of aminomethyl functionalised silanes *via* an α-lithiated amine: From their synthesis, stability and crystal structures to stereochemical issues†

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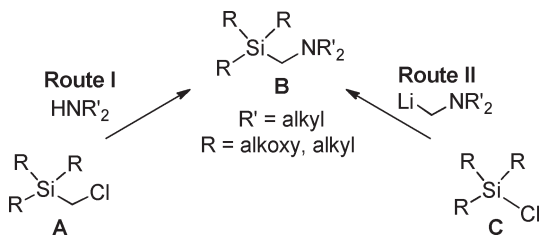
The preparation of aminomethyl functionalised silanes based on the α-lithiated amine, (1*R*,2*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine [(*R*,*R*)-TMCDA] is reported. This methodology can be applied for the synthesis of mono-aminomethyl substituted systems, but most remarkably also for di- and trifunctionalised compounds. The trapping of the lithiated amine is accompanied by transmetallation reactions resulting in the formation of (silylmethyl)silanes depending on the reaction temperature. The zinc(II) halide complexes of the mono-functionalised systems show the formation of exclusively one configuration of the stereogenic nitrogen atom, in which the spatially more demanding substituent exhibits the pseudo-equatorial position. The di- and trifunctionalised systems feature high sensitivity towards Si–C bond cleavage under re-formation of the (*R*,*R*)-TMCDA fragment.

Introduction

α-Functionalised silanes, above all alkoxysilanes, find various applications in industry such as for surface modification, adhesion promotion or the crosslinking of silicones.[1] Amongst others, amino, epoxy and glycidoxy, mercapto and sulfido substituents are used as functional groups. These functionalities are described to crucially influence the properties of the silane, which is commonly known as the so-called α-effect.[2] One intriguing example is the acceleration of the hydrolysis of the alkoxy functions upon the introduction of an aminomethyl function.[3] The preparation of the required α-aminosilanes of type **B** is usually accomplished by substitution reaction of a (chloromethyl)silane **A** with the corresponding secondary amine (Scheme 1, route I).[4] This synthetic route, however, lacks the accessibility of these silanes,[5] so that alternative preparation methodologies, especially *via* the cheap and in many varieties available chlorosilanes **C**, are desired. To accomplish the preparation of **B** starting from chlorosilanes α-amino-substituted carbanions are necessary. Due to the low acidity of the α-hydrogen atom and the involved hindered deprotonation this route has not been considered relevant until now.

In the course of our studies on Lewis base coordinated organolithium compounds, we recently reported on the direct lithiation of a series of tertiary methylamines, including, amongst others, the chiral (1*R*,2*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine [(*R*,*R*)-TMCDA, (*R*,*R*)-**1**] and the commonly used TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[6] These deprotonations occurred in high yields even at room temperature and on a preparative scale. As such, it was possible to apply the obtained lithiated building blocks to the introduction of a nitrogen function giving way to a series of new ligand systems.[7] Motivated by these results we aimed at expanding the applicability of these building blocks for the synthesis of aminomethyl functionalised silanes starting from simple chlorosilanes. Special focus was given to the preparation of oligo(aminomethyl) functionalised silanes, as these compounds seem to be difficult to access *via* the (chloromethyl)silane (route I, Scheme 1). To the best of our knowledge, only one example each of a tri- and tetra(aminomethyl) functionalised silane is known. Interestingly, while Tacke and coworkers succeeded in the preparation of silane **2** *via* route I,[8] Karsch proved the synthetic potential of their dilithiated diamine {[$LiCH_2N(Me)CH_2]_2$} as functionalised building block (Fig. 1).[9] This synthesis of spiro compound **3** underlines the great potential of α-amino-substituted carbanions for such functionalisations. Herein we report on the preparation of (aminomethyl)silanes on the basis of α-lithiated



Scheme 1 General preparation methods of (aminomethyl)silanes of type **B** *via* the (chloromethyl)silane **A** or the chlorosilane **C**.

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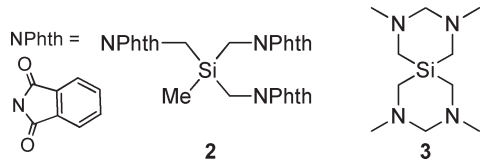


Fig. 1 Reported tri- and tetra(aminomethyl)silanes.[8,9]

(*R*,*R*)-TMCDA. Besides the introduction of one diamine moiety, the di- and tri-substitution reactions are also presented.

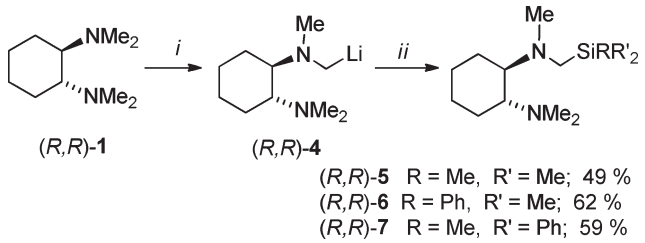
Results and discussion

Mono-functionalised silanes

To evaluate the potential of lithiated amines for the preparation of functionalised silanes, (*R*,*R*)-TMCDA [(*R*,*R*)-**1**] was first applied for the synthesis of mono-functionalised systems. (*R*,*R*)-**1** is readily available by racemic resolution of a mixture of all isomers (*RR*, *SS*, *cis*) with L-tartaric acid and subsequent methylation *via* Eschweiler–Clarke reaction.[10] Note, that also the racemic mixture of the amine is known to undergo deprotonation reaction of the *N*-methyl group.[7] However, the enantiomeric pure compound was chosen to ease analysis of the desired silyl compounds, especially the multiple functionalised systems.

For the preparation of the (aminomethyl)silanes the chiral diamine was treated with *tert*-butyllithium in n-pentane at room temperature for deprotonation of its methyl group. As outlined in Scheme 2 the thus obtained lithiated amine **4** was *in situ* reacted with different chlorosilanes at low reaction temperatures (for details see the experimental section). After aqueous work-up and distillation the (aminomethyl)-silanes (*R*,*R*)-**5**, (*R*,*R*)-**6** and (*R*,*R*)-**7** were obtained as colourless oils in only moderate yields of 49 to 62%. The dimethylphenyl compound (*R*,*R*)-**6** has already been described before in context of the preparation of Si-chiral compounds by diastereoselective deprotonation of its diastereotopic methyl groups.[11] All compounds were characterised by multinuclear NMR spectroscopy, elemental analysis and mass spectrometry. It is noteworthy, that due to the chiral side-arm the phenyl substituents in (*R*,*R*)-**7** are diastereotopic, so that two sets of signals are observed in the ^{1}H and ^{13}C NMR spectra.

The stereoinformation of the chiral nitrogen side-arm is retained during the whole reaction sequence of lithiation and trapping reaction. This is evidenced by optical rotation measurements and single-crystal X-ray diffraction analyses of the corresponding zinc(II) bromide complexes (see below) in combination with NMR studies. The zinc(II) bromide complexes were



Scheme 2 Preparation of functionalised silanes **5**–**7** *via* α-lithiated (*R*,*R*)-TMCDA, (*R*,*R*)-**1**. (i) *t*BuLi, pentane, −30 °C → rt; (ii) RR′$_2$SiCl.

obtained for the dimethylphenyl and the diphenylmethylsilane (*R*,*R*)-**6** and (*R*,*R*)-**7** by dissolving the corresponding silane in acetone or acetone/diethyl ether with an equivalent amount of the metal salt. After slow evaporation of the solvent the zinc bromide adducts were obtained as colourless crystals. The crystal structures of both compounds are depicted in Fig. 2. The zinc complexes are part of systematic studies on the catalysis of lactide ring-opening polymerisation. Analogous complexes with TMCDA-based diamine ligands have revealed to be efficient initiators for this transformation.[12]

Both complexes (R_C,R_C,R_N)-**8** and (R_C,R_C,R_N)-**9** crystallise as monomeric adducts in the monoclinic crystal system, space group $P2_1$. The asymmetric unit of (R_C,R_C,R_N)-**9** contains two molecules, one of which is shown in Fig. 2. For selected bond lengths and angles, see Table 1; for crystallographic details and structure refinement, see Table 3 and the supporting information.† In both structures, the zinc(II) bromide is coordinated by the TMCDA side-arm resulting in a distorted tetrahedral coordination environment of the zinc atom. The angles around the metal atom range from 87.8(1) to 117.0(1)° and 87.3(2) to 117.1(1)°, respectively, with the smallest angle being the bite angle to the diamino side-arm. The angles around silicon differ only slightly from the ideal tetrahedral angle. In both cases the *R*,*R*-configuration of the stereogenic carbon centres of the diamine is evident. The complexation also in solution is

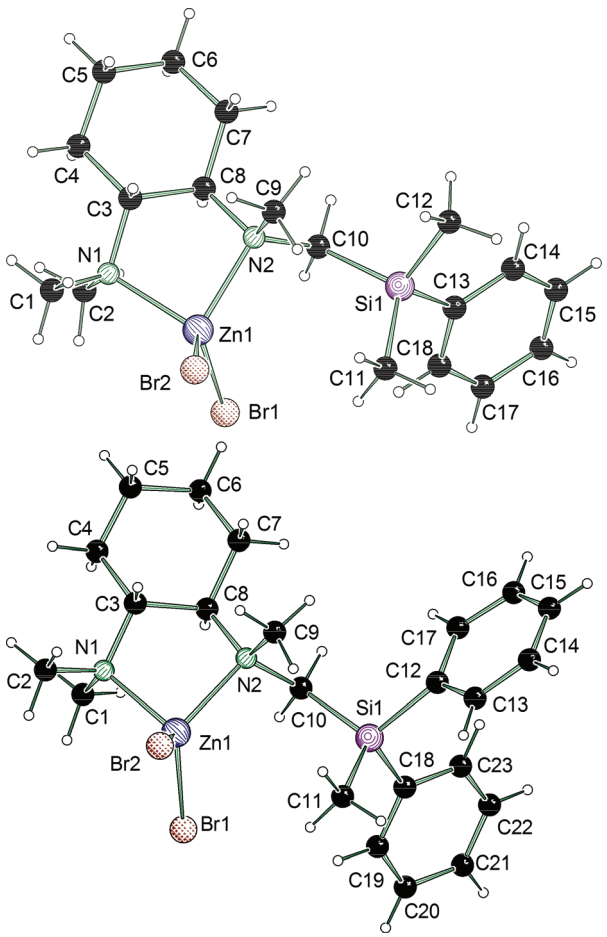


Fig. 2 Molecular structure and numbering scheme of the zinc complexes (R_C,R_C,R_N)-**8** (top) and (R_C,R_C,R_N)-**9** (bottom).

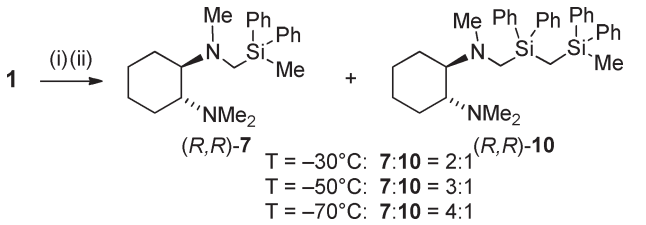
Table 1 Selected bond lengths (Å) and angles (°) for **8**, **9**, **12**

(R_C,R_C,R_N)-**8**			
Zn–Br(1)	2.349(1)	Zn–N(1)	2.088(3)
Zn–Br(2)	2.358(1)	Zn–N(2)	2.092(3)
Si(1)–C(10)	1.894(4)	Si(1)–C(12)	1.888(4)
Si(1)–C(11)	1.873(4)	Si(1)–C(13)	1.890(3)
N(1)–Zn–N(2)	87.8(1)	Br(1)–Zn–Br(2)	117.0(1)
N(1)–Zn–Br(1)	112.3(1)	N(2)–Zn–Br(1)	113.5(1)
N(1)–Zn–Br(2)	110.8(1)	N(2)–Zn–Br(2)	111.9(1)
C(10)–Si–C(11)	114.4(2)	C(10)–Si–C(13)	103.7(2)
C(10)–Si–C(12)	111.8(2)	C(11)–Si–C(12)	109.5(2)
(R_C,R_C,R_N)-**9**[a]			
Zn–Br(1)	2.354(1) 2.356(1)	Zn–N(1)	2.065(6) 2.077(6)
Zn–Br(2)	2.362(1) 2.367(1)	Zn–N(2)	2.093(6) 2.100(5)
Si(1)–C(10)	1.873(7) 1.878(6)	Si(1)–C(12)	1.881(7) 1.870(8)
Si(1)–C(11)	1.849(7) 1.818(7)	Si(1)–C(18)	1.895(6) 1.900(7)
N(1)–Zn–N(2)	87.3(2) 87.2(2)	Br(1)–Zn–Br(2)	117.1(1) 117.6(1)
N(1)–Zn–Br(1)	110.5(1) 111.5(1)	N(2)–Zn–Br(1)	114.1(15) 115.1(1)
N(1)–Zn–Br(2)	109.2(1) 109.6(1)	N(2)–Zn–Br(2)	114.6(1) 111.9(2)
C(10)–Si–C(11)	114.9(3) 112.0(3)	C(10)–Si–C(18)	105.3(3) 105.3(3)
C(10)–Si–C(12)	110.8(3) 112.0(3)	—	—
(R_C,R_C,R_N)-**12**			
Zn–Br(1)	2.351(1)	Zn–N(1)	2.085(2)
Zn–Br(2)	2.362 (1)	Zn–N(2)	2.100(2)
Si(1)–C(10)	1.906(3)	Si(1)–C(17)	1.880(3)
Si(1)–C(11)	1.873(3)	Si(1)–C(23)	1.857(2)
Si(2)–C(23)	1.870(2)	Si(2)–C(30)	1.882(3)
Si(2)–C(24)	1.884(3)	Si(2)–C(31)	1.864(2)
N(1)–Zn–N(2)	88.0 (1)	Br(1)–Zn–Br(2)	116.2(1)
N(1)–Zn–Br(1)	112.0(1)	N(2)–Zn–Br(1)	114.9(1)
N(1)–Zn–Br(2)	110.0(1)	N(2)–Zn–Br(2)	112.4(1)
C(10)–Si(1)–C(11)	109.4(1)	C(10)–Si(1)–C(23)	113.0(1)
C(10)–Si(1)–C(17)	103.1(1)	Si(1)–C(12)–Si(2)	120.2(1)
C(23)–Si(2)–C(24)	110.3(1)	C(23)–Si(2)–C(30)	107.6(1)
C(23)–Si(2)–C(31)	113.0(1)	—	—

[a] Complex **9** contains two molecules in the asymmetric unit. Values for both molecules are given.

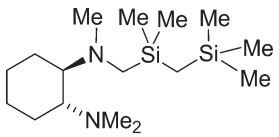
confirmed by NMR spectroscopy of the zinc(II) adducts. Upon coordination of the metal the configuration of the nitrogen atoms becomes fixed. As such the methyl groups of the $N(CH_3)_2$ moiety become diastereotopic and appear as two singlet resonances in the ^1H and ^{13}C NMR spectra (see SI†).

As the lithiation of TMCDA to **4** itself was found to occur quantitatively,[7] the trapping reactions according Scheme 2 were investigated more carefully to explain the moderate yields (49 to 62%) of the obtained mono-functionalised silanes **5**–**7**. Typically such substitution reactions of chlorosilanes with organolithium compounds are known to proceed quantitatively.[13] For this purpose, the treatment of (*R*,*R*)-**4** with diphenylmethylchlorosilane was accomplished at different reaction temperatures and the crude product (prior work-up) studied by NMR spectroscopy. Besides the simple substitution product (*R*,*R*)-**7** (Scheme 2), the formation of a second amino-functionalised compound was observed. The isolation finally revealed the (silylmethyl)silyl compound (*R*,*R*)-**10** as by-product of the trapping reaction. This compound is formed by deprotonation of the methyl group of the initially formed silane **7** and its subsequent reaction with still present chlorosilane. As investigated for the diphenylmethylsilane, this transmetallation reaction depends on the trapping



Scheme 3 Trapping reaction of diphenylmethylchlorosilane to (*R*,*R*)-**7** and (*R*,*R*)-**10** *via* transmetallation; (i) *t*-BuLi, −30 °C to rt, 4h; (ii) $Ph_2MeSiCl$, low temperature, aqueous work-up.

temperature with a decrease of transmetallation α to silicon at lower trapping temperatures. While at −30 °C compound (*R*,*R*)-**10** has been formed in half the amount of the simple trapping product, only a 4 : 1 mixture has been observed at −70 °C (Scheme 3). The same side reaction was also observed for the preparation of silane (*R*,*R*)-**5**, however with smaller amounts of the corresponding (silylmethyl)silyl compound (*R*,*R*)-**11**. Here, at −78 °C, only a 9 : 1 mixture was obtained, while at −30 °C a 3 : 1 mixture was obtained.



(*R*,*R*)-**11**

The observed transmetallation in the α-position is in line with the well-known anion-stabilizing ability of silyl groups, which is due to the high polarisability of Si and the presence of low-lying σ*-SiR orbitals allowing for negative hyperconjugation.[14] This stability of the silyl substituted carbanion corroborates with the thermodynamic preference observed in experiment. The formation of the transmetallation products (*R*,*R*)-**10** and (*R*,*R*)-**11** can be minimized by simple addition of the lithiated amine (*R*,*R*)-**4** to the chlorosilane. We have recently used this increased acidity of the methyl groups bound to silicon in diastereoselective deprotonation reactions to access Si-chiral compounds.[11]

Analogously to the simple trapping products (*R*,*R*)-**6** and (*R*,*R*)-**7**, the transmetallation product (*R*,*R*)-**10** was transferred into the corresponding zinc(II) bromide complex (R_C,R_C,R_N)-**12** by slow evaporation of a solution of (*R*,*R*)-**10** in acetone. (R_C,R_C,R_N)-**12** crystallises in the orthorhombic crystal system, in the space group $P2_12_12_1$. One additional solvent molecule crystallises in the asymmetric unit (not depicted in Fig. 3). For selected bond lengths and angles, see Table 1; for crystallographic details and structure refinement, see Table 3 and the supporting information.† Comparable to (R_C,R_C,R_N)-**8** and (R_C,R_C,R_N)-**9**, the zinc atom exhibits a distorted tetrahedral coordination by complexation through the amino side-arm, which again exhibits *R*,*R*-configuration at the stereogenic carbon atoms. The complex possesses structural features analogous to the presented zinc(II) bromide complexes (*R*,*R*)-**8** and (*R*,*R*)-**9** (Fig. 2).

An intriguing feature of all isolated zinc(II) bromide complexes is the selective formation of one specific configuration at the stereogenic nitrogen atom N(2) (see Fig. 2 and 3). Upon coordination of the zinc salt to the diamino side-arm the silyl

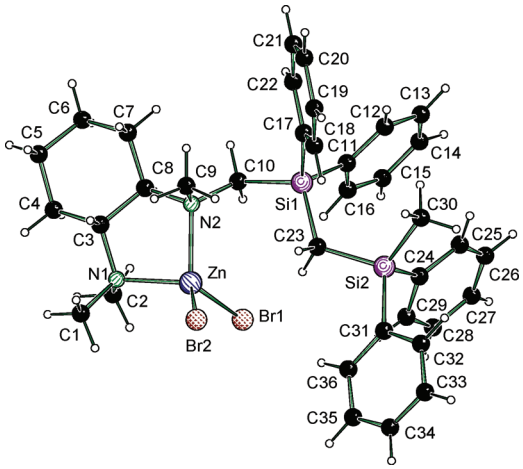
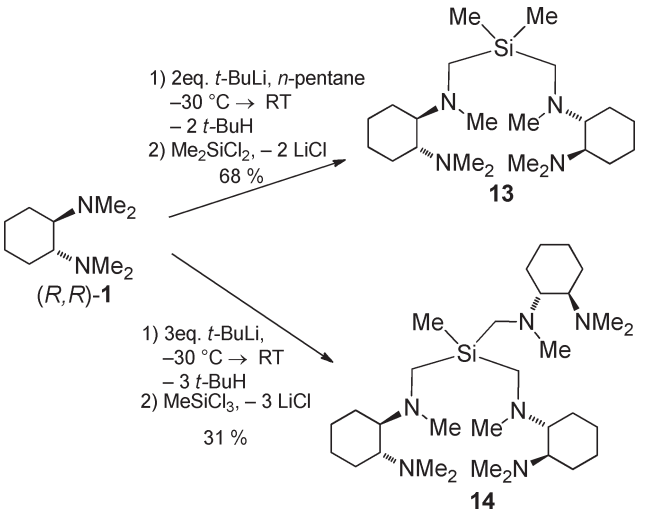


Fig. 3 Molecular structure of the zinc(II) bromide complex (R_C,R_C, R_N)-**12** of compound **10**.



Scheme 4 Preparation of multiple TMCDA functionalised silanes.

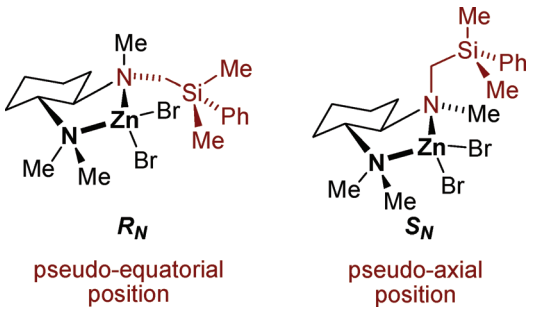


Fig. 4 Scheme of the preferred configuration at the stereogenic nitrogen atom in the $ZnBr_2$ adduct of (R_C,R_C,R_N)-**6**; arrangement of the spatially more demanding substituent (red) in pseudo-equatorial position.

substituted nitrogen atom becomes stereogenic. Most interestingly, all complexes feature *R*-configuration at the nitrogen. In this configuration, the sterically more demanding substituent adopts the pseudo-equatorial position of the five-membered ring, which is formed upon coordination of the metal salt to the diamino side-arm (Fig. 4). For a more detailed study, the zinc(II) chloride complexes of silanes (*R*,*R*)-**5** and (*R*,*R*)-**6** were also synthesised (for crystallographic details, bond lengths and ORTEP plots of these complexes, see ESI†). Comparable to the zinc(II) bromide complexes (Fig. 2, Fig. 3) the structures of the $ZnCl_2$ adducts feature monomeric compounds, all of which show the pseudo-equatorial arrangement of the spatially more demanding silyl substituent and thus one specific configuration of the stereogenic nitrogen atom. This selective formation of one configuration may be of interest for asymmetric transformations employing complexes in transition metal-catalysed reaction such as the presented zinc(II) adducts. Here, complexes with ligands based on the cyclohexanediamine framework have already gained wide applications.[10b,15] Especially, diamines with three different substituents at the nitrogen atom revealed to be more efficient for the induction of stereoinformation.[16] This is attributed to the closer arrangement of the stereocentre to the active metal centre compared to complexes with solely ligand chirality.

Bis- and tris(aminomethyl)-functionalised silanes

To further evaluate the potential of lithiated (*R*,*R*)-TMCDA as building block for the synthesis of organometallic compounds multiple functionalisations were attempted. The target molecules were also expected to serve as interesting multidentate ligand systems with intriguing coordination behaviour. For these multiple functionalisations the lithiated amine was cautiously treated with dichlorodimethylsilane and trichloromethylsilane (Scheme 4). After an aqueous work-up and Kugelrohr distillation the desired bis- and tris(aminomethyl)-functionalised silanes **13** and **14** were obtained in 68 and 31% yield as colourless oils. These compounds are rare representatives of oligo-aminomethyl functionalised silanes.[17] Especially, tris(aminomethyl)silanes are difficult to access by the common synthetic route *via* (chloromethyl)silane and the corresponding secondary amine (route I, Scheme 1). This is also due to the limited pathways to multiple chloromethyl substituted silanes.[18] To the best of our knowledge, **14** is even the first chiral tris(aminomethyl)silane.

The low yield of **14** can be attributed to the sensitivity of the compound towards moisture, leading to the Si–C bond cleavage under re-formation of (*R*,*R*)-TMCDA. Due to this reactivity—which has not been observed for any of the other presented silanes—the aqueous work-up resulted in the loss of product. Interestingly, the sensitivity of **14** is only observed in solution. The compound itself can be stored without any precautions for weeks.

The decomposition of **14** by Si–C bond cleavage was studied by NMR spectroscopy in non-dried benzene-d^6. We assumed that under these conditions hydrolysis would be slow enough to also detect intermediate products of the hydrolysis. Indeed, the decomposition occurs slow enough to be followed by NMR spectroscopy. Hydrolysis of 30 mg silane in 0.7 mL C_6D_6 is completed after 60 h. Fig. 5 depicts an extract of the NMR spectra showing the methyl functions at the nitrogen atoms of silane **14** (blue) and the NMe_2 groups of the formed (*R*,*R*)-TMCDA (**1**) (red). However, no further amine functionalised silanes could be detected during this decomposition process. This suggests an "auto-catalytic" process, in which the

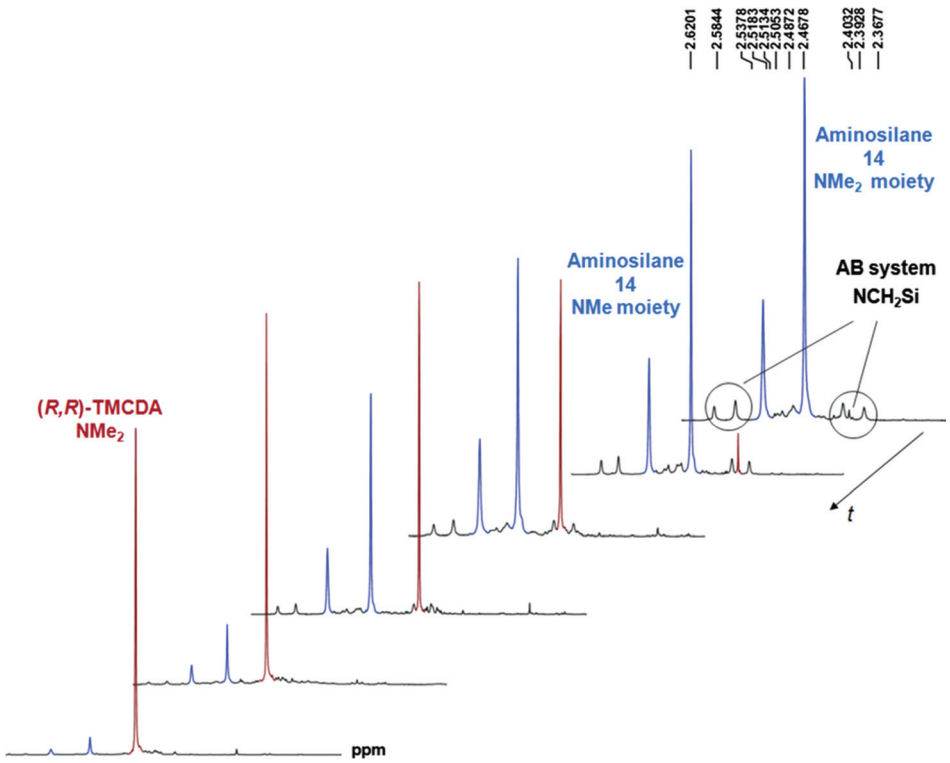
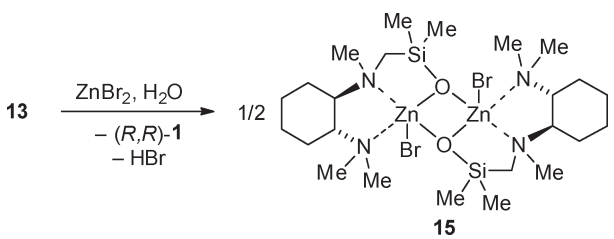


Fig. 5 Extract of ^{1}H NMR spectra in C_6D_6; decomposition of the tris(aminomethyl)-substituted silane **14** *via* Si–C bond cleavage.

cleavage of the second and also third side-arm occurs faster than the cleavage of the first Si–C bond, which means that the initially formed hydroxy species are more prone to decomposition than compound **14** itself.

In contrast to **14** the bis(aminomethyl)-functionalised silane **13** was revealed to be stable in solution. However, decomposition was observed during crystallisation attempts of the corresponding zinc(II) bromide complexes. Thereby, a solution of **13** in acetone was treated with an equivalent amount of the metal salt. In this case no simple adduct comparable to (R_C,R_C,R_N)-**8** or (R_C,R_C,R_N)-**9** could be isolated. Instead, the stable zinc silanolate **15**—with an Si–O–Zn fragment—as result of the cleavage of one TMCDA unit could be isolated (Scheme 5).[12,19] The formation of this compound has been described previously by treatment of the corresponding disiloxane with $ZnBr_2$.[20] The formation of **15** underlines the stability of these metallasilanolates, which have long been supposed to be unstable compounds and emphasises the increased sensitivity of multiple (aminomethyl) functionalised silanes towards Si–C bond cleavage. An analogous crystallization experiment of the tris(aminomethyl)-functionalised system **14** with $ZnBr_2$ exclusively lead to the decomposition product $ZnBr_2$·(*R*,*R*)-TMCDA resulting from the cleavage of all Si–C bonds. $ZnBr_2$·(*R*,*R*)-TMCDA could be isolated as crystalline solid in 79% yield. The failed isolation of any intermediate decomposition product as $ZnBr_2$ adduct is in line with the NMR experiments.



Scheme 5 Formation of zinc silanolate **15** *via* Si–C bond cleavage in **13**.

The observed sensitivities of compound **13** and **14** towards Si–C bond cleavage is consistent with previous observations of other groups dealing with aminomethyl substituted silanes.[17c,21] Investigations by Moreau and coworkers showed that the decomposition of a series of (aminomethyl)trialkoxysilanes during sol–gel applications led—analogous to our systems—to the corresponding methylamine and silica. The cleavage was a result of the nucleophilic attack of water and a Si–O$^-$, respectively, at the silicon. Most interestingly, the decomposition was found to proceed faster the more alkoxy functions that were present in the silane, *i.e.* the higher the "electrophilicity" of the Si atom.[21] This is in total agreement with the observed "autocatalytic" decomposition of **14**. As such, the intermediate di- and mono-(aminomethyl) functionalised hydroxysilanes should decompose faster than the still present **14** without hydroxyl groups bound to the silicon. This also explains the increased sensitivity of the tris(aminomethyl)-functionalised silane **14** compared with **13** or even the mono-substituted systems **5**, **6** and **7**. The cleavage of **13** upon treatment with zinc(II) bromide can thus also be explained by the increased electrophilicity of the Si atom due to quartenisation of the nitrogen atom upon coordination of the metal salt.

Conclusions

In conclusion we reported on the efficient use of the α-lithiated tertiary amine, (*R*,*R*)-TMCDA [(*R*,*R*)-**1**], for the preparation of (aminomethyl) functionalised silanes. The formation of a series of mono-functionalised systems proceeds with good yields accompanied by transmetallation of the initially formed silane leading to the corresponding (silylmethyl)silanes. Formed zinc(II) halide complexes of the presented TMCDA functionalised silanes showed the formation of monomeric adducts with one specific configuration at the stereogenic nitrogen atom. Thereby, the spatially more demanding substituent adopts the pseudo-equatorial position of the five-membered ring formed upon complexation of the metal salt by the diamine side-arm. Furthermore the potential of α-lithiated tertiary amines for the formation of multiple (aminomethyl) substituted silanes is depicted by the syntheses of compound **13** and **14** with two and three (aminomethyl) functionalities, respectively. These compounds revealed an increased sensitivity in solution towards Si–C bond cleavage under reformation of the diamine. This sensitivity was found to increase with number of (aminomethyl) substituents in the silane. We are currently looking into the mechanistic features of this interesting hydrolysis behaviour and the expansion of the preparation of (aminomethyl) functionalised silanes *via* other α-lithiated tertiary amines.

Experimental section

General considerations

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. H_2O is distilled water. The solvents used were dried over sodium and distilled prior to use. Cyclohexane-1,2-diamine was purchased from Aldrich, the chlorosilanes and *tert*-butyl lithium were provided by Wacker Chemie and Chemetall, respectively. The concentration of *tert*-butyl lithium was determined by titration against diphenylacetic acid before use. (*R*,*R*)-TMCDA (*R*,*R*)-**1** and (*R*,*R*)-**6** were prepared according to the literature.[6c,10] Enantiomeric purity of **1** was determined according the literature.[6e]

^1H, ^{13}C, ^{29}Si NMR spectra were recorded on DRX-300 and AMX-500 Bruker spectrometers at 22 °C. Assignment of the signals was supported by additional DEPT-135 and C,H-COSY experiments. All values of the chemical shift are in ppm regarding the δ-scale. All spin–spin coupling constants (J) are given in Hertz (Hz). GC-MS analysis were performed on a ThermoQuest TRIO-1000 (EI = 70 eV); Column; Zebron, Capillary GC Column, ZB-1. Optical rotation values were determined on a Jasco-polarimeter: P-1030 (cell path l = 1.00 dm; temperature: 20.0 °C, wave length λ = 589 nm).

A. General procedure for the preparation of aminomethyl functionalised silanes

(*R*,*R*)-TMCDA was dissolved in n-pentane and cooled to −30 °C. At this temperature *tert*-butyl lithium (solution in n-pentane) was added, the mixture allowed to warm to room temperature and stirred for an additional 3–4 h during which the formed precipitate of (*R*,*R*)-TMCDA completely dissolved. After cooling (for temperature, see each compound) the corresponding chlorosilane (1.4 eq.) was cautiously (partly vigorous reaction!!) added, the mixture again warmed to rt and stirred for 2 h. After addition of 10 mL diethyl ether and 10 mL of 2 M HCl_{aq} to dissolve the formed lithium chloride, the combined organic layers were extracted 3 times with 20 mL of 2 M HCl_{aq}. The aqueous layers were afterwards set to pH 12 with 2 M NaOH and finally extracted 3 times with 30 mL of diethyl ether and the combined organic layers were dried over Na_2SO_4. After removal of all volatile compounds *in vacuo*, the crude product was purified by Kugelrohr distillation.

Synthesis of (*R*,*R*)-5 and (*R*,*R*)-11. Using general procedure A, 3.90 g (22.9 mmol) (*R*,*R*)-TMCDA [(*R*,*R*)-**1**] dissolved in pentane were treated with 17.6 mL (29.9 mmol) *t*-BuLi. Trimethylchlorosilane was added at −30 °C. Kugelrohr distillation gave (*R*,*R*)-**5** (oven temperature: 128 °C, 3 × 10^{-2} mbar; yield: 2.72 g, 11.2 mmol, 49%) and (*R*,*R*)-**11** (oven temperature 148: °C, 3 × 10^{-2} mbar; yield: 1.21 g, 3.84 mmol, 17%) in a 3 : 1 ratio as colourless oils. Trapping of the lithiated amine at −78 °C gave a 8.8 : 1 ratio with an overall yield of 79%. Spectroscopic data of (*R*,*R*)-**5** ^1H NMR: (300.1 MHz, C_6D_6): δ = 0.13 [s, 9H; Si(CH_3)$_3$], 1.00–1.14 (m, 4H; 2 CH_2, cyclohexyl), 1.68–1.73 (m, 2H; CH_2, cyclohexyl), 1.78–1.87 (m, 2H; CH_2, cyclohexyl), 1.90 + 2.13 [AB system, $^2J_{AB}$ = 14.4 Hz, 2H; N(CH_2)Si], 2.26 [s, 3H; N(CH_3)CH_2Si], 2.27–2.33 [m, 2H; CHN], 2.31 [s, 6H; N(CH_3)$_2$]. {^1H}^{13}C NMR: (75.5 MHz, C_6D_6): δ = −0.96 [Si(CH_3)$_3$], 25.2 + 26.1 + 26.5 + 26.6 (CH_2, cyclohexyl], 40.7 [N(CH_3)CH_2Si], 41.0 [N(CH_3)$_2$], 45.5 [N(CH_2)Si], 64.7 (CHN), 67.8 (CHN). ^{29}Si NMR: (59.6 MHz, C_6D_6): δ = −0.62. Elemental analysis: Calc. for $C_{13}H_{30}N_2Si$: C 64.39, H 12.47, N 11.55; Found: C 64.48, H 12.20, N 11.15. GC-MS t_R = 11.53 min [80 °C (2 min) − 10 °C min^{-1} − 280 °C (5 min)]; *m*/*z* (%): 242 (22) (M^+), 169 (60) {[M − Si(CH_3)$_3$]$^+$}, 124 (100) {[$C_6H_9N(CH_3)CH_2$]$^+$}, 73 (45) {[Si(CH_3)$_3$]$^+$}, 58 (80) {[N(CH_3)$_2CH_2$]$^+$}. Spectroscopic data of (*R*,*R*)-**11**: ^1H NMR: (300.1 MHz, $CDCl_3$): δ = −0.27 (s, 2H; SiCH_2Si), 0.03 [s, 9H; Si(CH_3)$_3$], 0.03 + 0.04 [s, 6H; Si(CH_2)CH_2Si], 0.97–1.14 (m, 4H; 2 CH_2, cyclohexyl), 1.61–1.68 (m, 2H; CH_2, cyclohexyl), 1.8–1.82 (m, 2H; CH_2, cyclohexyl), 1.89 + 2.06 [AB system, $^2J_{AB}$ = 14.5 Hz, 2H; N(CH_2)Si], 2.14 [s, 3H; N(CH_3)CH_2Si], 2.27–2.33 [m, 2H; CHN], 2.30 [s, 6H; N(CH_3)$_2$]. {^1H}^{13}C NMR: (75.5 MHz, C_6D_6): δ = 0.65 (SiCH_2Si), 2.0 [Si(CH_3)$_3$], 3.0 (SiCH_2Si), 25.6 + 25.7 + 26.1 + 26.6 (CH_2, cyclohexyl), 40.8 [N(CH_3)CH_2Si], 40.9 [N(CH_3)$_2$], 46.5 [N(CH_2)Si], 64.7 (CHN), 67.7 (CHN). ^{29}Si NMR: (59.6 MHz, C_6D_6): δ = −0.11 + 0.45. GC-MS: t_R = 15.75 min [80 °C (2 min) − 10 °C min^{-1} − 280 °C (5 min)]; *m*/*z* (%): 314 (15) (M^+), 228 (23) [MH − CH_2Si(CH_3)$_3$], 169 (100) {[M − Si(CH_3)$_2CH_2$Si(CH_3)$_3$]$^+$}, 145 (20) {[Si(CH_3)$_2CH_2$Si(CH_3)$_3$]$^+$}, 124 (75) {[$C_6H_9N(CH_3)CH_2$]$^+$}, 73 (43) {[Si(CH_3)$_3$]$^+$}, 58 (48) {[N(CH_3)$_2CH_2$]$^+$}.

Synthesis of (*R*,*R*)-7 and (*R*,*R*)-10. Using general procedure A, 4.00 g (23.5 mmol) (*R*,*R*)-TMCDA in 25 mL pentane were treated with 20 mL (30.0 mmol) *t*-BuLi. Diphenylmethylchlorosilane was added at the temperatures given in Table 2. Kugelrohr distillation gave (*R*,*R*)-**7** (oven temperature 225 °C, 6 × 10^{-42}

Table 2 Obtained product ratios and yields depending on the trapping temperature

Trapping temperature	(*R*,*R*)-**7**	(*R*,*R*)-**10**	Total isolated yield
−30 °C	2.1	1	87%
−50 °C	3.3	1	74%
−70 °C	4.2	1	86%

mbar) and (*R*,*R*)-**10** (oven temperature 260 °C, 6×10^{-4} mbar) as colourless, highly viscous oils.

Spectroscopic data of diphenylmethylsilane (*R*,*R*)-**7**: ^{1}H NMR: (500.1 MHz, *d*-Tol): δ = 0.66 [s, 3H; Si(CH_3)], 0.87–1.05 [m, 4H; 2 × CH_2CH$_2$], 1.57–1.62 [m, 2H; CH_2CHN(CH$_3$)CH$_2$], 1.67–1.72 [m, 1H; CH_2CHN(CH$_3$)CH$_2$], 1.76–1.80 [m, 1H; CH_2CHN(CH$_3$)CH$_2$], 2.19 [s, 3H; N(CH_3)CH$_2$Si], 2.22 [s, 6H; N(CH_3)$_2$], 2.24–2.27 [m, 2H; 2 × C*H*N], 2.48 + 2.74 [AB system, $^{2}J_{AB}$ = 14.4 Hz, 2H; N(CH_2)Si], 7.02–7.22 (m, 6H; H_{arom}), 7.64–7.70 (m, 4H; H_{arom}). {^{1}H}^{13}C NMR: (125.8 MHz, *d*-Tol): δ = −3.6 [Si(*C*H$_3$)], 24.1 (*C*H$_2$CHN), 24.7 (*C*H$_2$CHN), 26.4 [(*C*H$_2$)$_2$CH$_2$], 26.2 [(CH$_2$)$_2$CH$_2$], 40.3 [N(*C*H$_3$)$_2$], 40.8 [N(*C*H$_3$)CH$_2$Si], 42.7 [N(*C*H$_2$)Si], 64.5 (*C*HN), 66.9 (*C*HN), 128.00 + 128.01 (CH_{meta}), 129.28 + 129.29 (CH_{para}), 135.1 + 135.2 (CH_{ortho}), 138.0 + 138.1 (C_{ipso}). ^{29}Si NMR: (99.4 MHz, *d*-Tol): δ = −11.2. Elemental analysis: Calc. for $C_{23}H_{34}N_2Si$: C 75.35, H 9.35, N 7.64; Found: C 75.48, H 9.20, N 7.35. $[\alpha]_D^{20}$ −6.8 (cyclohexane, 1.057 g/100 mL). GC-MS: t_R = 12.14 min [80 °C (2 min) − 10 °C min^{-1} − 280 °C (5 min)]; *m*/*z* (%): 366 (3) [M$^+$], 197 (32) {[Si(CH$_3$)Ph$_2$]$^+$}, 169 (100) {[M − Si(CH$_3$)Ph$_2$]$^+$}, 124 (58) {[C$_6$H$_9$N(CH$_3$)CH$_2$]$^+$}, 58 (100) {[N(CH$_3$)$_2$CH$_2$]$^+$}. Spectroscopic data of (*R*,*R*)-**10**: ^{1}H NMR: (500.1 MHz, CDCl$_3$): δ = 0.23 (s, 3H SiCH_3), 0.80–1.04 [m, 4H; CH_2, cyclohexyl], 0.96 (s, 2H; SiCH_2Si), 1.57–1.70 [m, 3H; CH_2, cyclohexyl], 1.79–1.81 [m, 1H; CH_2, cyclohexyl], 2.01 [s, 3H; N(CH_3)CH$_2$Si], 2.22 [s, 6H; N(CH_3)$_2$], 2.22–2.29 [m, 2H; C*H*N], 2.34 + 2.54 [AB system, $^{2}J_{AB}$ = 14.6 Hz, 2H; N(CH_2)Si], 7.27–7.36 (m, 12H; H_{arom}), 7.37–7.48 (m, 4H; H_{arom}) 7.55 (d, 2H, $^{3}J_{HH}$ = 6.2 Hz; H_{ortho}), 7.64 (d, 2H, $^{3}J_{HH}$ = 6.6 Hz; H_{ortho}). {^{1}H}^{13}C NMR: (125.8 MHz, CDCl$_3$): δ = −2.63 [Si(*C*H$_3$)], −2.18 (SiCH$_2$Si), 23.0 + 24.9 + 25.3 + 25.6 (*C*H$_2$ cyclohexyl), 39.9 [N(*C*H$_3$)CH$_2$Si], 40.3 [N(*C*H$_3$)$_2$], 43.9 [N(*C*H$_2$)Si], 63.9 (*C*HN), 65.8 (*C*HN), 127.46 + 127.48 + 127.57 + 127.59 (CH_{meta}), 128.78 + 128.84 +128.98 + 129.02 (CH_{para}), 134.21 + 134.25 + 135.1 + 135.4 (CH_{ortho}), 136.8 (br) + 137.4 + 138.8 (C_{ipso}). ^{29}Si NMR: (59.6 MHz, *d*-Tol): δ = −11.10, −8.04.

Synthesis of 13. Using general procedure A, 6.00 g (35.2 mmol) (*R*,*R*)-TMCDA [(*R*,*R*)-**1**] dissolved in 25 mL n-pentane were treated with 29 mL (43.5 mmol) *t*-BuLi. Trapping with 6.00 g (47.6 mmol) dimethyldichlorosilane at −50 °C. *Caution*: vigorous reaction. Kugelrohr distillation (oven temperature 200 °C, 4×10^{-4} mbar) gave **13** as a colourless, highly viscous oil (5.82 g, 15.9 mmol, 68%). ^{1}H NMR: (500.1 MHz, C$_6$D$_6$): δ = 0.44 [s, 6H; Si(CH_3)$_2$], 1.08–1.26 [m, 8H; 4 × CH_2CH$_2$], 1.73–1.78 [m, 4H; 2 × CH_2CHN], 1.89–1.91 [m, 2H; CH_2CHN], 1.98–2.00 [m, 2H; CH_2CHN], 2.19 + 2.42 [AB system, $^{2}J_{AB}$ = 14.2 Hz, 4H; N(CH_2)Si], 2.41–2.47 [m, 4H; 2 × C*H*N], 2.45 [s, 12H; N(CH_3)$_2$], 2.46 [s, 6H; N(CH_3)CH$_2$Si]. {^{1}H}^{13}C NMR: (125.8 MHz, C$_6$D$_6$): δ = −2.0 [Si(*C*H$_3$)], 24.9 (*C*H$_2$CHN), 25.4 (*C*H$_2$CHN), 26.17 + 26.18 [(*C*H$_2$)$_2$CH$_2$], 40.5 [N(*C*H$_3$)CH$_2$Si], 40.6 [N(*C*H$_3$)$_2$], 43.8 [N(*C*H$_2$)Si], 64.4 (*C*HN), 67.4 (*C*HN). ^{29}Si NMR: (99.4 MHz, C$_6$D$_6$): δ = −1.2. Elemental analysis: Calc. for $C_{22}H_{48}N_4Si$: C 66.60, H 12.19, N 14.12; Found: C 66.23, H 12.17, N 14.49. $[\alpha]_D^{20}$ −28.1 (cyclohexane, 0.827 g/100 mL); GC-EI/MS: t_R = 11.99 min [80 °C (2 min) − 10 °C min^{-1} − 280 °C (5 min)]; *m*/*z* (%): 381 (2) [(M − CH$_3$)$^+$], 227 (100) {[M − (C$_{10}$H$_{21}$N$_2$)]$^+$}, 170 (15) [(*R*,*R*)-TMCDA], 124 (25) {[C$_6$H$_9$N(CH$_3$)CH$_2$]$^+$}, 58 (60) {[N(CH$_3$)$_2$CH$_2$]$^+$}.

Synthesis of 14. Using general procedure A, 4.00 g (23.5 mmol) (*R*,*R*)-TMCDA [(*R*,*R*)-**1**] dissolved in 25 mL n-pentane were treated with 15 mL (25.5 mmol) *t*-BuLi. 1.5 g (10.0 mmol) methyltrichlorosilane was then slowly added at −70 °C. *Caution*: extremely exothermic reaction. Kugelrohr distillation (oven temperature: 290 °C, 4×10^{-4} mbar) gave **14** as a slightly yellow, highly viscous oil (1.35 g, 2.45 mmol, 31%). ^{1}H NMR: (400.1 MHz, C$_6$D$_6$): δ = 0.65 [s, 3H; SiCH_3], 1.15–1.31 [m, 12H; 6 × CH_2CH$_2$], 1.75–1.79 [m, 6H; 3 × CH_2CHN], 1.90–1.93 [m, 3H; CH_2CHN], 2.05–2.08 [m, 3H; CH_2CHN], 2.41 + 2.62 [AB system, $^{2}J_{AB}$ = 14.2 Hz, 6H; N(CH_2)Si], 2.41–2.54 [m, 6H; 6 × C*H*N], 2.49 [s, 18H; N(CH_3)$_2$], 2.56 [s, 9H; N(CH_3)CH$_2$Si]. {^{1}H}^{13}C NMR: (125.8 MHz, C$_6$D$_6$): δ = −3.0 [Si(*C*H$_3$)], 25.0 (2 × *C*H$_2$CHN), 26.20, 26.24 [(*C*H$_2$)$_2$CH$_2$], 40.6 [N(*C*H$_3$)$_2$], 40.8 [N(*C*H$_3$)CH$_2$Si], 42.7 [N(*C*H$_2$)Si], 64.5 (*C*HN), 67.5 (*C*HN). ^{29}Si NMR: (99.4 MHz, C$_6$D$_6$): δ = −1.4. Elemental analysis: Calc. for $C_{31}H_{66}N_6Si$: C 67.58, H 12.07, N 15.25; Found: C 67.17, H 12.59, N 14.72. $[\alpha]_D^{20}$ −33.5 (cyclohexane, 0.618 g/100 mL); GC-MS: t_R = 19.26 min [80 °C (2 min) − 10 °C min^{-1} − 280 °C (5 min)]; *m*/*z* (%): 381 (20) {[M − (C$_{10}$H$_{21}$N$_2$)]$^+$}, 170 (35) [(*R*,*R*)-TMCDA], 124 (25) {[C$_6$H$_9$N(CH$_3$)CH$_2$]$^+$}, 84 (100) {[N(CH$_3$)$_2$C$_3$H$_4$]$^+$}, 71 (63) [(C$_4$H$_9$N)$^+$], 58 (92) {[N(CH$_3$)$_2$CH$_2$]$^+$}.

B. General procedure for the synthesis of the zinc(II) bromide/chloride complexes

The silane and an equivalent amount of the zinc(II) salt were dissolved in acetone or a mixture of acetone/diethyl ether and stored at room temperature. Upon evaporation of the solvent, colourless crystals of the corresponding adduct are formed, which were washed with cold diethyl ether.

Synthesis of the zinc(II) bromide/chloride complexes of (*R*,*R*)-6. Using general procedure B, 100 mg (0.33 mmol) of silane (*R*,*R*)-**6** and 74 mg, 0.33 mmol zinc(II) bromide (45 mg, 0.33 mmol zinc(II) chloride) gave colourless crystals of (R_C,R_C,R_N)-**8** (161 mg, 30 mmol; 92%) (chloride: 128 mg, 0.29 mmol; 88%). $ZnBr_2$ adduct: ^{1}H NMR: (300.1 MHz, CDCl$_3$): δ = 0.54 [s, 3H; Si(CH_3)], 0.69 [s, 3H; Si(CH_3)], 1.10–1.37 (m, 4H; 2 CH_2, cyclohexyl), 1.83–1.86 (m, 2H; CH_2, cyclohexyl), 2.01–2.16 (m, 2H; CH_2, cyclohexyl), 2.33 [s, 3H; N(CH_3)], 2.43 [s, 3H; N(CH_3)], 2.55–2.57 [m, 2H; C*H*N], 2.63 [s, 3H; N(CH_3)], 2.67 + 2.91 [AB system, $^{2}J_{AB}$ = 13.8 Hz, 1H; N(CH_2)Si, D1 + D2], 7.34–7.36 (m, 3H; H_{arom}), 7.57–7.60 (m, 2H; H_{arom}). {^{1}H}^{13}C NMR: (75.7 MHz, CDCl$_3$): δ = −1.68 + −1.89 [Si(*C*H$_3$)$_2$], 21.8 + 22.4 + 24.2 + 24.3 (*C*H$_2$, cyclohexyl), 40.9 + 41.8 + 47.4 [N(*C*H$_3$)], 49.3 [N(*C*H$_2$)Si], 64.1 (*C*HN), 67.6

Table 3 Crystal data and structure refinement of all zinc(II) bromide complexes

Compound	(R_C,R_C,R_N)-**8**	(R_C,R_C,R_N)-**9**	(R_C,R_C,R_N)-**12**
CCDC No.	851902	851903	851904
Formula	$C_{18}H_{32}SiN_2ZnBr_2$	$C_{23}H_{34}SiN_2ZnBr_2$	$C_{39}H_{52}SiN_2ZnBr_2O$
Formula weight/g mol^{-1}	529.74	591.80	846.20
T/K	173(2)	173(2)	173(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1$ (4)	$P2_1$ (4)	$P2_12_12_1$ (19)
a/Å	11.5004(6)	12.3467(6)	12.2947(4)
b/Å	8.3851(4)	11.0348(6)	16.4427(5)
c/Å	11.6141(7)	19.5297(14)	19.7658(6)
β/°	96.489(5)	106.652(7)	—
Volume/Å^3	1112.80(10)	2549.2(3)	3995.8(2)
Z	2	4	4
D_c/Mg m^{-3}	1.581	1.542	1.407
μ(Mo Kα)/mm^{-1}	4.751	4.157	2.706
F(000)	536	1200	1744
Crystal dimensions/mm	0.30 × 0.20 × 0.10	0.40 × 0.40 × 0.10	0.30 × 0.20 × 0.10
Theta range/°	2.36 to 25.00	2.14 to 25.00	2.06 to 25.00
Index ranges	$-13 \le h \le 13$ $-9 \le k \le 9$ $-13 \le l \le 13$	$-14 \le h \le 14$ $-13 \le k \le 13$ $-22 \le l \le 23$	$-14 \le h \le 14$ $-19 \le k \le 19$ $-21 \le l \le 23$
Reflections collected	10 641	23 721	33 648
Independent reflections	3863 [R_{int} = 0.0310]	8910 [R_{int} = 0.0859]	7038 [R_{int} = 0.0456]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameter	3868/7/222	8910/1/531	7038/0/430
Goodness-of-fit on F^2	1.027 1.019	1.006 —	— —
Final R indices [$2\sigma(I)$]	R_1 = 0.0243 R_1 = 0.0255 wR_2 = 0.0550	R_1 = 0.0432 — wR_2 = 0.0674	— — wR_2 = 0.0392
R indices (all data)	R_1 = 0.0269 wR_2 = 0.0553	R_1 = 0.0649 wR_2 = 0.0691	R_1 = 0.0351 wR_2 = 0.0397
Absolute structure parameter	−0.001(8)	−0.045(8)	0.003(5)

(*C*HN), 127.8 (*C*H$_{meta}$), 129.2 (*C*H$_{para}$), 133.6 (*C*H$_{ortho}$), 137.4 (*C*$_{ipso}$). ^{29}Si NMR: (59.6 MHz, $CDCl_3$): $\delta = -5.5$.

Synthesis of the zinc(II) bromide/chloride complexes of (*R*,*R*)-7. Using general procedure B, 100 mg (0.27 mmol) of (*R*,*R*)-**7** and 61 mg (0.27 mmol) zinc(II) bromide (36.8 mg, 0.27 mmol zinc(II) chloride) gave colourless crystals of (R_C,R_C,R_N)-**9** (123 mg, 0.21 mmol; 78%) (chloride: 119 mg, 0.24 mmol; 88%). $ZnBr_2$ adduct: ^{1}H NMR: (300.1 MHz, $CDCl_3$): δ = 1.13–1.37 (m, 4H; 2 C*H*$_2$, cyclohexyl), 1.18 [s, 3H; Si(C*H*$_3$)], 1.86–1.88 (m, 2H; C*H*$_2$, cyclohexyl), 2.03–2.07 (m, 2H; C*H*$_2$, cyclohexyl), 2.19 + 2.48 + 2.65 [s, 3H; N(C*H*$_3$)], 2.53–2.61 [m, 2H; C*H*N], 3.09 + 3.25 [AB system, $^2J_{AB}$ = 14.3 Hz, 2H; N(C*H*$_2$)Si, D1 + D2], 7.29–7.35 (m, 3H; *H*$_{arom}$), 7.44–7.46 (m, 3H; *H*$_{arom}$), 7.55–7.58 (m, 2H; *H*$_{arom}$), 7.66–7.70 (m, 2H; *H*$_{arom}$). {^{1}H}^{13}C NMR: (7.5 MHz, $CDCl_3$): δ = −2.97 [Si(*C*H$_3$)$_2$], 21.9 + 22.6 + 24.3 + 24.4 (*C*H$_2$, cyclohexyl), 41.3 + 42.0 + 47.3 [N(*C*H$_3$)], 47.5 [N(*C*H$_2$)Si], 64.1 (*C*HN), 67.7 (*C*HN), 127.8 + 128.2 (*C*H$_{meta}$), 129.5 + 129.7 (*C*H$_{para}$), 134.5 +134.9 (*C*H$_{ortho}$), 135.0 + 135.33 (*C*$_{ipso}$). ^{29}Si NMR: 59.6 MHz, $CDCl_3$): $\delta = -10.5$.

Synthesis of the zinc(II) bromide complexes of (*R*,*R*)-10. Using general procedure B, 100 mg (0.18 mmol) of (silylmethyl)silane (*R*,*R*)-**8** and 40 mg (0.18 mmol) zinc(II) bromide gave colourless plates of (R_C,R_C,R_N)-**12** (125 mg, 0.16 mmol; 88%). ^{1}H NMR: (300.1 MHz, $CDCl_3$): δ = 0.13 (s, 3H SiC*H*$_3$), 1.04–1.198 [m, 6H; C*H*$_2$, cyclohexyl + SiC*H*$_2$Si], 1.77–1.85 [m, 2H; C*H*$_2$, cyclohexyl], 2.01–2.05 [m, 2H; C*H*$_2$, cyclohexyl], 2.07 + 2.50 + 2.67 [s, 3H; N(C*H*$_3$)], 2.52–2.62 [m, 2H; C*H*N], 2.84 + 3.31 [AB system, $^2J_{AB}$ = 14.0 Hz, 2H; N(C*H*$_2$)Si], 7.27–7.36 (m, 12H; *H*$_{arom}$), 7.45–7.49 (m, 4H; *H*$_{arom}$), 7.52–7.58 (m, 4H; *H*$_{arom}$). {^{1}H}^{13}C NMR: (75.5 MHz, $CDCl_3$): δ = −2.94 (SiCH$_3$), −2.47 (SiCH$_2$Si), 21.9 + 22.6 + 24.3 + 24.4 (*C*H$_2$, cyclohexyl), 41.2 + 42.0 [N(*C*H$_3$)$_2$], 47.4 [N(*C*H$_2$)Si], 47.5 [N(*C*H$_3$)CH$_2$Si], 64.2 (*C*HN), 67.7 (*C*HN), 127.5 + 127.9 (br) + 128.2 (*C*H$_{meta}$), 128.7 + 129.6 (br) + 129.8 (*C*H$_{para}$), 134.5 + 134.6 + 134.7 + 134.9 (*C*H$_{ortho}$), 135.1 +135.3 + 135.4 + 135.6 (*C*$_{ipso}$). ^{29}Si NMR: (59.6 MHz, $CDCl_3$): $\delta = -8.0, -10.5$.

Formation of zinc silanolate 15. Using general procedure B; 100 mg (0.25 mmol) silane **13** and 56 mg (0.25 mmol) zinc(II) bromide in 10 mL acetone gave colourless plates of **15** (86 mg, 0.11 mmol; 88%). For spectroscopic details see literature.[20]

Formation of (*R*,*R*)-TMCDA·ZnBr$_2$ (16). Using general procedure B; 100 mg (0.18 mmol) silane **14** and 123 mg (0.54 mmol) zinc(II) bromide in 10 mL acetone gave colourless plates of **16** (169 mg, 0.43 mmol; 79%). ^{1}H NMR: (500.1 MHz, $CDCl_3$): δ = 1.16–1.34 (m, 4H, C*H*$_2$ cyclohexyl), 1.84–1.89 (m, 2H; C*H*$_2$ cyclohexyl), 2.01–2.05 (m, 2H; C*H*$_2$ cyclohexyl), 2.42 [s, 6H; N(C*H*$_3$)$_2$], 2.57–2.60 (m, 2H; C*H*N), 2.63 [s, 6H; N(C*H*$_3$)$_2$]. {^{1}H}^{13}C NMR: (125.8 MHz, $CDCl_3$): δ = 22.3 + 24.2 (*C*H$_2$ cyclohexyl) 41.1 + 47.1 [N(*C*H$_3$)$_2$], 64.5 (*C*HN). Elemental analysis: Calc. for $C_{10}H_{22}N_2ZnBr_2$: C 30.37, H 5.61, N 7.08; Found: C 30.50, H 5.55, N 7.10.

Crystallographic details

Data collection of all compounds was conducted with CrysAlis CCD, Oxford Diffraction Ltd. CCD (D8 three-circle goniometer), cell determination, refinement and integration with CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.32.37; empirical absorption correction with CrysAlis RED using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The crystal structure determinations were effected at −100 °C (type of radiation: Mo Kα, α = 0.71073 Å). The structures were solved applying direct and Fourier methods using SHELXS-97 (G. M. Sheldrick, SHELXS97, University of Göttingen 1997) and refined with SHELXL-97 (G. M. Sheldrick, SHELXL97, University of Göttingen 1997). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data (see Table 3 and S1†). Table 3 and Table S1 (SI†) give further information about the data collection and structure refinement of all α-lithiated silanes. Further information (ORTEP plots, atomic coordinates and anisotropic displacement parameters) is available in the Supporting Information.†

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