

Functionalized Carbazoyl Hydro- and Allyl-Silanes

Pauline Hädinger^[a] and Alexander Hinz^{*[a]}*Dedicated to Prof. Axel Schulz on the occasion of his 55th birthday.*

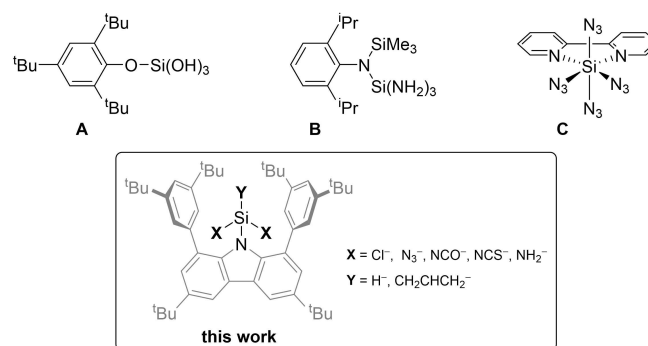
The synthesis and properties of silanes bearing a bulky carbazoyl substituent are described. Metathesis routes with different reagents under different conditions are required to obtain the compounds of the general formula $\text{RSi(X)}_2\text{H}$ and

$\text{RSi(X)}_2\text{All}$ ($\text{X} = \text{Cl}, \text{N}_3, \text{NCO}, \text{NCS}, \text{NH}_2, \text{All} = \text{CH}_2\text{CHCH}_2$). The silanes were studied by XRD, NMR and IR spectroscopy and all findings were corroborated by DFT methods.

Introduction

Functionalized silanes are of great interest, especially as building blocks in polymer chemistry and materials science.^[1] In many instances, with archetypical functional groups such as OH or NH_2 , self-condensation occurs which then leads to the formation of oligomers and polymers. Silicones, for example, consist of Si–O–Si linkages, which are formed by this process.^[2] When bulky substituents are introduced to silicon, the silanols can be kinetically stabilised and the self-condensation process is mostly suppressed. Consequently, it is possible to access defined oligomeric structures or silanols in their monomeric form.^[3] For instance, this was shown by Roesky who synthesized defined metallasiloxanes from stabilized silanetriols (A), (Scheme 1). The latter were prepared by controlled hydrolysis of trichlorosilanes with bulky oxygen- or nitrogen-bonded substituents.^[4] Similarly, Kuroda and Shimojima utilized *tert*-alkoxy groups to synthesize stable silanetriols as synthons for silica-based nanomaterials with well-regulated structures.^[5] Further work regarding defined, supramolecular assemblies based on stable organosilanols was for instance published by Jutzl^[6] and Jancik.^[7] Very recently, also fluorinated substituents such as $\text{C}(\text{C}_6\text{F}_5)_3$ or $\text{C}(\text{C}_6\text{H}_3\{\text{CF}_3\}_2)_3$ were employed by the Beckmann group and the stabilization of the monomeric species $\text{Ar}_3\text{COSiCl}_3$ and mono-condensation products $\text{Ar}_3\text{COSi(OH)}_3$ ($\text{Ar} = \text{C}_6\text{F}_5, \text{C}_6\text{H}_3\{\text{CF}_3\}_2$) was demonstrated.^[8]

Murugavel chose a different approach and trapped less stable organosilanetriols such as $[\text{2,6-MeC}_6\text{H}_3\text{N}(\text{SiMe}_3)\text{Si(OH)}_3]$ in amine matrices, thus thwarting condensation reactions.^[9] Recently, also the parent orthosilicic acid Si(OH)_4 was selectively synthesized by Sato and Shimada *via* a non-aqueous hydro-



Scheme 1. Selected silanes bearing functional groups.

genolysis reaction of benzyloxysilanes and isolated as hydrogen-bound crystals with tetrabutylammonium halides.^[10]

Aminosilanes show similar reactivity to silanols. For instance, the parent $\text{Si(NH}_2)_4$ is not stable and undergoes condensation reactions. However, bulky substituents can also be utilized to enable the synthesis of terphenyl-triaminosilane^[11] $\text{TerSi(NH}_2)_3$ as demonstrated by Power in 1993 or tetraaminosilane B (Scheme 1), which was later reported by Roesky.^[12] In the reaction of SiCl_4 with various amines, some selectivity was found by Passarelli and coworkers. In dependence of the R group and reaction conditions, various species of the type $\text{SiCl}_n(\text{NR}_2)_{4-n}$ ($n = 1, 2, 3, 4$) could be obtained.^[13]

With the introduction of other pseudohalide substituents to silanes, different issues arise. Mixed species of silicon halide/pseudohalides were studied early in the second half of the 20th century by means of vibrational spectroscopy. This allowed the identification of Si(NCS)_4 and Si(NCO)_4 as being preferentially formed over the isomeric Si(OCN)_4 and Si(SCN)_4 which could have been expected on the basis of either oxophilicity or similarity in atomic size of Si and S.^[14,15] The highly explosive $\text{Si(N}_3)_4$ was prepared by Wiberg.^[16] The explosivity could be diminished by adding a stabilizing bidentate base such as bipyridine (C) and phenanthroline (Scheme 1).^[17]

The aforementioned silicon pseudohalides were synthesized by metathesis reactions, but the reagents and conditions vary greatly. For instance, while for azide metathesis, predominantly NaN_3 was used, most of the cyanate reactions employ AgNCO

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and on rarer occasions, KNCO was used. For the preparation of $\text{Si}(\text{NCS})_4$, an early protocol involved $\text{Pb}(\text{NCS})_2$, which later was replaced by AgNCS , and eventually was improved with the use of NH_4NCS as thiocyanate source. As these requirements differ for each investigated system, the study of metathesis reactions of chlorosilanes with a bulky carbazolyl substituent (R) is warranted in this contribution.

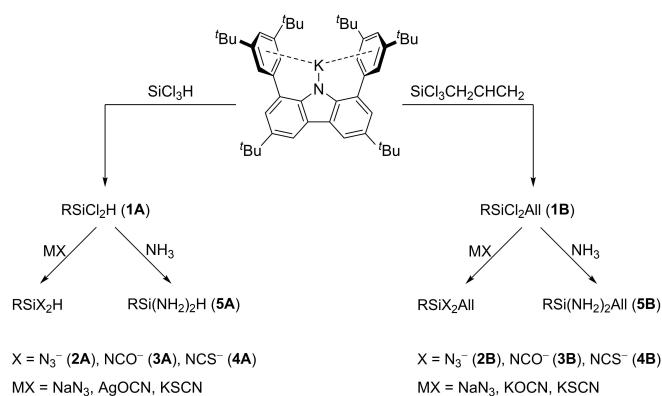
Carbazole-based ligands with sterically demanding substituents at the 1- and 8-position are known to stabilize reactive main group species. Examples include 1,8-diphenyl-3,6-dimethyl-carbazolyl-dimethylalane,^[18] 1,8-dimesityl-3,6-di-tert-butyl-carbazolyl-magnesiumiodide^[19] and 1,8-dimesityl-3,6-dimethyl-carbazolyl-dichlorogallane.^[20] By employing the 1,8-bis(3,5-di-tert-butyl-phenyl)-3,6-di-tert-butyl-carbazolyl system (R), our group recently reported on the generation of formally one-coordinate tetraarylium cations $[\text{RE}]^+$ (E=Si, Ge, Sn, Pb)^[21,22] and the attempted reduction of a carbazolyl-diiodoalane.^[23] Featuring this carbazole scaffold R, we now describe the synthesis and properties of two series of compounds, $\text{RSi}(\text{X})_2\text{H}$ and $\text{RSi}(\text{X})_2\text{All}$ (X=Cl, N₃, NCO, NCS, NH₂, All=CH₂CHCH₂).

Results and Discussion

Syntheses

Starting from the potassium carbazolidine RK, stepwise metathesis was planned to obtain functionalised carbazolyl hydro- and allyl-silanes (Scheme 2). The reaction of the potassium carbazolidine RK with the trichlorosilanes SiCl_3H and SiCl_3All (All = allyl = CH₂CHCH₂) in toluene proceeded smoothly, affording the carbazolyl-dichlorosilanes RSiCl_2H (**1A**) and RSiCl_2All (**1B**). Both compounds were obtained as off-white products after filtration and removal of all volatiles and recrystallized from *n*-hexane (**1A**) or toluene (**1B**). The dichlorosilanes were then used as starting materials for the introduction of pseudohalide and amine functions to silicon.

For the synthesis of pseudohalido-silanes, simple metal pseudohalides were employed for the metathesis reactions. Due to the low solubility of these salts in organic solvents, they were used in over stoichiometric amounts. Treating solutions of the dichlorosilanes **1A** and **1B** in thf with NaN_3 at ambient temperature led to the formation of the diazidosilanes $\text{RSi}(\text{N}_3)_2\text{H}$ (**2A**) and $\text{RSi}(\text{N}_3)_2\text{All}$ (**2B**). While for the hydro-silane **2A** the reaction was complete after 24 h hours, for the allyl derivative **2B** full conversion was only achieved after six days. In both



Scheme 2. Synthesis of functionalized carbazolyl hydro- and allyl-silanes.

cases, colorless crystals were obtained after extraction with toluene and slow concentration. Yet, for the hydro-silane **2A**, no crystals suitable for X-ray diffraction could be obtained from three different batches.

The reaction of RSiCl_2H (**1A**) with AgOCN in thf at 60 °C afforded the diisocyanatosilane $\text{RSi}(\text{NCO})_2\text{H}$ (**3A**) after two days. According to quantum chemical calculations, the isocyanate isomer is energetically favoured over the cyanate isomer by 262.55 kJ/mol. This prediction is also confirmed by spectroscopic experiments, as will be discussed later. Surprisingly, the reaction between AgOCN and allyl-dichlorosilane **1B** only led to a mixture of substitution products and full conversion to the diisocyanato derivative could not be achieved after three weeks. However, when KOCN was employed as the cyanate source and stirred with silane **1B** for three days at 60 °C, the quantitative formation of $\text{RSi}(\text{NCO})_2\text{All}$ (**3B**) was observed via ¹H NMR spectroscopy. In this case, the isocyanate isomer was calculated to be energetically favored by 236.30 kJ/mol over the cyanate isomer. Metathesis of the starting compounds **1A** and **1B** with KSCN afforded the substitution products $\text{RSi}(\text{NCS})_2\text{H}$ (**4A**) and $\text{RSi}(\text{NCS})_2\text{All}$ (**4B**) after stirring for 24 hours at 60 °C, respectively. Again, DFT calculations predict that the isothiocyanate isomers are more stable than the thiocyanate isomers by 183.79 kJ/mol for the hydro-silane and 210.04 kJ/mol for the allyl-silane and the obtained spectroscopic data are in good agreement. The carbazolyl-silanes **3A**, **3B**, **4A** and **4B** were isolated as colorless, crystalline products, respectively after removal of all volatiles from the reaction mixture, extraction with *n*-hexane and slow concentration.

All carbazolyl-pseudohalido compounds are thermally stable up to 240 °C. Surprisingly, the azido-silanes melt only at 270 °C and no decomposition was observed.

For the preparation of amino-functionalized carbazolyl-silanes, metathesis of RSiCl_2H (**1A**) with LiNH_2 in thf seemed straightforward and was initially attempted. Via ¹H NMR spectroscopy, the desired compound $\text{RSi}(\text{NH}_2)_2\text{H}$ (**5A**) could at first be observed in solution (Figure 1). The broad resonance at 4.85 ppm was assigned to the Si–H hydrogen atom, the NH₂ atoms yield a broad singlet at 0.07 ppm. Yet, the mono-substituted aminosilane was also present in the reaction



Dr. Hinz completed his PhD in 2015 under the supervision of Axel Schulz. After a postdoctoral stint with Jose Goicoechea at the University of Oxford, UK, he moved to the Karlsruhe Institute of Technology in 2018 to begin his habilitation with Frank Breher. Alexander Hinz's research focuses on low-coordinated main-group and transition-metal compounds with the aim of achieving complexes with the coordination number 1.

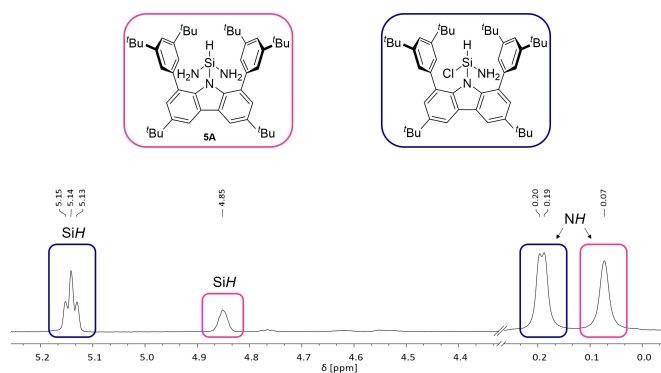


Figure 1. Extract from the ^1H NMR spectrum after the reaction of **1A** with LiNH_2 .

mixture, as indicated by the triplet at 5.14 ppm and the corresponding doublet at 0.2 ppm. Full conversion to the diaminosilane could not be achieved by adding more LiNH_2 to the reaction solution since this led to the formation of lithium carbazolidate, exclusively. As an alternative approach, we attempted the direct conversion of dichlorosilane **1A** with NH_3 . However, due to the easy cleavage of the carbazole-silicon bond by protonation, an excess of NH_3 had to be avoided. Therefore, we used a modified literature procedure to generate stoichiometric amounts of NH_3 .^[24] Accordingly, NaNH_2 was protonated by stearic acid upon heating and the emerging NH_3 was condensed to a solution of dichlorosilane **1A** in toluene. The reaction solution was then stirred under NH_3 atmosphere at -78°C for one hour.

After warming to room temperature, a fine, white precipitate was observed in the reaction mixture, indicating the formation of NH_4Cl . Removal of all volatiles, extraction with *n*-hexane and slow concentration allowed the isolation of the diaminosilane $\text{RSi}(\text{NH}_2)_2\text{H}$ (**5A**) as crystalline material. This synthetic procedure was then applied, starting from the allyl-dichlorosilane **1B** to synthesize the analogous allyl-diaminosilane $\text{RSi}(\text{NH}_2)_2\text{Al}$ (**5B**). In this case, more NH_3 needed to be present in the reaction flask to achieve a full conversion to the twofold amino-substituted product.

NMR Spectroscopy

By comparing NMR spectra of the functionalized carbazoly-silanes, differences in their electronic structures are revealed. For the series of hydro-silanes, the hydride ^1H NMR resonance is shifted from 5.72 ppm in RSiCl_2H (**1A**) to higher field upon substitution of the chlorine atoms with pseudohalide (**2A** 5.02 ppm, **3A** 4.62 ppm, **4A** 4.65 ppm) or amine (**5A** 4.85 ppm) functionalities. No correlation of the silane ^1H NMR resonance with its computed charge was found, as the charge only shows miniscule variation between -0.01 and -0.09 e. A similar effect as observed for the ^1H NMR signals was observed for the ^{29}Si NMR resonances. Compared to the starting material RSiCl_2H (**1A** -22.0 ppm), the isothiocyanate groups cause the strongest shift

to higher field (**4A** -75.5 ppm), followed by the isocyanate (**3A** -68.8 ppm) and the azide (**2A** -49.9 ppm) groups. For the ^{29}Si NMR resonance of the diaminosilane (**5A** -34.1 ppm), the shift to higher field is less marked than for the pseudohalide derivatives. By comparing the ^{29}Si NMR resonances within the series of allyl-silanes, the same trend can be noticed. While the ^{29}Si resonance in dichlorosilane **1B** is found at 0.79 ppm, it is observed shifted to -20.9 ppm (**5B**), -34.7 ppm (**2B**), -47.3 ppm (**3B**) and -52.8 ppm (**4B**) upon introduction of amine and pseudohalide substituents. This observation indicates that the electron-donating properties of the different functional groups decrease in the order NCS^- , NCO^- , N_3^- , NH_2^- .

The carbazole ^{15}N NMR resonance is only marginally influenced upon introduction of different functional groups to the silicon atom and is found in the range of 104.0 to 120.1 ppm. It is interesting to note that the NCO^- ^{15}N NMR resonances for the isocyanatosilanes are found at 35.1 ppm (**3A**) and 39.3 ppm (**3B**), whereas the NCS^- ^{15}N NMR resonances are observed significantly downfield shifted at 106.8 ppm (**4A**) and 111.4 ppm (**4B**). The ^{15}N NMR resonances for the NH_2 atoms in the diaminosilanes **5A** and **5B** only differ slightly and are found at 17.6 ppm and 19.5 ppm, respectively.

Concerning the two possible bonding motifs of the NCO and NCS substituents, the experimentally obtained NMR data for silanes **3A**, **3B**, **4A** and **4B** compare well to computed values of the N-bound isomers. This is most significantly demonstrated by the ^{29}Si , ^{15}N (NCX) and ^{13}C (NCX) NMR resonances, as is shown in Table 1 and Table 2, respectively.

IR Spectroscopy

For the hydro-silanes, $\nu(\text{SiH})$ vibrations are observed in the expected region for **1A** (2282 cm^{-1}), **4A** (2281 cm^{-1}) and **5A** (2192 cm^{-1}). Antisymmetric and symmetric $\nu(\text{NH})$ vibrations for diaminosilane **5A** are found at 3479 and 3391 cm^{-1} , respectively and at slightly lower energies of 3467 cm^{-1} and 3376 cm^{-1} for the allyl derivative **5B**.

Table 1. Selected NMR data for hydro-silanes **1A–5A** ($\text{X}=\text{O}$ or S). All resonances were recorded in C_6D_6 and are given in ppm. Computed values are given in *italics*.

	$^1\text{H}(\text{SiH})$	$^{13}\text{C}(\text{NCX})$ or $^1\text{H}(\text{NH})$	^{29}Si	$^{15}\text{N}(\text{Carb})$	$^{15}\text{N}(\text{funct.})^{[a]}$
1A (obs.)	5.72	–	-22.0	115.5	–
<i>RSiCl₂H</i>	4.3	–	2	126	–
2A (obs.)	5.02	–	-49.6	105.5	60.7, 183.4, 228.3
<i>RSi(NNN)₂H</i>	5.5	–	-48	112	71, 193, 234
3A (obs.)	4.62	122.7	-68.8	106.9	35.1
<i>RSi(NCO)₂H</i>	4.2	115	-78	126	51
<i>RSi(OCN)₂H</i>	3.9	99	-55	118	179
4A (obs.)	4.65	144.0	-75.6	106.6	104.7
<i>RSi(NCS)₂H</i>	4.1	142	-79	118	118
<i>RSi(SCN)₂H</i>	3.5	105	10	120	304
5A (obs.)	4.85	0.07	-34.1	105.1	17.6
<i>RSi(NH₂)₂H</i>	4.1	-0.6	-36	135	32

[a] Funct. = (NNN), (NCX), or (NH₂).

Table 2. Selected NMR data for allyl-silanes **1B–5B** (X=O or S). All resonances were recorded in C₆D₆. Computed values are given in *italics*.

	¹³ C(NCX) or ¹ H(NH)	²⁹ Si	¹⁵ N(Carb)	¹⁵ N(func.) ^[a]
1B (obs.)	–	0.79	108.9	–
<i>RSiCl₂All</i>		23	126	
2B (obs.)	–	–34.7	104.0	63.8, n.obs.
<i>RSi(N₃)₂All</i>		–46	117	74, 191, 236
3B (obs.)	123.6	–47.3	104.3	39.3
<i>RSi(NCO)₂All</i>	115	–55	122	55
<i>RSi(OCN)₂All</i>	102	–40	114	177
4B (obs.)	144.7	–52.8	102.6	111.4
<i>RSi(NCS)₂All</i>	142	–58	121	121
<i>RSi(SCN)₂All</i>	108	37	118	305
5B (obs.)	0.37	–20.9	120.1	19.5
<i>RSi(NH₂)₂All</i>	–0.3	–23	139	28, 34

[a] Funct. = (NNM), (NCX), or (NH₂).

For the antisymmetric stretching vibrations of the azide, isocyanate and isothiocyanate groups, strong IR bands are observed at characteristic energies. The corresponding values are compiled in Table 3. The occurrence of four ν_{as} bands for the silanes **3A**, **4A** and **4B** may be attributed to the presence of

Table 3. Selected IR data for silanes **2A–4A** and **2B–4B**. All values are given in cm^{–1}.

	ν_{as} (NNN)		ν_{as} (NCO)		ν_{as} (NCS)
2A	2172	3A	2305	4A	2095
	2157		2284		2081
			2268		2035
	2255		1998		
2B	2170	3B	2312	4B	2099
	2146		2275		2075
					2033
					2014

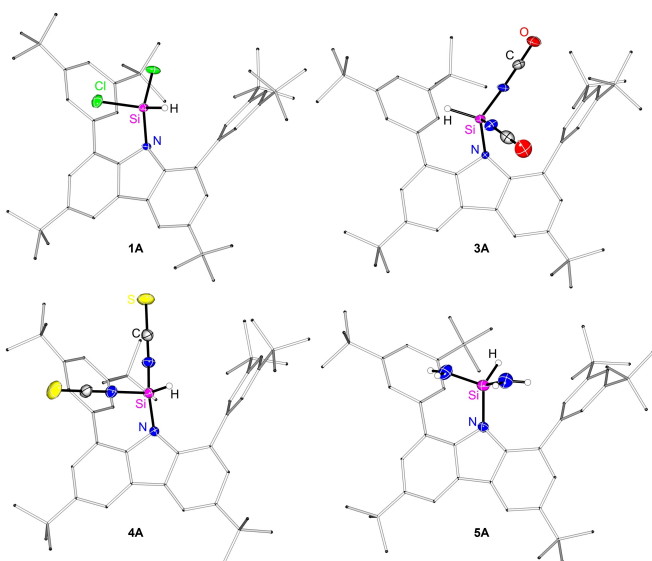


Figure 2. Molecular structures of the hydro-silanes RSiCl₂H (**1A**), RSi(NCO)₂H (**3A**), RSi(NCS)₂H (**4A**) and RSi(NH₂)₂H (**5A**). Thermal ellipsoids at 30% probability.

different rotamers, with respect to the position of the substituents at silicon.

Crystal structures

Molecular structures were determined by X-ray diffraction and are shown in Figure 2 and Figure 3. In all compounds, the substituents are arranged around the central silicon atom in a slightly distorted tetrahedral fashion. Surprisingly, in the hydro-silanes **1A**, **3A** and **4A**, the chlorine atom or one of the pseudohalide groups point into the cavity, formed by the arenes, whereas in the amino-derivative, this position is occupied by the hydride. Within the series of allyl-silanes, the allyl group points into the carbazole pocket in all cases. Generally, the silicon atom is bent out of the plane, spanned by the carbazole unit, by approximately 40°. This can be attributed to minimized steric hindrance between the substituents at silicon and the flanking arenes. Only for diaminosilane **5A**, this bending angle is found to be 25°, owing to the smaller bulk of the NH₂ groups.

Table 4 summarizes bonding parameters for the SiNNN or SiNCX linkages (X=O, S) in the pseudohalido-silanes. For azidosilane **2B**, bond metrics are comparable to the bulky trimesityl-azidosilane (**I**)^[25] or silyl-substituted azidosilane Mes₂(N₃)SiSiPh₂-tBu (**II**).^[25] Similar to compound **II**, in silane **2B**, the N₁–N₂ bonds are longer than the terminal N₂–N₃ bonds. However, while these bonds in **II** only differ by 2.3 pm, the deviation of 10.4 and 9.5 pm between the respective bond lengths is more distinct in **2B**.

Considering the isocyanate fragments in compounds **3A** and **3B**, smaller SiNC angles are observed for the hydro-silane, compared to the allyl-derivative. The other bond metrics only differ slightly and are in good agreement to those reported for the silyl-isocyanate (PhMe₂Si)₃CSiMe₂NCO (**III**).^[26] Bond lengths and angles within the isothiocyanate moieties in silanes **4A** and **4B** show no significant deviations for the two derivatives and are comparable to the values reported for triphenyl-isothiocyanatosilane (**IV**).^[27] The orientation of the Si–H in **5A** is different than in **1A**, **3A** and **4A**. This is likely due to packing effects, as

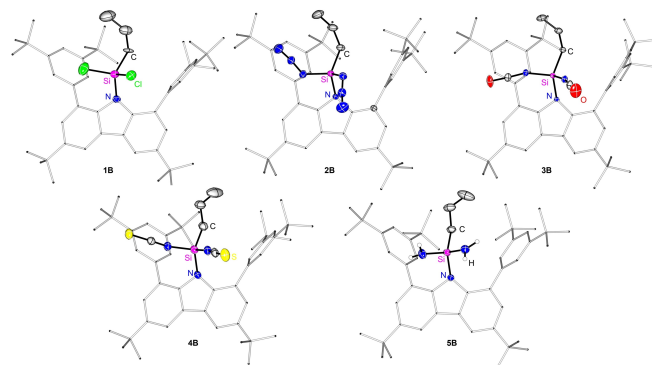


Figure 3. Molecular structures of the allyl-silanes RSiCl₂All (**1B**), RSi(N₃)₂All (**2B**), RSi(NCO)₂All (**3B**), RSi(NCS)₂All (**4B**) and RSi(NH₂)₂All (**5B**). Thermal ellipsoids at 30% probability.

Table 4. Selected bond parameters for the SiNNN linkage in **2B** or SiNCX linkages in **3A,B** (X=O) and **4A,B** (X=S). Bond lengths in Å, bond angles in °.

	Si–N	N ₁ –N ₂ or N–C	N ₂ –N ₃ or C–X	SiNN or SiNC	NNN or NCX
2B	1.7342(11)	1.226(2)	1.123(2)	124.63(10)	174.3(2)
	1.7182(11)	1.213(2)	1.119(2)	129.57(10)	173.5(2)
I ^[25]	1.814(2)	1.158(4)	1.170(4)	125.8(2)	173.7(3)
II ^[25]	1.782(4)	1.170(5)	1.147(6)	129.1(4)	174.9(5)
3A ^[a]	1.685(2)	1.203(3)	1.175(3)	140.3(2)	176.8(3)
	1.691(2)	1.186(3)	1.175(3)	153.5(2)	178.0(3)
3B	1.699(2)	1.170(3)	1.169(3)	160.2(2)	178.3(3)
	1.700(2)	1.164(3)	1.161(3)	167.0(2)	178.4(3)
III ^[26]	1.739(5)	1.135(8)	1.174(8)	155.7(5)	175.9(7)
4A	1.703(3)	1.178(3)	1.561(2)	156.2(4)	178.9(4)
	1.706(2)	1.178(5)	1.563(5)	177 (2)	175(3)
4B	1.717(3)	1.193(4)	1.564(4)	171.9(3)	177.9(3)
	1.700(3)	1.185(4)	1.572(4)	163.9(2)	178.1(3)
IV ^[27]	1.735(5)	1.156(4)	1.562(4)	170.7(2)	178.9(3)

[a] Parameters correspond to one molecule in the asymmetric unit.

the computed energy difference between both rotamers is small and NMR data indicate free rotation of the Si(X)₂H moiety.

Conclusion

Based on a bulky carbazole scaffold, we prepared hydro- and allyl-silanes, bearing pseudohalide or amine groups. Central intermediates for both series were the respective carbazolyldichlorosilanes. For the introduction of azide, isocyanate and isothiocyanate functionalities, the dichlorosilanes were subjected to metathesis with metal pseudohalides under various conditions. The synthesis of amino-substituted silanes proved to be more challenging and required the use of stoichiometric amounts of ammonia. The products were characterised by means of spectroscopy, X-ray diffraction and DFT methods.

Experimental Section

General considerations. All operations were conducted under dry argon atmosphere using Schlenk and glovebox techniques. Solvents were dried over sodium and distilled prior to use. The ligand RH and its corresponding potassium salt RK were prepared according to literature protocols.^[21] NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer. Reported chemical shifts are referenced to the ¹H and ¹³C NMR resonances of the deuterated solvent.^[28] Coupling constants *J* are given in Hertz as positive values regardless of their real individual sign. ¹H, ¹³C, ¹⁵N, ²⁹Si NMR spectra were obtained at 400.1, 100.6, 40.6, 79.5 MHz respectively. IR spectra were recorded on a Bruker Alpha spectrometer using the attenuated total reflection (ATR) technique on powdered samples. Elemental analyses were obtained with a Vario Micro Cube (Elementar Analysensysteme GmbH) in the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT).

RSiCl₂H (1A). At –78 °C a solution of SiCl₃H (approx. 590 mg, 4.35 mmol) in 3 ml toluene was added dropwise to a solution of RK (3.00 g, 4.33 mmol) in 80 ml toluene. The mixture was warmed to ambient temperature and was stirred overnight. The resulting

suspension was filtered, and the filtrate was concentrated to dryness. The yellow residue was then washed with 10 ml of *n*-hexane, allowing the isolation of RSiCl₂H as a pale-yellow solid (2.43 g, 3.22 mmol, 74%). Recrystallisation from *n*-hexane afforded colorless crystals. ¹H NMR (400.1 MHz, C₆D₆): δ (ppm) = 1.36 (s, 36 H, Ar-^tBuH), 1.37 (s, 18 H, Carb-^tBuH), 5.79 (s, *J*_{SiH} = 344.3 Hz, 1 H, SiH), 7.59 (t, *J*_{HH} = 1.8 Hz, 2 H, *p*-CH), 7.65 (d, *J*_{HH} = 1.8 Hz, 4 H, *o*-CH), 7.66 (d, *J*_{HH} = 2.0 Hz, 2 H, C^{2,7}H), 8.30 (d, *J*_{HH} = 2.0 Hz, 2 H, C^{4,5}H). ¹³C NMR (100.6 MHz, C₆D₆): δ (ppm) = 31.7 (s, Ar-C(CH₃)), 31.9 (s, Carb-C(CH₃)), 34.8 (s, Carb-C(CH₃)), 35.1 (s, Ar-C(CH₃)), 115.8 (s, C^{4,5}H), 122.6 (s, *p*-CH), 125.0 (s, *o*-CH), 130.3 (s), 132.2 (s), 141.0 (s), 141.7 (s), 146.4 (s, C^{3,6}), 151.3 (s, *m*-C). ¹⁵N NMR (40.6 MHz, C₆D₆): δ (ppm) = 111.5 (s). ²⁹Si NMR (79.5 MHz, C₆D₆): δ (ppm) = –22.0 (s). IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2956 (vs), 2903 (m), 2866 (m), ν (Si–H) 2282 (vw), 1592 (m), 1477 (m), 1393 (m), 1362 (s), 1291 (w), 1248 (m), 1221 (w), 1199 (w), 1181 (m), 1155 (vw), 1077 (w), 997 (vw), 943 (w), 914 (vw), 867 (s), 808 (m), 717 (m), 707 (m), 646 (vw), 585 (m), 568 (m), 512 (vw). EA [C₄₆H₆₅Cl₂N₅Si] found (calc.): C 75.65 (76.36) H 8.38 (8.68) N 1.64 (1.86).

RSiCl₂All (1B). At –78 °C a solution of SiCl₃CH₂CHCH₂ (approx. 606 mg, 3.45 mmol) in 3 ml toluene was added dropwise to a solution of RK (2.12 g, 3.04 mmol) in 80 ml toluene. The mixture was warmed to ambient temperature and stirred overnight. After filtration, the filtrate was evaporated to dryness and the yellow residue was extracted with 20 ml of toluene. Volatiles were removed in vacuo, allowing the isolation of RSiCl₂All as a pale-yellow solid (2.10 g, 2.64 mmol, 87%). Recrystallisation from toluene afforded colorless crystals. ¹H NMR (400.1 MHz, C₆D₆): δ (ppm) = 1.37 (s, 18 H, Carb-^tBuH), 1.38 (s, 36 H, Ar-^tBuH), 1.56 (dt, 2 H, *J*_{HH} = 7.8, 1.2 Hz, Si-CH₂), 4.55 (dq, *J*_{HH} = 16.8, 1.4 Hz, 1 H, H_a), 4.70 (ddd, *J*_{HH} = 10.1, 2.0, 1.0 Hz, 1 H, H_b), 5.25 (ddt, *J*_{HH} = 16.8, 10.0, 7.6 Hz, 1 H, H_c), 7.60 (t, *J*_{HH} = 1.9 Hz, 2 H, *p*-CH), 7.64 (d, *J*_{HH} = 2.1 Hz, 2 H, C^{2,7}H), 7.75 (s br, 4 H, *o*-CH), 8.23 (d, *J*_{HH} = 2.1 Hz, 2 H, C^{4,5}H). ¹³C NMR (100.6 MHz, C₆D₆): δ (ppm) = 29.5 (s, Si-CH₂), 31.8 (s, Ar-C(CH₃)), 31.9 (s, Carb-C(CH₃)), 34.8 (s, Carb-C(CH₃)), 35.1 (s, Ar-C(CH₃)), 115.7 (s, C^{4,5}H), 117.8 (s, Si-CH₂CHCH₂), 122.4 (s, *p*-CH), 125.6 (s br, *o*-CH), 128.2 (s, C^{2,7}H), 129.6 (s, Si-CH₂CHCH₂), 131.2 (s), 133.3 (s, C^{1,8}), 141.9 (s), 143.2 (s), 146.6 (s, C^{3,6}), 151.0 (s br, *m*-C). ¹⁵N NMR (40.6 MHz, C₆D₆): δ (ppm) = 108.9 (s). ²⁹Si NMR (79.5 MHz, C₆D₆): δ (ppm) = 0.78 (s). IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2959 (vs), 2903 (m), 2866 (m), 1634 (vw), 1593 (w), 1478 (w), 1462 (w), 1392 (w), 1378 (w), 1363 (m), 1290 (w), 1247 (w), 1198 (w), 1174 (m), 1107 (vw), 1074 (vw), 992 (vw), 940 (w), 907 (w), 869 (m), 841 (w), 794 (vw), 760 (w), 719 (w), 644 (vw), 611 (w), 571 (w), 550 (m).

RSi(N₃)₂H (2A). RSiCl₂H (213 mg, 0.265 mmol) and NaN₃ (174 mg, 2.67 mmol) were combined as solids and 15 ml thf were added. The suspension was sonicated for 1 hour and then stirred vigorously for 24 hours at ambient temperature. Volatiles were removed in vacuo. The oily residue was dissolved in 6 ml of toluene and filtered. The resulting solution was concentrated affording colorless, rod-shaped crystals. Mp.: 280 °C. ¹H NMR (400.1 MHz, C₆D₆): δ (ppm) = 1.38 (s, 18 H, Carb-^tBuH), 1.42 (s, 36 H, Ar-^tBuH), 5.02 (s, *J*_{SiH} = 311.3 Hz, 1 H, SiH), 7.64 (t, *J*_{HH} = 1.9 Hz, 2 H, *p*-CH), 7.66 (d, *J*_{HH} = 2.1 Hz, 2 H, C^{2,7}H), 7.71 (d, *J*_{HH} = 1.9 Hz, 4 H, *o*-CH), 8.32 (d, *J*_{HH} = 2.1 Hz, 2 H, C^{4,5}H). ¹³C NMR (100.6 MHz, C₆D₆): δ (ppm) = 31.7 (s, Ar-C(CH₃)), 31.9 (s, Carb-C(CH₃)), 34.8 (s, Carb-C(CH₃)), 35.2 (s, Ar-C(CH₃)), 115.7 (s, C^{4,5}H), 123.0 (s, *p*-CH), 124.3 (s, *o*-CH), 128.5 (s, C^{2,7}H), 130.0 (s), 131.5 (s), 141.0 (s), 141.1 (s), 146.3 (s, C^{3,6}), 151.4 (s, *m*-C). ¹⁵N NMR (40.6 MHz, C₆D₆): δ (ppm) = 60.7 (s), 105.5 (s, Carb-N), 183.4 (s), 228.3 (s). ²⁹Si NMR (79.5 MHz, C₆D₆): δ (ppm) = –49.6 (s). IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2961 (vs), 2903 (m), 2866 (m), $\nu_{as}(\text{NNN})$ 2172 (vs), $\nu_{as}(\text{NNN})$ 2157 (vs), 1592 (m), 1477 (w), 1392 (w), 1380 (w), 1362 (s), 1325 (m), 1291 (w), 1247 (w), 1226 (w), 1200 (m), 1183 (w), 1156 (vw), 1110 (vw), 1077 (vw), 1003 (vw), 946 (w), 916 (vw), 869 (s), 817 (m), 735 (vw), 591 (w).

RSi(N₃)₂All (2B). RSiCl₂All (300 mg, 0.377 mmol) and NaN₃ (250 mg, 3.49 mmol) were combined as solids and 18 ml thf were added. The suspension was sonicated for 2 hours and then stirred vigorously for 5 days at ambient temperature. Volatiles were removed in vacuo. The residue was dissolved in 15 ml of *n*-hexane and filtered. The resulting solution was evaporated to dryness and the residue was dissolved in toluene. Slow concentration at ambient temperature afforded colorless crystals (71.0 mg, 0.09 mmol, 24%). Mp.: 270 °C. ¹H NMR (400.1 MHz, C₆D₆): δ (ppm) = 1.25 (d, 2 H, J_{HH} = 7.8, 1.2 Hz, Si-CH₂), 1.38 (s, 18 H, Carb-^tBuH), 1.39 (s br, 36 H, Ar-^tBuH), 4.59 (dq, J_{HH} = 16.9, 1.5 Hz, 1 H, H_a), 4.67 (ddd, J_{HH} = 10.1, 1.9, 1.0 Hz, 1 H, H_b), 5.13 (ddt, J_{HH} = 16.8, 10.0, 7.8 Hz, 1 H, H_c), 7.62 (t, J_{HH} = 1.8 Hz, 2 H, *p*-CH), 7.66 (d, J_{HH} = 2.1 Hz, 2 H, C^{2,7}H), 7.74 (s br, 4 H, *o*-CH), 8.27 (d, J_{HH} = 2.1 Hz, 2 H, C^{4,5}H). ¹³C NMR (100.6 MHz, C₆D₆): δ (ppm) = 23.2 (s, Si-CH₂), 31.8 (s, Ar-C(CH₃)), 31.9 (s, Carb-C(CH₃)), 34.8 (s, Carb-C(CH₃)), 35.1 (s, Ar-C(CH₃)), 115.8 (s, C^{4,5}H), 118.2 (s, Si-CH₂CHCH₂), 122.9 (s, *p*-CH), 124.3 (s br, *o*-CH), 128.4 (s, C^{2,7}H), 129.1 (s, Si-CH₂CHCH₂), 130.6 (s, C^{4a,4b}), 132.2 (s), 141.9 (s), 142.1 (s), 146.3 (s, C^{3,6}), 151.3 (s br, *m*-C). ¹⁵N NMR (40.6 MHz, C₆D₆): δ (ppm) = 63.8 (s), 104.0 (s, Carb-N), 337.1 (s). ²⁹Si NMR (79.5 MHz, C₆D₆): δ (ppm) = -34.7 (s). IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2963 (s), 2905 (w), 2867 (w), ν_{as} (NNN) 2170 (vs), ν_{as} (NNN) 2146 (vs), 1634 (vw), 1594 (w), 1476 (w), 1393 (w), 1382 (w), 1362 (s), 1320 (w), 1290 (w), 1269 (vw), 1248 (w), 1200 (m), 1187 (m), 1153 (vw), 1104 (vw), 1075 (w), 994 (w), 939 (w), 908 (m), 869 (s), 848 (s), 795 (w), 774 (s), 718 (m), 710 (s), 676 (w), 645 (vw), 624 (w), 612 (m), 579 (s), 565 (s), 553 (w), 451 (w), 411 (vw), 384 (vw). EA [C₅₃H₆₉N₃S₂Si] found (calc.): C 75.02 (75.79) H 8.02 (8.61) N 11.94 (12.13).

RSi(NCO)₂H (3A). RSiCl₂H (200 mg, 0.265 mmol) and AgOCN (160 mg, 1.07 mmol) were combined as solids and 15 ml thf were added. The suspension was sonicated for 1 hour and then stirred vigorously at 60 °C for two days. Volatiles were removed in vacuo. The oily residue was dissolved in 4 ml of *n*-hexane and filtered. The resulting solution was concentrated affording colorless, rod-shaped crystals (62.5 mg, 0.081 mmol, 31%). Mp.: 275 °C. ¹H NMR (400.1 MHz, C₆D₆): δ (ppm) = 1.37 (s, 18 H, Carb-^tBuH), 1.39 (s, 36 H, Ar-^tBuH), 4.62 (s, J_{SiH} = 320.6 Hz, 1 H, SiH), 7.63 (t, J_{HH} = 1.8 Hz, 2 H, *p*-CH), 7.65 (d, J_{HH} = 2.0 Hz, 2 H, C^{2,7}H), 7.67 (d, J_{HH} = 1.8 Hz, 4 H, *o*-CH), 8.31 (d, J_{HH} = 2.0 Hz, 2 H, C^{4,5}H). ¹³C NMR (100.6 MHz, C₆D₆): δ (ppm) = 31.8 (s, Ar-C(CH₃)), 31.9 (s, Carb-C(CH₃)), 34.8 (s, Carb-C(CH₃)), 35.2 (s, Ar-C(CH₃)), 115.8 (s, C^{4,5}H), 122.7 (s, NCO), 123.0 (s, *p*-CH), 124.3 (s, *o*-CH), 130.1 (s), 131.6 (s), 141.2 (s), 141.5 (s), 146.3 (s), 151.6 (s, *m*-C). ¹⁵N NMR (40.6 MHz, C₆D₆): δ (ppm) = 35.1 (s, NCO), 106.9 (s, Carb-N). ²⁹Si NMR (79.5 MHz, C₆D₆): δ (ppm) = -68.8 (s). IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2960 (s), 2904 (w), 2867 (w), ν_{as} (NCO) 2305 (vs), ν_{as} (NCO) 2284 (vs), ν_{as} (NCO) 2268 (vs), ν_{as} (NCO) 2255 (vs), 1591 (w), 1477 (w), 1461 (w), 1393 (w), 1381 (vw), 1362 (m), 1291 (vw), 1248 (w), 1214 (vw), 1199 (w), 1184 (w), 1077 (vw), 1001 (vw), 944 (w), 870 (s), 826 (s), 717 (m), 649 (vw), 598 (m), 445 (vw), 428 (vw), 417 (vw), 404 (m), 397 (m), 391 (m), 383 (m).

RSi(NCO)₂All (3B). RSiCl₂All (365 mg, 0.460 mmol) and KOCN (300 mg, 3.70 mmol) were combined as solids and 20 ml thf were added. The suspension was sonicated for 1 hour and then stirred vigorously at 60 °C for three days. Volatiles were removed in vacuo. The oily residue was dissolved in 4 ml of *n*-hexane and filtered. The resulting solution was concentrated affording colorless, rod-shaped crystals (120 mg, 0.148 mmol, 32 %). Mp.: 261 °C. ¹H NMR (400.1 MHz, C₆D₆): δ (ppm) = 1.17 (dt, 2 H, J_{HH} = 7.9, 1.1 Hz, Si-CH₂), 1.38 (s, 18 H, Carb-^tBuH), 1.40 (s br, 36 H, Ar-^tBuH), 4.44 (dq, J_{HH} = 16.9, 1.4 Hz, 1 H, H_a), 4.64 (ddt, J_{HH} = 10.0, 1.8, 0.9 Hz, 1 H, H_b), 5.04 (ddt, J_{HH} = 16.8, 10.0, 7.9 Hz, 1 H, H_c), 7.62 (t, J_{HH} = 1.8 Hz, 2 H, *p*-CH), 7.66 (d, J_{HH} = 2.0 Hz, 2 H, C^{2,7}H), 7.76 (s br, 4 H, *o*-CH), 8.27 (d, J_{HH} = 2.1 Hz, 2 H, C^{4,5}H). ¹³C NMR (100.6 MHz, C₆D₆): δ (ppm) = 24.3 (s, Si-CH₂), 31.8 (s, Ar-C(CH₃)), 31.9 (s, Carb-C(CH₃)), 34.8 (s, Carb-C(CH₃)), 35.2 (s, Ar-C(CH₃)), 115.8 (s, C^{4,5}H), 117.9 (s, Si-CH₂CHCH₂), 123.1 (s, *p*-

CH), 123.6 (s, NCO), 124.3 (s br, *o*-CH), 128.4 (s, C^{2,7}H), 129.5 (s, Si-CH₂CHCH₂), 130.8 (s), 132.3 (s), 142.0 (s), 142.6 (s), 146.4 (s, C^{3,6}), 151.6 (s br, *m*-C). ¹⁵N NMR (40.6 MHz, C₆D₆): δ (ppm) = 104.3 (s, Carb-N). ²⁹Si NMR (79.5 MHz, C₆D₆): δ (ppm) = -47.3 (s). IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2961 (s), 2906 (w), 2868 (w), ν_{as} (NCO) 2312 (vs), ν_{as} (NCO) 2275 (vs), 1631 (vw), 1592 (w), 1463 (w), 1394 (w), 1382 (vw), 1363 (m), 1288 (vw), 1268 (vw), 1247 (w), 1199 (m), 1187 (w), 1173 (m), 1151 (vw), 1001 (vw), 1028 (vw), 990 (vw), 927 (vw), 910 (w), 872 (s), 848 (s), 773 (s), 721 (m), 709 (m), 645 (w), 625 (s), 608 (vs), 586 (vs), 553 (vw), 444 (vw).

RSi(NCS)₂H (4A). RSiCl₂H (420 mg, 0.556 mmol) and KSCN (264 mg, 2.72 mmol) were combined as solids and 18 ml thf were added. The suspension was sonicated for 1 hour and then stirred vigorously at 60 °C for 24 hours. Volatiles were removed in vacuo. The residue was dissolved in 4 ml of *n*-hexane and filtered. The resulting solution was concentrated, affording colorless crystals (178 mg, 0.201 mmol, 36%). Mp.: 246 °C. ¹H NMR (400.1 MHz, C₆D₆): δ (ppm) = 1.37 (s, 18 H, Carb-^tBuH), 1.44 (s, 36 H, Ar-^tBuH), 4.65 (s, J_{SiH} = 326.8 Hz, 1 H, SiH), 7.63 (m, 4 H, C^{2,7}H, *p*-CH), 7.67 (d, J_{HH} = 1.8 Hz, 4 H, *o*-CH), 8.27 (d, J_{HH} = 2.0 Hz, 2 H, C^{4,5}H). ¹³C NMR (100.6 MHz, C₆D₆): δ (ppm) = 31.9 (s, Carb-C(CH₃)), 31.9 (s, Ar-C(CH₃)), 34.9 (s, Carb-C(CH₃)), 35.2 (s, Ar-C(CH₃)), 115.8 (s, C^{4,5}H), 123.3 (s, *p*-CH), 124.2 (s, *o*-CH), 128.2 (s, C^{2,7}H), 130.2 (s), 131.6 (s), 140.6 (s), 141.2 (s), 144.0 (s br, NCS), 146.7 (s, C^{3,6}), 151.7 (s, *m*-C). ¹⁵N NMR (40.6 MHz, C₆D₆): δ (ppm) = 104.7 (s, NCS), 106.8 (s, Carb-N). ²⁹Si NMR (79.5 MHz, C₆D₆): δ (ppm) = -75.6 (s). IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2960 (s), 2867 (w), ν (SiH) 2281 (vw), ν_{as} (NCS) 2095 (m), ν_{as} (NCS) 2081 (m), ν_{as} (NCS) 2035 (m), ν_{as} (NCS) 1998 (vs), 1591 (m), 1477 (m), 1393 (m), 1363 (m), 1289 (w), 1268 (vw), 1248 (m), 1228 (w), 1215 (w), 1201 (m), 1153 (vw), 1104 (vw), 1076 (vw), 1042 (w), 997 (w), 943 (w), 912 (vw), 866 (vs), 814 (vs), 756 (vw), 717 (m), 707 (m), 665 (vw), 645 (w), 619 (vw), 575 (m), 546 (s), 528 (m), 507 (w), 479 (m).

RSi(NCS)₂All (4B). RSiCl₂All (400 mg, 0.504 mmol) and KSCN (280 mg, 2.88 mmol) were combined as solids and 18 ml thf were added. The suspension was sonicated for 2 hours and then stirred vigorously at 60 °C for 24 hours. Volatiles were removed in vacuo. The residue was dissolved in 15 ml of *n*-hexane and filtered. The resulting solution was slowly concentrated at 40 °C affording colorless crystals (143 mg, 0.170 mmol, 34%). Mp.: 257 °C. ¹H NMR (400.1 MHz, C₆D₆): δ (ppm) = 1.06 (dt, 2 H, J_{HH} = 7.8, 1.2 Hz, Si-CH₂), 1.38 (s, 18 H, Carb-^tBuH), 1.42 (s br, 36 H, Ar-^tBuH), 4.48 (dq, J_{HH} = 16.8, 1.4 Hz, 1 H, H_a), 4.67 (ddd, J_{HH} = 10.0, 1.8, 1.0 Hz, 1 H, H_b), 5.05 (ddt, J_{HH} = 16.8, 10.0, 7.8 Hz, 1 H, H_c), 7.63 (t, J_{HH} = 1.8 Hz, 2 H, *p*-CH), 7.67 (d, J_{HH} = 2.0 Hz, 2 H, C^{2,7}H), 7.83 (s br, 4 H, *o*-CH), 8.20 (d, J_{HH} = 2.1 Hz, 2 H, C^{4,5}H). ¹³C NMR (100.6 MHz, C₆D₆): δ (ppm) = 23.0 (s, Si-CH₂), 31.9 (s, Ar-C(CH₃)), 31.9 (s, Carb-C(CH₃)), 34.8 (s, Carb-C(CH₃)), 35.2 (s, Ar-C(CH₃)), 116.0 (s, C^{4,5}H), 118.6 (s, Si-CH₂CHCH₂), 123.3 (s, *p*-CH), 124.3 (s br, *o*-CH), 128.2 (s, Si-CH₂CHCH₂), 128.5 (s, C^{2,7}H), 130.8 (s), 132.0 (s), 141.4 (s), 142.3 (s), 144.7 (s br, NCS), 146.7 (s, C^{3,6}), 151.7 (s br, *m*-C). ¹⁵N NMR (40.6 MHz, C₆D₆): δ (ppm) = 102.6 (s, Carb-N), 111.4 (s, NCS). ²⁹Si NMR (79.5 MHz, C₆D₆): δ (ppm) = -52.8 (s). IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2962 (s), 2905 (w), 2867 (w), ν_{as} (NCS) 2099 (vs), ν_{as} (NCS) 2075 (vs), ν_{as} (NCS) 2033 (vs), ν_{as} (NCS) 2014 (vs), 1634 (vw), 1591 (m), 1477 (m), 1393 (m), 1380 (w), 1363 (s), 1291 (w), 1247 (m), 1216 (m), 1199 (m), 1180 (s), 1154 (w), 1108 (vw), 1075 (w), 1039 (w), 995 (w), 942 (m), 907 (s), 872 (s), 844 (s), 796 (w), 763 (s), 719 (s), 707 (s), 645 (w), 624 (s), 612 (s), 567 (vs), 547 (s), 534 (s), 516 (m), 488 (m), 460 (m), 424 (w). EA [C₅₃H₆₉N₃S₂Si] found (calc.): C 76.50 (75.75) H 8.01 (8.28) N 4.79 (5.00).

RSi(NH₂)₂All (5A). Modified procedure.^[24] In a Schlenk tube RSiCl₂H (200 mg, 0.265 mmol) were dissolved in 8 ml of toluene. In a second Schlenk tube NaNH₂ (62.2 mg, 1.59 mmol) and stearic acid (603 mg, 2.11 mmol) were combined as solids. Both Schlenk tubes were connected through a glass piece and the solution was degassed three times. In a static vacuum, the solids were slowly

heated to 120 °C while the solution was cooled to –196 °C. Then, the heater was removed, and the solution was stirred at –78 °C for 1 hour, resulting in a turbid suspension. All volatiles were removed in vacuo and the residue was dissolved in 4 ml of *n*-hexane. After filtration, the solution was concentrated affording colorless crystals (53.2 mg, 0.074 mmol, 28%). ¹H NMR (400.1 MHz, C₆D₆): δ (ppm) = 0.07 (s br, 4 H, NH), 1.33 (s, 36 H, Ar-^tBuH), 1.45 (s, 18 H, Carb-^tBuH), 4.85 (quin, *J*_{SiH} = 257.8 Hz, *J*_{HH} = 2.7 Hz, 1 H, SiH), 7.52 (t, *J*_{HH} = 1.8 Hz, 2 H, *p*-CH), 7.68 (d, *J*_{HH} = 2.0 Hz, 2 H, C^{2,7}H), 7.68 (d, *J*_{HH} = 1.8 Hz, 4 H, *o*-CH), 8.45 (d, *J*_{HH} = 2.1 Hz, 2 H, C^{4,5}H). ¹³C NMR (100.6 MHz, C₆D₆): δ (ppm) = 31.8 (s, Ar-C(CH₃)), 32.2 (s, Carb-C(CH₃)), 34.8 (s, Carb-C(CH₃)), 35.1 (s, Ar-C(CH₃)), 115.4 (s, C^{4,5}H), 121.5 (s, *p*-CH), 125.2 (s, *o*-CH), 127.4 (s, C^{2,7}H), 129.6 (s), 131.4 (s), 143.3 (s), 143.5 (s, C^{3,6}), 144.0 (s), 150.8 (s, *m*-C). ¹⁵N NMR (40.6 MHz, C₆D₆): δ (ppm) = 17.7 (s, *J*_{NH} = 50.2 Hz, NH₂), 105.1 (s, Carb-N). ²⁹Si NMR (79.5 MHz, C₆D₆): δ (ppm) = –34.1 (s). IR (ATR): $\tilde{\nu}$ (cm^{–1}) = $\nu_{\text{as}}(\text{NH})$ 3479 (vw), $\nu_{\text{s}}(\text{NH})$ 3391 (vw), 2952 (s), 2903 (w), 2865 (w), $\nu(\text{SiH})$ 2192 (vw), 1592 (m), 1539 (vw), 1479 (m), 1392 (m), 1376 (m), 1362 (s), 1291 (w), 1246 (m), 1216 (m), 1202 (m), 1181 (m), 1078 (w), 996 (m), 927 (m), 868 (vs), 795 (vw), 719 (s), 704 (m), 678 (vw), 647 (m), 550 (vw), 520 (m), 439 (m), 410 (vw), 380 (w).

RSi(NH₂)₂All (5B). Modified procedure.^[24] In a Schlenk tube RSiCl₂All (1.50 g, 1.89 mmol) were dissolved in 30 ml of toluene. In a second Schlenk tube NaNH₂ (1.03 g, 26.4 mmol) and stearic acid (10.5 g, 56.9 mmol) were combined as solids. Both Schlenk tubes were connected through a glass piece and the solution was degassed three times. In a static vacuum, the solids were slowly heated to 120 °C while the solution was cooled to –196 °C. Then, the heater was removed and the mixture was stirred at –78 °C for 1 hour, resulting in a turbid suspension. Then, the suspension was filtered and concentrated, affording colorless crystals. To remove remaining RH, the crystals were washed with *n*-hexane allowing the isolation of RSi(NH₂)₂All (260 mg, 0.344 mmol, 18%). ¹H NMR (400.1 MHz, C₆D₆): δ (ppm) = 0.38 (s br, 4 H, NH₂), 1.36 (s, 36 H, Ar-^tBuH), 1.41 (d, *J*_{HH} = 8.1 Hz, 2 H, Si-CH₂), 1.45 (s, 18 H, Carb-^tBuH), 4.42 (ddt, *J*_{HH} = 17.0, 2.6, 1.4 Hz, 1 H, H_a), 4.52 (ddt, *J*_{HH} = 10.0, 2.2, 1.0 Hz, 1 H, H_b), 5.17 (ddt, *J*_{HH} = 16.8, 10.1, 7.9 Hz, 1 H, H_c), 7.56 (t, *J*_{HH} = 1.8 Hz, 2 H, *p*-CH), 7.65 (d, *J*_{HH} = 2.1 Hz, 2 H, C^{2,7}H), 7.74 (d, *J*_{HH} = 1.8 Hz, 4 H, *o*-CH), 8.42 (d, *J*_{HH} = 2.1 Hz, 2 H, C^{4,5}H). ¹³C NMR (100.6 MHz, C₆D₆): δ (ppm) = 25.7 (s, Si-CH₂), 31.8 (s, Ar-C(CH₃)), 32.1 (s, Carb-C(CH₃)), 34.7 (s, Carb-C(CH₃)), 35.1 (s, Ar-C(CH₃)), 113.5 (s, Si-CH₂CH₂), 115.4 (s, C^{4,5}H), 121.8 (s, *p*-CH), 124.8 (s, *o*-CH), 130.4 (s), 131.9 (s, C^{1,8}), 134.7 (s, Si-CH₂CH₂), 143.7 (s), 144.2 (s), 144.6 (s), 151.2 (s br, *m*-C). ¹⁵N NMR (40.6 MHz, C₆D₆): δ (ppm) = 19.5 (s, NH₂), 120.1 (s, Carb-N). ²⁹Si NMR (79.5 MHz, C₆D₆): δ (ppm) = –20.9 (s). IR (ATR): $\tilde{\nu}$ (cm^{–1}) = $\nu_{\text{as}}(\text{NH})$ 3467 (vw), $\nu_{\text{s}}(\text{NH})$ 3376 (vw), 2961 (s), 2904 (w), 2866 (w), 1593 (m), 1536 (vw), 1478 (m), 1461 (w), 1392 (m), 1379 (w), 1363 (s), 1290 (w), 1247 (m), 1214 (m), 1200 (m), 1183 (m), 1162 (m), 1077 (w), 993 (w), 933 (m), 894 (vs), 870 (vs), 844 (m), 824 (w), 720 (s), 703 (m), 679 (vw), 645 (w), 594 (s), 532 (m), 474 (vw), 447 (m), 418 (w), 409 (w), 397 (w). 391 (vw). EA [C₅₁H₇₃N₃Si] found (calc.): C 80.11 (81.00) H 8.94 (9.73) N 5.48 (5.56).

Deposition Numbers 2131588 (for **1A**), 2131589 (for **1B**), 2131590 (for **1B**-hexane), 2131591 (for **2B**), 2131592 (for **3A**), 2131593 (for **3B**), 2131594 (for **4A**), 2131595 (for **4B**), 2131596 (for **5A**), and 2131597 (for **5B**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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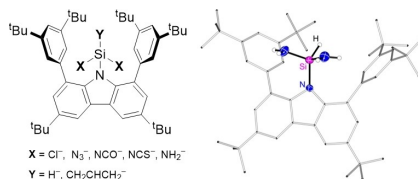
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RESEARCH ARTICLE

Two series of silanes bearing a bulky carbazolyl substituent were prepared starting from RSiCl_2H and RSiCl_2All (R = carbazolyl, All = allyl) by metathesis reactions, affording RSiX_2H and RSiX_2All (X = N_3 , NCO, NCS, NH_2).



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**Functionalized Carbazolyl Hydro-
and Allyl-Silanes**

