Molecular “Floppyness” and the Lewis Acidity of Silanes: A Density Functional Theory Study

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This paper is dedicated to Prof. Dr. Karl Hensen on the occasion of his 65th birthday

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A comprehensive set of Lewis acid-base adducts of silanes was investigated by means of the density functional theory geometry optimization [B3LYP/6–31G(d)], and thermochemical calculations, [B3LYP/6–311+G(2d,p)//B3LYP/6–31G(d)]. Complex formation was found to weaken Si–Cl and Si–Br bonds more than Si–F or Si–H bonds. Comparable distances between Si and a Lewis base L (L = NH_3, OH_2, F^-) are shorter in hexa- than in pentacoordinated complexes. The molecular structures of the pentacoordinated Si complexes allowed for a mapping of an S_N2 reaction pathway by correlating the lengths of the Si–X and Si–L bonds. Complex formation was found to be exothermic for most of the coordination compounds, and the analysis of the natural atomic charges revealed a high ionic character of the dative bonds. Formation of the anionic complexes and of $SiH_2X_2(py)_2$ is most exothermic with X = Cl or Br and otherwise most exothermic with X = F. Only small enthalpy differences were found between the *trans* and *cis* configurations of $SiF_4(py)_2$. The standard free enthalpy of complex formation is negative only for complexes between halosilanes and F^-, i.e. all other silane Lewis base adducts are thermodynamically unstable under standard conditions with respect to dissociation. It is inferred that the existence of some of the silicon complexes in the solid state or in solution is caused by stabilizing intermolecular forces, and silanes are classified as very weak Lewis acids. The thermochemistry of complex formation was analyzed in terms of molecular "floppyness" of the silanes and the energy of interaction between the deformed silane and the Lewis base. The enhanced complex stability of $SiCl_4(py)_2$ compared to $SiH_4(py)_2$ and of $GeF_4(NH_3)$, $[GeF_5]^-$ and $[GeF_6]^{2-}$ compared to the analogues silane adducts does not result from a stronger Lewis acid base interaction but from an increased "floppyness" of $SiCl_4$ and GeF_4 compared to SiH_4 and SiF_4, respectively.

Introduction

While many compounds of group 13 elements act as Lewis acids due to their electron deficiency, the driving force for the formation of hypervalent silanes must be different. Many adducts of silanes with Lewis bases have been characterized,[1] and hypervalent compounds have long since been the subject of many experimental[2] and theoretical[3] investigations; some are even of pharmaceutical interest.[4] Several review articles have been published in this field.[5] Hence, since Si atoms can participate in donor acceptor interactions, the corresponding silanes were said to be Lewis acids.

But does the Lewis acidity of, for example, $SiCl_4$ follow from the existence of $SiCl_4(py)_2$ *in the solid state*? And why does $SiCl_4(py)_2$ exist and $SiH_4(py)_2$ does not?[1f] Most complexes between silanes and typical Lewis bases are hitherto found only in the solid state or in polar solvents, some exist at very low temperatures only with matrix isolation,[6] and $SiF_4(NH_3)$ is the only example of a silane adduct known to the author, that has been detected in the gas phase, but at very low temperatures.[7]

Thus two questions arise: first, how does the Lewis acidity of silanes depend on their molecular properties, and second, is the existence of adducts between silanes and Lewis bases at room temperature at all enabled by intermolecular forces, in contrast to group 13 Lewis acids like BX_3, AlX_3 and GaX_3 (X = H, alkyl, halogen) whose adducts with Lewis bases are known to exist in the gas phase under normal conditions (see e.g. reference 8)? $SiH_2Cl_2(py)_2$ was recently calculated to be thermodynamically unstable under normal conditions with respect to dissociation into SiH_2Cl_2 and pyridine.[9] It is thus of interest to look at the thermodynamic stability of a more comprehensive set of silicon complexes, including different coordination numbers, donor atoms and substitution patterns of the silicon atom. Some of the molecules investigated exist in the solid state, i.e. $SiH_3Cl(OMe_2)$,[10] $SiH_2Cl_2(py)_2$,[1f,9] $SiH_2Br_2(py)_2$,[1f] $SiF_4(py)_2$,[11] $SiCl_4(py)_2$,[12] $SiF_4(NH_3)_2$,[13], $SiF_4(NH_3)$,[6] SiF_5^-,[14] and SiF_6^{2-},[15] the others are model compounds, i.e. $SiH_3X(NH_3)$, $SiX_4(NH_3)$ and $SiH_3X(OH_2)$, $SiH_2F_2(py)_2$, $SiH_4(py)_2$, $[SiH_3XF]^-$, $[SiH_4F]^-$, $[SiCl_4F]^-$, $[SiH_4F_2]^{2-}$ and $[SiCl_4F_2]^{2-}$ (X = F, Cl, Br for complexes of SiH_3X and SiH_2X_2 and X = H, F, Cl for complexes of SiX_4, py = pyridine).[16,18] To investigate the matter of “genuine” Lewis acidity of silanes, no molecules such as silatranes or 1-sila-8-dimethylaminonaphthalene, whose potential donor and acceptor sites are forced into close proximity, and where an interaction is favored by molecular steric strains, were considered. Furthermore, no chelating or macrocyclic

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Lewis bases were included in the study to avoid their stabilizing effect on complexes.

Geometry optimizations for molecules as large as $SiCl_4(py)_2$ (27 atoms, 166 electrons), with a full-electron Hartree-Fock (HF) method using a reasonable basis set [e.g. 6−31G(d)], followed by CI (configuration interaction) or MP*n* (n-th order Møller Plesset perturbation) calculations to account for electron correlation exceeded the limits of the available computational resources. Hence a DFT (density functional theory) approach[19,20] was chosen which includes dynamic electron correlation effects without requiring as many computational resources as the above quoted methods do. In the present paper, the results of DFT geometry optimizations and thermochemical calculations on coordination compounds of different silanes will be presented, and molecular factors influencing the Lewis acidity of and dative bonds[21,22] to silanes will be discussed

Results and Discussion

Molecular Structures

Selected structural parameters are given in Table 1 to 3 (See Figure 1 for a graphical overview of the complexes).

Table 1. Selected structural parameters from optimized geometries of SiH_3X and their Lewis acid base adducts

	$r_e(Si-X)$	x[a]	$r_e(Si-H)$	$r_e(Si-L)$	l[a]	$a(XSiH)$
SiH_3F (C_{3v})	161.3	1.000	148.5			109.2
$SiH_3F(NH_3)$ (C_{3v})	163.2	1.012	148.4	256.4	1.328	104.3
$SiH_3F(NMe_3)$ (C_3)	163.5	1.014	148.6	248.5	1.288	103.0
$SiH_3F(OH_2)$ (C_s)	162.3	1.006	148.3[b]	276.0	1.445	108.4[b]
$[SiH_3F_2]^-$ (D_{3h})	172.0	1.066	152.7	172.0	0.910	90.0
SiH_3Cl (C_{3v})	207.9	1.000	148.2			108.6
$SiH_3Cl(NH_3)$ (C_{3v})	213.6	1.027	147.9	250.8	1.299	102.2
$SiH_3Cl(OH_2)$ (C_s)	210.5	1.013	147.8[b]	273.4	1.431	105.5[b]
$SiH_3Cl(OMe_2)$ (C_s)	210.5	1.013	147.8[b]	271.7	1.423	105.5[b]
$SiH_3Cl(OMe_2)$[c]	214.2		-	227.2		99.4[b]
$[SiH_3ClF]^-$ (C_{3v})	261.4	1.257	148.8	167.6	0.887	81.6
SiH_3Br (C_{3v})	222.9	1.000	148.2			108.8
$SiH_3Br(NH_3)$ (C_{3v})	228.6	1.026	147.9	250.7	1.299	102.3
$SiH_3Br(OH_2)$ (C_s)	225.3	1.011	147.9[b]	273.6	1.432	105.7[b]
$[SiH_3BrF]^-$ (C_{3v})	276.0	1.238	148.6	167.4	0.886	81.4

[a] See text for definition of *x* and *l*. − [b] Averaged value over symmetrically nonequivalent Si−H bonds and X−Si−H angles. − [c] Single crystal X-ray diffraction structure from Reference 10. Atomic distances represent an r_α instead of an r_e structure.

Table 3. Selected structural parameters from optimized geometries of SiX_4, GeF_4, and their Lewis acid base adducts

	$r_e(Si-X)$	x[a]	$r_e(Si-L)$	l[a]	$a(X^aSiX^e)$[33]
SiH_4 (T_d)	148.6	1.000			
$SiH_4(py)_2$ (D_{2h})	156.0	1.050	203.6	1.055	
$[SiH_4F_2]^{2-}$ (D_{4h})	164.4	1.106	176.8	0.935	
$SiH_4(NH_3)$ (C_{3v})	148.4/149.7[b]	1.007	302.6	1.568	106.8
$[SiH_4F]^-$ (C_{3v})	152.9/161.3[b]	1.085	171.7	0.908	88.2
SiF_4 (T_d)	157.9	1.000			
$SiF_4(py)_2$ (D_{2h})	167.0	1.058	198.3	1.027	
$SiF_4(NH_3)_2$ (C_{2h})	166.9	1.057	197.4	1.023	
$[SiF_6]^{2-}$ (O_h)	172.0	1.089	172.0	0.910	
$SiF_4(NH_3)$ (C_{3v})	160.8/161.2[b]	1.021	214.4	1.111	98.1
$SiF_4(NMe_3)$ (C_3)	161.3/161.7[b]	1.024	217.0	1.124	96.8
$[SiF_5]^-$ (D_{3h})	164.2/167.3[b]	1.060	167.3	0.885	90.0
GeF_4	171.0	1.000			
$[GeF_6]^{2-}$	182.2	1.065	182.2	0.944	
$GeF_4(NH_3)$	174.0/173.3[b]	1.013	215.9	1.096	96.9
$[GeF_5]^-$	175.9/177.8[b]	1.040	177.8	0.921	90.0
$SiCl_4$ (T_d)	204.7	1.000			
$SiCl_4(py)_2$ (C_{2h})	221.6	1.083	204.6	1.060	
$[SiCl_4F_2]^{2-}$ (D_{4h})	232.7	1.137	164.5	0.870	
$SiCl_4(NH_3)$ (C_{3v})	210.3/211.7[b]	1.034	216.6	1.122	97.2
$[SiCl_4F]^-$ (C_{3v})	215.2/224.4[b]	1.096	164.5	0.870	90.0

[a] See text for definition of *x* and *l*. x is not given for equatorial Si−X bonds in $SiX_4(L)$. − [b] The first of the two values refers to the equatorial, the second to the apical Si−X bond.

The molecular geometry of the complexes may give an indication of the strength of the Lewis acid/base interaction in terms of atomic distances and distortion of silane and Lewis base from their ground state geometries. According to Pauling,[34] the bond length is an indication of the bond strength, i.e. the shorter Si−L bond (L = O for OH_2, OMe_2; L = N for NH_3, NMe_3 and py; L = F for F^-) should be the stronger one.[35] As different X and L are to be compared with each other, relative lengths are used instead of $r_e(Si-X)$ and $r_e(Si-L)$. Accordingly, $r_e(Si-X)$ is divided by $r_e(Si-X)$ of the parent silane to give the relative length $x = r_e(Si-X)/r_e(Si-X)_{silane}$ and $r_e(Si-L)$ is divided by the sum of the covalent radii of Si and L to give the relative length $l = r_e(Si-L)/[r_{cov}(Si) + r_{cov}(L)]$. (Covalent radii are taken from reference 36 and are 122, 118, 75, 73 and 71 pm for Ge, Si, N, O and F, respectively). In the complex anions, in $SiH_3X(L)$ and in $SiH_2X_2(py)_2$, $r_e(Si-L)$ decreases for a given complex with X in the order H > F > Cl > Br, and, for a given L, the relative lengths of the Si−X bond, *x*, increases in the same order, the only excep-

Table 2. Selected structural parameters from optimized geometries of SiH_2X_2 and their Lewis acid base adducts

	$r_e(Si-X)$	x[a]	$r_e(Si-H)$	$r_e(Si-N)$	l[a]	$\tau(CNSiX)$[b]
SiH_2F_2 (C_{2v})	160.1	1.000	147.9			
$SiH_2F_2(py)_2$ (D_{2h})	171.1	1.069	150.4	208.5	1.080	0.0
SiH_2Cl_2 (C_{2v})[c]	206.5	1.000	147.6			
$SiH_2Cl_2(py)_2$ (C_{2h})[c]	229.1	1.109	148.3	203.9	1.056	60.5
SiH_2Br_2 (C_{2v})	221.8	1.000	147.6			
$SiH_2Br_2(py)_2$ (C_{2h})	242.7	1.094	148.0	202.4	1.049	66.1

[a] See text for definition of *x* and *l*. − [b] Parameter represents the torsion between one N−C bond of pyridine and one Si−X bond. − [c] Values from reference 9.

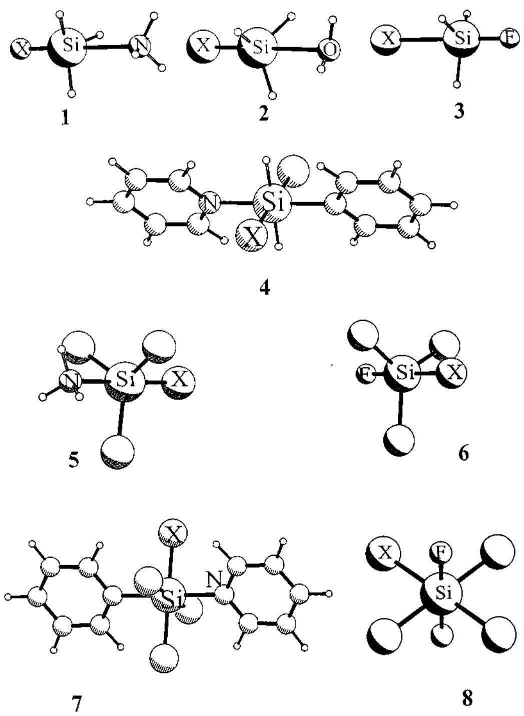

Figure 1. Molecular graphics of the hypervalent compounds investigated (only those systems are shown, in which X is varied) $SiH_3X(NH_3)$ **1**, $SiH_3X(OH_2)$ **2**, $[SiH_3XF]^-$ **3**, $SiH_2X_2(py)_2$ **4** (X = F, Cl, Br); $SiX_4(NH_3)$ **5**, $[SiX_4F]^-$ **6**, $SiX_4(py)_2$ **7**, $[SiX_4F_2]^{2-}$ **8** (X = H, F, Cl)

tions being $[SiH_4F]^-$ and $[SiH_3F_2]^-$. For the other complexes, $SiX_4(NH_3)$ and $SiX_4(py)_2$, Si−N is shortest with X = F.

The relative length x increases with L in the order L = O < N << F^- and the relative length l decreases in the same order. Thus, l and x suppose F^- to be the strongest of all Lewis bases studied in the present work.

Considering the electrically neutral amine-silane complexes, r_e(Si−N) is smaller in the hexacoordinated compounds $SiX_4(py)_2$, $SiH_2X_2(py)_2$ and $SiF_4(NH_3)_2$ than in the pentacoordinated $SiX_4(NH_3)$, $SiH_3X(NH_3)$, $SiH_3F(NMe_3)$ and $SiF_4(NMe_3)$, and smaller in $SiX_4(NH_3)$ and $SiF_4(NMe_3)$ than in $SiH_3X(NH_3)$ and $SiH_3F(NMe_3)$. The difference in r_e(Si−N) between $SiF_4(py)_2$ and $SiF_4(NH_3)_2$, and between $SiF_4(NMe_3)$ and $SiF_4(NH_3)$, is marginal, while r_e(Si−N) is shorter in $SiH_3F(NMe_3)$ than in $SiH_3F(NH_3)$. These results suppose that the Si−N distance is mainly determined by electronic and not by steric factors. The nature of the Si−L bond in $SiH_3X(L)$ and $SiX_4(L)$ was analyzed in terms of second order perturbation in a natural orbital basis (see Table 4). It is not the absolute values of these energies that are of interest, but, for comparable complexes, their relative orders. In complexes $SiH_3X(L)$, the interaction of the lone pair of L with the anti-bonding orbital of the apical Si−X bond, n(L)−σ*(Si−X), was found to play the major role, a result that rationalizes the considerable lengthening of the Si−X bond due to interaction of L with Si. Compared to n(L)−σ*(Si−X), the interaction between the lone pair of L and the anti-bonding orbitals of the equatorial Si−H bonds, n(L)−σ*(Si−H), is rather small. In $SiX_4(L)$, the apical Si−X bond is only slightly longer than the equatorial ones, and in $GeF_4(NH_3)$, $r_e(Ge-F^a)$ is even smaller than $r_e(Ge-F^e)$, a relation well reflected by the NBO interaction energies (see Table 4).

Structure Correlation

Interpreting the pentacoordinated complexes in terms of structure correlation[37] as “snapshots” of an S_N2 reaction path, with the nucleophile and the nucleofuge occupying the apical positions of a trigonal bipyramid, a smaller l requires a bigger x and vice versa. As can be seen from Figure 2a, the pentacoordinated complexes give a reasonably good correlation between x and l, in contrast to the hexacoordinated ones (see Figure 2b). The deformations of SiH_3X and SiX_4, as measured by the difference of a(HSiX) and

Table 4. Second order perturbation energies for the interaction of Lewis base L and SiH_3X, SiH_2X_2, SiX_4 and GeF_4 in an NBO basis[a]

	n(L)-σ*(Si−X)	n(L)-σ*(Si−Y)[b]		n(L)-σ*(E−X)[c]	n(L)-σ*(Ei−Y)[b,c]
$SiH_3F(OH_2)$	24.0	4.5[d] (3)	$SiH_4(NH_3)$	17.8	3.8 (3)
$SiH_3Cl(OH_2)$	28.8	5.9[d] (3)	$SiF_4(NH_3)$	51.2	46.6 (3)
$SiH_3Br(OH_2)$	31.0	6.2[d] (3)	$SiCl_4(NH_3)$	53.3	53.3 (3)
$SiH_3F(NH_3)$	44.7	9.5 (3)	$[SiH_4F]^-$	88.2	47.9 (3)
$SiH_3Cl(NH_3)$	56.1	12.8 (3)	$[SiF_5]^-$	72.0	65.8 (3)
$SiH_3Br(NH_3)$	59.8	13.1 (3)	$[SiCl_4F]^-$	51.9	47.4 (3)
$[SiH_3F_2]^-$	79.2	47.0 (3)	$GeF_4(NH_3)$	74.8	106.6 (3)
$[SiH_3ClF]^-$	131.3	36.7 (3)	$[GeF_5]^-$	79.0	127.1 (3)
$[SiH_3BrF]^-$	137.9	35.5 (3)			
	n(L)-$3p_z$(Si)[e]	n(X)-$3p_z$(Si)[e]		n(L)-$3p_z$(Si)[e]	n(X)-$3p_z$(Si)[e]
$SiH_2F_2(py)_2$	313.5 (2)	57.1 (2)	$SiH_4(py)_2$	387.3 (2)	–
$SiH_2Cl_2(py)_2$	378.8 (2)	40.5 (2)	$SiF_4(py)_2$	331.4 (2)[f]	57.6 (4)
$SiH_2Br_2(py)_2$	402.8 (2)	42.1 (2)	$SiCl_4(py)_2$	367.8 (2)	50.6 (4)

[a] Energies are given in kJ mol^{-1}. Values in parentheses represent the multiplicity of the given type of second order interaction in the actual complex. – [b] Y = H for complexes of SiH_3X, and Y = X^e for complexes of SiX_4. – [c] E = Si for SiX_4, E = Ge for GeF_4 – [d] Average value from three n(O)-σ*(Si−H) interactions. – [e] z axis of cartesian system is defined by the two L atoms, i.e. of all three 3p orbitals of Si, $3p_z$ can best overlap with the lone pairs of L. – [f] In $SiF_4(py)_2$, an additional n(N)−3s(Si) interaction of 299.4 kJ mol^{-1} is present.

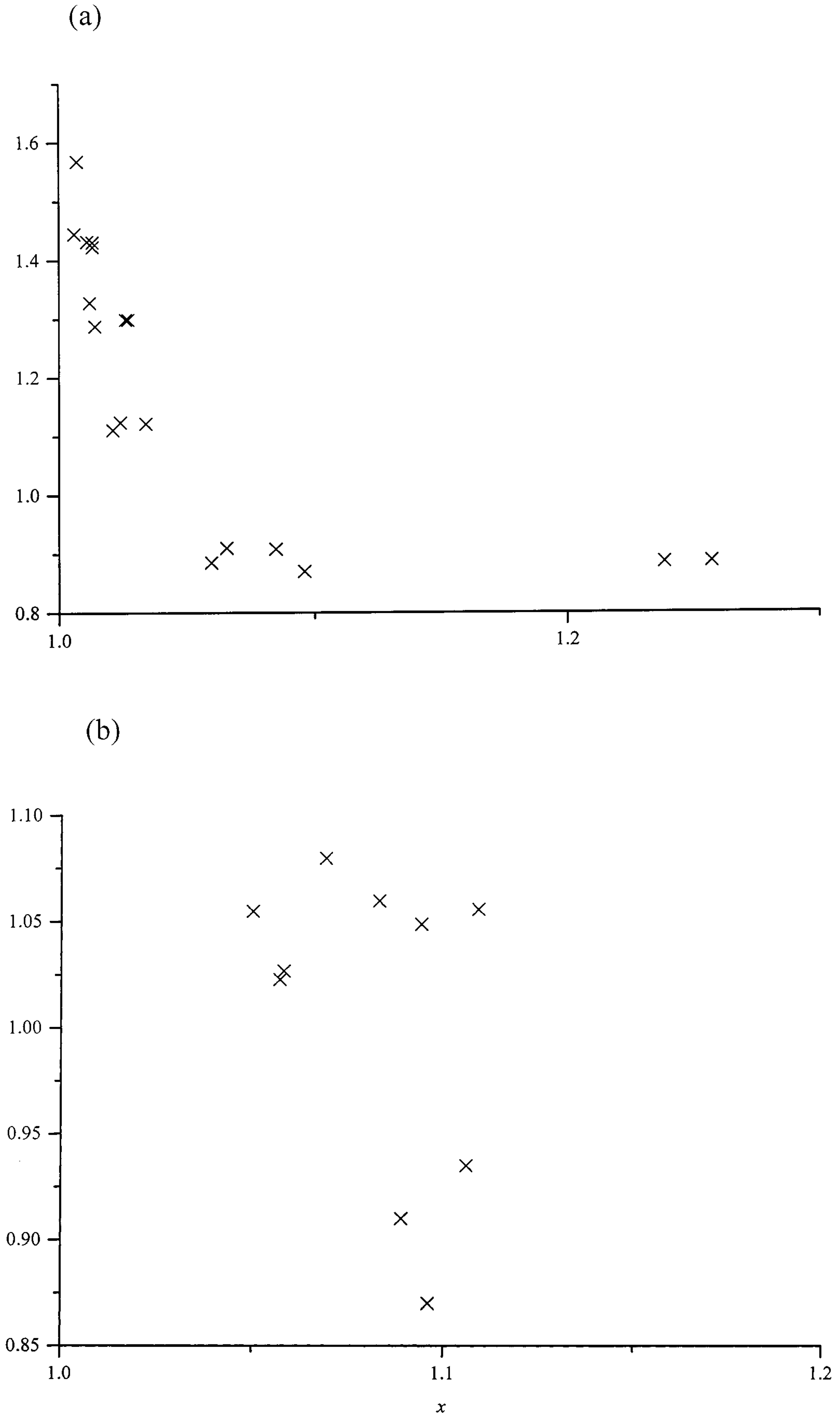

Figure 2. Correlation between the relative length of the Si−X bond, x, and the relative lengths of the Si−L bond, l, for (a) pentacoordinated (b) hexacoordinated Si complexes; for details see text

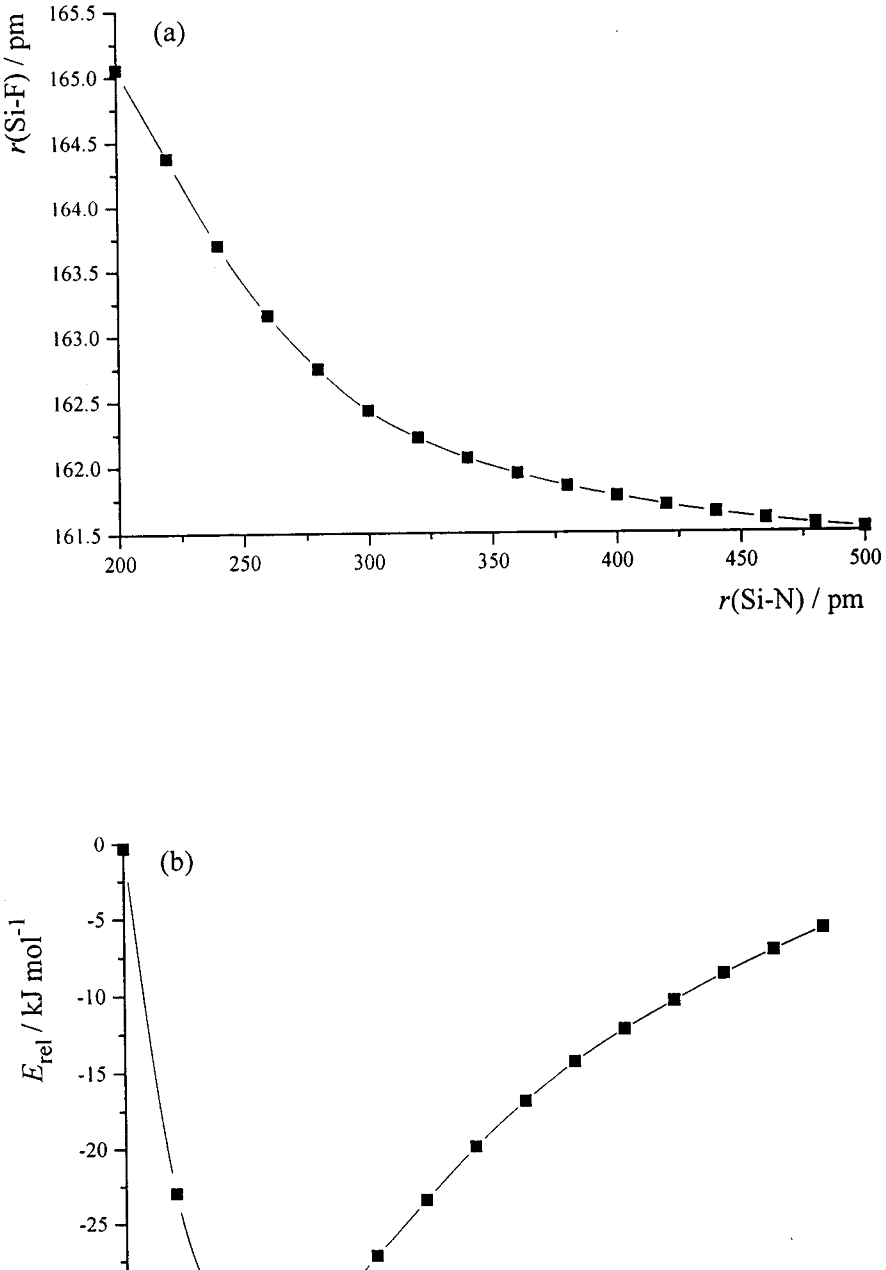

Figure 3. (a) Correlation between r(Si−N) and r(Si−F) in $SiH_3F(NH_3)$; (b) Relaxed potential energy scan (B3LYP/6−31G(d)) for r(Si−N) of $SiH_3F(NH_3)$; $E_{rel} = 0$ represents complete dissociation

$a(X^aSiX^e)$ between the complex and the silane, corroborate the structure correlation, as the approaching nucleophile L pushes the H and X^e atoms away towards X^a and narrows a(HSiX) and $a(X^aSiX^e)$. For $SiH_3F(NH_3)$, a relaxed potential energy scan was performed by changing r(Si−N) in a stepwise manner and optimization of the remaining parameters. The potential energy as a function of r(Si−N) (b) and a correlation of r(Si−N) with r(Si−F) (a) are given in Figure 3. The latter shows a typical pattern for a correlation with mutual weakening of the bonds as it occurs in an S_N2 mechanism, analogous to Figure 2a.

Comparison to Solid State Structures

$SiH_3Cl(OMe)_2$ presents a striking example of a dative bond to Si that is shorter in the solid state than in the isolated molecule (see Table 1). This difference is attributed to stabilizing intermolecular contacts in the solid state.[10] The shorter Si−O bond in the solid state corresponds to a longer Si−Cl bond, an example for structure correlation within different "phases". The considerable shift of the Si−O distance by changes in the molecular environment implies that the curvature of the potential energy surface, $\partial^2 V/\partial r_e(\mathrm{Si{-}O})^2$, at its minimum is small, i.e. the bond is weak. This weakness applies also for the Si−N bond in $SiH_3F(NH_3)$ (see Figure 3). *r*(Si−N) can be varied around the equilibrium distance over a range of 75 pm without increasing the energy by more than 5 kJ mol^{-1}.

Thermochemistry of Complex Formation: Structural "Stiffness" vs. Energy of Interaction

Since the energy, enthalpy and free enthalpy of complex formation are state functions, their values do not depend on the way in which the complex is formed. It is useful to divide the complex formation from silane (S) and Lewis base (L) into two steps. First, the molecules of the silane and the Lewis base are deformed from their ground state geometries, S(GS) and L(GS), to their complex geometry, S(CG) and L(CG), the energy required being $\Delta E_{\mathrm{def}}(\mathrm{S})$ [Equation (1a)] and $\Delta E_{\mathrm{def}}(\mathrm{L})$ [Equation (1b)].

$$\mathrm{S(GS)} \rightarrow \mathrm{S(CG)} \tag{1a}$$

$$\mathrm{L(GS)} \rightarrow \mathrm{L(CG)} \tag{1b}$$

In all complexes, $\Delta E_{\mathrm{def}}(\mathrm{L})$ proved to be only a small fraction of $\Delta E_{\mathrm{def}}(\mathrm{S})$, and only $\Delta E_{\mathrm{def}}(\mathrm{S})$ is further considered.

The deformed silane and Lewis base then interact and form the complex [Equation (2)].

$$\mathrm{S(CG)} + n\ \mathrm{L(CG)} \rightarrow \mathrm{SL}_n \tag{2}$$

The energy of the process shown in Equation (2), *V*, represents the strength of interaction. Since the energy required for Equation (1a) may even vary for the same silane and the same coordination number, a study of $\Delta E_{\mathrm{def}}(\mathrm{S})$ from the ground state geometry to a well defined distorted geometry was performed. For hexacoordinated complexes of SiH_2X_2 and SiX_4, the silane molecules were "flattened", i.e. the geometry optimization was performed with the symmetry restricted to D_{2h} for SiH_2X_2 and D_{4h} for SiX_4. To account for the pentacoordinated complexes of SiH_3X and SiX_4, the molecules were optimized with a trigonal pyramidal structure, which means that the HSiX angles in SiH_3X and the XSiX angles in SiX_4 between the unique X atom and the other X atoms were fixed to 90°. This symmetry is designated as "C_{3v}(tp)". The energy necessary for these kinds of deformations is a measure of the "floppyness" of the silane to adopt the geometry in a given complex. Values for $\Delta E_{\mathrm{def}}(\mathrm{S})$ are given in Table 7.

The standard enthalpy of complex formation, ΔH_c^{298}, and the standard free enthalpy of complex formation, ΔG_c^{298}, obtained in the present study exhibit partially very small absolute values (see Table 5a and 5b), hence counterpoise calculations are essential to correct them for the basis set superposition error (bsse).[31,32,38] Counterpoise-corrected

Table 5. (a) Enthalpies of complex formation, ΔH_c^{298}; (b) free enthalpies of complex formation, ΔG_c^{298}; (c) basis set superposition errors for the thermochemistry of complex formation; for details see text

(a)[a]

Silane	SiH_3X (CN_{Si} = 5)			SiX_4 (CN_{Si} = 5)		SiX_4 (CN_{Si} = 6)		SiH_2X_2 (CN_{Si} = 6)
Lewis base	NH_3	H_2O	F^-	NH_3	F^-	py	F^-	py
X = H				3.2	−143.2	123.1	200.1	
F	−13.2	−5.5	−214.7	−23.4	−296.0	−57.1	−89.1	2.4
Cl	−10.1	−3.9	−269.4	13.8	−306.3	3.8	−257.4	−15.9
Br	−10.4	−3.7	−294.3					−26.1

(b)[b]

Silane	SiH_3X (CN_{Si} = 5)			SiX_4 (CN_{Si} = 5)		SiX_4 (CN_{Si} = 6)		SiH_2X_2 (CN_{Si} = 6)
Lewis base	NH_3	H_2O	F^-	NH_3	F^-	py	F^-	py
X = H				27.4	−112.4	215.1	269.6	
F	23.4	22.7	−178.7	16.7	−260.9	38.3	−12.2	100.9
Cl	27.0	24.1	−237.8	60.3	−275.5	107.5	−188.8	80.4
Br	26.8	23.7	−262.6					71.8

(c)

Silane	SiH_3X (CN_{Si} = 5)			SiX_4 (CN_{Si} = 5)		SiX_4 (CN_{Si} = 6)		SiH_2X_2 (CN_{Si} = 6)
Lewis base	NH_3	H_2O	F^-	NH_3	F^-	py	F^-	py
X = H				1.6	8.3	3.2	17.2	
F	3.2	2.2	9.6	7.0	11.7	19.2	26.7	19.0
Cl	3.1	2.1	10.1	6.2	15.4	17.1	31.7	16.2
Br	3.1	2.1	9.0					15.0

[a] $SiH_3F(NMe_3)$: −16.4, $SiH_3Cl(OMe_2)$: −5.4, $SiF_4(NMe_3)$: −23.5, $SiF_4(NH_3)_2$: −62.3, $GeF_4(NH_3)$: −65.0, $[GeF_5]^-$: −347.3, $[GeF_6]^{2-}$: −191.7. – [b] $SiH_3F(NMe_3)$: 27.5, $SiH_3Cl(OMe_2)$: 25.9, $SiF_4(NMe_3)$: 25.8, $SiF_4(NH_3)_2$: 15.3, $GeF_4(NH_3)$: −26.1, $[GeF_5]^-$: −312.0, $[GeF_6]^{2-}$: −115.3.

Table 6. (a) Energies of deformation for the silanes from the ground state geometry to the geometry in the complexes ΔE_{def}(S) in kJ mol^{-1}; (b) counterpoise corrected energies of interaction, V^{cc}, for the silanes (CG) with the specified Lewis bases in kJ mol^{-1}; for details see text

(a)[a]

Silane	SiH_3X (CN_{Si} = 5)			SiX_4 (CN_{Si} = 5)		SiX_4 (CN_{Si} = 6)		SiH_2X_2 (CN_{Si} = 6)
Lewis base	NH_3	H_2O	F^-	NH_3	F^-	py	F^-	py
X = H				2.1	113.9	375.4	402.7	
F	4.2	0.2	105.1	75.2	219.9	285.6	333.0	218.7
Cl	10.2	2.0	197.9	78.0	196.5	285.1	368.7	229.1
Br	8.3	1.2	172.2					208.3

(b)[b]

Silane	SiH_3X (CN_{Si} = 5)			SiX_4 (CN_{Si} = 5)		SiX_4 (CN_{Si} = 6)		SiH_2X_2 (CN_{Si} = 6)
Lewis base	NH_3	H_2O	F^-	NH_3	F^-	py	F^-	py
X = H				−3.3	−247.0	−264.6	−178.2	
F	−21.8	−9.3	−310.3	−101.1	−505.8	−342.0	−397.8	−225.7
Cl	−25.5	−9.9	−460.5	−68.2	−490.0	−283.7	−599.4	−257.8
Br	−23.8	−8.7	−461.3					−249.6

[a] $GeF_4(NH_3)$: 64.9, $[GeF_5]^-$: 155.0, $[GeF_6]^{2-}$: 220.9. – [b] $GeF_4(NH_3)$: −132.0, $[GeF_5]^-$: −490.6, $[GeF_6]^{2-}$: −390.5.

Table 7. Energies of deformation, ΔE_{def}(silane) (kJ mol^{-1}) for structurally distorted silanes and GeF_4; for details see text

	ΔE_{def}		ΔE_{def}
SiH_3F (C_{3v} tp)	95.3	SiH_2F_2 (D_{2h})	207.5
SiH_3Cl (C_{3v} tp)	84.7	SiH_2Cl_2 (D_{2h})	206.3
SiH_3Br (C_{3v} tp)	78.5	SiH_2Br_2 (D_{2h})	197.4
SiH_4 [C_{3v}(tp)]	88.1	SiH_4 (D_{4h})	373.7
SiF_4 [C_{3v}(tp)]	199.2	SiF_4 (D_{4h})	261.1
GeF_4 [C_{3v}(tp)]	147.2	GeF_4 (D_{4h})	182.6
$SiCl_4$ [C_{3v}(tp)]	169.6	$SiCl_4$ (D_{4h})	252.8

values are indicated by the superscript “cc”. Differences in $\Delta H_{\mathrm{c}}^{298}$ between different complexes can subsequently be analyzed in terms of ΔE_{def}(S) vs. V^{cc}.

Lewis Bases with N or O Donor Atoms

The formation of $SiH_3X(L)$ from SiH_3X and L is more exothermic for L = NH_3 than for L = OH_2, a result that is in accordance with the n(L)−σ*(Si−X) energies already presented (vide infra), and reflects the enhanced Lewis basicity of NH_3 compared to H_2O. $\Delta H_{\mathrm{c}}^{298}$ of $SiH_3X(L)$ is more negative for X = F than for X = Cl or X = Br, and Table 6 reveals that this is due to the small ΔE_{def}, despite V^{cc} being smaller for $SiH_3F(L)$ than for $SiH_3Cl(L)$ or $SiH_3Br(L)$.

With $SiX_4(NH_3)$ on the other side, complex formation is exothermic only for X = F and even more endothermic for X = Cl than for X = H, and the differences in $\Delta H_{\mathrm{c}}^{298}$ between different X groups are much bigger than for $SiH_3X(NH_3)$. Both, ΔE_{def} and V^{cc}, are very small for SiH_4, in accordance with the long Si−N bond in $SiH_4(NH_3)$ (see Table 3). The reduced stability of $SiCl_4(NH_3)$ relative to $SiF_4(NH_3)$ can be attributed entirely to the stronger interaction between SiF_4 and NH_3 (see Table 6), with ΔE_{def} being about equal for the two complexes. As with $SiF_4(NH_3)$/$SiCl_4(NH_3)$, the increased stability of $SiF_4(py)_2$ relative to $SiCl_4(py)_2$ is due to the difference in V^{cc} and not in ΔE_{def}. It is striking that one of the “classical” silicon complexes, $SiCl_4(py)_2$,[1b] exhibits a positive $\Delta H_{\mathrm{c}}^{298}$, in contrast to the formation of *solid* $SiCl_4(py)_2$ from $SiCl_4$ and pyridine, which is distinctly exothermic. Formation of $SiH_4(py)_2$ is even less favored, but this is caused by $\Delta E_{\mathrm{def}}(SiH_4)$ being bigger than $\Delta E_{\mathrm{def}}(SiCl_4)$, while V^{cc} of $SiH_4(D_{4h})$ and $SiCl_4(D_{4h})$ with pyridine are nearly equal. This means that the different Lewis acidities of SiH_4 and $SiCl_4$ are not caused by different electron-withdrawing forces of the ligands, but are due to different ΔE_{def}.

The variable differences in $\Delta H_{\mathrm{c}}^{298}$ for penta- and hexacoordinated complexes of SiH_4 on one hand and of SiF_4/$SiCl_4$ on the other have their cause in different trends of $\Delta E_{\mathrm{def}}[SiX_4,C_{3v}(tp)]$ and $\Delta E_{\mathrm{def}}[SiX_4(D_{4h})]$ and in the different degrees of deformation of SiX_4 in $SiX_4(L)$. ΔE_{def} $[SiH_4,C_{3v}(tp)]$ is about 100 kJ mol^{-1} smaller and $\Delta E_{\mathrm{def}}[SiH_4(D_{4h})]$ about 100 kJ mol^{-1} bigger than the respective values for SiF_4 and $SiCl_4$.

Only recently, and also by means of DFT calculations, Gillespie and co-workers related the weaker Lewis acidity of BF_3 relative to BCl_3 to the higher energy that is necessary to achieve a pyramidalization of the former.[8] The authors take the greater strength of the B−F bond relative to the B−Cl bond, and ligand close-packing effects as the causes for this effect and favor them over the “classical” explanation in terms of an n(X)−p_{π}(B) interaction. In the present work, a second order perturbation analysis of $SiX_4(D_{4h})$ in an NBO basis reveals substantial stabilization for X = F and Cl (440 and 436 kJ mol^{-1} for each molecule, respectively) through an n(X)−$3p_{\pi}$(Si) interaction. In $SiF_4(py)_2$, and $SiCl_4(py)_2$, this kind of interaction is reduced to 232 and 204 kJ mol^{-1}, respectively, but is still considerably high. Due to the absence of lone pairs, this interaction cannot operate with X = H. The significantly lower $\Delta E_{\mathrm{def}}(D_{4h})$ for SiF_4 and $SiCl_4$ compared to SiH_4 cannot be due to bond strengths, as the Si−H bond is weaker than the Si−F and Si−Cl bonds, nor due to a stronger repulsion between X atoms, as H atoms are smaller and less charged than F atoms. Instead, the above mentioned n(X)−3p$_{\pi}$(Si) interaction (see Table 4), which stabilizes the deformed states of SiF_4 and $SiCl_4$, is seen to be responsible for the results outlined in Table 7.

Comparing $SiH_2X_2(py)_2$ and $SiX_4(py)_2$, ΔH_c^{298} of $SiF_4(py)_2$ is much more negative than ΔH_c^{298} of $SiH_2F_2(py)_2$, whereas ΔH_c^{298} of $SiCl_4(py)_2$ is slightly positive and ΔH_c^{298} of $SiH_2Cl_2(py)_2$ is negative (see Table 5a). Similar relations are found for $SiH_3X(NH_3)$/$SiX_4(NH_3)$ (X = F, Cl), where the formation of $SiF_4(NH_3)$ and $SiH_3Cl(NH_3)$, is much more exothermic than that of $SiH_3F(NH_3)$ and $SiCl_4(NH_3)$. Hence, SiH_2Cl_2 and SiF_4 are more Lewis acidic than SiH_2F_2 and $SiCl_4$, and SiH_3Cl and SiF_4, more acidic than $SiCl_4$ and SiH_3F. For the pyridine complexes, this order is due to $\Delta E_{def}(SiH_2X_2)$ being smaller than $\Delta E_{def}(SiX_4)$ and V^{cc} of $SiH_2Cl_2(py)_2$ bigger than that of $SiH_2F_2(py)_2$.

Considering the N and O donor complexes, V^{cc} is bigger in the hexacoordinated than in the pentacoordinated ones, which reflects the different r_e(Si−L), i.e. short Si−L bonds correspond to strong interactions and vice versa. These differences can be explained in terms of second order NBO interactions (see Table 4). In the pentacoordinated complexes, the Si−L bonds result mainly from n(L)−σ*(Si−X) interactions, while in hexacoordinated complexes, n(L)−3p$_z$(Si) interactions dominate. Due to a smaller difference in the NBO energies and a bigger overlap integral of n(L) and 3p$_z$(Si), compared to n(L) and σ*(Si−X), the second order n(L)−3p$_z$(Si) energy is considerably bigger than the n(L)−σ*(Si−X) energy.

In terms of ΔG_c^{298} (see Table 5b), none of the neutral Lewis bases NH_3, NMe_3, py, OH_2 and OMe_2 forms complexes with silanes that are thermodynamically stable under normal conditions. This is in accordance with results on some SiF_4-amine adducts which are completely dissociated in the gas phase under normal conditions.[39]

Figure 3b shows the results of a relaxed potential energy scan for $SiH_3F(NH_3)$ in which the potential energy is given as a function of r(Si−N). The curve represents a typical Morse-type potential. No barrier of activation occurs that could kinetically stabilize any thermodynamically labile complex towards dissociation or would prevent complex formation. The existence or nonexistence of this type of complex thus depends on thermodynamic factors only, with the solid state or polar environments providing additional stabilization.

A comparison of $SiF_4(NH_3)$ with $GeF_4(NH_3)$ reveals a higher thermodynamic stability of the latter (see Table 5). Approximately the same values of ΔE_{def} allow for a more enhanced distortion of GeF_4 (see Table 3), which, in turn, gives a stronger interaction with NH_3, as can be seen from V^{cc}.

F^- as Lewis Base

While NH_3, OH_2, their methyl derivatives and pyridine cannot substitute a halide or hydride from an Si center without charge separation, substitution reactions of silanes with F^- according to Equations (3a)−(3c) do not generate electric charges.

$$SiH_3X + F^- \rightarrow SiH_3F + X^- \tag{3a}$$

$$SiX_4 + F^- \rightarrow SiX_3F + X^- \tag{3b}$$

$$SiX_4 + 2\,F^- \rightarrow SiX_2F_2 + 2\,X^- \tag{3c}$$

For X = F, these reactions proceed in a thermochemically neutral manner, they are exothermic for X = Cl, Br and endothermic for X = H, in accordance with results of Gronert et al.[40]

The absolute value of ΔH_c^{298} as a function of the Lewis bases in complexes $SiH_3X(L)$, $SiX_4(L)$ and $SiX_4(L)_2$ is much bigger for L = F^- than for the neutral ligands (see Table 5). The heavier the atom X is, the more exothermic becomes the complex formation with L = F^-, $[SiH_4F_2]^{2-}$ being the only complex exhibiting positive ΔH_c^{298} and ΔG_c^{298}. All other F^- complexes are thermodynamically stable with respect to dissociation into silane and F^-.

Gutsev calculated $[SiF_6]^{2-}$ to be unstable towards dissociation into $[SiF_5]^-$ and F^-, and to exhibit a metastable octahedral geometry with respect to ionization ($[SiF_6]^{2-} \rightarrow [SiF_6]^- + e^-$, see also reference 18).[41] The thermodynamic instability of $[SiF_6]^{2-}$ is confirmed in the present study, with $\Delta H^{298} = -206.9$ and $\Delta G^{298} = -248.7$ kJ mol^{-1} for the reaction $[SiF_6]^{2-} \rightarrow [SiF_5]^- + F^-$ [B3LYP/6−311+(2d,p)//B3LYP/6−31G(d)]. Furthermore, formation of SiF_6^{2-} is not much more exothermic than that of $SiF_4(py)_2$ or $SiF_4(NH_3)_2$. The existence of SiF_6^{2-}must thus be due to intermolecular stabilization, either in the solid state or in solution.

As with $GeF_4(NH_3)$, $[GeF_5]^-$ and $[GeF_6]^{2-}$ are thermodynamically more stable than their silicon analogues. In contrast to $SiF_4(NH_3)$ and $GeF_4(NH_3)$, the degree of deformation of SiF_4 and GeF_4 in $[EF_5]^-$ and $[EF_6]^{2-}$ (E = Si, Ge) is the same. It is hence striking, that V^{cc} for $[EF_5]^-$ and $[EF_6]^{2-}$ is even more negative for E = Si, and the overall increased thermodynamic stability of $[GeF_5]^-$ and $[GeF_6]^{2-}$ results from significantly smaller values of $\Delta E_{def}(GeF_4)$ compared to $\Delta E_{def}(SiF_4)$ (see Table 6 and 7).

Table 8. ΔH^{298} for reactions according to Equations 3a−c

X =	H	Cl	Br
reaction 3a		−195.9	−241.1
3b	93.8	−212.9	
3c	162.0	−426.8	

The more negative ΔH^{298} (see Table 8) for a given reaction, the more negative is the corresponding ΔH_c^{298} (see Table 5). Notably, ΔH_c^{298} is always more negative than the corresponding ΔH^{298}, i.e. in contrast to anions with pentacoordinated carbon atoms, which represent transition states in S_N2 reactions, silanes form complexes, that are thermodynamically stable toward decomposition either into SiH_3X/SiX_4 and F^- or SiH_3F/$SiFX_3$ and X^-. With the anionic complexes, Haaland's distinction between covalent and dative bonds (see reference 22) comes to its limits. For example, the two Si−F bonds in $[SiH_3F_2]^-$ (D_{3h}) are equivalent by symmetry and the criterion of least-energy bond cleavage defines the Si−F bond that is broken first as dative, since dissociation would favorably be heterolytic, giving SiH_3F and F^-. The other one is subsequently defined as covalent, since least-energy cleavage will give SiH_3 and F instead of SiH_3^+ and F^-. Distinction between a covalent and a dative Si−F bond would thus be arbitrary. Taking $[SiH_3ClF]^-$, the first bond to be broken is either Si−F or Si−Cl, which would be defined as dative, giving either SiH_3Cl and F^- or SiH_3F and Cl^-, and leaving the other as covalent. This is an arbitrary distinction as well, but here between two nonequivalent bonds and this cannot be justified. It is suggested for such cases to extend Haaland's definition, and to define the dative bond as that whose heterolytic cleavage costs less energy, which in the present case is the Si−Cl bond. Thus, in contrast to the complexes with N/O donors, where the Si−L bond formed is the dative bond, in complexes with F^- as Lewis base, Si−Cl and Si−Br bonds become dative, as can be seen from ΔH^{298} in Table 8, which represent the enthalpy differences of the heterolytic bond cleavage [see Equations (3a)−(3c)]. It is this qualitative difference between F^- and N/O donors which is seen as the cause of the different trends of Lewis acidity outlined above.

Natural Atomic Charges

Atomic charges should indicate the ionic character of bonds in hypervalent Si compounds and its dependence on X and L. Natural atomic charges[28,29] are directly related to the eigenvalues of the density matrix expressed in terms of natural atomic orbitals and are thus more reliable than Mulliken atomic charges.[28]

The highest values for q_{Si} are always with X = F (see Table 9). q_{Si} varies little with L, if X = F and *decreases* in this case on coordination in all cases except $[SiH_3F_2]^-$. For X ≠ F, q_{Si} *increases* on coordination in most cases, and is most positive in the complex anions. An increase of charge of the central atom on coordination was previously found for $SiH_2Cl_2(py)_2$, $[SiH_4F]^-$ and $[SiH_5]^-$, but also for $[GeH_5]^-$ and $[SnH_5]^-$.[9,40] A similar relationship holds for q_X. It varies little for X = F, for which it is most negative (except for $[SiH_3XF]^-$) and it is more negative in the hypervalent than in the tetravalent silanes. Comparing $[SiX_4F]^-$ to $[SiX_4F_2]^{2-}$ and $SiF_4(NH_3)$ to $SiF_4(NH_3)_2$, q_X is more

Table 9. Natural atomic charges (a) of the Si atom, (b) of X and (c) of L (L = N for NH_3, NMe_3, py; L = O for H_2O, Me_2O; L = F for F^-).

(a)[a]

X =	H	F	Cl	X =	F	Cl	Br
SiX_4 (T_d)	0.63	2.46	1.38	SiH_2X_2 (C_{2v})	1.77	1.11	0.93
SiX_4 (D_{4h})	1.21	2.43	1.35	SiH_2X_2 (D_{2h})	1.74	1.17	0.99
SiX_4 [C_{3v}(tp)]	0.50	2.42	1.37	$SiH_2X_2(py)_2$	1.67	1.21	1.10
$SiX_4(NH_3)$	0.65	2.45	1.41	SiH_3X (C_{3v})	1.29	0.92	0.82
$[SiX_4F]^-$	0.90	2.40	1.61	SiH_3X [C_{3v}(tp)]	1.19	0.87	0.78
$SiX_4(py)_2$	0.85	2.44	1.47	$SiH_3X(NH_3)$	1.26	0.92	0.83
$[SiX_4F_2]^{2-}$	1.20	2.37	1.84	$SiH_3X(OH_2)$	1.27	0.92	0.92
				$[SiH_3XF]^-$	1.35	1.16	1.13

(b)[b]

X =	H	F	Cl		F	Cl	Br
SiX_4 (T_d)	−0.16	−0.62	−0.34	SiH_2X_2 (C_{2v})	−0.62	−0.38	−0.30
SiX_4 (D_{4h})	−0.30	−0.61	−0.34	SiH_2X_2 (D_{2h})	−0.63	−0.43	−0.34
SiX_4 [C_{3v}(tp)][c]	−0.13	−0.61	−0.34	$SiH_2X_2(py)_2$	−0.70	−0.57	−0.52
$SiX_4(NH_3)$[c]	−0.17	−0.64	−0.40	SiH_3X (C_{3v})	−0.61	−0.40	−0.32
$[SiX_4F]^-$ [c]	−0.30	−0.68	−0.49	SiH_3X [C_{3v}(tp)]	−0.66	−0.48	−0.42
$SiX_4(py)_2$	−0.29	−0.68	−0.47	$SiH_3X(NH_3)$	−0.64	−0.470	−0.41
$[SiX_4F_2]^{2-}$	−0.43	−0.73	−0.62	$SiH_3X(OH_2)$	−0.63	−0.43	−0.37
				$[SiH_3XF]^-$	−0.72	−0.79	−0.77

(c)[d]

X =	H	F	Cl		F	Cl	Br
$SiX_4(NH_3)$	−1.11	−1.15	−1.13	$SiH_2X_2(py)_2$	−0.53	−0.54	−0.54
$[SiX_4F]^-$	−0.71	−0.69	−0.67	$SiH_3X(NH_3)$	−1.12	−1.12	−1.11
$SiX_4(py)_2$	−0.50	−0.57	−0.58	$SiH_3X(OH_2)$	−0.94	−0.93	−0.93
$[SiX_4F_2]^{2-}$	−0.74	−0.73	−0.68	$[SiH_3XF]^-$	−0.72	−0.68	−0.68

[a] $SiF_4(NH_3)_2$: 2.40, $SiF_4(NMe_3)$: 2.47; $SiH_3F(NMe)_3$: 1.27; $SiH_3Cl(OMe)_2$: 0.92. – [b] $SiF_4(NH_3)_2$: −0.69; $SiF_4(NMe_3)$: −0.64; $SiH_3F(NMe)_3$: −0.64; $SiH_3Cl(OMe)_2$: −0.43. – [c] Abundance weighted average of apical and equatorial q_X. – [d] $SiF_4(NH_3)_2$: −1.13; $SiF_4(NMe_3)$: −0.59; $SiH_3F(NMe)_3$: −0.53; $SiH_3Cl(OMe)_2$: −0.58. $q_N(NH_3) = -1.11$, $q_N(NMe_3) = -0.49$, $q_N(py) = -0.45$, $q_O(H_2O) = -0.93$, $q_O(Me_2O) = -0.56$, $q_F(F^-) = -1.00$.

negative in the hexacoordinated complexes. In $SiX_4[C_{3v}(tp)]$, $SiX_4(NH_3)$ and $[SiX_4F]^-$, q_X is more negative for the apical than for the equatorial X. It is interesting to note that the reduced negative charge on the donor atom in NMe_3 compared to NH_3 (and as well in OMe_2 compared to OH_2) has little influence on q_{Si}.

For SiH_3X, SiH_2X_2 and their complexes, $q_{H(Si)}$ (not given in Table 9) becomes more negative in the order X = Br < Cl < F.

The increase in the charge difference between Si and X on complex formation in most cases gives a hint of a pronounced ionic nature of the interaction between Si and L, increasing in the order X = H < Br < Cl < F and, consequently, $SiH_3X < SiH_2X_2 < SiX_4$. In the course of the complex formation, electron density is shifted from and to the periphery of the molecule, i.e. X becomes more negatively and the H atoms of the ligands more positively charged. This shift will certainly favor intermolecular coulombic and charge-dipole interactions and hence gives a reasonable explanation for the stabilization of the otherwise unstable silane-amine complexes in polar solutions and in the solid state.

Alternative Complex Configurations: *cis* vs. *trans*

It has already been established [3d,22,42,43] that in pentacoordinated Si complexes with a trigonal bipyramidal configuration, the most stable structure has the Lewis base, i.e. the dative bond, in an apical rather than an equatorial position [*cf.* $SiF_4(NMe_3)$ vs. PF_4NMe_2 in ref.[22]]. In the present paper, $SiF_4(py)_2$ was chosen to investigate the case of *cis* (C_2) vs. *trans* (D_{2h}) configuration in distorted octahedral complexes. All known XRD structures of hexacoordinated Si complexes of the SiA_4B_2 type that are not configurationally strained, i.e. that do not contain chelating Lewis bases or the Si atom as a member of a ring system, exhibit a *trans*- rather than a *cis* configuration.[9,11−13,44,45]

Since the Si−N bond is longer in the *cis*- than in the *trans* complex, and, regarding the *cis* complex, the Si−F bonds *trans* to the Si−N bonds are shorter than the two Si−F bonds in mutual *trans* position (see Figure 4), the *trans*-effect of F is obviously stronger than that of N. The bond angles around the Si atom in *cis*-$SiF_4(py)_2$ are: $a(F^bSiF^b)$ 101.5, $a(F^aSiF^a)$ 161.7, $a(F^aSiF^b)$ 95.3 and 96.3, a(NSiN) 84.5, $a(NSiF^a)$ 82.9 and 83.5, $a(NSiF^b)$ 87.0 and 171.5° ("a" denotes the two F atoms *trans* to each other, "b" denotes the other two). In spite of the huge differences in their molecular structures, ΔH_c^{298} is surprisingly very similar for the two configurations, with a difference of only 7.6 kJ mol^{-1} in favor of the *trans* complex. The much stronger interaction due to a shorter contact distance between py and SiF_4(CG) in the *trans* complex is nearly entirely compensated by the energy of deformation, which is much bigger for the *trans* complex (285.6 kJ mol^{-1}) than for the *cis* complex (216.6 kJ mol^{-1}). Since the energy difference between the *cis* and *trans* configurations is rather small, the domination of the *trans* configuration in all SiA_2B_4 complexes in the solid state is assumed to be mainly a crystal packing effect.

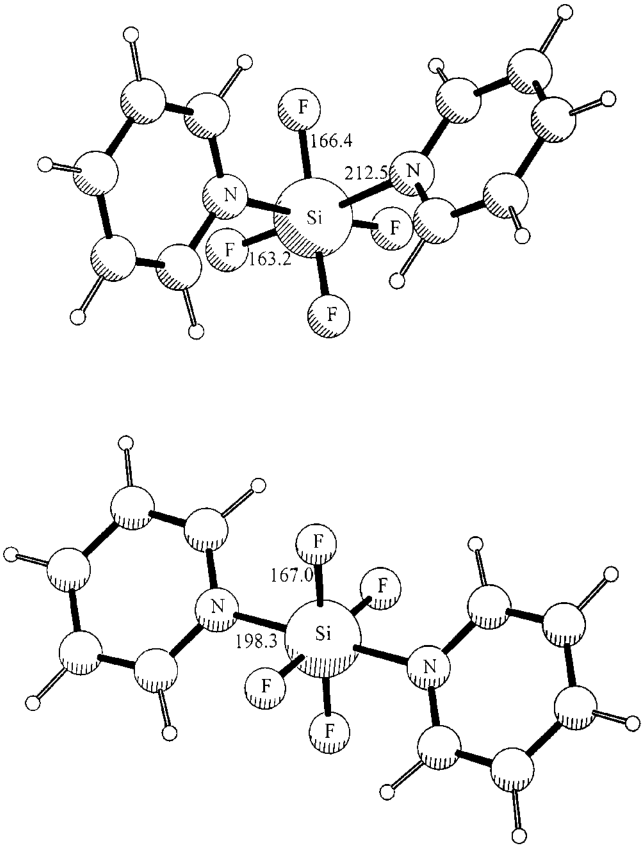

Figure 4. Molecular graphics of *cis*- (above) and *trans*-$SiF_4(py)_2$ with selected interatomic distances

Comparison of the B3LYP/6−311+G(2d,p)//B3LYP/6−31G(d) Approach to More Sophisticated Models and Experimental Results

$SiF_4(NH_3)$ is the only silane adduct with a known gas-phase structure, and it was taken as a probe for the reliability of the B3LYP/6−31G(d) geometry optimizations for the present subject.[46] Since the N and F atoms exhibit large negative charges according to NBO analyses (see Table 9), the geometry of $SiF_4(NH_3)$ was optimized with the B3LYP/6−311+G(2d,p) model to reveal the influence of diffuse functions on the molecular structure. Additionally, an MP2/6−311+G(2d,p) geometry optimization was performed to compare the MP2 and the B3LYP level. Furthermore, with $SiH_3F(NH_3)$, another comparison of the B3LYP and the MP2 model was performed.

The data in Table 10a demonstrate that r(Si−F) and $a(F^aSiF^e)$ agree very well between all theoretical models and the experiment. The Si−N bond is too long with all model chemistries, MP2/6−311+G(2d,p) giving the closest value. A good agreement between DFT- and MP2-optimized covalent bond lengths and angles is also achieved for $SiH_3F(NH_3)$.

The dative bond is far more sensitive to the chosen method of geometry optimization and the basis set than the covalent bonds are. Complex formation is estimated to be more exothermic with the MP2 method of electron correla-

Table 10. Selected parameters (a) from the experimental and theoretically optimized molecular structure of $SiF_4(NH_3)$; (b) from theoretically optimized molecular structure of $SiH_3F(NH_3)$

(a)

	B3LYP(I)[a]	B3LYP(II)[b]	MP2(I)[c]	MP2(II)[d]	exp[e]
$r(Si-F^a)$	161.2	160.9	160.9	161.2	161.2
$r(Si-F^e)$	160.8	160.5	160.3	160.8	160.8
$r(Si-N)$	214.4	213.0	210.8	214.4	209.0
$a(F^eSiF^a)$	98.1	97.7	97.7	97.7	97.7
ΔE_{form}	−33.1	−32.5	−41.3	−43.9	

(b)

	B3LYP(I)[a]	B3LYP(II)[b]	MP2(II)[d]
$r(Si-F)$	163.2	163.7	163.5
$r(Si-H)$	148.4	147.3	146.5
$r(Si-N)$	256.4	267.0	261.5
$a(HSiF)$	104.3	103.9	103.7
ΔE_{form}	−21.1	−21.4	−27.6

[a] B3LYP(I): B3LYP/6−311+G(2d,p)//B3LYP/6−31G(d). – [b] B3LYP(II): B3LYP/6−311+G(2d,p). – [c] MP2: MP2/6−311+G(2d,p). – [d] MP2/D95G(p,d) from ref.[47] – [e] Structure from ref.[7]

tion than with B3LYP, while diffuse functions have a minor influence.

Conclusion

The aim of the present work was to give a comprehensive study of the Lewis acidity of silanes and to have a closer look at its molecular origins. The method of partitioning the energy of complex formation into a deformation energy, ΔE_{def}, and an interaction energy, V, together with an analysis of the nature of the dative bond in terms of natural bond orbitals and natural atomic charges proved to be very useful for this purpose. Silanes were shown to be weak Lewis acids towards neutral N and O donor Lewis bases. The energy gained by interaction with these donor atoms is, in many cases, not much bigger, and in quite a few cases even smaller, than the energy necessary to change the geometry of the silane from the ground state to that in the complex, leading to comparably small values of ΔH_c^{298}. Since the formation of the complex reduces the number of molecules, ΔS_c^{298} of the system is negative. This fact leads to a positive value of ΔG_c^{298} for all complexes with N and O donor atoms. Only complexes of silanes with the very strong Lewis base F^- exhibit a negative standard free enthalpy of formation. A comparison of SiF_4 and GeF_4 shows that the latter is a stronger Lewis acid than SiF_4, but not due to a stronger interaction with Lewis bases, but due to a more floppy ground-state geometry, resulting in smaller ΔE_{def}. The DFT calculations in the present paper rationalize why complexes between silanes and N/O donating Lewis bases were never observed in the gas phase under standard conditions. The atomic charges, the changes in bond lengths during complex formation and, compared to N and O donors, the significantly more exothermic reactions of halosilanes with F^- suggest that the interaction between Si and the donor atoms exhibit an highly ionic character, increasing from SiH_3X to SiH_2X_2 to SiX_4 and from X = Br to Cl to F. Silanes are classified as very weak Lewis acids due to the "stiffness" of their molecular structure and only with very strong Lewis bases or stabilized by intermolecular forces in solution of the solid state, Lewis base adducts of silanes can exist at room temperature.

Experimental Section

Theoretical Methods

All calculations were performed on various servers of the Zentrum für Datenverarbeitung, Universität Mainz, using the GAUSSIAN94 software package.[23] The geometries of all molecules were fully optimized under the respective symmetry constraints using a 6−31G(d) basis set and density functional theory (DFT)[19] employing a combination of local, gradient-corrected, and exact exchange functionals according to the prescription of Becke[24] and the gradient-corrected correlation functional of Lee, Yang and Parr[25] [B3LYP/6−31G(d)] (for basis set terminology see e.g. reference 26). All stationary points were characterized by calculation of analytic force constants. With the same model chemistry, natural atomic charges were calculated and second order perturbation energies in a natural orbital basis were calculated.[27−29] Taking the B3LYP/6−31G(d) optimized geometries, single-point energies were calculated at the B3LYP level using Pople's 6−311+G(2d,p) basis set.[30] H^{298} and G^{298} were obtained from B3LYP/6−311+G(2d,p)//B3LYP/6−31G(d) energies and unscaled B3LYP/6−31G(d) thermal corrections. Using the B3LYP/6−31G(d) optimized geometries of the complexes, B3LYP/6−311+G(2d,p) counterpoise calculations were performed to correct the energy of interaction between Si and the donor atoms for the basis set superposition error (bsse).[31,32]

All thermochemical quantities (i.e. ΔE, ΔH, ΔG and V) are given in kJ mol^{-1}, all atomic distances in pm, all bond and torsional angles in degree and all charges in fractions of the elemental charge (1.609×10^{-19} C).

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[1] [1a] W. R. Trost, *Nature* **1952**, *169*, 289−290. – [1b] U. Wannagat, Z. Schwarz, H. Voss, *Z. Anorg. Allg. Chem.* **1954**, *277*, 73−88. – [1c] B. J. Aylett, *J. Inorg. Nucl. Chem.* **1958**, *5*, 292−295. – [1d] E. Schnell, *Monatsh. Chem.* **1962**, *93*, 1136−1144. – [1e] I. R. Beattie, *Quart. Rev. Chem. Soc.* **1963**, *17*, 382−405. – [1f] H. J. Campbell-Ferguson, E. A. V. Ebsworth, *J. Chem. Soc. A*, **1966**, 1508−1514; **1967**, 705−712. – [1g] U. Wannagat, K. Hensen, F. Vielberg, *Monatsh. Chem.* **1968**, *99*, 431−437.

[2] [2a] B. J. Helmer, R. West, R. J. P. Corriu, M. Poirier, G. Royo, A. de Saxce, *J. Organomet. Chem.* **1983**, *251*, 295−298. – [2b] A. R. Bassindale, T. Stout, *J. Chem. Soc., Chem. Commun.* **1984**, 1387−1389. – [2c] D. G. Anderson, A. J. Blake, S. Cradock, E. A. V. Ebsworth, D. W. H. Rankin, H. E. Robertson, A. J. Welch, *J. Chem. Soc., Dalton Trans.* **1986**, 91−95. – [2d] D. Kummer, S. C. Chaudhry, T. Debaerdemaeker, U. Thewalt,

Chem. Ber. **1990**, *123*, 945−951. − [2e] K. M; Kane, F. M. Lemke, J. L. Petersen, *Inorg. Chem.* **1995**, *34*, 4085−4091. − [2f] K. Hensen, F. Gebhardt, M. Bolte, *Z. Anorg. Allg. Chem.* **1997**, *623*, 633−636. − [2g] N. W. Mitzel, A. J. Blake, D. W. H. Rankin, *J. Am. Chem. Soc.* **1997**, *119*, 4143−4148. − [2h] P. Boudjouk, S. D. Kloos, B-K. Kim, M. Page, D. Thweatt, *J. Chem. Soc., Dalton Trans.* **1998**, 877−879. − [2i] H. H. Karsch, P. A. Schlüter, M. Reisky, *Eur. J. Inorg. Chem.* **1998**, 442−426.

[3] [3a] A. Greenberg, C. Plant, C. A. Venanzi, *THEOCHEM*, **1991**, *80*, 291−301. − [3b] M. S. Gordon, M. T. Carroll, J. H. Jensen, L. P. Davis, L. W. Burggraf, R. M. Guidry, *Organometallics* **1991**, *10*, 2657−2660. − [3c] G. I. Csonka, P. Hencsei, *J. Comput. Chem.* **1994**, *15*, 385−394. − [3d] J. M. Anglada, C. Bo, J. M. Bofill, R. Crehuet, J. M. Poblet *Organometallics* **1999**, *18*, 5584−5593.

[4] R. Tacke, D. Reichel, M., Kropfgans, P. G. Jones, E. Mutschler, J. Gross, X. Hou, M. Waeldbrock, G. Lambrecht, *Organometallics* **1995**, *14*, 251−262.

[5] [5a] S. N. Tandura, M. G. Voronkov, M. V. Alekseev, *Top. Curr. Chem.* **1986**, *131*, 99−156. − [5b] R. R. Holmes, *Chem. Rev.* **1990**, *90*, 17−31. − [5c] C. Chuit, R. J .P. Corriu, C. Reye, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371−1448.

[6] T. J. Lorenz, B. S. Ault, *Inorg. Chem.* **1982**, *21*, 1758−1761.

[7] R. S. Ruoff, T. Emilsson, A. I. Jaman, T. C. Germann, H. S. Gutowsky, *J. Chem. Phys.* **1992**, *96*, 3441−3446.

[8] B. D. Rowsell, R. J. Gillespie, G. L. Heard, *Inorg. Chem.* **1999**, *38*, 4659−4662.

[9] K. Hensen, T. Stumpf, M. Bolte, C. Näther, H. Fleischer, *J. Am. Chem. Soc.* **1998**, *120*, 10402−10408.

[10] A. J. Blake, S. Cradock, E. A. V. Ebsworth, K. C. Franklin, *Angew. Chem.* **1990**, *102*, 87−89; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 76−78.

[11] V. A. Bain, R. C. G. Killean, M. Webster, *Acta Cryst*. **1969**, *B25*, 156−159.

[12] O. Bechstein, B. Ziemer, D. Hass, S. I. Trojanov, V. B. Rybakov, G. N. Maso, *Z. Anorg. Allg. Chem.* **1990**, *582*, 211−216.

[13] C. Plitzko, G. Meyer, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1646−1650.

[14] F. Olbrich, R. J. Lagow, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1929−1932.

[15] W. C. Hamilton, *Acta Cryst.* **1962**, *15*, 353−360.

[16] Due to the presence of protic hydrogen atoms, $SiH_3X(NH_3)$, $SiH_3X(OH_2)$ (X = Cl, Br) and $SiCl_4(NH_3)$ are thermodynamically unstable with respect to the formation of di-/oligosilazanes and NH_4X (L = NH_3), or disiloxanes and HX (L = H_2O).[17] Since this reaction channel does not interfer with the subject studied, these compounds can still serve as models for dative Si−N and Si−O interactions.

[17] R. Fessenden, J. Fessenden *Chem. Rev.* **1961**, *61*, 361−388.

[18] Only a few isolated dianionic species were calculated to be stable towards a single electron oxidation according to $A^{2-} \rightarrow A^{-} + e^{-}$ (personal correspondence, Dr. Thomas Sommerfeld, University of Perugia, Italy.) and it is suspected that none of the dianions investigated herein are members of this set. This aspect was anyhow not subject of the present study.

[19] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, **1989**.

[20] T. Ziegler, *Chem. Rev.* **1991**, *91*, 651−667.

[21] In the present study, covalent and dative bonds are distinguished according to the definition of Haaland.[22] A chemical bond between two atoms is called covalent, if the lowest energy channel of dissociation leads to a homolytic cleavage, and dative if it is cleaved heterolytically.

[22] A. Haaland, *Angew. Chem.* **1989**, *101*, 1017−1032; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992−1007.

[23] GAUSSIAN 94, Revision E.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**.

[24] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652.

[25] C. Lee, W. Yang, R. G. Parr, *Phys. Rev.* **1988**, *B37*, 785−789.

[26] W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, Ab initio *Molecular Orbital Theory*; Wiley, New York, **1986**.

[27] The term "model chemistry" refers to a distinct method of calculation combined with a distinct basis set e. g. B3LYP/6−311+G(2d,p), see also reference 26.

[28] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, 83, 735−746.

[29] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899−926.

[30] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650−654.

[31] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553−566.

[32] D. W. Schwenke, D. G. Truhlar, *J. Chem. Phys.* **1985**, *82*, 2418−2426.

[33] The indices "a" and "e" refer to apical and equatorial positions in a trigonal pyramidal or a trigonal bipyramidal structure.

[34] L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd ed., Cornell University Press, **1960**.

[35] Recent ab initio investigations on complexes with dative Al→W interactions revealed bigger dissociation energies for adducts with longer bonds. See R. A. Fischer, M. M. Schulte, J. Weiss, L. Zsolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehme, S. F. Vyboishchikov, *J. Am .Chem. Soc.* **1998**, *120*, 1237−1248.

[36] *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Ed. L. Sutton, Spec. Publ. No 11 and 18, The Chemical Society, London **1958** and **1965**.

[37] H. B. Bürgi, *Perspectives in Coordination Chemistry* (Eds.: A. F. Williams, C. Floriani, A. E. Merbach), p. 1−29, Helvetica Chimica Acta, Basel, **1992**.

[38] In this respect, recently published energy calculations for coordinative Si−N interactions which were not corrected for the bsse are to be taken with care. See: H. Bock, Z. Havlas, V. Krenzel, *Angew. Chem.* **1998**, *110*, 3305−3307; *Angew. Chem. Int. Ed.* **1998**, *37*, 3163−3166.

[39] C. J. Porritt, *Chem. Ind. (London)* **1979**, 215.

[40] S. Gronert, R. Glaser, A. Streitwieser, *J. Am. Chem. Soc.* **1989**, *111*, 3111−3117.

[41] G. L. Gutsev, *Chem. Phys. Lett.* **1991**, *184*, 305−309.

[42] C. J. Marsden, *Inorg. Chem.* **1983**, *22*, 3177−3178.

[43] J. A. Deiters, R. R. Holmes, *J. Am. Chem. Soc.* **1987**, *109*, 1686−1692.

[44] H. Fleischer, K. Hensen, T. Stumpf, *Chem. Ber.* **1996**, *129*, 765−771.

[45] M. Kettner, Ph.D. Thesis, University of Frankfurt/Main, **1999**.

[46] From the experiment, an r_g structure was obtained, while ab initio and DFT geometry optimizations lead to r_e structures. Since the experiment was performed at a temperature of 3 K, r_e and r_g should not differ too much for bond lengths, with $r_g > r_e$.

[47] A. R. Rossi, J. M. Jasinski, *Chem. Phys. Lett.* **1990**, *169*, 399−404.

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