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Synthesis of electron-rich, planarized silicon(IV) species and the theoretical analysis of dimerizing aminosilanes

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Abstract: Equipping silicon(IV) with electron-rich, geometrically constrained NNN- and ONO-tridentate substituents leads to aminosilanes with increased Lewis acidity – expressed through the formation of Si_2N_2 rings by head-to-tail dimerization. Depending on the substituents, the dimerization can be controlled for the first time, yielding monomeric, structurally reversible and dimeric states. The monomeric species display substantial distortions from tetrahedral towards planar geometry at silicon. The dimerization and the Lewis acidity of aminosilanes are rationalized by (conceptual) DFT, NBO, ETS-NOCV and QTAIM methods. The preorganization at silicon, London dispersion between the substituents and resonance phenomena inside the formed Si_2N_2 tetracycles are identified as driving forces for the dimerization. Comparison with selected aminosilanes permits general conclusions on the Lewis acidity of silicon species and on the aggregation of amphiphilic compounds.

Introduction

Molecular main-group element compounds with unusual geometries are of longstanding interest, owing to their particular (physico)chemical features, which are enabled by the deformation of the central element.^[1] Such species have mainly been studied for group 13-16 elements and revealed peculiar structures and unexpected reactivity. The increase of Lewis acidity in group 13 species by pyramidalization has been proposed theoretically^[2] and confirmed by experiment.^[3] Seminal studies by Arduengo et al. demonstrated the electronic and geometrical effects of electron-rich and geometrically constrained substituents on group elements (e.g. in unusual T-shaped phosphorous 15 compounds).^[4] An essential feature of the electron-rich ligands is the transfer of electron density to the central atom, leading to a formally reduced state with specific reactivity.^[4c, 5] The capability of such compounds for main-group element mediated reversible bond activations lead to a recent burst of research activities and catalytic applications.^[6] For group 14 elements, the corresponding chemistry is less developed. Intramolecular electron transfer was observed in the tin compound 1 (figure 1a) derived from SnCl₄

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and HN[CH₂(O)^tBu]₂, with significant charge reorganization from the initial Sn(IV) to a formal stannylene Sn(II) species.^[7] An analog intramolecular electron transfer was described by Driess et al. for germanium(IV), even though the presence of a Ge(II) intermediate could be supported only by secondary reaction products.^[8] Very surprisingly, the realization of corresponding monomeric silicon-based compounds is still pending. One exclusive attempt was reported.^[9] No intramolecular charge transfer was found, but a surprising dimerization of the primary reaction products was observed (2, figure 1b). The proposed parent monomeric species have neither been detected nor could the dimerization process be prevented by installation of a bulky group at silicon. Instead, this modification led to a radical type dimerization in the ligand backbone, indicating particular reactivity of the eventual monomeric units. It should be stressed, that the ability for hypercoordination at silicon^[10] in a monomeric state, combined with the electron releasing nature of redox-active substituents,[11]



Figure 1. a/b) Previously studied electron-rich, geometrically constrained group 14 compounds based on the $HN[CH_2(O)'Bu]_2$ ligand show an intramolecular electron transfer for tin (a) or irreversible dimerization for silicon (b), c) amphiphilic silicon-Lewis base compounds which tend to dimerize in the solid state and d) the herein described electron-rich, geometrically constrained Si(IV)-NNN and -ONO compounds.

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is promising for new bond activation processes mediated by silicon - the most abundant element in the earth crust. Understanding and prevention of the dimerization leading to compounds like 2 would thus mean a major step towards the exploration of new modes of ligand-element cooperativity with silicon(IV) compounds. In comparison to other silicon donor/acceptor complexes, the dimerization of 2 in solution is astonishing, since aminosilanes are not considered as effective Lewis acids towards neutral donors. However, the driving forces for the dimerization of compounds 2, as well as for other aminosilanes like 3 and 4 (figure 1c) have not been considered in detail.^{[12],[13]} The present work will serve several objectives in a combined synthetic and computational approach (figure 1d): I) The synthesis of a variety of silicon(IV) compounds with geometrically constrained triamido (NNN3-, 5/6) and amidodiphenolato (ONO3-, 7) substituents is achieved and permits the unprecedented control over the dimerization process leading to either monomeric. structurally reversible or dimeric species. Acute distortions from tetrahedral towards planar geometries in the monomeric compounds disclose the amplification of silicon Lewis acidity by preorganization. II) The solvation-corrected Gibbs free energies of the dimerization process are calculated by state-of-the art computational theory. Strong dispersive forces which act as driving force in the dimerization process are found. A detailed analysis employing conceptual DFT, NBO, ETS-NOCV and QTAIM rationalizes the effect of planarization and inspects the nature of Si-N bonding in this new class of compounds. Unique stabilizing factors in the dimers are identified and compared with aminosilanes 3 and 4, allowing for more general conclusions on Lewis acidity at silicon and the aggregation of amphiphilic species.

Results and Discussion

Synthesis

The synthesis of triamido-silicon (MeNNN-SiR', **5a-d**, PrNNN-SiR', 6a-b, scheme 1) or amido-diphenolato-silicon (ONO-SiR', 7a-b) compounds based on bis(2-methylaminophenyl)amine (H₃^{Me}NNN, 8),^[6c] bis(2-isopropylaminophenyl)amine (H₃^{,Pr}NNN, 9)^[6c] and N,N-bis(3,5-di-tert-butyl-2-phenoxy)amine (H₃ONO, **10**)^[14] are described first. Spectroscopic and structural discussion of the products will be given subsequently in a comparative perspective. Hydro- and chlorosilanes 5a,b/6a,b (scheme 1) were obtained by reaction of the corresponding arylamines 8/9 and HSiCl₃ or SiCl₄ in the presence of stoichiometric amounts of NEt₃ in toluene or CH₃CN, showing full conversion at NMR scale after one hour at rt. Preparative scale reactions yielded the desired products after removal of the salts by extraction with toluene or Et₂O and recrystallization from toluene or Et_2O . Derivatives with R' = Ph, *n*Hexyl (**5c,d**) were readily accessible by a convenient $B(C_6F_5)_3$ catalyzed (2 mol%) dehydrogenative coupling of a 1:1 mixture of 8 and R'SiH₃ in toluene (scheme 1).^[15] Reaction profiling indicated the internal Si-N bond coupling as the final step toward the products and full conversion without any byproduct except dihydrogen (see figure SI1). The catalytic amount of B(C₆F₅)₃ was removed by crystallization/precipitation of 5c/5d from cold Et₂O or

CH₃CN respectively and the desired products were easily obtained on gram scale with up to 91 % yield. Initial attempts to apply the NEt₃ based method (suitable for the preparation of compounds 2) starting with the neutral H₃ONO ligand 10 failed. Instead, the very efficient formation of a neutral, hexacoordinate silicon(IV) complex Si[ONOH]₂ (11) was observed for HSiCl₃ and PhSiCl₃ as electrophiles, with the concomitant liberation of H₂ or C₆H₆, respectively (scheme 1, see SI for the structural analysis of 11, reminiscent of similar neutral SiO₄N₂ complexes).^[16] Such mild conditions for the cleavage of Si-C bonds are remarkable and have already been observed during the reaction of diols with carbon substituted siloxanes.^[17] Obviously, the relatively weak base NEt₃ leads to insufficient deprotonation of 10 (or of silicon bound intermediates) and conditions acidic enough for a fast and irreversible intramolecular protonolysis of the substituent (H or Ph) at silicon. In contrast, such acidic protons in the adjacencies of silicon are not present with the diketo-amine ligand (HN[CH₂(O)^tBu]₂) in the synthesis of **2**, where deprotonation occurs at the enolic positions. Indeed, upon application of the much stronger base benzyl potassium in toluene and the subsequent addition of PhSiCl₃ or TipSiCl₃ (Tip = 2,4,6triisopropyl) respectively, the desired compounds 7a-b were obtained in overall good yields (scheme 1). The obtained colorless compounds vary from highly to slightly air sensitive with fast and intense coloration upon exposure to air, indicating redoxreactions due to the strong electron donating ability of the redoxactive substituents. The moisture sensitivity of NNN compounds 5/6 (readily reacting with traces of H₂O) is much more pronounced compared to the ONO species 7. Comprehensive aspects of the highly promising (redox)-reactivity of 5-7 will be given in future contributions from our laboratory.



Scheme 1. Synthesis of NNN-SiR' compounds (5/6) by nucleophilic reaction or dehydrogenative coupling, the undesired reaction to the octahedral silicon complex 11 and synthesis of ONO-SiR' (7) compounds after deprotonation with BnK.

Spectroscopy

The structures in solution were studied by multi-nuclear / -dimensional solution NMR spectroscopy. ²⁹Si/¹H NMR HSQC/HMBC spectroscopy serves as a useful tool for the determination of the Si-coordination, as the chemical shift strongly depends on the coordination state.^[18] The experimentally determined ²⁹Si-NMR chemical shifts of compounds 5-7 are presented in comparison with the DFT calculated values of the monomeric and dimeric species in table 1 (spin-orbit relativistic solvent corrected DFT, ZORA-SO-PBE0(COSMO, and CH₂Cl₂)/TZ2P, for further details, see SI).^[19] For the ^{Me}NNN ²⁹Si-NMR compounds 5a,b, the shifts derived (-61.0 ppm, -80.4 ppm, typical for λ^5 -coordinate silicon) indicated dimerization in solution. A head-to-tail type arrangement of 5a,b in solution was supported by ¹H NOESY spectroscopy, showing cross-peaks between the NMe-groups and aromatic protons H6 (ortho to central N) as well as between Si-H and H6 (see figures SI2/3). Such a spatial proximity is impossible in a monomeric state and confirms a symmetric aggregation structure as proposed in scheme 1. In marked contrast, compounds 5c,d exist as monomers in solution, indicated by the less negative ²⁹Si NMR shifts of -3.4 ppm and 9.8 ppm, respectively. Mild liquid injection field desorption ionization spectrometry (LIFDI) was performed to gain insight into the gas phase aggregation state.^[20] The dimeric nature of 5a persists in the gas phase, indicated by a dimer molecular mass peak (m/z = 506.2). Interestingly though, a peak at m/z = 253.1 also revealed the presence of the monomeric species, hence indicating a certain reversibility of the aggregation process for 5a. Species 5b-d were found monomeric also in the gas phase. With the PrNNN derived compound 6a, reversible dimerization was observed by ¹H and ²⁹Si-HMBC/HSQC VT-NMR spectroscopy. The ²⁹Si-HSQC NMR spectra at rt suggested the presence of monomeric species (-14.9 ppm). However, upon gradually cooling the solution to -40°C, the formation of a new species was detected, with increasing proportion at lower temperatures (up to 1:1 at -90 °C, see figures SI4-7). The ²⁹Si-HSQC NMR spectra at low temperature revealed a chemical shift of -59.0 ppm for the new species, in good agreement to the calculated shift of the dimeric form. The process was entirely reversible, giving back the pristine monomeric compound at room temperature.^[21] Although there exist a variety of neutral intramolecular and/or ionic intermolecular temperature dependent coordination-equilibria in silicon compounds,^[22] there is only one example of a neutral intermolecular coordination equilibrium.[23] By consequence, this is the first demonstration of a reversible dimerization of an amphiphilic silicon compound in solution. Chlorosilane 6b prevailed monomeric in solution (-14.8 ppm), thus standing in contrast to the related MeNNN chlorosilane derivative **5b**, which was observed only as a dimer at rt. Similarly, ONO based compounds 7 were evaluated in solution. In this case, the phenylsilane 7a was observed as dimer, based on negative peak in the ²⁹Si-HMBC NMR spectra (-66.5 ppm), but which is monomeric in the case of the ^{Me}NNN-substituent (5c).

Table 1. Measured and calculated ²⁹ Si-NMR chemical shifts for 5-7.				
δ(²⁹ Si) exp. ^[a] δ(²⁹ Si) calc. ^[b]		δ(²⁹ Si) calc. ^[b]		
(CD ₂ Cl ₂)	monomer	dimer		
-61	-7.8	-61.1		
-80.4	-15	-80		
-3.4	-6	-37.5		
9.8	7.6	-62.4		
-14.9 (25°C)/	-10.5	-57.6		
-59.0 (-90°C)				
-14.8	-17	-80.9		
-66.5	-7.8	-69.7		
0	-4.1	N. N.		
	sured and calculated δ(²⁹ Si) exp. ^[a] (CD ₂ Cl ₂) -61 -80.4 -3.4 9.8 -14.9 (25°C)/ -59.0 (-90°C) -14.8 -66.5 0	sured and calculated ²⁹ Si-NMR chemical s δ(²⁹ Si) exp. ^[a] δ(²⁹ Si) calc. ^[b] (CD ₂ Cl ₂) monomer -61 -7.8 -80.4 -15 -3.4 -6 9.8 7.6 -14.9 (25°C)/ -10.5 -59.0 (-90°C) -14.8 0 -4.1		

^[a]experimental (CD₂Cl₂ at RT) ^[b] DFT calculation (ZORA-SO-PBE0(COSMO, CH₂Cl₂)/TZ2P) relative to δ ⁽²⁹Si) calc. TMS = 0 ppm

This observation is surprising, as one would expect the fourfold *t*Bu-substituted ONO-substituent to be more hindered towards dimerization by Pauli repulsion. Also, the aggregation of the ONO class of compounds was successfully controlled by installation of the bulky 2,4,6-triisopropylphenyl-group (Tip) at silicon (**7b**), with the ²⁹Si-chemical shift of 0.0 ppm now lying well in the range of tetracoordinate silicon.

By consequence, the aggregation state of electron-rich aminosilanes in solution can be either controlled by the choice of substituents directly bound to silicon, or by modification of the NNN groups. This flexibility allows for the generation of 'selfprotecting' (reversible dimerizing) systems and the future investigation of the influence of aggregation on the reactivity towards various substrates and the redox chemistry.

Solid-state structures

Solid-state structures were obtained by X-ray diffraction for compounds **5a-c**, **6a-b**, **7a-b** (figure 2, for **5a** and **6b** see SI). Selected bond lengths and angles can be found in table 2. In all cases, the metric oxidation state of the aryl rings of the substituents confirmed the fully reduced, trianionic nature of the triamido or amido-diphenolato groups – in line with its colorless appearance. The observed aggregation states (monomeric/dimeric) were in full agreement with the structural interpretations based on spectroscopy, as will be discussed in the following, grouped by monomeric (**5c**, **7b**) and dimeric structures (**5a**, **5b**, **6a**, **7a**).

The molecular structure of phenyl-substituted triamido silane **5**c is shown in figure 2a, revealing a tetravalent silicon. The Si-C1 bond (1.850 Å) and the central Si-N1 bond (1.745 Å) show no exceptional lengths, whereas the two outer silicon nitrogen bonds (Si-N2/N3) are shortened (1.722 Å).^[24] The most remarkable features of the structure are the N1-Si-C1 and the N2-Si-N3 angles: they are significantly enlarged from the ideal tetrahedral angle to 126.2°/129.8°, respectively. A structural survey in the CCSD revealed those angles as record values for tetravalent silicon(IV).^[25] ^[26] No close contacts to neighboring molecules or solvent molecules were observed in the packing structure,





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Figure 2. Molecular structures of compounds a) 5c, b) 5b, c) 6a, d) 7b, e) 7a; probability level of displacement ellipsoids 50%, bond length and bond angles can be found in table 2. For 5a and all further details of X-ray structure determination, see SI.

Table 2. X-ray structural determined selected bond length (in Å) and bond angles (in °) for 5a-c, 6a and 7a-b

NNN	5a (R' = H)	5b (R' = CI)	5c (R' = Ph)	6a (R' = H)	ONO	7a (R' = Ph)	7b (R' = Tip)
Si-N1	2.0385 (15)	2.0399(15)	1.7458(14)	1.996(3)	Si-N1	2.6061(33)	1.749(2)
Si-N2	1.7403 (16)	1.7263(15)	1.7222(14)	1.749(2)	Si-02	1.6355(16)	1.6612(17)
Si-N3	1.7423 (17)	1.7350(15)	1.7268(15)	1.748(2)	Si-O3	1.6365(17)	1.6635(17)
Si-R	1.446 (19)	2.1542(8)	1.8495(17)	1.437(24)	Si-R	1.873(3)	1.854(2)
Si-N1'	1.8782 (15)	1.8526(15)		1.893(2)	Si-N1'	1.7459(18)	
N1-Si-R	178.31(80)	175.22(4)	126.17(7)	173.70(90)	N1-Si-R	171.05(5)	128.35(10)
N2-Si-N3	132.94 (8)	124.77(7)	129.67(12)	129.03(11)	01-Si-O2	122.09(9)	121.07(8)
N1-Si-N1'	82.32(7)	79.80(7)		81.05(11)	N1-Si-N1'	78.47(8)	

excluding solid state effects as the reason for the obtuse bond angles. Rather, the distortion is caused by strong π -donation and the constrained geometry of the substituent, as will be considered more in detail in the theoretical section. The ONO-derived 7b (figure 2d) also crystallizes as a monomer and shows similarity to 5c: Si-N1, Si-O2/O3 and Si-C1 bond lengths are unexceptional, whereas again the N1-Si-C1 angle at the tetravalent silicon atom is distorted to 128.4°. The O2-Si-O3 angle is not as much enlarged as the N2-Si-N3 in 5c (121.1° vs. 129.8°), in agreement with a lesser ability of the oxygen atoms to act as π -donors, hence underpinning an electronic origin of the distortion from tetrahedral geometry towards planarity. X-ray structural analysis of compounds 5a, 5b, 6a, 7a revealed dimeric structures with pentacoordinate silicon atoms. Two formally monomeric units are dimerized in head-to-tail fashion and are horizontally displaced towards each other, forming rhomboid Si₂N₂-rings as the central motif (N1-Si-N1' angle: 78.4-82.3°). The coordination geometry around silicon in all dimeric compounds can be described as trigonal-bipyramidal with the N1 and R substituents occupying the axial positions, slightly distorted towards tetragonal-pyramidal geometry with the N1' substituent at the apical position on a N1/N2(O2)/N3(O3)/R plane. Compounds 5a (see SI), 6a (figure 2c) and 7a (figure 2d) have C_i molecular point symmetry, with the inversion center lying in the center of the planar Si₂N₂-ring, whereas **5b** (figure 2b) posseses C_2 symmetry with the rotation axis in the middle of the slightly folded (22.1°) tetracycle. The Si-N2/N3 and Si-O2/O3 bond lengths match that of hypercoordinated silicon compounds like for example the structurally related (aza)silatranes, as do the Si-R bond lengths.^[27] In comparison to the monomeric species 5c and 7b,

the bond distances towards silicon increase slightly, as is usually observed when going from tetra- to pentacoordination. The most notable changes between the monomeric and dimeric species occurred in the "intramolecular" (axial) Si-N1 bonds (1.99-2.61 Å) which are increased considerably and are in all cases longer than the newly formed "intermolecular" (equatorial) Si-N1' bond (1.75-1.89 Å). In general, the Si-N bond lengths within the Si_2N_2 rings are shorter (for Si-N1') or longer (for Si-N1) than the sum of Si and N covalent radii (1.82 Å), [28] but for both cases within the range of experimentally measured values of intramolecular Si-N donor/acceptor complexes.^[10a] Regarding bond lengths, the dimerization can be considered as double donor/acceptor N1'→Si interaction between hypothetical monomeric units. The equatorial Si-N1' bonds that have been formed during dimerization go at the expense of the previous Si-N1 bond in the monomers. A detailed description of the dimerization, the origin of the geometrical distortion and the bonding situation in those compounds will be given in the next section.

Quantum theoretical analysis of the dimerization process of amphiphilic silicon compounds

From a very limited Lewis acidity and basicity perspective, the dimerization in compounds like **2** and **5-7** is unexpected. Even though several silicon donor-acceptor complexes with strong donors (e.g. NHCs) are known, common tetravalent silicon(IV) compounds are not considered as potent Lewis acids and are rather disfavored for the formation of stable bimolecular (*intermolecular*) adducts with weak neutral donors *in solution*.^[10] Especially aminosilanes should feature as both weak donors and

weak acceptors since nitrogen atoms attached to silicon have decreased basicity (charge delocalization towards silicon).^[29] This delocalization should increase the electron density at silicon and thus decrease its Lewis acidity.^[30] Thermodynamic data on the dissociation of SiF₄-nitrogen adducts show, that it is the crystal lattice energy of the adducts and not the formation enthalpy in the gas phase, which is crucial for the stability of the complexes in the solid state.[31] Theoretical studies on the dissociation energies of neutral, pentacoordinate silicon compounds with dative N→Si bonds found indeed, that the dissociation enthalpy usually ranges below 10 kcal mol⁻¹, ^[12c, 32] and that it is not the Lewis acidity of the silicon but rather the lattice energy that drives the formation of the dative bonds.^[33] The precipitation of stable silicon-nitrogen adducts from solution has been demonstrated, but it is unclear, to which extend the lattice energy is responsible.^[34] The only example of a reversible solution state complexation with moderate neutral nitrogen donors was reported for PhCCSiF₃.^[23] Amphiphilic silicon species with amine donor groups may in principle dimerize in a head-to-tail fashion by the formation of two intermolecular donor/acceptor interactions. However, various aminosilanes have been found to be monomeric in the gas phase. in solution as well as in the solid state.^[35] In contrast, H₂CISi-NMe₂ (4, scheme 1c) crystallizes in a head-to-tail dimeric arrangement,[36] but the dimerization was not observed in solution and the gas phase.^[37] Even the amphiphilic silicon compound **3**, with formally stronger Lewis acidic (-SiF₃) and basic (-NMe₂) sides as compared to 2, 5-7, forms adducts only in the solid state.[12d] Even the potentially more Lewis acidic compound TfOSi(NMe₂)₃ does not dimerize in solution.[38]

Fleischer^[39] and others^[40] argued, that the reason for the moderate Lewis acidity of silicon compounds is the high deformation energy from the tetrahedral to trigonal-bipyramidal form. Early theoretical studies on the inversion barrier of silicon(IV) demonstrated, that π -donor/ σ -acceptor ligands lower the energy of the planar transition state.^[26n, 41] Consequently, one could conjecture, that increased association energies can indirectly be achieved by deliberate lowering of the deformation energy of the silicon species through π -donor/ σ -acceptor ligands and geometrical preorganization / planarization. The strategy of planarization has never been stressed nor used in the context of silicon Lewis acids. By consequence, the careful inspection of the origin in the surprising aggregation process of amphiphilic silicon species **5-7** in solution is highly beneficial.

It appeared, that the bonding situations and driving forces in **5-7** were difficult to describe with a single quantum theoretical tool. However, to keep the matter simple and readable, the stabilizing factors will be emphasized only by the most relevant methods in the following, even if alternative tools confirmed the hypotheses redundantly (summarized in figure 5). For the full computational details, see SI.

Exact energies and the influence of dispersion

The first requirement for a meaningful theoretical analysis was the assessment of the exact energies of the dimerization process of compounds **3-7**. Comparison with available solid state structural data distinguished the B3LYP-D3(BJ)/def2-TZVPP level of theory ideal for geometry optimizations.

 Table 3. Calculated energies (in kcal mol⁻¹) for the dimerization process of 3-7.

		∆E(PW6B95- D3(BJ,abc)/QZVPP) ^a	∆Ga ^b	exp. dimer	ΔΔE(B3LYP (D3)-B3LYP) ^d
3	F ₃ SiCH ₂ NMe ₂	-12.1	8.9	no	-16.8
4	Me ₂ NSiH ₂ Cl	-4.1	12.1	no	-3.0
5a	MeNNNSiH	-35.0	-10.9	yes	-31.2
5b	MeNNNSiCI	-27.5	-2.3	yes	-37.6
5c	MeNNNSiPh	-4.7	21.0	no	-43.0
5d	MeNNNSiEt	-7.2	20.2	no	-39.1
6a	[₽] rNNNSiH	-33.6 (-36.0°)	-6.8	yes	-38.3
6b	₽rNNNSiCI	-13.7	16.5	no	-36.7
7a	ONOSiPh	-40.9	-9.2	yes	-52.5

^[a] pure electronic energies, ^[b] Gibbs free energy including thermal and solvent correction (COSMO-RS), ^[c] by SCS-MP2/QZVPP, ^[d] difference of electronic energies obtained at B3LYP/TZVPP level with and without dispersion correction (D3(BJ)).

For example, the experimentally measured, large C1-Si-N1-bond angle of 5c (126.1°) was reproduced very well (126.4°), thus confirming also the absence of crystal packing effects that lead to such an obtuse bond angle. The solvent-corrected, association Gibbs free energies for the monomers were obtained at the accurate meta-hybrid PW6B95-D3(BJ,abc),COSMO-RS(CH₂Cl₂)/def2-QZVPP level (ΔG_a , table 3).^[42] The values agree perfectly with the experimental observations ($\Delta G_a < 0$ for dimerization observed in solution). Comparison with the pure electronic energies shows, that the inclusion of entropy and solvation disfavors the dimerization. In fact, the pure electronic energies are all attractive and spread over a range of up to 50 kcal mol⁻¹ difference in association energy. Certainly, this large variance and the relative ordering cannot be explained by general Lewis-acidity trends (e.g. more electronegative substituents at silicon lead to stronger binding). To estimate the influence of London dispersion, energies were obtained with and without dispersion correction at the B3LYP/def2-TZVPP level, since the B3LYP functional does not account for medium-range electron correlation effects responsible for dispersion.^[43] The differential values $\Delta \Delta E$ (B3LYP(D3)-B3LYP) show that dispersion forces play a massive role in the associations in favor of the dimers 5-7, amounting for up to 52 kcal mol⁻¹ for ONOSiPh 7a. Dispersion has a significant effect even for 3, but is only marginal for 4. Calculations of a hypothetical ONO derivative without *t*Bu-groups revealed a contribution of 15 kcal mol⁻¹ by the dispersive attraction between these polarizable groups (see SI). The attractive, non-covalent forces between the substituents were further justified by an NCI-plot (see figure SI8). That the association of densely substituted Lewis acid/Lewis base pairs is strongly influenced by dispersion interaction has been recognized for several classes of compounds.^[42b, 44] However, the herein observed magnitude of dispersive stabilization is remarkable for a dative association, and was thus identified as the first influence on the surprising stability of dimers 5-7 (see figure 5).

Influence of preorganization and electrostatic attraction

A closer look at the intrinsic Lewis acidity of the monomers was considered by comparison of 3, 4 and 6a (for atom numbering, see figure 3a). Especially, compound 3 (Me₂NCH₂SiF₃) seems abnormal, as it shows a much weaker tendency towards dimerization as one would expect based on the electronegativity of the substituents in a SiF₃ moiety - even after the neglect of dispersion.^[45] To assess the orbital situation in the monomers, aminosilanes 4_{Mon} , 3_{Mon} and $6a_{Mon}$ were analyzed by conceptual DFT and NBO theory.^[46] Visual inspection of the frontier orbitals for **6a_{Mon}** revealed a significant deformation of the HOMO from the nitrogen lone pair towards silicon and a localized LUMO with pzshape at silicon (see SI for all FMOs and Fukui dual descriptors). This deformation is much less pronounced for 4_{Mon} , and virtually absent for 3_{Mon} . The observed orbital perturbations in $6a_{Mon}$ bear a strong resemblance to the features found in planar silicon transition states.^[41a] The geometrical distortion from the tetrahedral angle (experimentally observed in the N1-Si-C1 angle of 126° for 5c, see above) describes indeed the situation of silicon deformation towards planarity and results from the ability of the ONO and NNN ligand frameworks to act as a π -donor/ σ -acceptor. additionally supported by geometric strain of the ligand. Second order perturbation energies obtained by NBO analysis in 6a_{Mon} reveal that the threefold nitrogen lone- pair donation into the $\sigma^*(SiN)$ - and $\sigma^*(SiH)$ -NBOs amount to 40.5 kcal mol⁻¹, thus providing energy to compensate for the deformation at silicon. The perturbation energies do not have any true physical meaning but are helpful for the relative ranking of stabilizing orbital interactions. The Si-N²/N³ $\sigma\text{-NBOs}$ in $\textbf{6a}_{\text{Mon}}$ are located to 79 % at nitrogen and show considerable π -back-donation of 4 % from the nitrogen lone-pair into the silicon acceptor orbitals. These findings indicate high ionicity of the Si-N bonds and rationalize the experimentally observed shortening of the Si-N²/N³ bonds in 5c. The planarization of **6a**_{Mon} has a tremendous effect on the Lewis acidity: the species is preorganized and should have a reduced deformation energy during adduct formation. This hypothesis was confirmed by energy decomposition analysis (EDA) for 3, 4 and 6a, with the intuitive fragmentation into two closed shell monomeric species (for full details, see SI).^[47] The preparation energy for the deformation of the relaxed monomeric fragments to the geometries in the dimers is much larger for 3 (46.8 kcal mol-1), compared to **6a** (32.0 kcal mol⁻¹). The interaction energy between the prepared fragments in 3 is substantial, but it is compensated by the high preparation energy. By consequence, the preorganization and the low deformation energy at silicon was identified as the second contribution to the stability of dimers 5-7 (see figure 5).

EDA also revealed, that the electrostatic attraction between the fragments is the most dominant contribution in all studied dimers. The favorable Coulomb attraction is obvious, if the high positive atomic charges at silicon and negative ones at nitrogen are considered (NBO or QTAIM, see SI). *Thus, the electrostatic attraction was disclosed as the third stabilizing factor for the dimerization.* However, the importance of electrostatic attraction is decreasing in going from species **3** (58 %) over **4**

(57 %) to 6a (50 %). Accordingly, the importance of orbital interactions increases in the opposite order.

Specific orbital interaction in the dimers

The increasing contribution of orbital interactions in order of 3/4 to 6a indicated the possibility of specific stabilizing orbital interactions in the dimers of 6a, which were thus analyzed by the ETS-NOCV scheme (extended transition state (ETS) method for energy decomposition analysis combined with the natural orbitals for chemical valence (NOCV) theory).[48] The dimers were fragmented into closed shell species similar to the EDA, yielding NOCV deformation densities, which qualify and quantify the types of the orbital interactions in the dimerization process. Only the main conclusions obtained by the ETS-NOCV analysis shall be sketched here in a schematic representation (figure 3a); for all details of ETS-NOCV and fragment orbitals, see SI. For 3, only the σ -expected type donor/acceptor interaction between N' and Si was found (blue arrows). For 4, the same σ -type donor/acceptor interaction was found (NOCV 2), but a second, more critical deformation density revealed charge depletion in the entire Si-N bonding region, by the participation of the Si-N σ -bonding electrons in the monomer during the dimerization (NOCV 1, green arrows). In 6a, the orbital interaction is even more complex, revealing three significant NOCVs, which are difficult to express in terms of a simple orbital picture. Like in 4, the strongest interaction is characterized by the depletion of charge density in the Si-N¹ bonding region. (NOCV 1, 129.1 kcal mol⁻¹, green arrows).



Figure 3. a) Schematic representation of the electron charge deformations and energies for 3, 4 and 6a as obtained by ETS-NOCV, b) proposed resonance phenomenon in compounds like 6a.

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The second NOCV represents the expected donor/acceptor interaction between N1 and Si' (NOCV 2, 31.8 kcal mol⁻¹, blue arrows). A last, a rather unintuitive charge deformation channel was identified (NOCV 3, 14.9 kcal mol⁻¹, red arrows), in which the acceptor orbital is entirely delocalized across the aromatic rings, but accepts electron density through the nitrogen atom N¹. Importantly, this latter interaction describes a N¹/N¹' electron exchange path - an interaction that is also observed by QTAIM analysis (see below). Simply speaking, the coordinating nitrogen atoms in 4 and 6a deliver electron density to the "intermolecular" silicon (Si'), that it forwards to the neighboring N' and that can be used again for coordination to Si, closing the cycle. Such a situation could also be described as resonance phenomenon between interchanging formally dative and covalent bonds inside the Si₂N₂-ring (see figure 3b), that should stabilize any (semi)metal amine dimer by a corresponding resonance mixing of the respective wavefunctions. Is this phenomenon expressed in some other quantum theoretically derived orbital or topological signature? Indeed, second order perturbation energies from NBO analysis of dimeric **6a** reveal a huge energy gain (212 kcal mol⁻¹) by hyperconjugation^[49] from the in-plane Si-N¹ σ -bonds into the geminal $\sigma^*(Si-N^{1'})$ NBOs (figure 4a, for individual energetic contributions, see SI).



Figure 4. a) Most relevant NBO interactions for the stabilization of dimeric species 6a as revealed by second order perturbation analysis and the contour diagram of the PNBOs for geminal hyperconjugation from $\sigma(Si-N^1) \rightarrow \sigma^*(Si-N^{1'})$, b) Laplacian of the electron density in the Si_2N_2 plane of 6a, positive $\nabla^2\rho$ (charge depletion) in blue and negative (charge concentration) in red, together with values of delocalization indices (red numbers) all relating to nitrogen N¹ (upper right).

The overlap diagram of the preorthogonalized NBOs (PNBOs) of σ -(Si-N¹) with σ^* -(Si-N¹) reveals, that the overlap integral is maximized by tilting of the Si₂N₂-ring towards a smaller N¹-Si-N¹- angle, as is indeed expressed experimentally for all species by the rhomboid instead of a square tetracycle (figure 4a). This kind of interaction is occurring between all σ/σ^* -(Si-N¹)/(Si-N¹) as well as the σ/σ^* -(Si-H)/(Si-N¹) combinations (eightfold), amounting for the large total energy gain. Such intermolecular perturbations can be found to a certain degree also in the NBO analysis of **4**, but are not pronounced in **3**.

With particular regard to the proposed Si₂N₂-bond delocalization, the electron density topologies were investigated using Bader's theory of atoms in molecules (QTAIM).^[50] The explanation and a full set of bond descriptors for 3, 4 and 6a can be found in the SI. Recent topological studies on hypercoordinate silicon species emphasized the ionic bond character of silicon to electronegative substituents.^[51] Accordingly, closed shell character for all bonds to silicon and highly positive atomic charges, with small covalent contributions was found (table 4). The electron densities of the newly formed Si-N¹ bonds in 3 and 4 are lower than any other Si-E bond in the monomers, and all other descriptors are consistent with its weak, dative nature and closed shell character of intermediate type.^[52] The most interesting results can be drawn from the comparison of the bonds to silicon in monomeric and dimeric species of 6a. All Si-E bonds, except the Si-N¹ bond in 6a_{Mon}, are little affected by the dimerization, generally revealing increased ionicity upon pentacoordination. In the monomeric form of 6a, the three Si-N bonds are almost identical. In contrast, after dimerization, the Si-N¹ and Si-N¹ bonds inside the Si₂N₂ ring become almost similar, but differ substantially from the four Si-N2/3 bonds. The visual inspection of $\mathcal{P}^2 \rho$ in the plane of the Si₂N₂ring (figure 4b) in dimeric 6a supports the picture of similar Si-N¹ and Si-N1' bonds, with non-negligible charge transfer from the nitrogen lone-pair regions towards silicon, but the electron density concentrations still located in the nitrogen atomic basin. The two nitrogen lone-pairs unify to one charge concentrated donation area with proliferations towards silicon (see SI for VSCCs). The nature of the Si-N¹/Si-N¹ bonds is still predominantly closed shell, yet a remarkable decrease in the $G(\mathbf{r}_{BCP})/\rho(\mathbf{r}_{BCP})$ ratio (Lagrangian kinetic energy per electron) is observed upon dimerization. Since $\rho(\mathbf{r}_{BCP})$ in the Si₂N₂ ring bonds gets lower if compared to the Si-N¹ bond in the monomer, the major proportion in the lowering of $G(\mathbf{r}_{\text{BCP}})/\rho(\mathbf{r}_{\text{BCP}})$ upon dimerization must arise from the reduction in $G(\mathbf{r}_{BCP})$ itself. It is well known, that the kinetic energy is directly related to the amount of delocalization. Thus, a reason could be delocalization occurring inside the Si₂N₂ ring electrons, as already indicated by the ETS-NOCV and NBO analyses. The proposed resonance between the four internal Si-N bonds is further substantiated by the delocalization indices, based on the pairdensity (Fermi-hole) integration over the QTAIM derived atomic basins. The delocalization index guantifies the magnitude of electron sharing between different atoms and reveals extraordinary exchange pathways.[53] The three center delocalization indices (δ (A-B-C)) for the coordinating N¹ towards selected atoms over silicon are given in table 4 (for 6a also in figure 4b, for atom naming in compounds 3, 4 see figure 3a).

Table 4. QTAIM derived descriptors for selected bonds in monomeric and dimeric species of 3, 4 and 6a.

Compound	$\rho(r_{BCP})$	₽ ² (r _{BCP})	$G(r_{BCP})/\rho(r_{BCP})$	δ (A -B- C)	
6a _{Mon}					
SiN <i>i</i> Pr	0.1333	0.5358	1.485		
SiN	0.1324	0.4958	1.436		
SiH	0.1254	0.1485	0.939		
6a				6a	
SiN <i>i</i> Pr	0.1251	0.4610	1.403	0.004 (N ¹ -Si-H)	
SiN	0.0782	0.1642	1.000	0.181 (N ¹ -Si-N ¹ ')	
SiH	0.1238	0.1507	0.947	0.129 (N ¹ -Si-N ²)	
SiN'	0.0975	0.2466	1.121	0.060 (N ¹ -Si'-N ² ')	
4 _{Mon}					
SiN	0.1405	0.6031	1.550		
SiCI	0.0927	0.1831	1.015		
SiH	0.1272	0.1612	0.958		
4				4	
SiN	0.1200	0.3592	1.258	0.018 (N-Si'-Cl')	
SiCl	0.0815	0.1349	0.925	0.169 (N-Si'-N')	
SiH	0.1292	0.1629	0.964	0.136 (N-Si-CI)	
SiN'	0.0545	0.0575	0.708	0.108 (N-Si'-H')	
				0.059 (N-Si-H)	
3 _{Mon}					
SiF (avg)	0.1372	0.9216	2.012		
SiC	0.1365	0.1122	0.897		
3				3	
SiF _{eq} (avg)	0.1280	0.8082	1.910	0.003 (N-Si'-F'ax)	
SiFax	0.1255	0.7797	1.889	0.119 (N-Si'-F' _{eq})	
SiC	0.1246	0.1029	0.866	0.094 (N-Si'-C')	
SiN'	0.0587	0.0612	0.739	A.	

For a full set of descriptors, see SI. All values are given in atomic units. The last column contains the three-center delocalization indices between A and C in **A**-B-**C**.

Two observations are remarkable: 1) In all cases (3, 4 and 6a). only marginal exchange is found between the nitrogen and the substituent placed trans to this nitrogen - a result similarly obtained by Molina et al., which accounts for the fact that the bonding in such hypercoordinate SiX₅ species may not be described by the classical 3c-4e bonding model, and consistent with our findings of ETS-NOCV.^[54] 2) There is a strong delocalization between the equatorial and axial substituents. Remarkably, the delocalization index for N1-Si-N1' inside of the Si₂N₂ ring of **6a** exceeds the value for the other two eq.-ax. (N1-Si-N2/3) significantly (0.181 vs. 0.129). This observation substantiates the interpretation that the Si-N¹ bonds inside the central Si₂N₂ exhibit a stabilizing σ -type delocalization. To a slightly weaker extent, the same signature is found in 4, but is absent in 3, in which such a delocalization is impossible.[55] [56] Thus, the effect of resonating dative and covalent bonds in dimeric aminosilanes was identified as the fourth effect on the remarkable stability of aminosilanes 5-7 (figure 5). Importantly, this effect should be effective for other amphiphilic species like for example aluminum amides.[57]

Conclusions

In the present work, we described the first synthesis of electronrich, geometrically constrained silicon(IV) compounds with the triamido- (NNN) and amido-diphenolato- (ONO) substituents and

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rationalized their particular properties. By variation of the substituents at silicon or at the NNN substituents, the inevitable dimerization, which was recently observed in related species, could be controlled for the first time, yielding either monomeric, structurally reversible or dimeric species. The monomeric species revealed substantial distortion at silicon towards planarity - a record value reported for Si(IV) thus far. Solution-corrected association Gibbs free energies of the dimerization reaction perfectly reproduced the experimental results. Attractive London dispersion between the large substituents was disclosed as the first crucial factor for the efficient dimerization. Planarized silicon compounds like 5-7 feature a preformed coordination side with kinetically favorable localized electrophilicity and low deformation energy at silicon. The low deformation energy in 5-7 was identified as the second factor for the efficient dimerization. EDA and atomic charges revealed electrostatic attractions between the monomers as the third dominant factor, however with increasing contribution of orbital interactions upon planarization at silicon. Besides the expected σ -donor/acceptor interaction, additional stabilization through participation of the σ -bond electrons of the central Si-N¹ bond was found. The indication of a σ -bond delocalization was supported by significantly stabilizing geminal hyperconjugations inside the Si₂N₂-ring and by biased QTAIM derived three center electron delocalization indices as well as the decrease in the kinetic energy density of the electrons involved in the central Si₂N₂ ring. This resonance phenomenon is thus identified as last stabilizing factor for the efficient dimerization for this specific example, and might similarly play a decisive role for other amphiphilic dimerizing species.



Dispersive attraction between ligands (DFT-D3, NCI-analysis)

Low deformation energy at (preorganized) silicon (NBO, EDA, Fukui, TS)

Electrostatic attraction between Si and N (EDA, atomic charges)

σ-bond resonance of SiN-bonds (NBO, ETS-NOCV, QTAIM)

Figure 5. Summarized factors contributing to the efficient dimerization of geometrically constrained, electron-rich silicon compounds 5-7.

In light of the usually rather moderate Lewis acidity of silicon species, the herein described efficient dimerization is remarkable. The present work gives the explanation and presents a combined experimental and theoretical account of the strategy of preorganization in silicon Lewis acids. The disclosed influences of dispersion, geometrical strain, deformation energy (preorganization) and charge delocalization/resonance should

extend the perception of Lewis acidity at silicon and contribute to the currently active field of neutral silicon Lewis acids.^[58] Given the redox-activity of the electron-rich substituents in combination with the unquenched nature of the now accessible monomeric aminosilanes, a promising potential for ligand-element cooperativity with this new class of compounds is offered – an objective of current interest and ongoing research in our group.

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Keywords: main-group chemistry • unusual geometries • amphiphilic compounds • silicon • dative bonding

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significantly in formal atomic charge (and most likely orbital ordering, see ref 26n) and cannot be classified as Si(IV).

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Geometrically constrained, electronrich aminosilanes are synthesized, imparting control over a unique dimerization process. Quantum theoretical analyses of the process permit general conclusions on the Lewis acidity of silicon compounds and on dimerizing amphiphilic species.



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Synthesis of electron-rich, planarized silicon(IV) species and the theoretical analysis of dimerizing aminosilanes