Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 2667–2673 **2667**
DOI: 10.1021/ic901620e

Reactions of Hydridochlorosilanes with 2,2′-Bipyridine and 1,10-Phenanthroline: Complexation versus Dismutation and Metal-Catalyst-Free 1,4-Hydrosilylation

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Received August 13, 2009

Stable in the solid state and isolable in high yields are adducts of H_2SiCl_2, $HSiCl_3$, and $RSiCl_3$ (R = Me, Ph) with the N,N′-chelating ligands 1,10-phenanthroline (phen; **1c**), 2,2′-bipyridine (bipy; **1b**), and (to a limited extent) *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda; **1a**). The products were comprehensively characterized via multinuclear solution and solid-state NMR spectroscopy, including analysis of the ^{29}Si NMR chemical shift anisotropy tensors, Raman spectroscopy, elemental analyses, and, for $SiCl_4$(phen) (**2c**), $HSiCl_3$(bipy) (**3b**), H_2SiCl_2(bipy) (**4b**), $MeSiCl_3$(phen) (**5c**), and $PhSiCl_3$(phen) (**6c**), single-crystal X-ray structure analyses. The latter revealed that the nonchlorine substituents (i.e., H, Me, and Ph) are exclusively trans-disposed to the N-donor atoms of the chelating ligands. A dismutation of the complexes $HXSiCl_2$(bipy) and $HXSiCl_2$(tmeda) (X = H or Cl) was observed in polar solvents at elevated temperatures. This reaction is more pronounced when phen is used instead of bipy or tmeda. For $MeHSiCl_2$(phen), in addition to undergoing H−Cl redistribution accompanied by the formation of **5c**, an unexpected 1,4-hydrosilylation was observed. The latter was proven NMR-spectroscopically and by a single-crystal X-ray structure analysis of the product $MeSiCl_2$(4H-phen) (**7**), a pentacoordinated silicon compound with a trigonal-bipyramidal arrangement of the subsituents and the methyl group located in an equatorial position.

Introduction

Hydridochlorosilanes of the type H_xSiCl_{4-x} play a crucial role in the production process of ultrapure silicon (the Siemens process), in addition to being starting materials for numerous organosilicon compounds.[1] Among products derived from hydridochlorosilanes, adducts with additional donor molecules have attracted particular attention.[2] This might imply that compounds of the type H_xSiCl_{4-x}(donor)$_2$ with $x = 1$ or 2 are already well-known from the literature. In contrast to pyridine adducts H_xSiCl_{4-x}(Rpy)$_2$ (Rpy = pyridine and substituted pyridines), which have been studied and the molecular structures of which have been analyzed carefully,[3] only two structurally characterized complexes H_xSiCl_{4-x}(donor) comprising a bidentate N,N′-chelating ligand have been described so far: In the 1960s, Campell-Fergusson and Ebsworth reported the reaction of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) with $SiHCl_3$ in a 1:1 ratio to give (tmeda)$SiHCl_3$ (Scheme 1):

Scheme 1. Reaction of Trichlorosilane with tmeda

The poor solubility of the reaction product indicated polymeric or ionic structures.[4] X-ray diffraction analysis, however, revealed the monomeric structure of the complex.[5]

In sharp contrast with related hydridochlorosilane complexes, the products of the reactions of silicon tetrahalides with 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) as chelating N(sp^2)N′(sp^2)-donor building blocks are well-known.[6]

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Published on Web 02/16/2010

In this context, it was pointed out that the compounds SiX_4(bipy) and SiX_4(phen) are more stable than their pyridine analogues $SiX_4(py)_2$, a principle of general applicability.[7] Kummer et al. reported that, with reference to the same silane, the complex stability increases in the order py < bipy < phen.[8] In another particular case, a comparative study showed that dissociation of the crystalline adduct of silicon tetrachloride with bipy commences at noticeably higher temperatures than a similar decomposition of the pyridine adduct,[9] and computational studies support these findings.[10]

Whereas in trans-N-donor-substituted silanes (e.g., with pyridine ligands) the four formally covalently bound groups, e.g., Si−X and Si−H, are forced to arrange in the equatorial plane of an almost octahedral coordination sphere, investigations on bipy and phen complexes of silanes still lack the information as to which coordination sites (trans- or cis-N) will be occupied by Si−X (X = F, Cl, Br), Si−H, and Si−C groups.[11]

Herein we report the systematic investigation of hexacoordinated silicon compounds from hydridochlorosilanes (H_2SiCl_2, $HSiCl_3$, $MeHSiCl_2$, and $PhHSiCl_2$) and chlorosilanes ($SiCl_4$, $MeSiCl_3$, and $PhSiCl_3$) with the N,N′-chelating ligands tmeda, bipy, and phen. Differences between bipy and phen with respect to complexation versus dismutation as competitive reactions became clear, and an unexpected 1,4-hydrosilylation was found to take place at the phen ligand.

Experimental Section

All reactions were carried out under an atmosphere of dry argon using the Schlenk technique. Solvents were dried and purified by standard methods.

Cross-polarization/magic angle spinning (CP/MAS) NMR spectra were recorded on a 400 MHz Bruker Avance WB spectrometer using a 7 mm probe with zirconia rotors and KelF inserts operating at 400.23, 100.61, and 79.51 MHz for ^{1}H, ^{13}C, and ^{29}Si NMR spectra, respectively. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) using Q_8M_8 [octakis(trimethylsiloxy)octasilsesquioxane] and adamantane as the external standard for ^{29}Si and ^{13}C NMR, respectively. If not otherwise mentioned, CP/MAS spectra were recorded at ν_{spin} = 4 kHz and ^{13}C NMR using the TOSS sequence.

Raman spectra were recorded on a Bruker RFS 100/S instrument operating with a Nd/YAG laser. Determination of the chlorine content of compounds **3b** and **4b** was performed by hydrolysis of 0.19 g of **3b** and of 0.21 g of **4b** in 100 mL of a diluted sodium hydroxide solution, followed by chloride quantification with ion chromatography (Dionex ICS-2000, eluent 22 mM KOH, column AS11_HC, electrical conductivity measurement). C, H, and N analyses were performed using a vario microcube (Elementar).

Single-crystal X-ray diffraction data were collected on a Bruker Nonius X8 APEX2 CCD diffractometer using Mo Kα radiation. Structures were solved with direct methods and refined with full-matrix least-squares methods. All non-H atoms were anisotropically refined. C-bound H atoms were placed in idealized positions and isotropically refined (riding model). Si-bound H atoms were found by analysis of the residual electron density and refined without bond-length restraints. Structure solution and refinement of F^2 against all reflections were carried out with the software *SHELXS-97* and *SHELXL-97* [G. M. Sheldrick, Universität Göttingen (1986−1997)]. The structure of **5c** was determined from a data set collected from a twin [twin law: (1, 0, 0)(0, 1, 0)(0, 0, −1), populations 58% and 42%], the twinning of which resulted from the monoclinic angle being close to 90°. In a similar manner, compound **4b** crystallized as a twin because of the combination of very similar crystallographic axes *a* and *b*, together with very similar angles α and *β*. Thus, the structure was refined using the twin matrix (0, 1, 0)(1, 0, 0)(0, 0, 1), resulting in a population of 3% for a twin component and a significant decrease of the *R* factor (by ca. 0.01). Data of the structural determination and refinement for the hereinpresented crystal structures are summarized in the supporting Information (Tables S1 and S2).

Starting materials H_2SiCl_2 (Degussa), $HSiCl_3$ (Acros), $SiCl_4$ (Acros), $HSiCl_2Me$ (Aldrich), $HSiCl_2Ph$ (Aldrich), $MeSiCl_3$ (Merck), $PhSiCl_3$ (ABCR), 1,10-phenanthroline (Chempur), 2,2′-bipyridine (ABCR), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (Merck), and pyridine (Riedel de Haen) were commercially available. Solid compounds were dried under vacuum for several hours. All chlorosilanes were used as supplied.

General Procedure for the Syntheses of 3−4a, 2−4b, and 2−4c. The respective silane (5 mmol) was dissolved in toluene (20 mL) and stirred at −78 °C, and the desired N,N′-chelating ligand (10 mmol) was added as a solid (tmeda as a liquid). The products precipitated as colorless solids. The suspension was stirred for 1 h at −78 °C and then allowed to slowly adjust to ambient temperature. The white precipitate was filtered off, washed with toluene, and dried under vacuum. Modifications to this procedure are outlined if applicable.

The compounds **5−6b**, **5−6c**, and **2a** were prepared according to the following general route: To the solid N,N′-chelating ligand (10 mmol), which was stirred at −78 °C, was added the silane (4 mL). The products precipitated as colorless solids. The suspension was stirred for 1 h at −78 °C and was then allowed to slowly adjust to ambient temperature. The precipitate was filtered off, washed with the respective silane, and dried under vacuum. Modifications to this procedure are outlined if applicable. Spectroscopic and analytical details are provided in the Supporting Information.

Yields for Compounds 2−6b, 2c, 5−6c, and 2−4a. $SiCl_4$(bipy) (**2b**): 1.58 g (4.85 mmol; 97%). $HSiCl_3$(bipy) (**3b**): 1.44 g (4.94 mmol; 99%). H_2SiCl_2(bipy) (**4b**): 1.35 g (4.96 mmol; 99%). $MeSiCl_3$(bipy) (**5b**): 1.48 g (4.84 mmol; 96.8%). $PhSiCl_3$(bipy) (**6b**): 0.92 g (2.50 mmol; 50%). $SiCl_4$(phen) (**2c**): 1.72 g (4.91 mmol; 98.3%). $MeSiCl_3$(phen) (**5c**): 1.57 g (4.76 mmol; 95.2%). $PhSiCl_3$(phen) (**6c**): 1.0 g (2.55 mmol; 51.1%). $SiCl_4$(tmeda) (**2a**): 1.20 g (4.2 mmol; 83.9%). $HSiCl_3$(tmeda) (**3a**): 1.20 g (4.80 mmol; 95.4%). H_2SiCl_2(tmeda) (**4a**): 1.05 g (4.8 mmol; 96.7%).

Results and Discussion

In analogy to the previously described direct reaction of H_2SiCl_2[3f] and $HSiCl_3$[12] with pyridines, the straightforward formation of the octahedrally coordinated silicon compounds of bipy (**2−4b**) and phen (**2−4c**) was expected (Scheme 2, top). Furthermore, tmeda was used as an N,N′-chelating ligand (Scheme 2, bottom).

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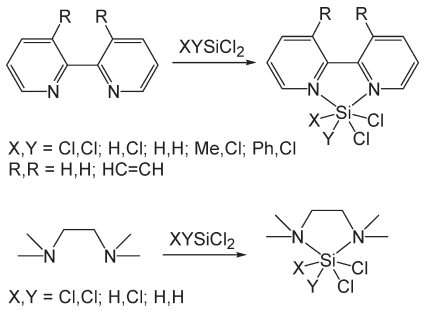
Scheme 2. Reactions of Various Chlorosilanes with bipy, phen, and tmeda



The silicon-complex stability of the N,N′-chelating ligands under investigation increases in the order tmeda < py < bipy < phen. Whereas tmeda fails to form stable adducts with $MeSiCl_3$ or $PhSiCl_3$ (target products **5a** and **6a**, respectively), thus limiting our series of $XYSiCl_2$(tmeda) complexes, the desired products **2**−**6b** and **2**−**6c** were accessible from bipy and phen, respectively. (The tetrachlorosilane adducts of bipy, phen, and tmeda have already been reported in the literature.[6,13]) CP/MAS ^{29}Si NMR spectra revealed hexacoordination of the Si atoms of all of the above products,[14] and coordination of the tmeda ligand [two N(sp^3)-donor atoms] is accompanied by a significant downfield shift of the resonance with respect to the signals of the bipy and phen complexes of the same silane [comprising two N(sp^2)-donor atoms]. The poor solubilities of these complexes rendered solution NMR spectroscopy unsuitable. Retention of the Si-bound H atoms (if applicable) is supported by Raman spectroscopy (Table 1).

Crystal Structures of the Hexacoordinated Silicon Complexes. In addition to the spectroscopic characterization described above, recrystallization of the bipy complexes **3b** and **4b** as well as the phen adducts **2c**, **5c**, and **6c** afforded crystals suitable for X-ray diffraction analyses (Figure 1 and Table 2). Despite the different chelators used and the different non-Cl substituents bound to the Si atom, these five complexes exhibit a number of mutual structural features. In addition to their slightly distorted octahedral Si-coordination sphere, all of them have a Cl−Si−Cl axis in common, which is directed almost perpendicularly to the idealized plane of and slightly bent toward the chelating ligand. Furthermore, the lengths of the Si−Cl bonds, which are trans-disposed to one another, are significantly longer than the trans-N-situated Si−Cl bonds of **3b**, **2c**, **5c**, and **6c**. Both the trans-Cl- and the trans-N-situated Si−Cl bonds are significantly longer than those in tetracoordinated chlorosilanes (e.g., 201.9 pm for tetrachlorosilane[15]). Even in the case of the phen complexes, the (more or less) rigid phen moiety responds to the coordinative requirements of the Si atom as a Lewis acidic center: e.g., in the case of **2c**, the angles N1−C12−C11 and N2−C11−C12 decreased from 117.1(1)° and 119.0(1)°[16] to 115.5(2)° and 115.7(2)°. The trans-N-situated Si-bound H atom(s) of adducts **3b** and **4b** appear particularly noteworthy because this feature clearly distinguishes bipy complexes such as **3b** from the related tmeda complex **3a**, which was reported to comprise *fac*-arranged Si−Cl bonds and a trans-Cl-situated Si−H bond. An explanation as to the origin of the configurational difference between **3b** and **3a** is provided by the steric demand of the chelating ligands. Whereas in compound **3b** (the same holds for **4b**) intermolecular interactions between the axial Cl atoms and the H atoms of neighboring bipy moieties stabilize the crystal packing, the Cl−Si−H axis in **3a** obviously serves the minimization of intramolecular repulsive forces between the tmeda methyl groups and the Si-bound monodentate substituents. In **5c**, the Si-bound phenyl group is arranged almost perpendicularly to the phen ligand, most likely in order to minimize steric repulsion. A similar donor atom arrangement (that is, two Si−Cl bonds trans to each other in addition to a Si-bound phenyl group trans-disposed to an imine N atom) has been described previously.[17]

In addition to the isotropic ^{29}Si NMR shift, the chemical shift anisotropy (CSA) tensor components of the hydridochlorosilane adducts **3b** and **4b** were extracted from spinning side-band spectra, and the directions of the principal components with respect to the Si-coordination spheres were analyzed with the aid of computational analyses based on the crystal structures of these complexes.

The experimentally obtained data (entries "exp" in Table 3) are reproduced very well with both B3LYP and HF (with a particularly good match of the B3LYP results) in the case of the dichlorosilane complex **4b**, whereas B3LYP fails to provide satisfactory data for the trichlorosilane(bipy) adduct **3b**. The use of HF instead of B3LYP helps to reduce these errors only in part. The general shape of the CSA tensor, however, is reproduced to an extent that allows for a discussion of its orientation with respect to the Si-coordination sphere (Figure 2). Whereas the CSA tensor for the trichlorosilane(bipy) adduct **3b** is surprisingly similar to that of the adduct $HSiCl_3$(4-*tert*-butylpyridine)$_2$, which comprises trans-disposed N-donor sites instead of the cis N−Si−N situation of **3b**, the change from trans- to cis-disposed N-donor sites effects the CSA tensor properties of the dichlorosilane complexes noticeably. In particular, the ^{29}Si NMR resonance is shifted to higher field upon transition to the chelate complex. This shift of the isotropic signal is mainly caused by an even more pronounced upfield shift of principal component (11). In complexes $HRSiCl_2$-(4-*tert*-butylpyridine)$_2$ (R = H, Cl), this CSA tensor component was shown to point along the Cl−Si−Cl axis, being particularly influenced by the orthogonal substituents (N and H donors). The same directionality applies to **4b**, with (11) pointing along the Cl−Si−Cl axis and the very similar components (22) and (33) being situated in the SiN_2H_2 plane. Thus, in complex **4b**, this pronounced upfield shift of the ^{29}Si NMR resonance [with respect to H_2SiCl_2(4-*tert*-butylpyridine)$_2$] can be attributed to the strong chelating effect of the bipy ligand. The develop-

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Table 1. CP/MAS ^{29}Si NMR Data and ν(Si−H) Raman Bands [cm^{-1}] for Compounds **2a**−**2c**, **3a**−**3c**, **4a**−**4c**, **5b**, **5c**, **6b**, and **6c**

	tmeda		bipy		phen	
silane	^{29}Si NMR [ppm]	ν(Si−H) [cm^{-1}]	^{29}Si NMR [ppm]	ν(Si−H) [cm^{-1}]	^{29}Si NMR [ppm]	ν(Si−H) [cm^{-1}]
$SiCl_4$	**2a**		**2b**		**2c**	
	−160.1		−179.5		−179.7	
$HSiCl_3$	**3a**		**3b**		**3c**	
	−145.3	2145, 2174	−169.5	2137	−171.1	a
H_2SiCl_2	**4a**		**4b**		**4c**	
	−131.5	2080, 2205	−161.0	2050, 2081	−163.3	a
$MeSiCl_3$	**5a**[b]		**5b**		**5c**	
			−155.2		−152.4	
$PhSiCl_3$	**6a**[b]		**6b**		**6c**	
			−153.5		−153.1	

[a] Dismutation. [b] Not stable at room temperature and under cooling.

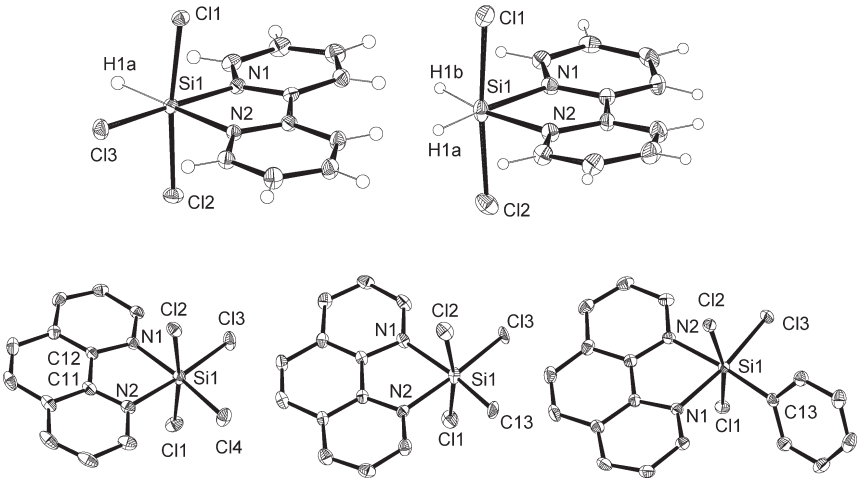

Figure 1. Molecular structures of **3b** and **4b** (on top from left to right) and **2c** (one of the two independent complex molecules in **2c**$_2$·MeCN), **5c** (in a crystal of **5c**·THF), and **6c** (bottom from left to right). ORTEP drawing with 50% probability thermal ellipsoids. H atoms omitted for clarity in the case of **2c**, **5c**, and **6c**. Atoms C13 and Cl3 in compound **5c** are disordered with sof of 46% and 54%.

Table 2. Selected Bond Lengths and Angles for Compounds **3b**, **4b**, **2c**, **5c**, and **6c**

	3b	**4b**	**2c**	**5c**	**6c**
Si−N1 [pm]	193.6(2)	196.0(4)	197.3(2)	202.1(6)	200.4(2)
Si−N2 [pm]	196.7(2)	196.2(4)	197.1(2)	199.6(6)	202.4(2)
Si−Cl1 [pm]	222.6(1)	227.9(2)	218.5(1)	222.4(3)	223.0(1)
Si−Cl2 [pm]	222.1(1)	225.3(2)	220.5(1)	222.2(3)	221.9(1)
Si−Cl3 [pm]	217.2(1)		214.3(1)	214.6(4)	218.9(1)
Si−Cl4 [pm]			214.4(1)		
Si−C13 [pm]				183.7(19)	191.7(2)
N1−Si−N2 [deg]	80.87(8)	79.02(17)	81.84(7)	80.12(19)	80.13(6)
Cl1−Si−Cl2 [deg]	172.55(4)	174.71(9)	172.08(3)	169.34(11)	166.94(3)

ment of the CSA characteristics of the trichlorosilane complex $HSiCl_3$(4-*tert*-butylpyridine)$_2$ upon chelation by bipy, however, hints at another (at least one) effect on the shielding of the Si nuclei in these complexes, which might be capable of overcompensating for the stronger shielding caused by the chelator. It is known from various examples of hexacoordinated silicon complexes that the introduction of five-membered chelate rings in the Si-coordination sphere causes a downfield shift of the ^{29}Si NMR resonance with reference to similar systems bearing six-membered chelates, e.g., those depicted in Scheme 3. Thus, the introduction of the five-membered bipy chelate can be expected to exert similar effects on the shielding of the Si nuclei in the herein reported complexes.

Dismutation of Hydridochlorosilanes. Si−Cl versus Si−H dismutation reactions, as pointed out in previous reports,[5] represent a serious competitor to hydridochlorosilane complexation in polar solvents. The reactions of trichlorosilane and dichlorosilane with tmeda and bipy led to the formation of hexacoordinated silicon compounds **3a** and **3b** as well as **4a** and **4b**, respectively. Under the synthesis conditions applied (−78 °C), compounds **4a** and **4b** precipitated immediately. There was no indication for dismutation reactions even upon variation of the solvent used (toluene and *n*-hexane). The same observation was made for the reaction of trichlorosilane and dichlorosilane with tmeda.

In the Raman spectrum, as expected, the target products exhibit their characteristic Si−H valence vibration bands. The shift to larger wave numbers for the trichlorosilane complexes (with reference to the related dichlorosilane complex) can be explained by electron withdrawal from the Si−H bond, hence bond strengthening, caused by the additional halide substituent.[21] Furthermore, the Si−H valence vibration bands of these complexes are shifted to lower wave numbers with respect to the tetracoordinated silanes H_2SiCl_2 and $HSiCl_3$. This shift is accompanied by broadening of the signal, which can be attributed to increased ionic contributions to the Si−H bonding situation.[3f]

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Table 3. Experimental CP/MAS ^{29}Si NMR Data of Selected Compounds silane·(L)

silane	L	a	δ_{iso} [b]	δ_{11}	δ_{22}	δ_{33}	Ω [c]	κ [c]
$HSiCl_3$	bipy	exp	−169.5	−123.4	−178.1	−207.0	83.6	−0.31
		B3LYP	−160.8	−119.4	−163.0	−200.0	80.6	−0.08
		HF	−169.2	−126.8	−180.4	−200.4	73.6	−0.46
$HSiCl_3$[12]	(4-*tert*-butylpyridine)$_2$	exp	−170.0	−126.6	−183.3	−202.0	75.5	−0.45
H_2SiCl_2	bipy	exp	−161.0	−85.1	−194.2	−203.4	118.4	−0.84
		B3LYP	−161.8	−86.3	−194.2	−204.9	118.6	−0.82
		HF	−164.5	−93.0	−197.3	−203.2	110.2	−0.89
H_2SiCl_2[3f]	(4-*tert*-butylpyridine)$_2$	exp	−149.6	−49.5	−189.3	−210.0	160.5	−0.70

[a] Method: exp = experimental, B3LYP = calculated on the B3LYP/6-311G+(2d,p) level, and HF = calculated on the HF/6-311G+(2d,p) level. Both CSA tensor calculations on the B3LYP and HF levels were performed on the molecular structures obtained from X-ray diffraction analyses after optimization of the H-atom positions on the MPW1PW91/6-311G(d,p) level. [b] Chemical shift in the solid state. [c] Herzfeld−Berger convention,[20] $\Omega = \delta_{11} - \delta_{33}$, $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$.

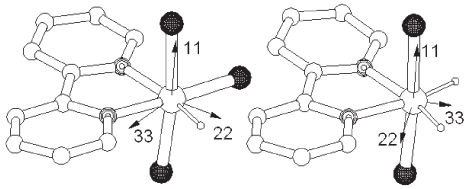
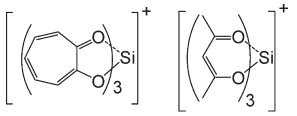


Figure 2. Orientation of the ^{29}Si CSA tensor components δ_{11}, δ_{22}, and δ_{33} with respect to the molecules **3b** (left) and **4b** (right). Atomic spheres are drawn at arbitrary size, Cl atoms are black, and N atoms are filled with circles.

Scheme 3. Cationic Silicon Trichelate Complexes Bearing Exclusively Five-Membered $[Si(trop)_3]^{+}$[18] (Left) and Six-Membered O,O-Chelates $[Si(acetylacetonato)_3]^{+}$[19] (Right)[a]



-139.6 -194.4

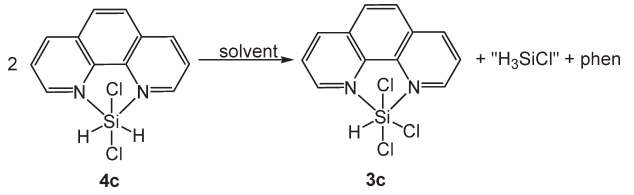
[a] CP/MAS ^{29}Si NMR spectroscopic data (δ_{iso}) are given below the formulas. Note: Although the six Si−O bonds in each of above compounds are almost equal among each other, the ketoenolate canonical form was chosen to illustrate the similarities between the O,O ligands, i.e., three O,O-ketoenolate monoanionic ligands with an unsaturated [C(sp^2)] backbone.

In contrast with the formation of bipy adducts **3b** and **4b**, the reactions of H_2SiCl_2 and $HSiCl_3$ with phen, e.g., in *n*-hexane or toluene, resulted in Si−H versus Si−Cl redistribution, including complexation of dismutation products (Scheme 4).

In addition to the pronounced susceptibility of monochlorosilane to dismutation reactions, the tendency for complexation of hydridosilanes with N-containing ligands decreases from tetrachlorosilane to monosilane.[22] This combination of effects is presumably the major reason for monochlorosilane(phen) adducts still being unobserved in the course of our investigations. (Note: The potential redistribution product monosilane was not observed so far during our investigations.)

The reaction of H_2SiCl_2 with phen to produce **4c** in tetrahydrofuran (THF; under reflux or at room temperature) results in the formation of dismutation products as well. A solid consisting of a mixture of **3c** and **4c** was obtained, as indicated by CP/MAS ^{29}Si NMR spectroscopy (Figure 3).

Scheme 4. Dismutation of **4c** in Solution



4c **3c**

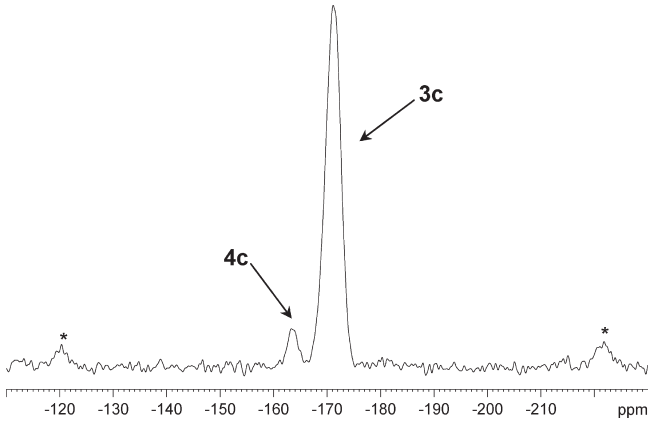


Figure 3. CP/MAS ^{29}Si NMR spectrum of the solid product obtained by the reaction of phen with dichlorosilane in THF at 65 °C after 1 h (asterisks mark spinning side bands of **3c**).

The supernatant, a red solution, exhibited a signal at $\delta = -99$ ppm in the ^{29}Si NMR spectrum, which indicates the formation of at least one additional byproduct, a compound comprising a pentacoordinated silicon compound.[23]

Hydrosilylation of phen with Organohydridochlorosilanes. Because the formation of a pentacoordinated silicon compound in a reaction between dichlorosilane and phen was completely unexpected, further attention was paid to this phenomenon. Kummer et al. have already observed a rearrangement reaction of an Si−X moiety in the phen coordination clamp, i.e., a silyl shift (X being a silyl substituent) to the phen ligand backbone.[24] In related studies dealing with Si−H activation in higher coordinated silicon compounds, hydride shifts to C=N and N=N moieties have also been

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(24) Kummer, D.; Chaudry, S. C.; Depmeier, W.; Mattern, G. *Chem. Ber.* **1990**, *123*, 2241–2245.

observed.[25] A hydrosilylation of a phen C=N bond (i.e., rearrangement of the Si−H bond) would provide an explanation for the formation of the pentacoordinated silicon compound. Because the pentacoordinated silicon complex lacks an Si−H bond (vide infra), the dismutation product $HSiCl_3$(phen) may be considered as a key intermediate, which underwent Si−H cleavage in the case of an intramolecular hydride rearrangement. In addition to trichlorosilane, organodichlorosilanes $RHSiCl_2$ should exhibit the same capability of transferring the H atom of a Si−H moiety onto an imine (or phen) C=N moiety, with the obvious advantage of their lower susceptibility to hydrogen versus chlorine dismutation.

The reaction between methyldichlorosilane and phen in THF at −5 °C resulted in the formation of a poorly soluble crystalline compound, which dissolved upon heating and afforded a yellowish crystalline solid upon cooling. The CP/MAS ^{29}Si NMR spectrum of this solid revealed the formation of one hexacoordinated silicon compound (δ_{iso} = −151.6 ppm). Raman spectroscopic data indicated the absence of the characteristic Si−H valence vibration. Both of these spectroscopic data and the determination of the unit cell parameters proved this solid to be the dismutation product **5c**, which was obtained in high yield (60% with respect to a quantitative formation of $MeSiH_3$ + $2MeSiCl_3$ as dismutation products). For comparison, the synthesis of **5c** from $MeSiCl_3$ and phen in THF under similar conditions (the same ratio of $MeSiCl_3$−THF) resulted in a similar yield (63%), thus rendering the observed yields (ca. 40% less than theoretical) a matter of solubility in THF.

^{29}Si NMR spectra of the remaining solution revealed signals at δ = −68.2, −73.7, −76.3, −76.8, and −78.5 ppm. A Raman spectrum of the solid obtained upon removal of the solvent lacks the characteristic Si−H valence vibration. Additionally, a CP/MAS ^{29}Si NMR spectrum recorded upon removal of the solvent supported the formation of pentacoordinated silicon compounds (δ = −79 ppm, broad) rather than the signal in solution being a result of rapid equilibration between compounds with tetra- and hexacoordinated Si atoms. From this solution, further crystalline solids were obtained that, in addition to yellowish crystals of **5c**, contained a few red crystals. An X-ray diffraction analysis of the latter confirmed both the formation of a pentacoordinated silicon compound (**7**) and the hydride shift to the phen ligand (Figure 4).

In contrast with the silyl rearrangement found by Kummer et al.[24] and the hydride shifts reported by Kost et al., Kawashima et al., and Wagler et al.,[25] all of which are 1,3-shift reactions, the rearrangement of a Si-bound hydride, giving rise to the formation of **7**, represents a 1,5 shift, i.e., a 1,4 addition of the Si−H moiety to phen (Scheme 5). Our observations, i.e., (i) the predominant formation of $MeSiCl_3$ as the dismutation product (as its phen adduct **5c**), (ii) the emergence of various ^{29}Si NMR signals characteristic of pentacoordinated silicon

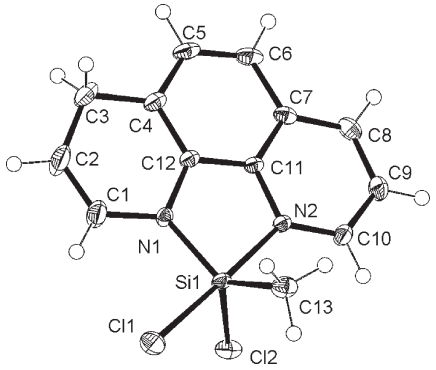
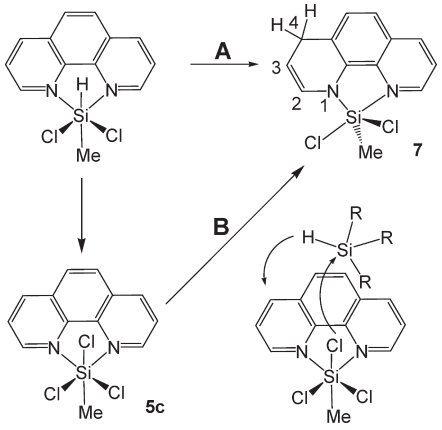


Figure 4. Molecular structure of **7** (ORTEP diagram with 50% probability ellipsoids). Atoms Si1, Cl1, N1, N2, and C3−C12 of the molecule are situated on a crystallographically imposed mirror plane. Hence, the positions of C1, C2, C13, and Cl2 (not located in this plane) suffer from symmetry-imposed disorder with a sof of 0.5 for each position. Selected bond lengths [pm] and angles [deg]: Si1−Cl1 221.1(1), Si1−Cl2 203.0(3), Si1−C13 189.5(14), Si1−N1 177.6(2), Si1−N2 200.4(2), N1−C1 142.2(3), N1−C12 140.6(3), C1−C2 133.9(4), C2−C3 149.7(4), C3−C4 150.5(3); N2−Si1−Cl1 178.3(1), N1−Si1−Cl1 95.2(1), N1−Si1−C13 117.3(7).

Scheme 5. Two Alternative Routes toward **7**: Intramolecular Hydrogen Shift (A) and Intermolecular Hydrogen Transfer from a Hydridosilane (e.g., MeH_2SiCl) to **5c** (Route B)



complexes, (iii) the preference for trans-N-located Si−H bonds in **3b** and **4b**, and (iv) the crystallographically proven formation of a 1,4-dihydrophenanthroline ligand supporting the hypothesis that the hydride Si−H transfer to the phen moiety occurs in an intermolecular fashion (reaction of **5c** with MeH_nSiCl_{3-n}, route B) rather than intramolecularly upon formation of $MeHSiCl_2$(phen) (route A; Scheme 5).

For the reaction between phenyldichlorosilane and phen in THF, a similar reaction was observed. A red solution and a poorly soluble crystalline compound were obtained. The CP/MAS ^{29}Si NMR spectrum of the latter indicated the formation of a hexacoordinated silicon compound (δ_{iso} = −153.1 ppm; **6c**). Raman spectroscopic data again demonstrated a lack of the characteristic Si−H valence vibration. ^{29}Si NMR spectra of the remaining solution revealed a signal at δ = −85.3 ppm. Final evidence for the general possibility of an intermolecular Si−H transfer to the phen backbone is provided by the reaction between **5c** and $PhHSiCl_2$. Whereas ligand exchange [under formation of $PhHSiCl_2$(phen)] and subsequent intramolecular rearrangement should produce a silicon compound with a characteristic ^{29}Si NMR signal at

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−85 ppm, intermolecular hydrogen transfer from $PhHSiCl_2$ to the $MeSiCl_3$-coordinated phen backbone and chlorine transfer from the $MeSiCl_3$ moiety to the phenylsilicon moiety should deliver a compound that produces a ^{29}Si NMR signal at ca. −77 ppm. The ^{29}Si NMR spectrum acquired from a mixture obtained by the reaction of **5c** with $PhHSiCl_2$ in THF exhibited signals at 13.8 ppm ($MeSiCl_3$), −0.3 ppm ($PhSiCl_3$), and −76.6 ppm but no signal in the range −80 to −90 ppm, thus providing an additional hint at an intermolecular Si−H transfer to the phen ligand.

So far, there are no crystallographic data available for silicon complexes of 1,4-dihydrophenanthroline. The coordination behavior of this 4H−phen derivative, however, is closely related to the manner in which 1,2,3,4-tetrahydrophenanthroline is setting up trigonal-bipyramidal coordination spheres about halide-substituted silicon centers,[26] thus rendering extensive discussion of the molecular structure of **7** superfluous.

Conclusions

Hydridochlorosilanes were shown to undergo various reactions with the bidentate chelators bipy and phen, i.e., complexation, dismutation, and hydrosilylation of the ligand. Whereas the reactivity patterns of tetrachlorosilane and organotrichlorosilanes with the above ligands are limited to adduct formation, organodichlorosilanes proved unstable in the bipy and phen braces. In particular, $RSiHSiCl_2$(bipy) underwent dismutation to yield $RSiCl_3$(bipy). In contrast to these two alternatives, hydrosilylation of the ligand was found as a reasonable alternative in related phen systems. Rather than being a competitor with dismutation, this hydrosilylation appears to be a subsequent reaction upon dismutation. In this context, the first crystal structure of a silicon complex bearing a 1,4-dihydrophenanthroline ligand, which was formed by the unexpected 1,4-hydrosilylation reaction (or hydrogen 1,5 shift), was presented. In addition to the formal hydride 1,5 shift, further experimental data support the hydrogenation of the phen ligand to arise from an intermolecular hydrogenation reaction that involves dismutation products. Trichlorosilane and dichlorosilane may exhibit the same reactivity patterns.

The first crystallographic evidence was delivered for hydridochlorosilane complexes of bipy. In contrast with the already known $HSiCl_3$(tmeda) complex, the silane(bipy) adducts exhibit Si−H bonds trans-situated with respect to the N-donor sites. In addition to this difference, the tmeda complexes, although accessible as stable solids, were found to be noticeably less stable than the bipy complexes with respect to their Si−N bonds. That is, dissociation into tmeda and the respective silane was found in solution.

The synthetic potential of the reversible complexation−dissociation, with particular focus on Si−H activation and the use of Si-coordinated ligands as precursors in ligand−hydrogenation reactions, will be the subject of further investigations.

Acknowledgment. The German Research Foundation (DFG, Bonn, Germany) and TU Bergakademie Freiberg are acknowledged for financial support of this research.

Supporting Information Available: Further details of the experimental procedures, CP/MAS ^{29}Si NMR data of compounds **2**−**4a**, **2**−**6b**, **2c**, **5**−**6c**, and **7**, and X-ray structure analysis data and CIF files for **2c**, **3b**, **4b**, **5c**, **6c**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication nos. CCDC-733072 (**2c**), CCDC-733074 (**3b**), CCDC-733071 (**4b**), CCDC-733076 (**5c**), CCDC-733073 (**6c**), and CCDC-733075 (**7**). Copies of the data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K., via www.ccdc.cam.ac.uk/data_request/cif, fax (international) +44-1223/336-033, or e-mail deposit@ccdc.cam.ac.uk.

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