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A Disilane with a Hypercoordinate Silicon Atom: Coordination of an Imine Ligand versus Si−Si Bond Splitting

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An imine−amine-substituted disilane (NN)MeSi−SiMe(ONO) [(NN) ≡ PhN$(CH_2)_2$NPh; (ONO) ≡ *o*-O-*p*-MeO−C_6H_3−C(Ph)=N−C_6H_4-*o*-O] involving a penta- as well as a tetracoordinate silicon atom was synthesized. This ligand combination gives rise to a stable disilane with a hypercoordinate silicon atom by the imine donor action, while a 1,1-dichlorosilane ($MeCl_2Si$)−SiMe(ONO) is not available due to Si−Si bond cleavage with formation of the pentacoordinate monosilane SiClMe(ONO).

Introduction

The chemistry of hypercoordinate silicon complexes, which has been intensely investigated during the past decades, still delivers new insights into this class of compounds. The weak Si−Si bond may easily be activated by hypercoordination of one Si atom in order to be cleaved and to undergo rearrangement reactions, e.g., the disproportionation of disilanes via donor-stabilized silylenes[1] or the 1,4-addition of disilanes to 1,2-diimines[2] and 1,2-diones.[3] Another kind of Si−Si bond cleavage under formation of a Si−C bond was recently reported[4] (Scheme 1, top). Construction of oligosilane backbones may also be mediated by hypercoordinate silicon species.[5]

The role of electron-transfer steps in various reactions at the Si atom including Si−Si bond cleavage has been discussed.[6] Recently, Mochida et al. reported an interesting kind of Si−Si bond cleavage by interaction with the strong electron acceptor tetracyanoethylene (TCNE).[7] Besides Si−Si bond activation via hypercoordination, many reactions such as the *N*-methylimidazole-catalyzed disilane-disproportionation[1] may also be based on hidden electron-transfer steps since imine moieties may act not only as lone-pair donors but also as electron acceptors. Unfortunately, there are only a few examples of oligosilanes bearing hypercoordinate Si atoms with additional imine-like ligands.[8]

Nevertheless, many attempts have been made to prepare isolable di- and oligosilanes with hypercoordinate silicon atom(s). They are expected to exhibit novel chemical and physical properties. Low-energy UV absorption bands resulting from an *all-trans* arrangement of a hypercoordinate pentasilane (1)[9] and the stabilization of a tetrakis(dimethylamino)ethylene radical cation by a pentaccoordinate trisilanide anion (2)[10] as well as the formation of disilanes with two pentacoordinate Si atoms within the coordination sphere of bridging carboxylato ligands (3)[11] (Chart 1) represent impressive examples.

Scheme 1

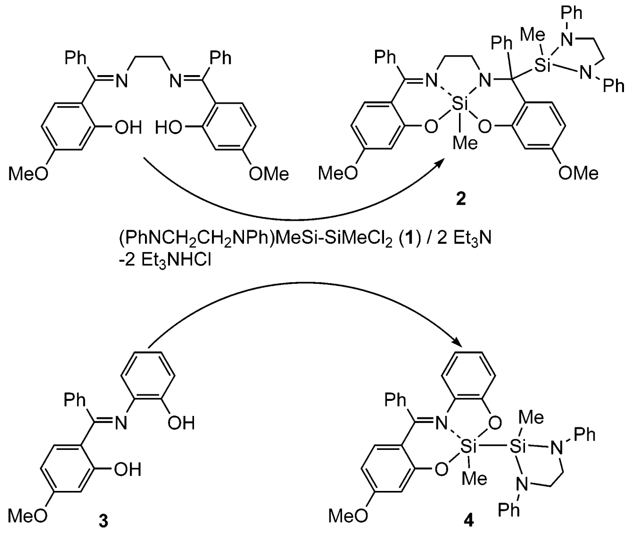
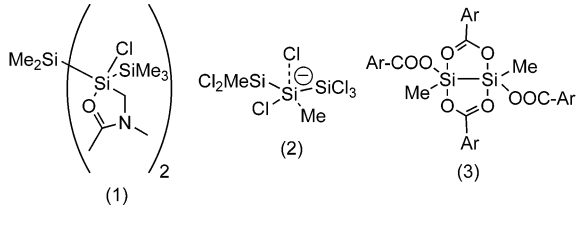


Chart 1



Now, we report the synthesis of a disilane bearing a tetra- and a pentacoordinate Si atom, the hypercoordination of which is realized by imine donor action and which does not undergo disproportionation or rearrangement reactions.

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[1] (a) Trommer, K.; Herzog, U.; Schulze, N.; Roewer, G. *Main Group Met. Chem.* **2001**, *24*, 425. (b) Herzog, U.; Schulze, N.; Trommer, K.; Roewer, G. *Main Group Met. Chem.* **1999**, *22*, 19.

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[10] Knopf, C.; Herzog, U.; Roewer, G.; Brendler, E.; Rheinwald, G.; Lang, H. *J. Organomet. Chem.* **2002**, *662*, 14.

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Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 4, 6, and 8

	4 (CCDC-602907)	**6** (CCDC-602906)	**8**·0.5dioxane (CCDC-621904)
empirical formula	$C_{36}H_{35}N_3O_3Si_2$	$C_{31}H_{33}N_3OSi_2$	$C_{23}H_{22}NO_4SiCl$
formula mass, g mol^{-1}	613.85	519.78	439.96
collection T, K	296 (room temp)	203(2)	296 (room temp)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	12.5431(3)	8.3473(3)	10.167(1)
b, Å	8.8949(2)	12.1119(5)	10.609(1)
c, Å	29.0676(7)	14.4510(6)	11.468(1)
α, deg	90	76.460(1)	116.999(2)
β, deg	99.748(1)	86.513(1)	92.598(3)
γ, deg	90	83.449(1)	97.476(3)
V, Å^3	3196.24(13)	1410.26(10)	1085.1(2)
Z	4	2	2
ρ_{calcd}, Mg/m^3	1.276	1.224	1.347
F(000)	1296	552	460
θ_{max}, deg	27.0	26.0	27.5
no. of collected rflns	42 007	18 744	15 067
no. of indep rflns	6968	5525	4896
R_{int}	0.0301	0.0265	0.0279
no. of rflns used	6968	5525	4896
no. of params	400	334	271
GOF	1.076	1.084	1.092
R1, wR2 ($I > 2\sigma(I)$)	0.0393, 0.1089	0.0345, 0.0909	0.0381, 0.1048
R1, wR2 (all data)	0.0564, 0.1171	0.0437, 0.0942	0.0555, 0.1105
max., min. res electron dens (e Å^{-3})	0.292, −0.202	0.315, −0.263	0.349, −0.303

Results and Discussion

As recently reported, the Si−Si bond of 1-methyl-1-(methyldichlorosilyl)-2,5-diphenyl-2,5-diazasilolidine ($(PhNCH_2CH_2NPh)SiMe-SiMeCl_2$) (**1**),[12] a disilane still bearing a $SiCl_2$ moiety enabling further manipulation, is easily cleaved when reacted with a tetradentate Salen-like ligand (Scheme 1, top).[4]

In order to determine whether only a hexacoordinate disilane would be subject to Si−Si bond cleavage or whether a pentacoordinate disilane would also exhibit such reactivity, **1** was treated with the tridentate *N*-(*o*-hydroxyphenyl)salicylidenimine-derived (Salop-type) ligand **3** under similar conditions as reported for the preparation of **2**. In this case, however, the Si−Si bond was retained and disilane **4** with a pentacoordinate Si atom was isolated as an intense red compound (Scheme 1, bottom). Its molecular structure was determined by X-ray structure analysis (Figure 1, Table 1).

The pentacoordinate silicon atom of **4** is housed within a trigonal bipyramidal environment (87.1% TBP[13]). Surprisingly, the oxygen donor atoms of the tridentate ligand are axially situated in this molecule [O1−Si1−O3 171.73(5)°]. Unlike our observations Tacke et al.[14] published pentacoordinate Si complexes involving a related tridentate ligand [derived from *N*-(*o*-hydroxyphenyl)acetylacetonimine], but with axially situated Si−N and equatorially located Si−O bonds. The Si−N bond [Si1−N1 1.888(1) Å] in **4** is much shorter than in most other examples of neutral pentacoordinate Si complexes with a N→Si dative bond. A neutral pentacoordinate silicon complex with a notable short dative N→Si bond [1.9496(9) Å] was reported by Kost et al.[15] The Si−Si distance in **4** [2.3532(6) Å] is in the range of common disilane bond lengths (compare to 2.358(1) Å in **1**[4]). Surprisingly, the Si−C bonds [Si1−C21 1.866(2) Å, Si2−C22 1.865(2) Å] have the same length despite the different coordination numbers of the silicon atoms.

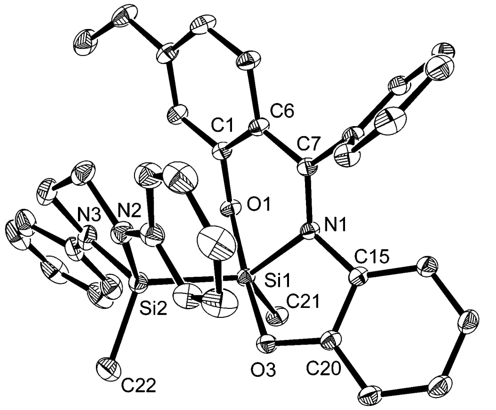

Figure 1. Molecular structure of **4** in the crystal (ORTEP plot with 20% probability ellipsoids, hydrogen atoms omitted for clarity).

The ^{29}Si NMR data collected in chloroform solution of **4** reveal the different coordination patterns of the two Si atoms with resonances at 1.5 and −71.2 ppm. The phenyl group of the tridentate ligand system is not freely rotating, but the phenyl groups of the diazasilolidine are. This conclusion was derived from the fact that 32 signals appear in the ^{13}C NMR spectrum of **4**. This parallels similar behavior found for analogous tetradentate Salen-like ligands.

In order to determine the special features of **4** that can be attributed to its hypercoordinate disilane-Si atom, another disilane was prepared from **1**. The reaction of **1** with an imine−enamine-tautomerizable bidentate ligand **5** yielded the colorless disilane **6**, which involves two differently substituted tetracoordinate Si atoms ($\delta^{29}Si = -4.7$ and −5.2 ppm in chloroform) (Scheme 2), as proven by its molecular structure (Figure 2, Table 1).

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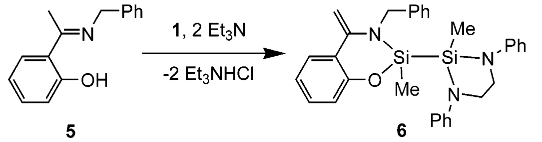
[12] Knopf, C.; Wagler, J.; Brendler, E.; Borrmann, H.; Roewer, G. *Z. Naturforsch.* **2004**, *59b*, 1337.

[13] The progress between TBP and SQP coordination geometry (% TBP) was determined using the equation % TBP = 100%(Angle 1 − Angle 2)/60°, in which Angle 1 is the widest angle X−Si−Y within the pentacoordinate geometry (i.e., the axial angle) and Angle 2 is the widest angle in the equatorial plane with respect to the axis defined with Angle 1. This general equation was derived from the special form % TBP = 100%(|Angle N−Si−N − Angle O−Si−O|)/60°, which has been used by Kost et al.: Kost, D.; Kingston, V.; Gostevskii, B.; Ellern, A.; Stalke, D.; Walfort, B.; Kalikhman, I. *Organometallics* **2002**, *21*, 2293.

[14] Seiler, O.; Burschka, C.; Metz, S.; Penka, M.; Tacke, R. *Chem.−Eur. J.* **2005**, *11*, 7379.

[15] Kost, D.; Gostevskii, B.; Kocher, N.; Stalke, D.; Kalikman, I. *Angew. Chem., Int. Ed.* **2003**, *42*, 1023.

Scheme 2



Surprisingly, the Si−Si bond in **6** [2.3723(5) Å] is slightly longer than in **4**. According to Gutmann's rules,[16] an increase in bond length with increasing coordination number should be expected. (The structural features of the enamine moiety are similar to those reported for other tetra- and even pentacoordinate silicon enamines.[17]) Regarding the Si−Si bond, the comparison between **4** and **6** points to the stability of this disilane moiety in **4**, which may be due to the equatorial situation of the Si−Si bond within a trigonal bipyramidal coordination sphere and the resulting short interatomic distance.[18]

The striking difference between **4** and **6** is the dark red color of **4**, but **6** is colorless instead. **4** represents a donor−acceptor-substituted disilane (electron-rich amide moieties, electron-deficient imine). Charge transfer in mononuclear hexacoordinate silicon complexes with a tetradentate Salen-like ligand as an imine-functionalized electron acceptor and also *N*,*N*′-diphenylethylenediamine as electron donor was recently proven by UV/vis spectroscopy and supported by quantum chemical calculations.[19] **4** bears this kind of substitution pattern. Unlike **4**, both chelates of **6** can be referred to as electron-rich features (amide as well as enamine). Analysis of the UV/vis spectrum of **4**, however, reveals that the conjugate π-electron system of the tridentate ligand can be assumed as the major reason for the color: **4** exhibits a discernible absorption band at 464 nm (ϵ = 6400 L·mol^{-1}·cm^{-1}) (Figure 3).

Complex **4** is very sensitive toward hydrolysis. Thus, the preparation and investigation of extremely diluted solutions of **4** had to be conducted very carefully. As demonstrated in solutions of **4** and **3**, respectively, the absorption band at about 464 nm is not caused by the potential hydrolysis product **3**. Tridentate Salop-type ligands such as **3** exhibit a strong absorption band in their UV/vis spectra at about 350 nm. Depending on the structural features of the complexes of these ligands, this band may be shifted to significantly lower energies. Pettinari et al. observed such intense red-shifts with Salop complexes of tin,[20] and Reyes et al. reported on related tin[21] and boron[22] complexes, the extinction properties of which were tuned by donor−acceptor-substitution patterns on the Salop backbone. In these Sn complexes the lowest-energy absorption band of the tridentate ligand system is shifted from about 350 nm to about 470 nm by (O$_{\text{axial}}$, N$_{\text{equatorial}}$, O$_{\text{axial}}$) coordination at the pentacoordinate Sn atoms. The extinction coefficient of the absorption band of **4** at 464 nm indicates a similar kind of red-shift of the lowest-energy absorption band of the tridentate ligand, which is located at about 350 nm for **3**. In monosilane complexes of **3** (**I**[23] and **II**,[23] Figure 3b) this absorption band is shifted only to wavelengths up to 385 and 386 nm, respectively. A comparison between the structural features of **4**, the silicon complexes **I**,[23] **II**,[23] and **8** (see further), and the tin complexes reported by Pettinari et al.[20] and Reyes et al.[21] reveals the special structural feature of **4** that can be regarded as the reason for this striking red-shifted absorption band. This crucial feature is embodied by the trigonal bipyramidal coordination sphere with the Salop ligand's O atoms in axial and the imine N atom in equatorial position. As a result thereof, the Si−N bond is only slightly longer than the Si−O bonds. **4** is the only one of the Si complexes exhibiting this feature, which is also found with the intensely colored pentacoordinate tin complexes with Sn−N bonds being only slightly longer than the axially situated Sn−O bonds.

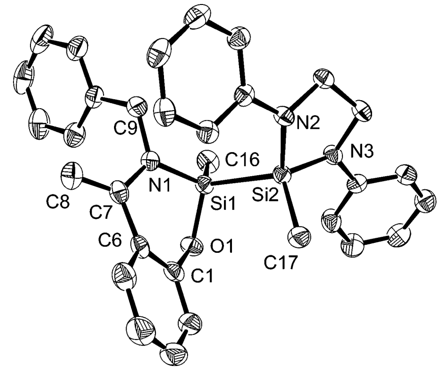


Figure 2. Molecular structure of **6** in the crystal (ORTEP plot with 50% probability ellipsoids, hydrogen atoms omitted for clarity).

Further attempts to synthesize disilanes with one or two pentacoordinate Si atom(s) bearing the tridentate ligand system **3** led to Si−Si bond cleavage (Scheme 3). The addition of a THF solution of 1 equiv of **3** to a cold solution of dimethyltetrachlorodisilane did not lead to **7a**, nor did the addition of dimethyltetrachlorodisilane to a cold solution of 2 equiv of **3** lead to **7b**. In both cases the disilane underwent disproportionation or oxidative Si−Si bond cleavage, which resulted in the formation of the pentacoordinate monosilane **8** in significant amounts, as proven by ^{29}Si NMR spectra of the crude reaction mixtures.[24]

Complex **8**, a yellow crystalline solid, was isolated as a THF solvate (**8**·0.5THF) from the reaction between **3** and tetrachlorodimethyldisilane in 1:1 molar ratio. Crystals of **8**·0.5dioxane, suitable for X-ray analysis, were grown from

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(16) Gutmann, V. *Coord. Chem. Rev.* **1975**, *15*, 207. Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225.

(17) (a) Wagler, J.; Böhme, U.; Roewer, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1732. (b) Wagler, J.; Schley, M.; Gerlach, D.; Böhme, U.; Brendler, E.; Roewer, G. *Z. Naturforsch.* **2005**, *60b*, 1054. (c) Wagler, J.; Böhme, U.; Brendler, E.; Thomas, B.; Goutal, S.; Mayr, H.; Kempf, B.; Remennikov, G. Ya.; Roewer, G. *Inorg. Chim. Acta* **2005**, *358*, 4270.

(18) Other di- and oligosilanes bearing pentacoordinate Si atoms with an equatorially situated Si−Si bond were reported by (respective Si−Si bond lengths in Å): (a) Kira, M.; Sato, K.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 3747 [2.403(3)]. (b) Reference 9 [2.3480(9) and 2.3353(8)]. (c) El-Sayed, I.; Hatanaka, Y.; Muguruma, C.; Shimada, S.; Tanaka, M.; Koga, N.; Mikami, M. *J. Am. Chem. Soc.* **1999**, *121*, 5095 [2.329(1), 2.3395(6), 2.3362(5), 2.3447(7)]. (d) Toshimitsu, A.; Saeki, T.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 9210 [2.348(1)]. (e) Toshimitsu, A; Hirao, S.; Saeki, T.; Asahara, M.; Tamao, K. *Heteroat. Chem.* **2001**, *12*, 392 [2.333(1), 2.368(1), 2.3563(6), 2.3711(9)]. Those with bulky substituents (e.g., triphenylsilyl group, ref a] exhibit notably longer equatorial Si−Si bonds. Most of the Si−Si interatomic distances, however, are close to 2.35 Å, the Si−Si bond length found in **4**.

(19) Wagler, J.; Gerlach, D.; Böhme, U.; Roewer, G. *Organometallics* **2006**, *25*, 2929.

(20) Pettinari, C.; Marchetti, F.; Pettinari, R.; Martini, D.; Drozdov, A.; Troyanov, S. *Inorg. Chim. Acta* **2001**, *325*, 103.

(21) Reyes, H.; García, C.; Farfán, N.; Santillan, R.; Lacroix, P. G.; Lepetit, C.; Nakatani, K. *J. Organomet. Chem.* **2004**, *689*, 2303.

(22) Reyes, H.; Munoz, B. M.; Farfán, N.; Santillan, R.; Rojas-Lima, S.; Lacroix, P. G.; Nakatani, K. *J. Mater. Chem.* **2002**, *12*, 2898.

(23) Wagler, J.; Brendler, E. *Z. Naturforsch.*, manuscript in preparation.

(24) (a) Additionally to the isolation of crystalline **8**·0.5THF from the reaction mixture (see Experimental Section) a ^{29}Si INEPT NMR spectrum of the filtrate was recorded. It exhibits various signals between 36 and −94 ppm. (b) In a modified reaction, addition of 1 equiv of tetrachlorodimethyldisilane to a solution of Et$_3$N + 2 equiv of ligand **3**, however, produced a mixture that exhibits various ^{29}Si NMR signals between −84 and −94 ppm. Several smaller further signals can be found between 0 and −63 ppm. Compound **8** (−81.5 ppm) represents only a minor component of this mixture.

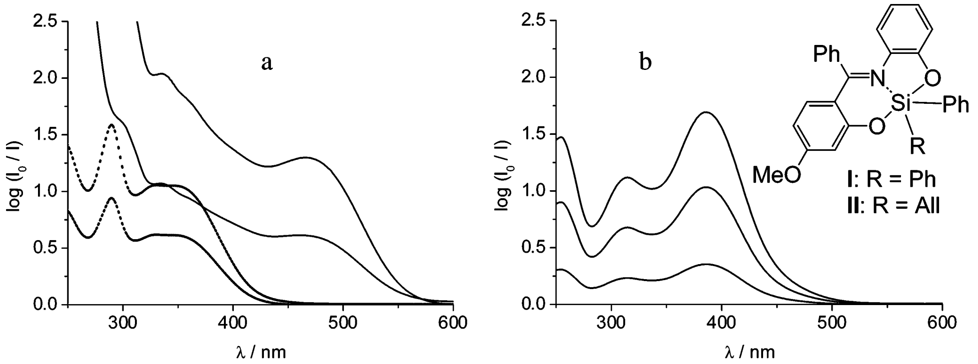
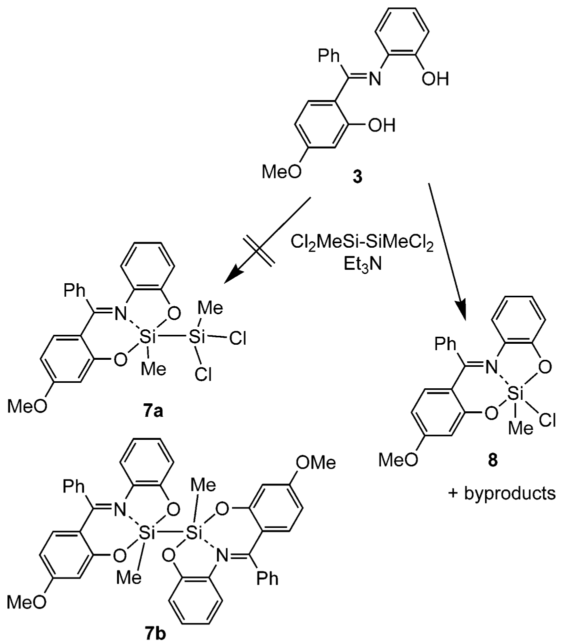


Figure 3. (a) UV/vis spectra of **3** (dotted lines, 0.6 and 1.0 mmol·L^{-1}) and **4** (straight lines, 1.0 and 2.0 mmol·L^{-1}); b) UV/vis spectra of **I** (0.2, 0.6, and 1.0 mmol·L^{-1}), the UV/vis spectrum of **II** is almost identical (all spectra obtained from chloroform solutions in quartz cuvettes, $d = 1$ mm).

Scheme 3



dioxane (Figure 4, Table 1). In contrast to **4**, the tridentate ligand system is arranged in a TBP coordination sphere (70% TBP[13]) with the imine N atom in the axial position and the oxygen donor atoms in equatorial ones. Therefore, many differences in bond lengths and angles around the pentacoordinate Si atoms in **4** and **8** are found and listed in Table 2. The transformation from one kind of trigonal bipyramid in the case of **4** into the other one in the case of **8** is clearly demonstrated by the values of the bond angles given in Table 2. Due to the axial positions of the O donor atoms in **4**, the Si−O bonds are significantly longer than those in **8**. Vice versa, the equatorial location of the imine N atom in **4** goes hand in hand with a striking shortening of the Si−N distance. The Si1−C21 bond, which is equatorially situated in both cases, is hardly influenced by the different arrangements of these TBP coordination spheres, thus being similar within the range of the standard deviation. The closer Si−N contact in **4**, however, causes a slightly longer imine C═N bond in this complex.

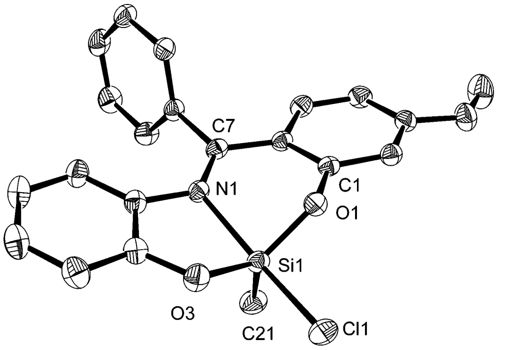


Figure 4. Molecular structure of **8** in the crystal of **8**·0.5dioxane (ORTEP plot with 30% probability ellipsoids, hydrogen atoms and dioxane molecule omitted for clarity).

Table 2. Selected Bond Lengths [Å] and Angles [deg] in 4 and 8·0.5Dioxane

	4	**8**·0.5dioxane
Si1−N1	1.888(1)	2.039(1)
Si1−O1	1.787(1)	1.675(1)
Si1−O3	1.809(1)	1.677(1)
Si1−C21	1.866(2)	1.851(2)
Si1−Si2 (**4**), Si1−Cl1 (**8**)	2.3532(6)	2.1705(6)
C7═N1	1.323(2)	1.302(2)
O1−Si1−O2	171.73(5)	126.41(6)
N1−Si1−Si2 (**4**), N1−Si1−Cl1 (**8**)	119.47(4)	168.51(5)
N1−Si1−C21	112.91(7)	91.95(7)

Conclusion

The special Si coordination sphere of compound **4** [TBP arrangement of the (ONO) tridentate ligand with axially situated Si−O bonds and equatorially located Si−N bond] gives rise to an intense intraligand absorption band at 463 nm in its UV/vis spectrum. Although one of the Si atoms in **4** is hypercoordinate, the Si−Si bond is not notably weakened. The C═N bond is stretched in contrast to the situation that has been found in many other hypercoordinate Si complexes bearing 2-iminomethylphenolate ligands.[25] The strong chelating effect of ligand **3** as well as the bidentate *N,N′*-diphenylethylenediamine system contribute to the formation and stability of **4**. There is no monodentate electronegative substituent remaining at the hypercoordinate Si atom that could be transferred to the next Si atom to give rise to the formation of either a donor-stabilized silylene via the conventional disilane disproportionation reaction or monosilane complexes such as **8**. Thus, **4** can also be considered an isolable model compound for hypercoordinate disilane species in disilane disproportionation reactions.

Pentacoordinate silicon atoms are expected to play essential roles in electron-transfer processes, and earlier attempts have been made to explore these properties for applications such as

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(25) (a) Wagler, J.; Böhme, U.; Brendler, E.; Blaurock, S.; Roewer, G. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2907. (b) Wagler, J.; Roewer, G. *Z. Naturforsch.* **2005**, *60b*, 709.

luminescent devices and sensors.[26] Even novel bonding situations in (colorless!) hypercoordinate silicon complexes have been referred to as CT effects.[27] In the case of **4** the coordination sphere around the hypercoordinate silicon atom plays an essential role in the red-shift of an intraligand absorption band. Referring to first investigations on Salop−Sn complexes,[20,21] a “push−pull” tuning of oligo- and disilane complexes such as **4** opens access to a new class of oligosilane compounds that are worth being considered as candidates for tunable nonlinear optical properties.

Experimental Section

All the following manipulations were carried out under an inert atmosphere of dry argon. THF, dioxane, and hexane were distilled from sodium/benzophenone, and triethylamine was distilled from calcium hydride and stored over 3 Å molecular sieves. Chloroform (stabilized with amylene) was dried over 3 Å molecular sieves. NMR spectra were recorded on a Bruker DPX 400 ($CDCl_3$ solution with TMS as internal standard) and a Bruker Avance 400 WB (CP/MAS spectra). Elemental analyses were carried out on a Foss Heraeus CHN-O-Rapid. UV/vis spectra were recorded on a Specord S100 UV/vis spectrometer using quartz cuvettes.

X-ray structural data were recorded on a Bruker-Nonius-X8-APEX2-CCD diffractometer with Mo Kα radiation. The structures were solved with direct methods (SHELXS-97) and refined with full-matrix least-squares methods (refinement of F^2 against all reflections with SHELXL-97). All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in idealized positions (riding model) and refined isotropically.

By analogy with previously published methods,[28,29] ligands **3** and **5** were prepared in condensation reactions using 2-hydroxy-4-methoxybenzophenone, *o*-aminophenol, triethyl orthoformate, and piperidine in dry ethanol (**3**) as well as 2-hydroxyacetophenone and benzylamine in ethanol (**5**). Synthesis of silane **1** was previously published.[12]

4: A solution of ligand **3** (1.40 g, 4.38 mmol) and triethylamine (1.0 g, 10 mmol) in THF (50 mL) was stirred at −10 °C, and a solution of silane **1** (1.65 g, 4.50 mmol) in THF (20 mL) was added dropwise within 10 min. The resulting dark red mixture was stirred at −10 °C for an additional 5 min, when the triethylamine−hydrochloride was filtered and washed with THF (5 mL). The volume of the filtrate was reduced to 10 mL under reduced pressure, and the red solution was stored at 8 °C for 3 days. The red crystalline product was filtered, washed with THF (2 mL), and dried under vacuum (yield: 1.20 g). A further fraction of **4** was obtained upon addition of hexane (10 mL) to the filtrate. Yield (total): 1.46 g (2.38 mmol, 54%). Mp (sealed capillary, not corrected): 184 °C. Anal. Calcd for $C_{36}H_{35}N_3O_3Si_2$: C, 70.44; H, 5.75; N, 6.85. Found: C, 70.30; H, 5.83; N, 6.79. ^{1}H NMR ($CDCl_3$): δ 0.45, 0.74 (2s, 6H, Si−CH_3), 2.9−3.4 (3 m, 4H, N−CH_2CH_2−N), 3.77 (s, 3H, O−CH_3), 5.63 (d, 1H, ar, $^3J_{HH}$ = 8.0 Hz), 6.06 (d, 1H, ar, $^4J_{HH}$ = 2.8 Hz), 6.13 (dt, 1H, ar, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz), 6.24 (dd, 1H, ar, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.4 Hz), 6.6−7.5 (mm, 18H, ar). ^{13}C NMR ($CDCl_3$): δ 1.4, 4.7 (Si−CH_3), 45.0, 45.2 (N−CH_2CH_2−N), 55.7 (O−CH_3), 103.2, 109.3, 113.1, 114.3, 114.8, 115.0, 115.4, 116.8, 116.9, 117.9, 121.1, 128.6, 128.8, 128.9, 129.0 (2x), 129.4, 130.2, 130.6, 134.0, 134.1 (ar), 148.2, 148.3 (phenyl C−N), 157.0, 167.0, 167.1, 170.6 (ar C−O, C═N). ^{29}Si NMR: δ 1.5, −71.2 ($CDCl_3$); −2.5, −69.5 (CP/MAS).

6: A solution of silane **1** (3.59 g, 9.78 mmol) and triethylamine (2.50 g, 24.7 mmol) in THF (40 mL) was stirred at ambient temperature, and a solution of the ligand **5** (2.20 g, 9.78 mmol) in THF (20 mL) was added dropwise over a period of 5 min. The triethylamine hydrochloride was removed by filtration and washed with THF (15 mL). Removal of all volatiles from the filtrate and recrystallization of the oily product from toluene afforded colorless crystals of **6**, which were filtered, washed with toluene (4 mL) and hexane (8 mL), and dried under vacuum. Yield: 3.29 g (6.33 mmol, 65%). Mp (sealed capillary, not corrected): 151 °C. Anal. Calcd for $C_{31}H_{33}N_3OSi_2$: C, 71.63; H, 6.40; N, 8.08. Found: C, 71.25; H, 6.47; N, 7.73. ^{1}H NMR ($CDCl_3$): δ 0.25, 0.37 (Si−CH_3), 3.3−3.5 (mm, 4H, N−CH_2CH_2−N), 3.71, 3.89 (2d, N−CH_2−Ph, $^2J_{HH}$ 17.2 Hz), 3.71, 4.55 (2 s, C═CH_2), 6.7−7.3 (mm, 18H, ar), 7.60 (d, 1H, ar, $^3J_{HH}$ = 8.0 Hz). ^{13}C NMR ($CDCl_3$): δ −0.4, 1.4, (Si−CH_3), 45.2, 45.4 (N−CH_2CH_2−N), 47.5 (N−CH_2−Ph), 86.4 (C═*C*H_2), 114.9, 115.0, 118.3 (2×), 120.6, 121.9, 124.9, 126.2, 126.4, 126.9, 128.2, 129.4 (2×), 129.5, 138.3 (ar), 145.0 (*C*═CH_2), 147.2, 147.4 (phenyl C−N), 151.4 (ar C−O). ^{29}Si NMR: δ −4.7, −5.2 ($CDCl_3$).

8: A solution of 1,1,2,2-tetrachlorodimethyldisilane (1.20 g, 5.26 mmol) and triethylamine (2.00 g, 19.8 mmol) in THF (50 mL) was stirred at −15 °C, and a solution of ligand **3** (1.50 g, 4.68 mmol) in THF (20 mL) was added dropwise within 10 min. The resulting mixture was stored at 8 °C overnight, then the triethylamine hydrochloride was filtered and washed with THF (10 mL). The solvent was removed from the filtrate under vacuum, and the residue was dissolved in THF (2 mL). Addition of hexane (4 mL) and storage at 8 °C for 2 weeks afforded **8**·0.5THF as a yellow crystalline powder, which was filtered, washed with a mixture of 0.5 mL of THF and 1.5 mL of hexane, and briefly dried under reduced pressure. Yield: 0.52 g (1.20 mmol, 26% relative to **3** used). The THF content was determined by ^{1}H NMR spectroscopy. Crystals of **8**·0.5dioxane were obtained by recrystallization from dioxane. Anal. Calcd for **8**·0.5dioxane $C_{23}H_{22}NO_4SiCl$: C, 62.79; H, 5.04; N, 3.18. Found: C, 62.90; H, 5.19; N, 3.28. ^{1}H NMR ($CDCl_3$): δ 0.57 (s, 3H, Si−CH_3), 3.89 (s, 3H, O−CH_3), 5.82 (d, 1H, ar, $^3J_{HH}$ = 8.0 Hz), 6.4−6.6 (m, 2H, ar), 6.80 (d, 1H, ar, $^4J_{HH}$ = 2.4 Hz), 6.90 (d, 1H, ar, $^3J_{HH}$ = 8.8 Hz), 7.1−7.7 (mm, 7H, ar). ^{13}C NMR ($CDCl_3$): δ 4.6 (Si−CH_3), 56.0 (O−CH_3), 105.2, 111.1, 115.4, 116.8, 119.7, 120.8, 127.1, 129.9 (2×), 130.8, 131.2, 133.5, 134.6 (ar), 152.4, 158.3, 166.0, 166.5 (ar C−O, C═N). ^{29}Si NMR ($CDCl_3$): δ −81.6.

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Supporting Information Available: Crystallographic data of **4**, **6**, and **8**·0.5dioxane. This material is available free of charge via the Internet at http://pubs.acs.org.

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