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Ni(II) complexes with thioether-functionalized silylamide ligands. Synthesis and crystal structures of $[\text{Ni}\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{S}-t\text{-Bu})_2\}]$, $[\text{Ni}\{\text{Ph}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SMe})_2\}]$ and $[\text{Ni}\{\text{Ph}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SPh})_2\}]$

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Abstract: Thioether-functionalized aminosilanes $\text{R}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{SR}')_2$ with $\text{R}=\text{Me}$, Ph and $\text{R}'=t\text{-Bu}$, Me , Ph were synthesized from the corresponding dichlorosilanes R_2SiCl_2 and lithiated aniline derivatives $\text{LiNH}-\text{C}_6\text{H}_4-2-\text{SR}'$. Treatment of the functionalized aminosilanes $\text{R}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{SR}')_2$ with two eq. of $n\text{-BuLi}$ and subsequent reaction with nickel(II) halides NiX_2 ($\text{X}=\text{Cl}$, Br) or $[\text{Ni}(\text{acac})_2(\text{TMEDA})]$ led to the formation of the Ni(II) complexes $[\text{Ni}\{\text{R}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SR}')_2\}]$. The X-ray single-crystal structure determinations of the nickel complexes revealed that the thioether-functionalized silylamides $\text{R}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SR}')_2$ act as tetradentate ligands. The nickel atoms exhibit a distorted square-planar coordination with Ni–N and Ni–S bond lengths in the range of 186.4(3)–186.9(2) pm and 217.5(1)–221.5(1) pm, respectively.

Keywords: aminosilanes; complexes; nickel; single crystal X-ray diffraction; thioethers.

1 Introduction

Complexes containing silylamide ligands $\text{R}_2\text{Si}(\text{NR}')_2$ were first described around four decades ago by Veith and Bürger, who reported on the stannylene compound $[\text{SnMe}_2\text{Si}(\text{N}-t\text{-Bu})_2]$ [1] and the titanium derivative $[\text{Ti}\{\text{Me}_2\text{Si}(\text{N}-t\text{-Bu})_2\}_2]$ [2]. Since this time, silylamide chemistry has developed continuously [3]. Silylamides are versatile ligands which can be easily tuned by variation of the residues R and R' . For example, the application of the sterically demanding $\text{Me}_2\text{Si}(\text{NDipp})_2$ ligand (Dipp: 2,6-*i*-Pr₂C₆H₃) allowed the formation of dinuclear zinc complexes with Zn–Zn bonds [4]. Apart from steric requirements, the coordination properties of silylamide

ligands can be customized by the introduction of additional side arm donor functions. The first studies go back to 2004 when Passarelli et al. synthesized functionalized silylamides $[\text{Me}_2\text{Si}(\text{NCH}_2\text{CH}_2\text{X})_2]^{2-}$ ($\text{X}=\text{OR}$, NR_2) and applied them for the generation of zirconium polymerization catalysts [5]. Recently, we found that thioether-functionalized silylamides $[\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{SR}')_2]^{2-}$ ($\text{R}'=\text{Me}$, Ph) can be successfully used for the synthesis of Cu(I), Ag(I), Au(I), and Tl(I) complexes [6, 7]. Particularly in the case of the Cu(I), Ag(I) and Au(I) compounds, the presence of thioether side arms leads to an improved thermal stability. Moreover, thioether-functionalized silylamides should also be suitable for the complexation of divalent metal ions. Depending on the type of the M(II) center, the N,N',S,S' donor set could support different coordination modes, e.g. square planar or tetrahedral. Currently we are studying the coordination behaviour of thioether-functionalized silylamides in Fe(II), Ni(II) and Co(II) complexes and here we report our first results on some nickel(II) derivatives.

2 Results and discussion

2.1 Synthesis of the aminosilanes and the nickel(II) complexes

The thioether-functionalized aminosilanes $\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{S}-t\text{-Bu})_2$ (**1**), $\text{Ph}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{SMe})_2$ (**2**) and $\text{Ph}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{SPh})_2$ (**3**) were synthesized from the corresponding chlorosilanes R_2SiCl_2 and the lithiated aniline derivatives $\text{LiNH}-\text{C}_6\text{H}_4-2-\text{SR}'$ according to Scheme 1. After recrystallization from toluene-*n*-hexane mixtures, the aminosilanes were obtained as pale yellow, air sensitive solids which are readily soluble in polar solvents like toluene and THF and less soluble in *n*-hexane. Compounds **1–3** were characterized by spectroscopic methods (¹H, ¹³C, ²⁹Si NMR and IR). The ²⁹Si NMR spectra consist of singlet signals with chemical shifts in the range between $\delta=-32.0$ and -11.3 ppm (Table 1). In the IR spectra the characteristic $\nu(\text{NH})$ bands were found between 3318 and 3341 cm⁻¹.

In order to synthesize the corresponding nickel(II) complexes, the aminosilanes were treated with two

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Scheme 1: Synthesis of the aminosilanes **1–3** and the nickel(II) complexes **4–6**.

Table 1: ^{29}Si NMR shifts for the aminosilanes **1–3** and the nickel(II) complexes **4–6**.

Compound	No.	$\delta(^{29}\text{Si})/\text{ppm}$
$\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2\text{-S-}t\text{-Bu})_2$	1	–11.3
$\text{Ph}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2\text{-SMe})_2$	2	–31.1
$\text{Ph}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2\text{-SPh})_2$	3	–32.0
$[\text{Ni}\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2\text{-S-}t\text{-Bu})_2\}]$	4	1.6
$[\text{Ni}\{\text{Ph}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2\text{-SMe})_2\}]$	5	–22.6
$[\text{Ni}\{\text{Ph}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2\text{-SPh})_2\}]$	6	–22.2

equivalents of *n*-BuLi and next reacted with anhydrous Ni(II) halides NiX_2 ($\text{X} = \text{Cl}, \text{Br}$) in refluxing THF (Scheme 1). During the reactions the nickel(II) halides were slowly dissolved and the reaction mixtures turned dark green. After removal of the volatiles in a vacuum, toluene was added and the insoluble parts were filtered off. Next the filtrates were layered with *n*-heptane to precipitate the nickel complexes $[\text{Ni}\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2\text{-S-}t\text{-Bu})_2\}]$ **4**, $[\text{Ni}\{\text{Ph}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2\text{-SMe})_2\}]$ **5** and $[\text{Ni}\{\text{Ph}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2\text{-SPh})_2\}]$ **6** as deep green crystals in yields of 53%, 19% and 30%, respectively. The main disadvantage of this synthesis route arises from the low solubility of the nickel(II) halides which requires long reaction times. In order to improve the preparations, the Ni(II) halides were replaced by $[\text{Ni}(\text{acac})_2(\text{TMEDA})]$ which is more soluble in organic solvents. At room temperature a blue solution of $[\text{Ni}(\text{acac})_2(\text{TMEDA})]$ in THF reacts rapidly with the silylamide reagent $\text{Li}_2\text{R}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2\text{-SR}')_2$ to give a deep green reaction mixture along with a precipitate of $\text{Li}(\text{acac})$. After removal of $\text{Li}(\text{acac})$ and recrystallization of the raw product from toluene-*n*-heptane the nickel complexes **4**, **5** and **6** were obtained in yields of 69, 60 and 72%, respectively.

The nickel complexes **4–6** are readily soluble in THF and toluene to give intensively green coloured air sensitive solutions. In non-polar solvents like *n*-hexane the complexes are much less soluble. On contact with air, the solid samples slowly decompose.

Compounds **4–6** are diamagnetic and the complexes were characterized by ^1H , ^{13}C and ^{29}Si NMR spectroscopy. In the case of compound **4** the ^1H NMR signals of the methyl and the *t*-Bu groups display a small downfield shift (0.05 and 0.43 ppm, respectively) with respect to the corresponding signals of the aminosilane **1**. A similar downfield shift of 0.3 ppm is observed for the SMe signal of compound **5**. The ^{29}Si NMR spectra consist of singlet signals with chemical shifts $\delta = 1.6$, –22.6 and –22.2 ppm, respectively. In comparison with the corresponding aminosilanes $\text{R}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2\text{-SR}')_2$ these signals are shifted by 8.5–12.9 ppm to lower field.

2.2 Crystal structures

In order to get more detailed insight into the molecular structures, X-ray crystal structure determinations were carried out for compounds **1**, **4**, **5**, and **6**. Details of the data collection and the refinements are collected in Table 2.

2.2.1 $\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2\text{-S-}t\text{-Bu})_2$ (**1**)

Compound **1** forms orthorhombic crystals, space group *Pbca*, $Z=8$. The crystal structure consists of discrete molecules without any unusually short intermolecular contacts (Fig. 1). The molecular structure displays a silicon atom which is nearly tetrahedrally coordinated by

Table 2: Crystallographic data and details of data collection and crystal structure refinement of compounds **1**, **4**, **5** and **6**.

Compound	1	4	5	6
Empirical formula	$C_{22}H_{34}N_2S_2Si$	$C_{22}H_{32}N_2NiS_2Si$	$C_{26}H_{24}N_2NiS_2Si$	$C_{36}H_{28}N_2NiS_2Si$
Formula weight/ $g \cdot mol^{-1}$	418.72	475.41	515.39	639.52
Temperature/K	200	200	213	200
Radiation	MoK α	MoK α	MoK α	MoK α
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
Unit cell dimensions				
<i>a</i> /pm	1401.75(7)	1408.2(2)	1584.4(1)	1848.4(4)
<i>b</i> /pm	1259.20(6)	1391.9(1)	972.64(4)	1038.95(9)
<i>c</i> /pm	2740.2(1)	1307.4(1)	1516.1(1)	1562.4(2)
β /deg	90	113.40(1)	97.94(1)	99.88(1)
Volume/pm ³	4836.8(4) · 10 ⁶	2351.9(4) · 10 ⁶	2314.0(2) · 10 ⁶	2956.1(7) · 10 ⁶
<i>Z</i>	8	4	4	4
Calculated density/ $g \cdot cm^{-3}$	1.15	1.34	1.48	1.44
Absorption coefficient μ/mm^{-1}	0.3	1.1	1.1	0.9
Crystal size/mm ³	0.30 × 0.28 × 0.17	0.41 × 0.32 × 0.03	0.14 × 0.08 × 0.05	0.38 × 0.22 × 0.14
θ range for data collection/deg	3.85–25.00	4.14–25.00	2.46–25.00	2.26–25.00
Reflections collected/unique	20661/4248	9318	10533/2029	9936/2888
R_{int}	0.0448	0.0357	0.0554	0.0367
Data/restraints/parameters	4248/0/252	9318/0/129	2029/0/146	2888/0/191
Goodness-of-fit on F^2	0.786	0.885	1.029	1.020
$R_1 [I > 2\sigma(I)]$	0.0285	0.0406	0.0296	0.0260
wR_2 (all data)	0.0576	0.0955	0.0740	0.0698
Res. densities (max/min)/ $e \text{ \AA}^{-3}$	0.19/−0.16	0.36/−0.39	0.37/−0.21	0.31/−0.28
Diffractometer	STOE IPDS 2T	STOE IPDS 2T	STOE IPDS 2	STOE IPDS 2T

Fig. 1: Molecular structure of compound **1** in the crystal.

Displacement ellipsoids at the 50% probability level. H atoms are omitted for clarity, except NH. Selected bond lengths (pm) and angles (deg): Si–N(1) 172.3(2), Si–N(2) 172.3(2), Si–C(1) 184.7(2), Si–C(2) 184.8(2), C(3)–N(1) 139.2(2), C(4)–S(1) 176.9(2), C(9)–S(1) 185.0(2), C(13)–N(2) 139.0(2), C(14)–S(2) 177.1(2), C(19)–S(2) 184.8(2); N(1)–Si–N(2) 111.3(1), C(1)–Si–C(2) 110.7(1), N(1)–Si–C(1) 103.9(1), N(1)–Si–C(2) 113.3(1), N(2)–Si–C(1) 114.3(1), N(2)–Si–C(2) 103.6(1), Si–N(1)–C(3) 132.3(1), Si–N(2)–C(13) 131.7(1), C(4)–S(1)–C(9) 104.5(1), C(14)–S(2)–C(19) 104.8(1).

two methyl groups and the N atoms of two 2-(*t*-butylthio)anilido units. The Si–N bonds have identical lengths of 173.2(1) pm which is in agreement with the Si–N bond lengths observed in the SPh derivative $Me_2Si(NH-C_6H_4-2-SPh)_2$ (173.2(1) pm) [6] and other diaminosilanes, e.g. $Me_2Si(NHPh)_2$ (172.7–173.9 pm) [8], $Me_2Si\{NH(2,6-Me_2C_6H_3)\}_2$ (174.3 pm) and $Ph_2Si\{NH(2,6-Me_2C_6H_3)\}_2$ (172.8 pm) [9]. The N–H groups are involved in weak intramolecular hydrogen bonding with N···S distances of 305.5(2)–305.8(2) pm. Approximately the same values have been observed for $Me_2Si(NH-C_6H_4-2-SPh)_2$ (304.0(2)–305.0(2) pm) [6].

2.2.2 Nickel complexes 4–6

Compounds **4–6** form monoclinic crystals, space group *C2/c*. In each case the crystal structure consists of isolated $[Ni\{R_2Si(N-C_6H_4-2-SR')_2\}]$ units without any unusually short intermolecular contacts (Figs. 2–4). The nickel and the silicon atoms reside on special positions (1/2, *y*, 1/4) of the space group *C2/c* and thus the complexes exhibit crystallographic C_2 (2) symmetry. The nickel atoms adopt an almost planar coordination by two nitrogen atoms and two sulfur atoms of the silylamido ligand. The maximum deviation from the mean plane through the atoms Ni, N, N', S and S' ranges from 16.9

Fig. 2: Molecular structure of compound **4** in the crystal. Displacement ellipsoids at the 50% probability level. H atoms are omitted for clarity. Symmetry operator $i: 1-x, y, 1/2-z$. Selected bond lengths (pm) and angles (deg): Ni–S 221.5(1), Ni–N 186.4(3), Si–N 170.2(3), Si–C(11) 185.4(5), C(1)–N 135.8(5), C(6)–S 177.8(4), C(7)–S 188.4(3); N–Ni–Nⁱ 79.6(2), N–Ni–S 88.2(1), N–Ni–Sⁱ 164.5(1), S–Ni–Sⁱ 105.4(1), N–Si–Nⁱ 89.0(2), Si–N–Ni 95.7(1), C(1)–N–Si 143.3(3), C(1)–N–Ni 120.6(3), C(6)–S–C(7) 102.9(2), C(6)–S–Ni 96.9(1), C(7)–S–Ni 103.9(1).

Fig. 4: Molecular structure of compound **6** in the crystal. Displacement ellipsoids at the 50% probability level. H atoms are omitted for clarity. Symmetry operator $i: 1-x, y, 3/2-z$. Selected bond lengths (pm) and angles (deg): Ni–S 219.1(1), Ni–N 186.0(1), Si–N 170.9(1), C(1)–N 136.1(2), C(6)–S 178.5(2), C(7)–S 178.8(2); N–Ni–Nⁱ 80.6(1), N–Ni–S 88.6(1), N–Ni–Sⁱ 164.5(1), S–Ni–Sⁱ 104.0(1), N–Si–Nⁱ 89.6(1), C(1)–N–Si 141.7(1), C(1)–N–Ni 120.4(1), C(6)–S–Ni 97.4(1), C(7)–S–Ni 110.9(1), C(6)–S–C(7) 102.2(1).

Fig. 3: Molecular structure of compound **5** in the crystal. Displacement ellipsoids at the 50% probability level. H atoms are omitted for clarity. Symmetry operator $i: 1-x, y, 3/2-z$. Selected bond lengths (pm) and angles (deg): Ni–S 217.5(1), Ni–N 186.9(2), Si–N 170.7(2), C(1)–N 135.7(3), C(6)–S 177.9(2), C(7)–S 181.1(3); N–Ni–Nⁱ 81.3(1), N–Ni–S 88.5(1), N–Ni–Sⁱ 163.0(1), S–Ni–Sⁱ 104.4(1), N–Si–Nⁱ 91.0(1), Si–N–Ni 93.9(1), C(1)–N–Si 144.2(2), C(1)–N–Ni 120.1(1), C(6)–S–C(7) 103.9(1), C(6)–S–Ni 97.9(1), C(7)–S–Ni 114.7(1).

pm (**4**) to 24.5 pm (**5**) and in all cases the N atoms are more dislocated than the sulfur atoms. For the silicon atoms a roughly tetrahedral coordination is found with relatively small N–Si–N angles (89.0(2)–91.0(1)°) due

to the formation of the SiN₂Ni four-membered ring. In comparison with the aminosilane **1** the N–Si–N angle is reduced by approximately 20°. The sulfur atoms adopt a pyramidal coordination with the R' groups in mutual *trans* orientation with respect to the NiS₂N₂ plane. The Ni–N bond lengths in compounds **4**–**6** are ranging from 186.4(3)–186.9(2) pm and the Ni–S bond lengths vary from 217.5(1) to 221.5(1) pm. A comparison of the Si–N bond lengths in compound **1** with those in the corresponding Ni complex **4** reveals a small decrease from 172.3(2) to 170.2(3) pm. The same effect is observed for the C–N bond lengths which change from 139.2(2) to 135.8(5) pm and additionally the Si–N–C angle is increased by approx. 12°. Contrary to this the Si–C bond lengths (**1**: 184.8(2), **4**: 185.4(5) pm) and the C–Si–C angles (**1**: 110.7(1)°, **4**: 109.6(4)°) are barely affected by the formation of the nickel complex. The Ni–N bond lengths in compounds **4**–**6** are comparable to those that have been observed in homoleptic nickel amides. In [Ni₂(μ-NPh₂)₂(NPh₂)₂] the Ni–N bond lengths are ranging from 183.7(9) pm for the terminal and 189.9(9)–191.6(9) pm for the bridging NPh₂ groups [10]. Comparatively short Ni–N bonds were found in two-coordinated nickel(II) complexes of the type [Ni(NHR)₂] (R = C₆H₃-2,6(C₆H₂-2,4,6-*i*-Pr)₂: 182.8(2) pm; R = C₆H₃-2,6(C₆H₂-2,4,6-Me)₂: 181.2(3)–181.9(3) pm) [11], [Ni(2,6-Dipp₂C₆H₃NH)₂]

(Dipp = 2,6-*i*Pr₂C₆H₃, 181.8(3) pm) [12], [Ni(NMesBMes₂)₂] (Mes = 2,4,6-Me₃-C₆H₂, 186.5(2)–186.7(2) pm) [13], [Ni{N(SiMe₃)(Dipp)}₂] (179.9(1) pm) [14]. The slight elongation of the Ni–N bonds in compounds **4–6** is due to the increased coordination number of nickel atoms and the influence of the thioether groups in *trans* position to the N atoms. Complexes **4–6** display Ni–S bond lengths which are in the expected range. According to the CSD database tetra-coordinated nickel(II) complexes with thioether ligands exhibit Ni–S bond lengths from 208.7 to 236.0 pm with a median value of 218.3 pm (lower quantile: 216.1 pm, upper quantile: 220.4 pm, 400 entries). [15]. The marginal elongation of the Ni–S bonds in compound **4** (221.5(1) pm) compared to compounds **5** and **6** (217.5(1)–219.1(1) pm) might be due to the steric requirements of the bulky *t*-Bu groups.

In comparison with the related Ag(I) and Au(I) complexes [M₂{Me₂Si(N-C₆H₄-2-SR')₂}(PMe₃)₂] (M = Ag, R' = Ph; M = Au, R' = Me, Ph) which display rather large M–S distances of 283.8(2)–341.2(1) pm, the Ni–S interaction in complexes **4–6** is much stronger. This different coordination behavior of the thioether groups in the related Ag(I)/Au(I) complexes on one hand and the Ni(II) derivatives on the other hand mainly arises from the different preferences of the metal centers involved. In the case of the Ag(I)/Au(I) complexes the coordinative saturation is assured by the presence of the amide and phosphine ligand and thus, the contribution of the thioether coordination is less essential. Contrary to this, Ni(II) centers usually prefer coordination number 4 (or higher) unless the bulkiness of the ligands enforces lower coordination numbers, cf. [Ni(NHR)₂] [11–14]. In the case of compounds **4–6** the Ni coordination spheres are completed by the neighbouring thioether groups. The geometric arrangement of the amido N atoms and the thioether sulfur atoms renders the sidearm-functionalized [R₂Si(N-C₆H₄-2-SR')₂]²⁻ ligands perfect for tetradentate planar coordination. Apart from Ni(II), other metal centers with *d*⁸ (Pd(II), Pt(II)) or *d*⁴ configuration (Cr(II)) could be interesting candidates to form square planar complexes with the thioether-functionalized silylamide ligands. These topics are currently investigated.

3 Experimental

3.1 General

All experiments were carried out in flame dried glassware under argon atmosphere using Schlenk techniques.

The solvents were purified by distillation from sodium/benzophenone.

The NMR spectra were recorded with an Agilent Technologies 500 MHz DD2 spectrometer and an Agilent Technologies 400 MHz VNMRs instrument at *T* = 27°C. The chemical shifts of ¹H, ¹³C and ²⁹Si were referenced relative to tetramethylsilane. CDCl₃ was freshly distilled from CaH₂. IR spectra were recorded on a BRUKER Tensor 27 equipped with a diamond ATR unit. Elemental analyses were performed on a VARIO EL instrument (Elementar Analysensysteme GmbH, Hanau). Mass spectra were collected on an Advion expression CMS spectrometer equipped with an APCI/ASAP ion source (capillary voltage: 150 V, capillary temperature: 220°C, source voltage: 15 V, APCI source temperature: 300°C, corona discharge 5 μA).

The commercially available compounds *n*-butyllithium, 2-methylthio-aniline, 2-phenylthio-aniline were used without further purification. Me₂SiCl₂ and Ph₂SiCl₂ were freshly distilled prior to use. 2-(*t*-butylthio)aniline [16] and [Ni(acac)₂(TMEDA)] [17] were prepared according to literature methods.

3.2 Crystal structure determinations

The crystal structure of compound **4** was determined from a twinned crystal. From the diffraction pattern two domains were identified and indexed separately. The integration of the intensity data was carried out for both domains including the overlapping reflections using the X-Area program [18]. From the refinement of the BASF parameter the ratio of both domains was determined as 0.63: 0.37. The crystal structures of compounds **1**, **4**, **5**, and **6** were solved by Direct Methods with the program SHELXT and refined with SHELXL [19] using OLEX2 [20]. Figures were generated with DIAMOND [21].

CCDC 1884701(**1**), 1884704 (**4**), 1884705 (**5**), and 1884706 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.3 General procedure for the synthesis of the aminosilanes 1–3

A solution of 90–200 mmol of the aniline derivative (H₂N-C₆H₄-2-SR, R = *t*-butyl, Me, Ph) in 50–80 mL of THF is treated with an equimolar amount of *n*-BuLi (2.5 M in hexane) at *T* = –78°C. After stirring for 30 min the reaction

mixture is warmed to room temperature. Next the stoichiometric amount of dichlorosilane R_2SiCl_2 is slowly added at -20°C . After warming to room temperature the reaction mixture is stirred for 12 h. Afterwards the volatiles are removed under reduced pressure and toluene (40–80 mL) is added. The precipitated LiCl is removed by filtration, washed with a few mL of toluene and afterwards the filtrate is evaporated nearly to dryness. After addition of 25–50 mL of *n*-pentane the solution is kept at -25°C to precipitate the product as a pale yellow solid, which is filtered off, washed with small portions of *n*-pentane and dried in vacuo. Yields: 80–90%.

3.3.1 $\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{S}-t\text{-Bu})_2$ (1)

$\text{C}_{22}\text{H}_{34}\text{N}_2\text{S}_2\text{Si}$ (418.7 g mol $^{-1}$): C found 63.0 (calcd. 63.1), H 7.54 (8.2), N 6.7 (6.7). M. p.: 148°C (decomposition). –MS (negative mode): 417.3 [M–H] $^-$. –IR: $\tilde{\nu}=3397(\text{w})$, 3318(m), 2965(m), 2923(w), 2898(w), 2861(w), 1635(w), 1588(m), 1567(m), 1478(s), 1445(m), 1376(m), 1363(m), 1304(s), 1257(s), 1221(w), 1166(m), 1150(m), 1122(w), 1057(w), 1035(m), 920(s), 901(s), 848(w), 830(s), 798(s), 753(vs), 697(w), 679(w), 661(m), 570(s), 533(m), 488(m), 446(m), 428(m), 322(s), 263(vs) cm $^{-1}$. – ^1H NMR (CDCl_3): $\delta=7.5$ (m, 2H, 3-CH), 7.23 (m, 2H, 5-CH), 6.98 (m, 2H, 6-CH), 6.58 (m, 2H, 4-CH), 5.85 (s, 2H, NH), 1.21 (s, 18H, *t*-Bu), 0.27 (s, 6H, SiCH_3). – ^{13}C NMR (125 MHz, CDCl_3): $\delta=150.1$ (1-CN), 139.3 (3-CH), 130.6 (5-CH), 118.1 (2-CS), 117.7 (4-CH), 115.1 (6-CH), 47.8 (CS, *t*-Bu), 31.0 (CH_3 , *t*-Bu), –1.6 (SiCH_3). – ^{29}Si NMR (100 MHz, CDCl_3): $\delta=-11.3$ (s).

3.3.2 $\text{Ph}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{SMe})_2$ (2)

$\text{C}_{26}\text{H}_{26}\text{N}_2\text{S}_2\text{Si}$ (458.71 g mol $^{-1}$): C found 67.59 (calcd. 68.08), H 5.56 (5.71), N 6.22 (6.11), S 14.31 (13.98). M. p.: 148°C (decomposition). –IR: $\tilde{\nu}=3317(\text{w})$, 3067(vs), 3023(vs), 2918(vs), 1585(m), 1567(m), 1476(vs), 1446(m), 1428(m), 1395(vw), 1366(s), 1293(s), 1277(m), 1261(s), 1213(vw), 1160(vw), 1113(s), 1061(vw), 1034(m), 997(vw), 970(vw), 916(s), 891(s), 847(vw), 792(w), 752(vs), 743(s), 712(vs), 699(s), 685(m), 595(m), 574(m), 498(vs), 467(s), 424(m), 360(w), 337(m), 300(vw), 263(vw), 237(w) cm $^{-1}$. – ^1H NMR (CDCl_3): $\delta=7.78$ (m, 4H, *m*-SiPh), 7.43 (m, 8H, *o*, *p*-Ph, 3- C_6H_3 -H), 7.02 (m, 2H, 6- C_6H_3 -H), 6.95 (m, 2H, 5- C_6H_3 -H), 6.70 (m, 2H, 4- C_6H_3 -H), 5.81 (s, 2H, NH_2), 2.39 (s, 6H, CH_3). – ^{13}C NMR (125 MHz, CDCl_3): $\delta=146.8$ (1-CN), 134.6 (*m*-SiPh), 134.2 (3-CH), 133.82 (*i*-SiPh), 130.6 (5-CH), 129.3 (*p*-SiPh), 128.6 (*o*-SiPh), 123.3 (2-CS), 119.5 (4-CH), 116.7 (6-CH), 19.0 (CH_3). – ^{29}Si NMR (100 MHz, CDCl_3): $\delta=-31.1$ (s).

3.3.3 $\text{Ph}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{SPh})_2$ (3)

$\text{C}_{36}\text{H}_{30}\text{N}_2\text{S}_2\text{Si}$ (582.86 g mol $^{-1}$): C found 74.08 (calcd. 74.19), H 5.28 (5.19), N 5.00 (4.81), S 11.92 (11.00). M. p.: 146°C (decomposition). –MS (negative mode): 581.2 [M–H] $^-$. –IR: $\tilde{\nu}=3341(\text{vw})$, 3309(w), 3066(vw), 3016(vw), 1585(m), 1568(m), 1477(vs), 1447(m), 1428(m), 1372(s), 1298(s), 1261(m), 1187(w), 1156(vs), 1113(m), 1081(w), 1068(w), 1055(w), 1034(m), 997(vw), 920(m), 898(s), 848(w), 787(w), 738(vs), 714(s), 689(vs), 593(m), 565(m), 526(m), 504(vs), 473(vs), 455(s), 351(m), 325(m), 308(m), 290(m), 233(m) cm $^{-1}$. – ^1H NMR (CDCl_3): $\delta=7.55$ (m, 2H, 6- C_6H_3 -H), 7.25 (m, 20H, *o*, *m*, *p*-SiPh, *o*, *m*, *p*-SPh), 6.99 (m, 2H, 4- C_6H_3 -H), 6.85 (m, 2H, 3- C_6H_3 -H), 6.74 (m, 2H, 5- C_6H_3 -H), 5.65 (s, 2H, NH_2). – ^{13}C NMR (125 MHz, CDCl_3): $\delta=148.1$ (1-CN), 137.5 (3-CH), 136.7 (*i*-SPh), 134.4 (*m*-SiPh), 132.9 (*i*-SiPh), 131.4 (5-CH), 130.5 (*p*-SiPh), 129.2 (*o*-SiPh), 128.3 (*m*-SiPh), 127.0 (*o*-SPh), 125.8 (2C, *p*-SPh), 119.4 (4-CH), 117.7 (2-CS), 117.0 (6-CH). – ^{29}Si NMR (100 MHz, CDCl_3): $\delta=-32.0$ (s).

3.4 Synthesis of the nickel complexes 4–6

3.4.1 $[\text{Ni}\{\text{Me}_2\text{Si}(\text{N}-\text{C}_6\text{H}_4-2-\text{S}-t\text{-Bu})_2\}]$ (4)

3.4.1.1 Method A

A solution of 0.67 g (1.6 mmol) of $\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{S}-t\text{-Bu})_2$ (1) in 30 mL THF is treated with 1.28 mL (3.2 mmol) of a 2.5 M solution of *n*-BuLi in *n*-hexane at $T=-70^\circ\text{C}$. After warming to room temperature the solution of $\text{Li}_2\text{Me}_2\text{Si}(\text{NC}_6\text{H}_4-2-\text{S}-t\text{-Bu})_2$ is slowly added to a suspension of 207.4 mg (1.6 mmol) of NiCl_2 in 10 mL THF. Then the reaction mixture is refluxed for 4 h. After cooling to room temperature the volatiles are removed and toluene (15 mL) is added. Next the insoluble parts are removed by filtration and the filtrate is layered with *n*-heptane. Within a few days the products precipitates in the form of green crystals. Yield: 0.36 g (53%).

3.4.1.2 Method B

A solution of 0.60 g (1.4 mmol) of $\text{Me}_2\text{Si}(\text{NH}-\text{C}_6\text{H}_4-2-\text{S}-t\text{-Bu})_2$ (1) in a mixture of 25 mL *n*-hexane and 25 mL THF is treated with 1.15 mL (2.86 mol) of a 2.5 M solution of *n*-BuLi in *n*-hexane at $T=-70^\circ\text{C}$. The solution is warmed to -50°C and a solution of 0.53 g (1.4 mmol) of $[\text{Ni}(\text{acac})_2(\text{TMEDA})]$ in 5 mL of *n*-hexane is added. On warming to room temperature the reaction starts at -20°C and a deep green reaction mixture is obtained. After stirring at room temperature the volatiles are removed under reduced pressure and afterwards toluene (50 mL) is added. The insoluble Li(acac) is

removed by filtration and next the filtrate is layered with *n*-heptane in order to precipitate the product. Yield: 0.47 g (69%). $\text{C}_{22}\text{H}_{32}\text{N}_2\text{NiS}_2\text{Si}$ (475.41 g mol⁻¹): C found 56.01 (calcd. 55.6), H 6.5 (6.8), N 5.8 (5.9). –IR: $\tilde{\nu}$ = 2976(w), 2956(w), 2918(w), 2861(w), 1597(m), 1566(m), 1518(m), 1458(s), 1437(sh), 1364(w), 1345(m), 1296(w), 1261(w), 1242(m), 1198(w), 1149(m), 1120(w), 1044(w), 1020(m), 979(w), 953(w), 920(w), 829(m), 771(s), 734(s), 719(m), 667(w), 658(w), 628(w), 551(w), 497(sh), 483(s), 461(m), 437(m), 407(m), 372(w), 347(m), 329(m), 273(m) cm⁻¹. ¹H NMR (CDCl₃): δ = 7.05 (m(br), 2H, 3-CH), 6.95 (m(br), 2H, 5-CH), 6.46 (m(br), 2H, 6-CH), 6.3 (m(br), 2H, 4-CH), 1.64 (s, 18H, *t*-Bu), 0.32 (s, 6H, SiCH₃). ¹³C NMR (125 MHz, CDCl₃): δ = 161.6 (1-CN), 133.8 (3-CH), 130.6 (5-CH), 117.7 (2-CS), 116.1 (4-CH), 112.3 (6-CH), 55.0 (CS, *t*-Bu), 30.5 (CH₃, *t*-Bu), 3.4 (SiCH₃). ²⁹Si NMR (100 MHz, CDCl₃): δ = 1.6 (s).

3.4.2 [Ni{Ph₂Si(N-C₆H₄-2-SMe)₂}] (5)

The nickel complex **5** was obtained by method A from 0.96 g (2.1 mmol) of Ph₂Si(NH-C₆H₄-2-SMe)₂ (**2**) 1.7 mL (4.2 mmol) of a 2.5 M solution of *n*-BuLi in *n*-hexane and 459 mg (2.1 mmol) of NiBr₂. Yield: 0.33 g (19%).

In the case of method B the synthesis was carried out with 1.53 g (3.34 mmol) of Ph₂Si(N-C₆H₄-2-SMe)₂, 2.7 mL (6.68 mol) of a 2.5 M solution of *n*-BuLi in *n*-hexane and 1.246 g (3.34 mmol) [Ni(acac)₂(TMEDA)]. Yield: 1.03 g (60%).

$\text{C}_{26}\text{H}_{24}\text{N}_2\text{NiS}_2\text{Si}$ (515.39 g mol⁻¹): C found 60.2 (calcd. 60.6), H 4.7 (4.7), N 5.2 (5.4). –IR: $\tilde{\nu}$ = 3059(w), 3016(w), 1572(m), 1482(m), 1459(s), 1440(m), 1426(m), 1365(w), 1338(s), 1293(m), 1261(w), 1248(w), 1181(w), 1152(w), 1108(m), 1023(m), 996(w), 979(w), 953(m), 829(w), 777(m), 733(s), 721(w), 702(s), 647(m), 522(s), 499(s), 486(s), 450(m), 434(m), 420(m), 375(w), 336(w), 310(w), 269(m) cm⁻¹. ¹H NMR (CDCl₃): δ = 7.8 (m, 4H, *m*-Ph), 7.4 (m; 6H; *o*, *p*-Ph), 7.1 (m, 2H, 3-CH), 6.9 (m, 2H, 5-CH), 6.6 (m, 2H, 6-CH), 6.4 (m, 2H, 4-CH), 2.69 (s, 6H, SCH₃). ¹³C NMR (125 MHz, CDCl₃): δ = 159.4 (1-CN), 138.1 (3-CH), 134.6 (*m*-Ph), 131.1 (*i*-C-SiPh), 130.4 (5-CH), 129.0 (*p*-Ph), 127.8 (*o*-Ph), 120.9 (2-CS), 117.6 (4-CH), 114.4 (6-CH), 25.2 (SMe). ²⁹Si NMR (100 MHz, CDCl₃): δ = -22.6 (s).

3.4.3 [Ni{Ph₂Si(N-C₆H₄-2-SPh)₂}] (6)

The nickel complex **6** was obtained by method A from 0.90 g (1.6 mmol) of Ph₂Si(NH-C₆H₄-2-SPh)₂ (**3**) 1.2 mL (3.1 mmol) of a 2.5 M solution of *n*-BuLi in *n*-hexane and 339 mg (1.6 mmol) of NiBr₂. Yield: 0.55 g (30%).

In the case of method B the synthesis was carried out with 1.65 g (2.8 mmol) of Ph₂Si(N-C₆H₄-2-SPh)₂ (**3**) 2.3 mL (5.7 mol) of a 2.5 M solution of *n*-BuLi in *n*-hexane and 1.056 g (2.83 mmol) of [Ni(acac)₂(TMEDA)]. Yield: 1.31 g (72%).

$\text{C}_{36}\text{H}_{28}\text{N}_2\text{NiS}_2\text{Si}$ (639.52 g mol⁻¹): C found 67.8 (calcd. 67.6), H 4.5 (4.4), N 4.2 (4.4). –IR: $\tilde{\nu}$ = 3044(w), 1576(m), 1460(s), 1440(m), 1427(m), 1367(w), 1339(s), 1297(m), 1263(w), 1249(w), 1184(w), 1157(w), 1122(sh), 1109(s), 1067(m), 1023(w), 999(w), 979(w), 953(m), 918(m), 827(w), 782(m), 748(m), 733(s), 718(m), 713(m), 700(s), 688(s), 646(m), 616(w), 543(w), 524(m), 506(m), 484(s), 454(m), 440(m), 380(w), 325(w), 293(m), 255(m), 226(w) cm⁻¹. ¹H NMR (CDCl₃): δ = 7.9 (m, 4H, *m*-SiPh), 7.52 (m, 4H, *m*-SPh), 7.4 (m, 6H, *o*, *p*-SiPh), 7.26 (m, 6H, *o*, *p*-SPh), 7.0 (m, 2H, 3-CH), 6.9 (m, 2H, 5-CH), 6.6 (m, 2H, 6-CH), 6.3 (m, 2H, 4-CH). ¹³C NMR (125 MHz, CDCl₃): δ = 160.0 (1-CN), 138.0 (*i*-C-SPh), 133.4 (*i*-C-SiPh), 134.7, 132.3, 130.7, 129.8, 129.7, 128.9, 127.9, 127.2 (Ph), 120.4 (2-CS), 117.7 (4-CH), 114.7 (6-CH). ²⁹Si NMR (100 MHz, CDCl₃): δ = -22.4 (s).

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