Pentacoordination at Fluoro-Substituted Silanes by Weak Lewis Donor Addition

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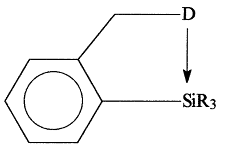
Quantum chemical calculations at the ab initio level indicate that Lewis donors such as amine or water form weak donor–acceptor complexes with fluoro-substituted silanes. The strength of the donor–acceptor formation increases with increasing degree of fluorine substitution. Amine and water form strong adducts only for tetrafluorosilane. The higher element homologues of Lewis donors, such as phosphane and sulfur dihydride, do not in essence coordinate. A considerable role in donor–acceptor formation is exerted by chelation effects which impose intramolecular interactions on functionalized ligands. The corresponding structures are explored.

Introduction

Corriu and co-workers have presented pioneering contributions in a series of experimental studies on the understanding of pentacoordination at silicon.[1−3] The results of these investigations further increased the knowledge of nucleophilic substitution at silicon.[4,5] For the extension of the coordination sphere at the silicon center aromatic ligands with a dimethylamino-functionalized side chain were mainly used, as indicated in Scheme 1. In this structure the Lewis donor is forced into close proximity to the substituted silane unit resulting in a D−A complex (D = donor, A = acceptor). Only a few species with other donor elements in the side chain are known.[5−11] Recently a structural investigation of an alkoxy-substituted pentacoordinated silicon compound has been reported (**1**, D = OCH_3)[13] (Scheme 1).



D = OR, NR_2

R = alkyl, aryl, F, OR

1

Scheme 1

Pentacoordination at silicon is usually monitored by ^{29}Si NMR spectroscopy[14] as the coupling to adjacent nuclei (^{19}F, ^{1}H) is influenced by pentacoordination.[15] This indicates that the stability of the pentacoordinated species is dictated by the electronegative fluorines at the silicon centre. Information about the varying strength of the donor-silicon interaction is also drawn from temperature-dependent NMR studies.[13] To this end an interesting 1,3-sigmatropic fluorine migration within a 2-phospha-1,3-disilaallyl derivative has been observed[16] thus indicating facile coordination at the silicon center with fluorine as a donor. One of the major questions is the magnitude of these bonding effects and how they are affected by the nature of the Lewis bases involved in the adduct formation.

Lewis bases can be classified into two categories, either as hard or soft donors, as discussed in detail in the pioneering work of Pearson et al.[17,18] In the present investigations we report quantum chemical calculations at an ab initio level which have a bearing on this problem. We will discuss the role of hard (NH_3, OH_2) and soft (PH_3, SH_2) donors for possible interaction with fluorosilanes. Fluorine atoms as substituents were chosen because they mimic best the effect of electronegative substituents attached to a silicon centre. In the experiment the coordination to a substituted silane is verified by intramolecular donor addition of an aromatic ligand functionalized with a donor side chain, e.g. compound **1**. Corresponding models will be explored in the last section of this publication. The details of the quantum chemical calculations are given in the Theoretical Section.

Results and Discussion

Qualitative Considerations

The donor−acceptor formation between an amine, phosphane, etc. and a silane is shown schematically in Scheme 2.

The parent silane possesses two sets of triply degenerate molecular orbitals (t_2 with T_d symmetry) constituted from the p-orbitals at the central silicon atom and the adjacent hydrogen atoms.[19] In addition, the s-orbital at the silicon atom forms a bonding and antibonding molecular orbital (a_1) with the neighbouring hydrogen atoms. Under the C_{3v} symmetry adopted in the donor−acceptor complex the t_2 orbitals reduce to (a_1 +e). A corresponding donor−acceptor interaction takes place by transfer of electron density from the n-orbital of the donor fragment (a_1) (lone pair

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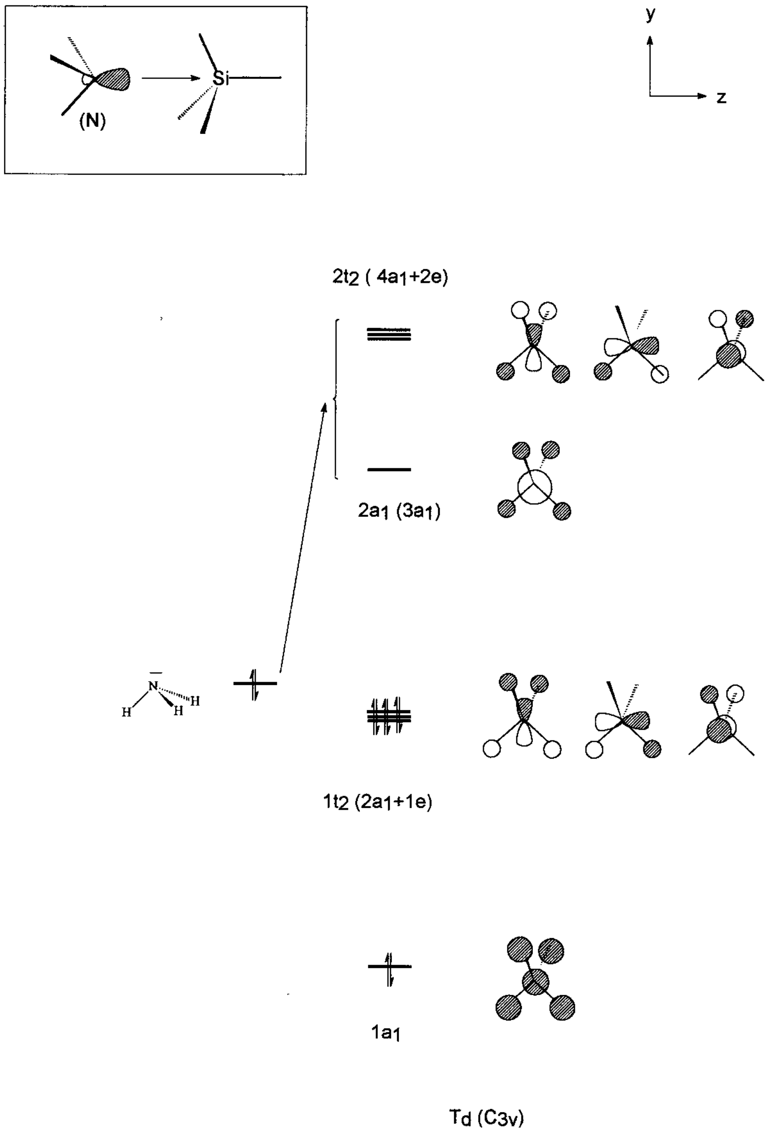


Scheme 2

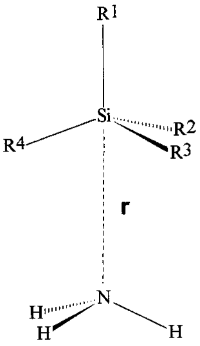
orbital at NH_3, PH_3) into the antibonding orbitals (a_1) of the silane fragment. According to second-order perturbation theory[20–22] such a donor–acceptor interaction can be assumed to increase with the lowering of the ionization potential of the donor orbital, given the same acceptor. In other words PH_3 should be a better donor than NH_3 since the ionization potential of the former (9.9 eV) is smaller than that of the latter (10.9 eV); likewise OH_2 (12.6 eV) is a poorer donor than SH_2 (10.5 eV).[21] It is equivalent to the assignment that nitrogen is more electronegative than phosphorus. Thus within the concept of Pearson's classification into hard and soft donors an amine is the harder donor than a phosphane.[23] Within the Klopman formulation of second-order perturbation theory[22] the interaction of the donor (nucleophile) and the acceptor (electrophile) is given according to Equation 1,

$$\Delta E = -\frac{Q_{nuc}Q_{elec}}{\varepsilon R} + \frac{2(c_{nuc}c_{elec}\beta)^2}{E_{HOMO(nuc)} - E_{LUMO(elec)}} \qquad (1)$$

with ε as the local dielectric constant (of the reaction medium), Q_{nuc} and Q_{elec} as the total charges at the overlapping atoms, E_{HOMO} and E_{LUMO} the molecular orbital energies of the donor (nucleophile) and the acceptor (electrophile) and ß as the overlap integral between the nucleophile and electrophile (for a detailed definition see ref.[22a]). The first term in this equation is simply the Coulombic repulsion or attraction. This term, which contains the total charge Q on each atom, is obviously important when ions or polar molecules are reacting together. The second term refers to the HOMO–LUMO interaction, as indicated schematically in the previous scheme. A priori one can differentiate between two extreme cases where either the coulombic term or the second term dominates. In the latter case one would expect that with decreasing ionization potential of the donor the adduct stability increases thus giving the opposite stability order, i.e. $OH_2 < NH_3$ for adduct formation. In general one assumes[20,21] that coulombic contributions are only important for interactions between charged species. This is not the case at hand as the Lewis donors and acceptors are neutral. From the qualitative discussion it is also clear that a possible HOMO−LUMO interaction, according to Equation (1), increases with the lowering of the LUMO energies of the silanes. This can be done by replacing the hydrogens with electronegative substituents. In this case at hand we have probed the effect on silanes successively substituted by fluorine. Such a situation is also observed experimentally,[15] where the shielding in the ^{29}Si NMR spectrum is changed by addition of amine to fluorine substituted silanes.

The Donor Adducts

In order to reveal the various factors which contribute to the overall donor-silicon stability we first determined the equilibrium structures for a selected variety of donor-adducts with NH_3, OH_2 and PH_3, SH_2 as donors, and with increasing fluorine substitution at the silicon center. In general the adducts tend to form a trigonal bipyramid, as shown in Scheme 3.



Scheme 3

The most relevant bonding parameter for the encounter complexes is given by r, the distance of the donor atom from the silicon center. Moreover, one has to differentiate between fluorine substitution at an equatorial (R^2, R^3, R^4) and/or an axial (R^1) position. The effect of substitution in both cases was investigated.

The binding energies (exothermic, in kcal/mol) of the various adducts together with the bonding parameter r (in Å) are collected in Table 1.

Table 1. Coordination of NH_3 (first entry) and OH_2 (second entry) at substituted silanes; D−A distances (in Å) and adduct energies (exothermic, in kcal/mol)

Structure	R^1	R^2	R^3	R^4	r [Å]	DZP[a]	TZP[b]
(1)	H	H	H	H	3.100	1.9	0.9
					3.264	1.9	0.9
(2)	H	F	H	H	2.839	3.6	2.2
					3.133	4.3	1.7
(3)	F	H	H	H	2.571	5.8	4.9
					2.76	4.1	3.1
(4)	H	F	F	H	2.588	4.2	2.6
					2.946	5.1	2.4
(5)	F	F	H	H	2.459	6.5	5.1
					2.748	5.6	3.6
(6)	F	F	F	H	2.275	7.1	5.2
					2.685	6.4	4.1
(7)	H	F	F	F	2.175	5.3	3.5
					2.838	4.0	2.2
(8)	F	F	F	F	2.114	10.2	8.5
					2.645	5.9	4.0

[a] MP2(fc)/6−31 g** plus zero-point vibrational energy correction. − [b] CCSD(t)/6−311+g**//MP2(fc)/6−31 g** plus zero-point vibrational energy correction, at level a).

Overall the binding energies for the addition of an amine are fairly small. They increase with increasing fluorine substitution and are at a maximum for SiF_4. A fluorine in the axial position exerts a stronger acceptor effect towards the amine than in the corresponding equatorial position (e.g., structure 3 vs. 2 in Table 1) and the resulting adducts are slightly (ca. 2 kcal/mol) more stable. This reflects the well-known tendency that electronegative substituents in a trigonal bipyramid prefer the axial rather than the equatorial position, as already well rationalized on the basis of one-electron considerations.[19] We have also probed the results on the basis of more sophisticated calculations. By this we mean single point calculations on the equilibrium geometries with the CCSD(t)/6−311+g** method. The results thus obtained (see Table 1) are similar, although the adduct energies are somewhat smaller.

Our analysis indicates fairly small adduct energies for amine and water coordination. For addition to SiF_4 the strengths of the stabilities is in the order OH_2 (4.0 kcal/mol) < NH_3 (8.5 kcal/mol) [at the TZP level, see Table 1]. The latter donor possesses a lower ionization potential than the former.[20] In order to gain a more detailed understanding we have also evaluated adduct formation for the donors PH_3 and SH_2. The results of these investigations are summarized in Table 2.

Table 2. Donor−acceptor binding energies (exothermic, in kcal/mol) of SiF_4 with PH_3 and SH_2

Donor	r [Å]	DZP[a]	TZP[b]
SH_2	3.656	1.6	2.4
PH_3	3.741	1.9	2.4

[a] MP2(fc)/6−31 g** plus zero-point vibrational energy correction. − [b] CCSD(t)/6−311+g**//MP2(fc)/6−31 g** plus zero-point vibrational energy correction, at level a).

Only the tetrafluorosilane, which exerts the strongest acceptor properties, was examined. As before the binding energies of the various donors are fairly small. The energy results indicate that the coordination ability of the tetrafluoro-substituted silane is much smaller for these two donors i.e. they are negligibly small.

On the basis of the Klopman concept[21,22] it is apparent that the electrostatic interactions [first term in Equation (1)] are not the dominant contribution to the overall stability of the resulting adducts otherwise the donor OH_2 would form a stronger adduct towards SiF_4 than NH_3, which is not the case. Since the energy contributions for the binding of the donors are rather weak a further bisection into various contributions was not attempted. The fact that the donors PH_3 and SH_2 form only very weak adducts is also in agreement with the recently explored dual-parameters equation for the stability of silylene adducts.[24] Accordingly, the resulting stability of a donor−acceptor complex depends on: (a) the donor ability (as measured by the ionization potential) and (b) the stability of a hypothetically covalent D(onor)−Si bond.[24] For the present system it means that a covalent D−Si bond is almost comparable for the series OH_2 and NH_3, or alternatively for SH_2 and PH_3. For the former two donors it is stronger than for the latter two donors, although the stabilities for all the investigated cases are fairly small.

The Chelation Effect

In the experiment the donor centre is coordinated intramolecularly to the silane unit, in structures such as **1**. The aromatic ligand exerts conformational rigidity which forces the donor fragment towards the silicon centre. This should enhance a possible donor−acceptor interaction. In order to reveal this aspect in more detail we performed quantum chemical calculations (MP2/6−31 g**) on **1** with the donors D = $-OH$, $-NH_2$, $-SH$, $-PH_2$. Only the results for the former two donor structures will be summarized here (Scheme 4).

The silicon center was substituted by three fluorine atoms which take up one axial and two equatorial positions. The substitution pattern was chosen in order to maximize the donor−acceptor interaction. For D = $-SH$ and $-PH_2$ no coordination was observed. In other words for these cases the donor function rotates away from the silicon center. In general the D−Si distances for the intramolecularly coordinated cases are shorter (N−Si 2.176, O−Si 2.441 Å) than in the corresponding adducts for bimolecular addition (N−Si 2.275, O−Si 2.685 Å) for the trifluoro-substituted cases, see Table 1). Thus on this basis the chelation effect by intramolecular coordination of the donor to the silicon center seems slightly more strongly pronounced for oxygen than for nitrogen coordination. The D−Si bond ratios for intra- versus intermolecular donor coordination are: N (2.275/2.176 = 1.046, O 2.685/2.441 = 1.100). It must be noted that the actual D−Si distances in the intramolecular coordinated complexes are dependent on the substituents (alkyl, silyl) at the donor. In addition the D−Si bond energies are rather weak and therefore also depend on the chosen computational level.[25]

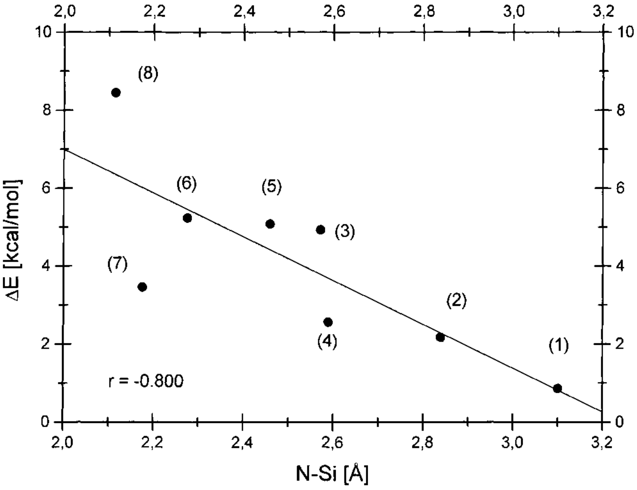


Figure 1. Linear correlation of N−Si distances (in Å) versus binding energies (negative, in kcal/mol) for amine coordination to substituted silanes

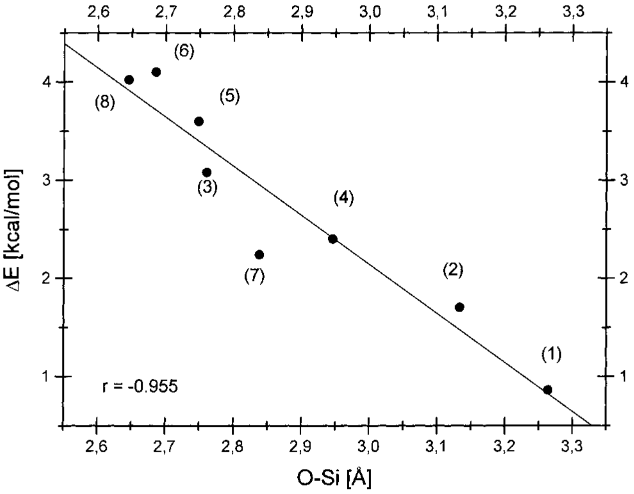


Figure 2. Linear correlation of O−Si distances (in Å) versus binding energies (negative, in kcal/mol) for water coordination to substituted silanes

To a first approximation the binding energies can be linearly related to the equilibrium bond lengths of the resulting donor−acceptor complexes. A rationale for this approach is given in the Experimental Section. A correspond-

Scheme 4

ing dependence of both quantities for amine and water addition is shown in Figure 1 (amine coordination) and Figure 2 (water coordination).

Accordingly, for both cases approximate linear relationships are apparent. It indicates that considerable changes in bond lengths (e.g. by 10%) cause only small changes in the resulting binding energies. On this basis it is evident that intramolecular coordination, such as in **1**, largely determines the actual equilibrium D−Si bond lengths, and, as we have seen, it is more pronounced for water than for amine coordination. Utilizing the linear relationship given in Figures 1 and 2 one can predict an extrapolation of the binding energies in the intramolecularly coordinated complexes **1**. They should be comparable and in the order of approx. 10 kcal/mol. Thus the binding energies are expected to be slightly larger than for the intermolecularly coordinated cases.

^{29}Si NMR Chemical Shifts

It is informative to analyze the effect of coordination on the chemical shifts of the silicon centers. We have calculated the corresponding ^{29}Si NMR chemical shifts for the cases of amine addition. A list of these values, obtained at the RHF and MP2 level of sophistication, are summarized in Table 3.

Table 3. d^{29}Si NMR shifts at RHF and MP2 level, with reference TMS

Compound	RHF[a,b]	MP2[a,b]	exp.[b]
TMS	0.0	0.0	0.0
$SiH_3^{(+)}$	280.4	303.7	(264)[c]
SiH_4	−92.3	−110.1	−93.1[d]
SiH_3F	−26.9	−24.1	−17.4[d]
SiH_2F_2	−35.3	−28.0	−28.5[d]
$SiHF_3$	−80.2	−73.7	−77.9[d]
SiF_4	−117.2	−109.0	−109.9[d]
H_4Si-NH_3	−89.1	−106.8	
$H_3SiF(eq)-NH_3$	−37.3	−35.8	
$H_3SiF(ax)-NH_3$	−63.3	−66.2	
$H_2SiF(eq)$-F(eq)$-NH_3$	−57.7	−51.0	
$H_2SiF(ax)$-F(eq)$-NH_3$	−69.9	−64.3	
HSiF(ax)F(eq)-F(eq)$-NH_3$	−112.1	−104.2	
HSiF(eq)F(eq)-F(eq)$-NH_3$	−114.0	−104.1	
SiF_4-NH_3	−145.6	−134.4	

[a] Basis set 6−311+g(2d,p). − [b] Chemical shifts relative to TMS: δ(^{29}Si) = σ(TMS) − σ(silane) [MP2 values]. σ(TMS) = 385.8 [367.2] ppm. − [c] C. Maerker, J. Kapp, P.v.R. Schleyer, in *Organosilicon Chemistry II*, Eds., N. Auner and J. Weis, VCH, 1996. − [d] Experimental values: H.C. Marsmann, *NMR Basic Principles and Progress, 17*, Springer, Berlin, **1981**.

For convenience we have also included here the values for tetramethylsilane (TMS) and the parent silyl cation. The results indicate a strong effect of electron correlation on the NMR chemical shifts only for the cases with low-lying empty orbitals, e.g., as the silyl cation, as seen by a comparison of the RHF versus MP2 values. For the other cases the computed chemical shifts at the RHF level are similar to those at the MP2 level. Is there a relationship between the changes in chemical shifts by coordination and adduct energies? In order to reveal a possible dependence between both quantities, we analyzed a linear relationship, as illustrated in Figure 3.

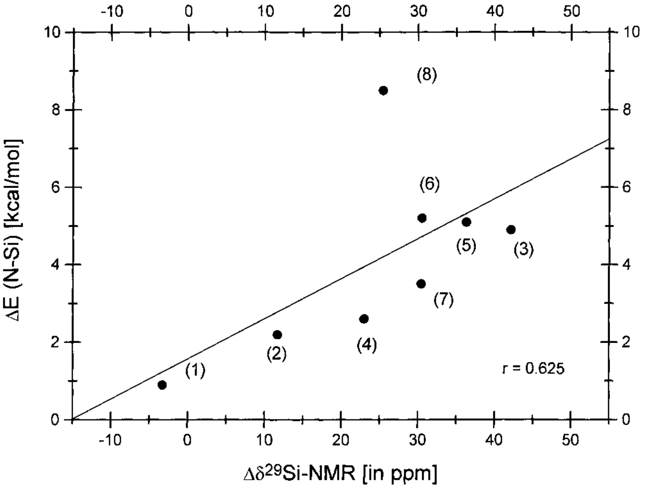


Figure 3. Linear correlation of amine adduct energies in (kcal/mol) versus differences in chemical shifts [Δδ^{29}Si = δ^{29}Si (silane) − d^{29}Si (silane−NH$_3$)]

We note that such a relationship is empirical, there is no theoretical justification for it. The difference in ^{29}Si NMR chemical shifts are given as the chemical shift of the amine-coordinated silane minus the chemical shift of the corresponding uncoordinated silane, at the MP2 level of sophistication (see Table 3). Our investigations indicate that a rough relationship between both quantities approximately exists, however the linear correlation is rather poor (r = 0.625).

Conclusions

The results of our investigations can be summarized as follows:

(1) Lewis donors, such as NH$_3$, PH$_3$, OH$_2$ and SH$_2$ form only weak donor−acceptor complexes with silanes. The effect of electronegative substituents was probed for fluorine. With increasing fluorine substitution the Lewis acidity is slightly increased.

(2) The donors NH$_3$ and OH$_2$ exert comparable donor properties, the former is slightly stronger than the latter whilst the higher element homologues PH$_3$ and SH$_2$ possess only negligible donor properties versus the substituted silane. The donor variety was studied for donation towards the best acceptor tetrafluorosilane. Within the Klopman concept one could describe the complexes by weak HOMO−LUMO interactions.

(3) For the intramolecular coordination shorter D−Si distances are observed than for intermolecular (bimolecular) coordination. Overall the resulting D−Si bonds are rather weak, in other words the chelating effects are dictating the equilibrium geometries

Experimental Section

Theoretical: The energy optimization of structures were performed using ab initio calculations with the valence double-ζ basis set, 6−31 g** of Pople et al.[26,27] Since donor−acceptor complexes are strongly determined by a superposition of covalent and ionic structures[28] all calculations were carried out at the MP2 level of optimization. Equilibrium geometries were identified by the corresponding vibrational analysis within the harmonic approximation. Further single-point calculations were done at the equilibrium geometries, utilizing the 6−311+g** basis set for first and second row elements.[29,30] This basis set has been considered of triple-zeta quality (TZP), since the 6−311 g basis set (triple split in the valence s- and p-shell) is augmented by one set of diffuse functions.[31] The basis sets utilized were augmented by a single set of polarization functions[32] at all atoms and the latter in addition by a set of diffuse functions.[33] Full details are given in the discussion. The NMR calculations were carried out with an enlarged basis set [6−311+g(2d,p)] at the optimized geometries. The isotropic shielding values were computed with the Gauge-Independent Atomic Orbital method (GIAO).[34,37] All calculations were performed with the Gaussian 98 set of programs.[38]

The Linear Bond Length-Bond Energy Relationship: Following the principal considerations of Pauling,[39] the energy of a bond as a function of the bond length is simply given by $E(r) = A - B \times \ln (r)$, where A and B are constants and r the bond length. For small changes in the bond lengths this formula can be expanded in a Taylor series, resulting in an approximate linear relationship between the bond energy and the distance. Such an approximation holds true only for small changes in bond energies, as in the case at hand.

Acknowledgments

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[1] R. J. P. Corriu, C. Guerin, *J. Organomet. Chem*. **1980**, *198*, 231−320.

[2] R. J. P. Corriu, J. C. Young, in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai and Z. Rappoport, John Wiley and Sons, New York, **1989**, 1241−1288.

[3] C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *Chem. Rev*. **1993**, *93*, 1371−1448.

[4] R. R. Holmes, *J. Am. Chem. Soc*. **1984**, *106*, 3745−3750.

[5] J. A. Deiters, R. R. Holmes, *J. Am. Chem. Soc.* **1987**, *109*, 1686−1692; *ibid.* **1987**, *109*, 1692−1696.

[6] F. P. Boer, F. P. van Remoortere, *J. Am. Chem. Soc*. **1970**, *92*, 801−807.

[7] K. D. Onan, A. T. Mc Phail, C. H. Yoder, R. W. Hillyard, *J. Chem. Soc., Chem. Commun.* **1978**, 209−210.

[8] A. A. Macharashvili, V. E. Shklover, Yu. T. Struchkov, Yu. I. Baukov, E. P. Kramarova, G. I. Oleneva, *J. Organomet. Chem.* **1978**, *327*, 167−172.

[9] E. A. Zelbst, V. E. Shkloever, Yu. T. Struchkov, Yu. L. Frolov, A. A. Kashaev, L. I. Gubanova, V. M. D′yakov, M. G. Voronkov, *Zh. Strukt. Khim*. **1981**, *22*, 82.

[10] A. A. Macharasvili, V. E. Shklover, Yu. T. Struchkov, M. G. Voronkov, B. A. Gostevsky, I. D. Kalikhman, O. B. Bannikova, V. A. Pestunovich, *J. Organomet. Chem.* **1988**, *340*, 23−29.

[11] A. A. Macharasvili, V. E. Shklover, N. Yu. Chernikova, M. Yu. Antipin, Yu. T. Struchkov, Yu. I. Baukov, G. I. Oleneva, E. P. Kramarova, A. G. Shipov, *J. Organomet. Chem*. **1989**, *359*, 13−20.

[12] T. K. Prakasha, S. Srinivasan, A. Chandrasekaran, R. O. Day, R. R. Holmes, *J. Am. Chem. Soc.* **1995**, *117*, 10003−10009.

[13] A. Mix, U. H. Berlekamp, H.-G. Stammler, B. Neumann, P. Jutzi, *J. Organomet. Chem.* **1996**, *521*, 177−183.

[14] N. Auner, R. Probst, F. Hahn, E. Herdtweck, *J. Organomet. Chem*. **1993**, *459*, 25−41.

[15] R. J. P. Corriu, C. Guérin, B. Henner, Q. Wang, *Organometallics* **1991**, *10*, 2297−2303.

[16] M. Driess, S. Rell, H. Pritzkow, R. Janoscheck, *Angew. Chem.* **1997**, *109*, 1384−1387; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 1326.

[17] R. G. Pearson, *J. Am. Chem. Soc*. **1963**, *85*, 3533−3539; R. G. Pearson, *Hard and Soft Acids and Bases Principles in Organic Chemistry*, Academic Press, New York, **1977**; R. G. Pearson, *Chemical Hardness*, Wiley-VCH, Weinheim **1977**.

[18] D. Bergmann, J. Hinze, *Angew. Chem*. **1996**, *108*, 162−176*; Angew. Chem. Int. Ed. Engl*. **1996**, *35*, 150−163.

[19] [19a] B. M. Gimarc, *Molecular Structure and Bonding*, Academic Press, New York, **1979**. − [19b] W. W. Schoeller, A. Sundermann, M. Reiher, *Inorg. Chem*. **1999**, *38*, 29−37.

[20] M. Klessinger, *Elektronenstruktur organischer Moleküle*, Verlag Chemie, Weinheim, **1982**.

[21] I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, John Wiley & Sons, London **1976**.

[22] [22a] L. Salem, *J. Am. Chem. Soc*. **1968**, *90*, 543−552; *ibid*. **1968**, *90*, 553−566. − [22b] G. Klopman, *J. Am. Chem. Soc*. **1968**, *90*, 223−234.

[23] According to Pearson[17] the hardness of the donor is defined as:

$$\lambda = \frac{1}{2}(I_p - E_a)$$

where I_p is the ionization potential and E_a the electron affinity of the donor or acceptor.

[24] W. W. Schoeller, R. Schneider, *Chem. Ber.* **1997**, *130*, 1013−1020.

[25] W. W. Schoeller, A. Rozhenko, unpublished results. A detailed discussion of this more computationally interesting aspect will be given elsewhere.

[26] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys*. **1971**, *54*, 724−728; W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257−2261.

[27] P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209−214. P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta*, **1973**, *28*, 213−222.

[28] R. S. Mulliken, *J. Am. Chem. Soc*. **1952**, *74*, 811−824; R. S. Mulliken, *J. Phys. Chem*. **1952**, *56*, 801−822; R. S. Mulliken, W. B. Person, *Molecular Complexes*, Wiley-Interscience, New York, **1969**.

[29] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639−5648.

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

[31] R. S. Grev, H. F. Schaefer III, *J. Chem. Phys*. **1989**, *91*, 7305−7306.

[32] M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265−3269.

[33] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comput. Chem*. **1983**, **4**, 294.

[34] K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc*. **1990**, *112*, 8251−8260.

[35] K. Wolinski, A. J. Sadlej. *Mol. Phys.* **1980**, *41*, 1419−1430.

[36] R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789−807.

[37] [37a] R. McWeeny, *Phys. Rev.* **1962**, *126*, 1028−1034. − [37b] F. London, *J. Phys. Radium, Paris* **1937**, *8*, 397.

[38] *Gaussian 98* (Revision A.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C.

Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanyakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian, Inc*. Pittsburgh PA, **1998**.

[39] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 3rd edition, **1960**.

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