Donor Complexes of Silylene, Germylene, and Stannylene☆

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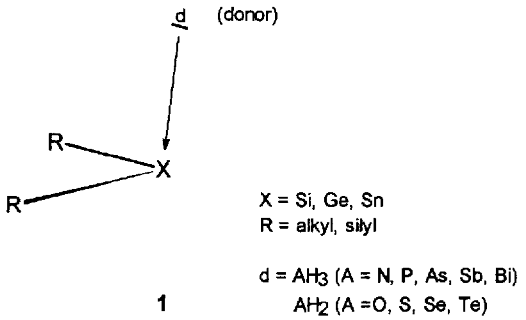
The complexes of various donor molecules, AH_3 (A = N, P, As, Sb, Bi) and AH_2 (A = O, S, Se, Te) with silylene, germylene, and stannylene ($^1A_1$ ground state) were studied by means of quantum chemical investigations at ab initio level utilizing all valence electron basis sets and relativistic corrected effective core potential methods. Accordingly, the donor molecules are weakly bound, the association energies are in the range of 15–30 kcal per mole. The exothermic energies for adduct formation, i.e., the resulting binding energies for the donor complexes, decrease in the order silylene > germylene > stannylene. The population analysis indicates for NH_3 and BiH_3 only a weak bonding towards the XH_2 fragment (X = Si, Ge, Sn) while the higher homologues (A = P, As, Sb) form ylide structures, 1.2-dipolaric in nature. The addition of two donor molecules has been studied for silylene and is much less favourable than donor mono-addition. For the donor mono-addition a dual parameter relationship between (a) the HOMO energies of the donor (n-orbital of the AH_3 unit, n, p-orbitals for AH_2) and (b) the covalent bond energies (from the literature) versus the binding energies of the donor-acceptor compounds was examined. This dual parameter equation describes satisfactorily the essential features of the stabilities of the donor-acceptor structures.

It is now well established that silylene adopts a singlet ground state ($^1A_1$), in contrast to methylene which prefers a triplet ground state ($^3B_2$)[1]. Singlet ground states have also been established for the higher element homologues, germylene[2] and stannylene[3]. Their role as intermediates in reactions have been inferred from a variety of techniques. These include kinetic and product studies as well as spectral observation in inert matrices. One possible way to stabilize such reactive entities is by addition of suitable donor molecules. Such an attempt has been studies in detail for silylenes via intermolecular[4] or intramolecular[5] ligand addition. The intramolecular coordination of Lewis bases has been successfully applied to the stabilization of silanediyl transition-metal complexes[6] as well as the isolation of doubly bonded silicon species[7,8]. The donor-acceptor adduct formation of silylenes has been investigated by recording the changes in the electronic spectrum of silylenes[4c,e]. From the viewpoint of theory a variety of high level ab initio investigations on silylene and its reactions are available[9]. Noticeable is the recent work on silylene insertion reactions into the X–H bonds (X = N, O, F, P, S, Cl)[10,11]. An investigation dedicated to bonding between silylenes and amines has been adressed[12].

In the present study we report quantum chemical calculations on the complete series of model compound **1** (X = Si, Ge, Sn; R = H, SiH_3) with various donor molecules (AH_3 = NH_3, PH_3, PF_3, AsH_3, BiH_3 and AH_2 = OH_2, SH_2, SeH_2, TeH_2).

This variety was chosen in order to get a deeper insight into the nature of possible stabilization of a silylene, germylene and stannylene unit towards stabilization with all sorts of donor molecules. On this basis a unique picture of possible donor stabilization of silylene, germylene and stannylene will emerge. The simplest representative in this series is methylenephosphorane, **2**, which has been scrutinized in detail by experiment as well as quantum chemical theory[13].

Scheme 1



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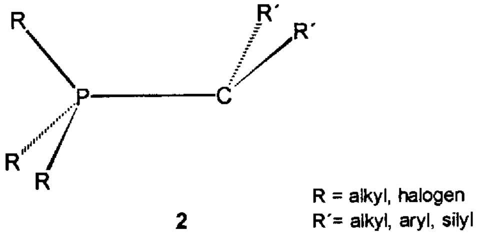
Scheme 2



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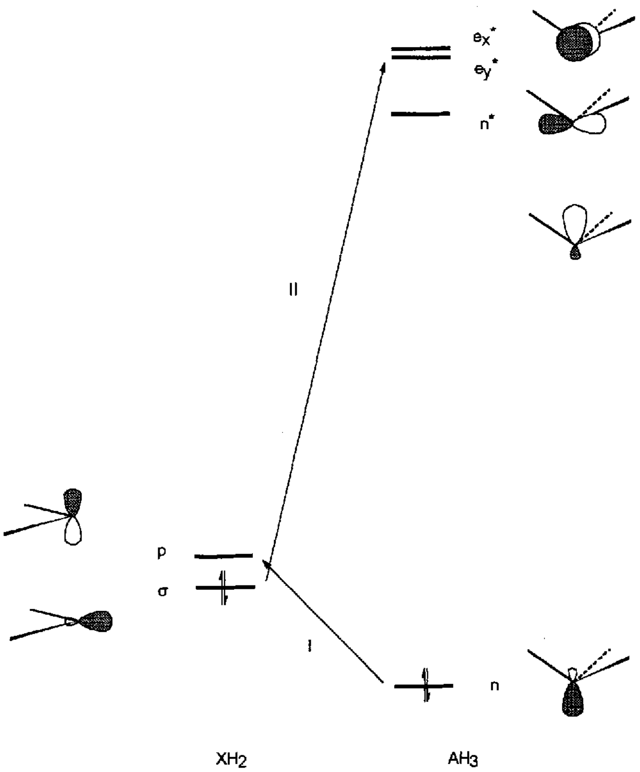
For the quantum chemical calculations we used relativistic effective core potentials with a double-ζ description of the valence space, augmented by a double set of polarization functions at the heavy atoms plus a single set of polarization functions at the hydrogen atoms (computational level M1). Furthermore, for the particular case of donor addition to silylene a further basis set (level M2) was probed, in order to analyze the importance of charge separation in the formed ylid structures on the resulting bond energies. The basis set included in addition a single set of diffuse sp-functions at the heavy atoms. Since donor-acceptor complexes are described by a mixture of covalent and ionic valence bond structures[14], a necessary prerequisite is the proper account for electron correlation in the wavefunction. All of our optimized geometries were derived at a MP2 level of optimization, in order to account for the proper balance of covalent and ionic structures in the overall wavefunction. In one case, a detailed analysis of bonding in silylenephosphorane and its substituent effects, the influence of additional f-functions in the basis set was tested. All computational aspects are given in detail in the experimental section.

Results and Discussion

1. Qualitative Considerations

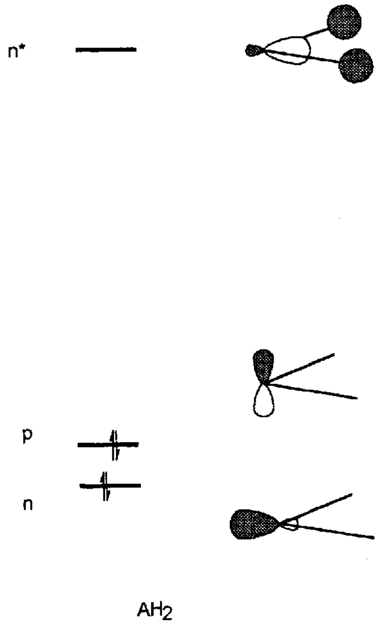
We first consider bonding in a qualitative model: the interaction of an AH_3 system (A = N, P, As, Sb, Bi) with the XH_2 (X = Si, Ge, Sn) unit. A corresponding interaction diagram is shown in Scheme 3.

Scheme 3



The frontier orbitals of the XH_2 unit are that of a carbene[15]. In the energy lowest singlet state ($^1A_1$) the electron pair resides in the σ-orbital (HOMO) while the p-orbital is the LUMO. In the AH_3 unit (A = N, P, As, Sb, Bi) the HOMO is the n-orbital[15a] while the n* refers to the LUMO. Close in energy to the LUMO is a degenerate pair of antibonding orbitals (e_x*, e_y*). These are constituted from antibonding interaction of the p-orbitals at the central atom with the hydrogen s-orbitals[15a]. Mutual orbital interaction of both fragments can take place in either one of two ways. In interaction of type I, electron density is transferred from the n-orbital of the AH_3 unit into the empty p-orbital of the carbene type species [$n(AH_3) \rightarrow p(XH_2)$]. Alternatively, electron density can be transferred via a type-II interaction, from the σ-orbital of the XH_2 unit into one component (e_y*) of the degenerate set of antibonding orbitals of the AH_3 fragment. One expects that the type-I interaction is the dominant one and hence preferentially electron density is transferred from the AH_3 fragment into the XH_2 fragment. It causes a depletion of electron density at the former fragment and an increase of electron density at the latter unit. Similar considerations apply to an AH_2 (A = O, S, Se, Te) fragment.

Scheme 4



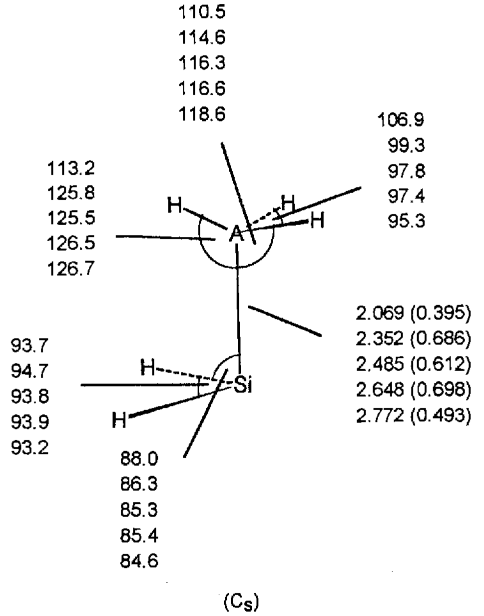
The HOMO is the p-orbital, close in energy to the n-orbital, both orbitals located at the central atom. The LUMO, n*, refers to a hybrid orbital with antibonding overlap towards the peripheral atoms[15a]. Again interaction with the XH_2 fragment is expected to occur by dominant type-I interaction [$p, n(AH_2) \rightarrow p(XH_2)$].

2. Numerical Results

The structural parameters as obtained for the silaylides were first evaluated. They are reported in Figure 1.

As a common feature of all the investigated structures, the AH_3 unit is almost perpendicular suited to the plane of the silylene unit, its n-orbital dives into the empty p-orbital. Throughout the adducts adopt C_s symmetry. With increasing atomic weight of A (N < P < As < Sb < Bi) the angle ∡(ASiH) decreases below 90°.

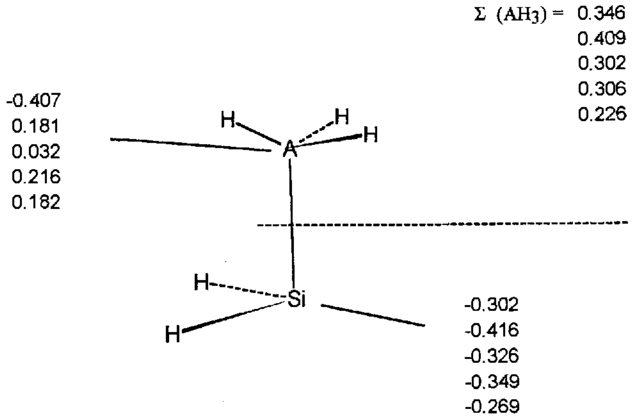
Figure 1. Structural parameters for silaylides; bond lengths are in Å and bond angles in °, from top to bottom AH_3, A = N, P, As, Sb, Bi; in parentheses are Löwdin bond orders



X-ray structure determinations on these coordinate are known for silylene. They reveal a large Si−N separation of about 2.05 Å[6b]. It may be compared with the normal Si−N distance of, about 1.72 Å calculated for silylamine[10]. The experimental findings agree with the computational observations. For the higher homologues (A = P, As, Sb, Bi) the A−Si distances refer to slightly extended single bonds. In parentheses to the given values are in addition the bond orders determined by a Löwdin population analysis[16] (given the SCF wavefunction at level M1). According to the Löwdin bond orders (Figure 1, values in parentheses) the N−Si bond is essentially weaker than the corresponding bonds with higher element homologues P to Bi. For the latter elements there is again a weakening in the apparent bond order (from Sb to Bi). The least favourable interaction between Bi and Si might be attributed to a bad match in overlap between a third row (Si) with a sixth row (Bi) element. A more quantitative analysis of computed binding energies as a function of the AH_3 (AH_2) unit is given in Section 3. For the series of donor-acceptor complexes resulting for germylene and stannylene we predict a bonding picture which is similar. However, the resulting donor-acceptor adducts are in general weaker than the corresponding adducts with silylene. For all of the investigated cases a dual parameter equation is sufficient to describe the binding energies as a function of (a) the HOMO frontier orbitals of the donors and (b) covalent bonding energies taken from the literature. The matter is analyzed in more detail in Section 3 (vide infra).

We note that all investigated compounds refer to energy minima on the hypersurfaces, as witnessed by corresponding vibrational analysis at electron correlation level (MP2) of optimization. Silylenephosphorane has been the subject of previous quantum chemical investigations[17], the results of these investigations are in perfect agreement with our findings. Further investigations of the electron density distributions within the optimized structures reveal a dominant type-I interaction. Essential features of the electron distributions are shown in Figure 2.

Figure 2. Löwdin populations (charge densities) for silylene compounds; from top to bottom A = N, P, As, Sb, Bi



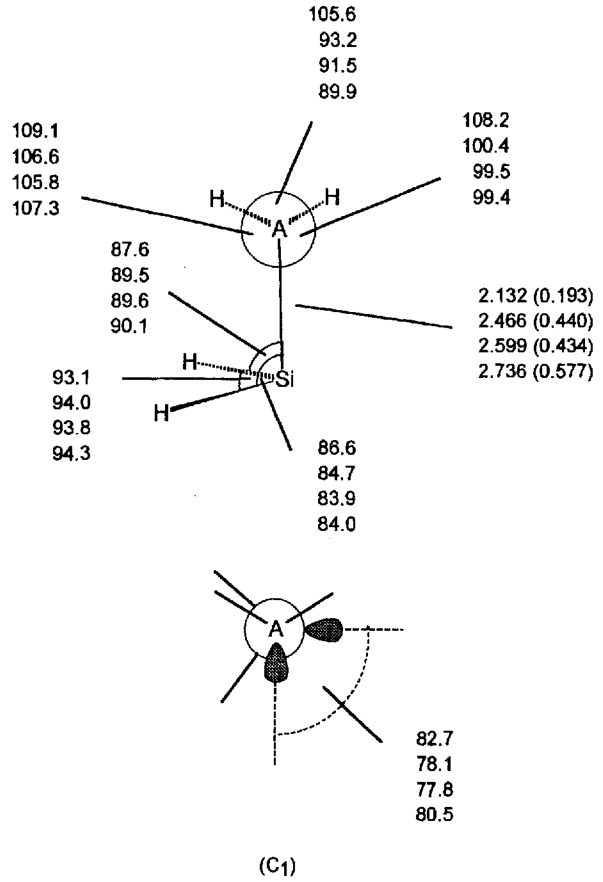
Electron density is strongly withdrawn at the AH_3 unit and accumulated at the silicon atom. The donation of electron density towards silicon is most strongly pronounced for PH_3 and most weakly for NH_3 and BiH_3. For the former case it might be attributed to the large electronegativity of N (versus Si) and for the latter to the decreased overlap; the match for overlap towards silicon becomes less favourable with increasing atomic weight of the donor element.

Next we investigated the donor-acceptor complexes of the AH_2 (A = O, S, Se, Te) unit with silylene. The resulting equilibrium geometries (C_1 symmetry at geometrical equilibrium) are collected in Figure 3.

Throughout these structures prefer a equilibrium geometry in which the lone pairs are in gauge position to each other. This in fact is not surprising since the resulting systems are isoelectronic to P_2H_4 which is known to preferentially adopt a similar geometry[18]. For addition of OH_2 to silylene the resulting Si−O bond is also rather long. The bond order (0.193, value in parentheses) reveals a very weak bond, even weaker than for NH_3 bound to silylene (0.395, Figure 1). Again for the higher element homologues (AH_2, A = S, Se, Te) a stronger bond is observed, although the resulting bonds are in essence weaker than the corresponding central bonds resulting from addition of the AH_3 fragments. The residual bonding features are similar to the previous discussed geometries (see Figure 1), the AH_2 are almost perpendicular suited to the plane spanned by the silylene unit. For the OH_2 mono-addition complex our findings agree with the recent quantum chemical work on silylene insertion into the O−H bond[11]. These studies predict a sizable energy barrier (23.4 kcal/mol) for rearrangement to the more stable silanole geometrical isomer[11].

Of particular interest are the binding energies of the adducts. They are collected in Table 1 and refer to the reaction for adduct formation, i.e. to reaction 1.

Figure 3. Structural parameters for silylene with an AH_2 fragment; bond lengths are in Å and bond angles in °; from top to bottom A = O, S, Se, Te; in parentheses are Löwdin bond orders



$$AH_3\,(AH_2) + SiH_2\,(^1A_1) \rightarrow H_3A(H_2A) \cdots SiH_2 \qquad (1)$$

The energy balances obtained for reaction 1 are all negative, in other words the adduct formations are exothermic. A listing of the energy quantities are presented in Table 1.

Table 1. Binding energies (negative, in kcal/mol) for adduct formation, at various levels of sophistication, for silylene ($^1A_1$ configuration) with various AH_3 and AH_2 units

AH_3, AH_2	M1[a]	M2[b]	M3[c]
NH_3	29.3	28.7	24.6
PH_3	24.8	24.9	20.9
AsH_3	19.9	19.9	16.3
SbH_3	20.3	20.4	17.1
BiH_3	14.3	14.0	11.3
OH_2	17.3	14.7	13.2
SH_2	16.2	15.9	12.4
SeH_2	16.0	12.5	12.5
TeH_2	18.1	18.0	14.7

[a] Method M1 = MP2/CEP-31g(2d,1p). – [b] Method M2 = M1 + 1 set of diffuse sp-functions at all atoms, geometry optimization at M1 level. – [c] Method M3 = M1 + zero point vibrational energy (ZPE) correction.

The corrections for zero-point vibrational energy (level M3) tend to decrease the binding energies. Level M2 differs from level M1 in inclusion of a further additional set of diffuse sp-functions (at all atoms). This was tested since the resulting structures are dipolaric in nature. The diffuse functions do not essentially alter the resulting binding energies already obtained at level M1. At the best computational level (M3) the resulting binding energies are in the range of 15–25 kcal/mol.

In order to ascertain our results by even better quantum chemical procedures we have further tested various other methods for the simplest representative, silylenephoshorane, ($H_3P{-}SiH_2$).

Table 2. Substituents effects for binding energies (negative, in kcal/mol), at MP2(fc)/3-21g(1d) level of sophistication

Complex	ΔE
$H_2Si\cdots PH_3$	26.1 (21.0[a]; 24.7[b]; 20.7[c]; 21.9[d]; 25.4[e])
$H_2Si\cdots PF_3$	30.0
$H_2Si\cdots PCl_3$	27.2
$(H_3Si)_2Si\cdots PH_3$	36.3
$(H_3Si)_2Si\cdots PF_3$	41.6

[a] MP2(fc)/6-31g(1d,1p). – [b] MP2(fc)/6-31g(2d,1p). – [c] MP2(fc)/6-31g(2d,1p) + zero point vibrational energy (ZPE) correction. – [d] MP4(fc)/6-31g(2d,1p)//MP2(fc)/6-31g(2d,1p). – [e] MP4(fc)/6-31g(2d1f,1p)//MP2(fc)/6-31g(2d,1p).

We also tested this case with various substitution patterns, i.e. silyl groups at silicon, and fluorines at phosphorus. As a result large binding energies are obtained, in agreement with the finding on the related methylenephosphorane[13c]. This confirms the picture of charge separation in the donor-acceptor complex. Their stabilities are further increased by a suitable combination of substituents. In the next step we record our findings on the higher element

Table 3. Binding energies (negative, in kcal/mol) for adduct formation with germylene ($^1A_1$ ground state); bond lengths are in Å

AH_2, AH_3	M1[a]	M3[b]	r(GeA)	BO[c]
NH_3	24.9	20.9	2.201	0.310
PH_3	19.7	16.3	2.484	0.570
AsH_3	16.1	13.0	2.620	0.491
SbH_3	16.8	14.0	2.774	0.575
BiH_3	12.1	9.5	2.901	0.345
OH_2	15.0	11.5	2.278	0.150
SH_2	13.6	10.3	2.632	0.353
SeH_2	13.6	10.6	2.751	0.333
TeH_2	15.3	12.3	2.883	0.444

[a] Method M1 = MP2/CEP-31g(2d,1p). – [b] Method M3 = M1 + zero point vibrational energy (ZPE) correction. – [c] Löwdin populations; bond orders at M1 level.

Table 4. Binding energies (negative, in kcal/mol) for adduct formation with stannylene ($^1A_1$ ground state); bond lengths are in Å

AH_2, AH_3	M1[a]	M3[b]	r(SnA)	BO[c]
NH_3	23.0	19.4	2.402	0.204
PH_3	15.3	12.5	2.750	0.389
AsH_3	12.7	10.2	2.878	0.306
SbH_3	13.2	10.8	3.028	0.431
BiH_3	9.5	7.4	3.160	0.219
OH_2	14.7	11.6	2.452	0.111
SH_2	11.7	9.0	2.875	0.262
SeH_2	11.9	9.3	2.994	0.225
TeH_2	12.8	10.4	3.142	0.296

[a] Method M1 = MP2/CEP-31g(2d,1p). – [b] Method M3 = M1 + zero point vibrational energy (ZPE) correction. – [c] Löwdin populations; bond orders at M1 level.

homologues germylene and stannylene. The structures and energies were obtained as before in a similar manner. The results are collected in Table 3 for germylene and in Table 4 for stannylene.

The situation is comparable to that of silylene. The ordering of stabilities is very alike to the previous case, nevertheless the overall binding energies for adduct formation are essentially smaller. This makes it evident that the adducts with higher element homologues are difficult to verify by experiment.

3. Relation to HOMO Energies

At the beginning of our report we proposed a simple model in which bonding in the adducts is rationalized in terms of an interaction diagram of a XH_2 (X = Si, Ge, Sn) with an AH_3 (AH_2) fragment. Accordingly, the donor-acceptor bond formation is constituted by a dominant type-I interaction, i.e., transfer of electron density from the n-orbital (HOMO) of the AH_3 (AH_2) unit into the empty p-orbital (LUMO) at the XH_2 unit. Thus the energy profit by mutual orbital interaction is given by equation I.

$$\delta E = \frac{\beta(AX)^2}{E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}} \qquad \text{(I)}$$

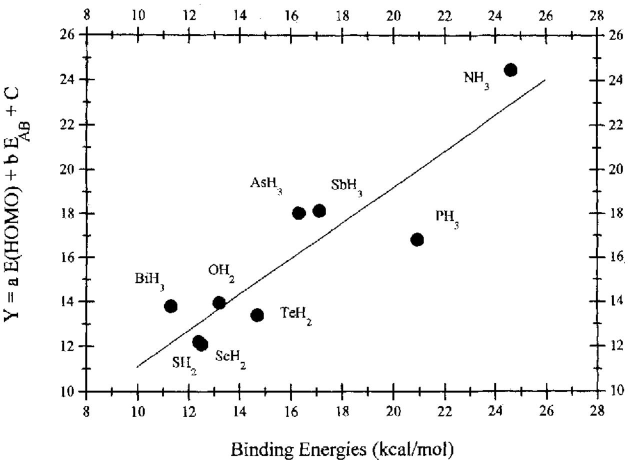
Such an interaction is within differential frontier orbital theory[19] to a first order given by additive changes in (a) the overlap integral (β_{AX}) between AH_3 (AH_2) and XH_2 and (b) the orbital energy differences between HOMO (donor) and LUMO (acceptor).

A priori, two extreme cases can be recognized. (a): The bond strength in the donor-acceptor formation is determined by the nominator in equation I. Thus the resulting binding energies would be determined by the A–X bond energies. Apparently this is not the case, e.g., the Si–O bond is rather strong (111 kcal/mol)[20] while the Si–N bond is weaker (80 kcal/mol)[20]. It is in contrast to the binding energies (Table 1) for donor-acceptor formation, e.g. NH_3 addition (24.6 kcal/mol at M3 level) results a stronger bond than OH_2 addition (13.2 kcal/mol, M3 level) towards silylene. (b): Alternatively, the adduct formation would be controlled by the denominator in equation I. Then the least electronegative donor fragment (BiH_3) should yield the largest binding energies. However, this is not the case, e.g. NH_3 forms stronger donor-acceptor adducts than BiH_3.

Consequently, the energy for donor-acceptor formation is determined by two opposing trends. According to differential orbital theory[19] the interaction energy given by equation I can be related to equation II, with E_{AX} (the approximate for the overlap integral β_{AX}) as the energy for covalent bond formation[20] and E_{HOMO} as the energy of the donor orbital. We have tested such a relationship, with bond energies E_{AX} taken from literature values[20] (see Appendix). A plot of the binding energies from the quantum chemical considerations versus the calculated values according equation II is recorded in Figure 4.

$$E \text{ (donor-acceptor)} = aE_{AX} + bE_{\mathrm{HOMO}} + c \qquad \text{(II)}$$

Figure 4. Binding energies E (negative, in kcal/mol, obtained at M3 level) versus dual parameter equation II

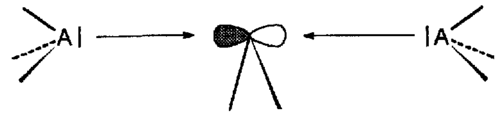


The linear relationship between both quantities (a = 0.567, b = −8.904, c = 79.490) yields a fair agreement (r^2 = 0.811). The two constants a and b have opposite sign which indicates that strong electronegative donors (e.g., OH_2) may form only weak donor-acceptor bonds. The dual parameter equation II, here in detail outlined for the addition of the donor variety to silylenes also holds true for germylene and stannylene additions (see Appendix). We have not included in our considerations the different substituted silylenephosphanes (see Table 2). For the case of the PF_3 addition it may well be possible that d-orbitals play an enhanced role in bonding. As a consequence the simple picture for donor-acceptor interaction emerging in equation II has to be modified (e.g., for the participation of different acceptor orbitals).

4. Addition of Two Donor Molecules

The addition of two donor molecules (AH_3, A = N, P, As, Sb, Bi) leads to a trigonal bipyramide **3**.

Scheme 5

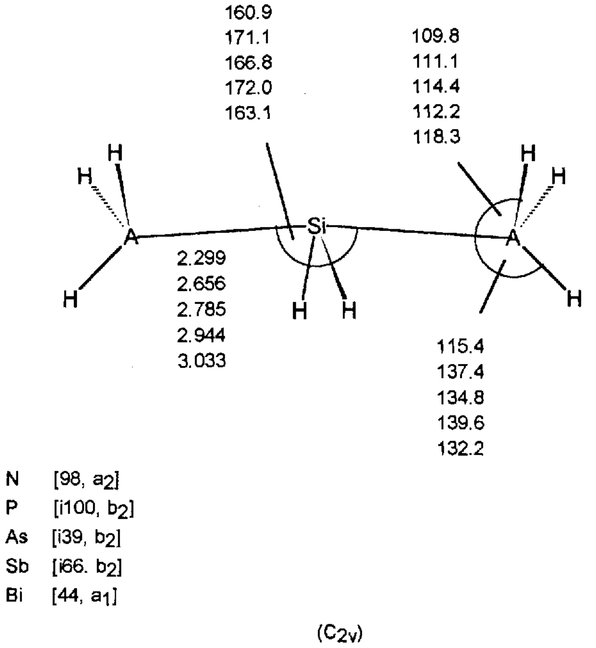


3

Since the central atom (Si, Ge, Sn) is a higher main group element its nonbonding s-orbital is strongly stereochemically active[21]. Hence, the axial bonds are comprised of a 4-electron 3-center bond, e.g., as well established for bonding in $I_3^{(-)}$[22]. Thus, one expects the axial bonds to be on average longer than the corresponding ones obtained for mono-addition of the donor molecules. We have evaluated the bonding feature for the AH_3 cases (A = N, P, As, Sb, Bi). The important geometrical features of the resulting bipyramides are collected in Figure 5.

Of the investigated species only the cases A = N and Bi are energy minima on the corresponding electronic hyper-

Figure 5. C_{2v} geometrical equilibrium geometries of trigonal bipyramidal obtained at M1 level; bond lengths are in Å units, bond angles in °; values in brackets refer to energy lowest vibrations (in cm^{-1})



surfaces. The other homologues refer to first-order saddle points (transition state geometries). Further geometry relaxation causes a slight drop in energy and the two axial bonds become unsymmetrical; e.g., for A = P and As the following situation results: P, C_{2v} (PSi = 2.656 Å) [C_1, PSi = 2.388, 3.244 Å] geometry 0.0 [−0.7 kcal/mol at MP2 level; −0.6 kcal/mol at MP2 level plus further zero-point vibrational correction (unscaled)]; As, C_{2v} (AsSi = 2.785 Å) [C_1, AsSi = 2.621, 3.015 Å] geometry 0.0 [−0.03] kcal/mol at MP2 level (without zero-point energy correction). Hence these investigations indicate that the structures with two donor molecules at the silylene unit are only transient, they refer to rather loose donor-acceptor complexes. This picture is in fact confirmed by further inspection of the energetic situation which results for addition of the second donor molecule to the mono-adduct, i.e., reaction 2.

$$H_2Si \cdots AH_3 + AH_3 \rightarrow H_3A \cdots SiH_2 \cdots AH_3 \qquad (2)$$

Table 5. Energy balances (negative, in kcal/mol) for reaction 2

AH_3	M1[a]	M3[b]
NH_3	6.5	4.8
PH_3	1.6	1.0
AsH_3	3.0	2.6
SbH_3	3.1	2.7
BiH_3	4.9	4.4

[a] Method M1 = MP2/CEP-31g(2d,1p). – [b] Method M3 = M1 + ZPE correction (unscaled).

The corresponding energy balances are listed in Table 5. In agreement with the previous discussion the donor bis-adducts are only weakly stable with regard to decomposition into mono-adducts and the corresponding AH_3 fragments.

Conclusions

The adduct formation of silylene, germylene and stannylene towards AH_3 (A = N, P, As, Sb, Bi) and AH_2 (A = O, S, Se, Te) fragments has been studied. The conclusions of our study are as follows:

Bonding in the resulting donor complexes is predominantly achieved by transfer of electron density from the n-orbital of the AH_3, AH_2 fragment into the vacant p-orbital of the XH_2 (X = Si, Ge, Sn) unit. However, a simple model for the stabilities, i.e., relationship between HOMO energies of the donor molecules and corresponding stabilities of donor-acceptor complexes, does not hold. A rather satisfactory approach to the understanding of the donor-acceptor stabilities is given within differential frontier orbital theory[19] which yields a dual parameter equation (eq. II). The binding energies are determined by two opposing trends, (a) the HOMO-LUMO interaction and (b) the bond energy as one would obtain from covalent bond formation.

In the NH_3 complexes the n → p electron transfer is rather weak enabling the addition of a second NH_3 to form a stable trigonal bipyramidal structure. However, the latter can easy undergo fragmentation into the corresponding mono-adduct plus amine. For the case of AH_2, A = P to Bi, ylide structures result. As has been shown for the case of silylenephosphorane the stabilities of the adducts are mainly product controlled. Suitable substituents which stabilize the charge separation increase the stability of the resulting ylide structure.

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Appendix

Computational Details: All of the quantum chemical calculations were carried out with the Gaussian 94 set of programs[23] and the Gamess program[24]. The relativistic effective core potentials were taken from Stevens, Basch and Krauss[25] with a double-ζ basis set for the valence space. All heavy atoms were augmented by a double set of polarization functions (6d), as provided by Schmidt[26]. To the hydrogens a single set of polarization functions was added. The choice of a set of diffuse sp-functions was also given with respect to the same authors[26]. The RHF and MP2[27] calculations were conducted by analytically determined nuclear coordinate gradients. The force constants for the effective core potential calculations were performed by the method of numerical differences. If Pople-type basis sets[28] were used, they are documented in the text. In these cases the second derivatives with respect to the nuclear coordinates were also determined analytically. – The notations of basis sets for the relativistic effective core potentials is as follows: M1 level, MP2/CEP-31g(2d,1p); M2 level, MP2/CEP-31+g(2d,1p); M3 = level M1 + zero-point vibrational energy correction (at level M1). The bond orders and atomic charges were all determined at M1 basis set level. Löwdin populations are obtained by use of Mulliken's formula after transformation of the wave function to a symmetrically orthogonal basis[16,24]. The atomic charges and populations are basis set dependent, hence, always the same computational level (M1) was used. The further addition of one set of diffuse sp-functions (M2 level) does not essentially alter the populations. – Preliminary calculations indicate that the proper geometry parameters are already obtained with a single set of d-functions at the heavy atoms. Nevertheless the elaborate valence basis sets were used. Additional f-functions do not exert considerable changes in the geometries. They were probed only in some cases, since their additional use considerably slows down the numerical calculations. A complete list of frontier orbital energies, population details (charge densities at atoms and bond orders) as well as equilibrium geometries is available on request.

Dual Parameter Equation: For the dual parameter equation II appropriate values E_{AA} were taken from the literature[20]. The heteropolar bond energies E_{AX} were compiled according to the Pauling relationship[29]: $E_{AB} = 1/2\ (E_{AA} + E_{BB}) + 23(x_A - x_B)^2$ with x_A and x_B as the electronegativity values according to the Allred-Rochow scale[30]. The used covalent bond energies and electronegativities are collected in Table 6. The HOMO energies (negative, in eV) are: (a) for AH_3 species, A = N 11.7, P 10.5, As 10.3, Sb 9.7, Bi 9.9; (b) for AH_2 species (p, n orbitals), A = O (13.7, 15.7), S (10.3, 13.6), Se (9.6, 13.0), Te (8.6, 12.0). For the AH_2 fragments the average mean of the n and p orbitals was taken as HOMO energy.

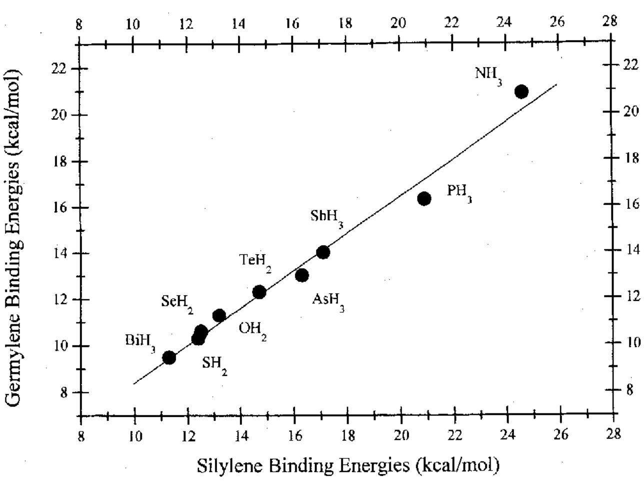
Table 6. Values for dual parameter equation II; E_{AA} are in kcal/mol

A	E_{AA}	x_A[c]
Si	54[a]	1.74
N	38[a]	3.07
P	50[a]	2.06
As	43[a]	2.20
Sb	34[a]	1.82
Bi	25[b]	1.67
O	34[a]	3.50
S	63[a]	2.44
Se	38[a]	2.48
Te	33[a]	2.01

[a] Values from ref.[20]. – [b] Values from ref.[29]. – [c] Allred-Rochow scale[30].

The dual parameter equation equally holds for donor-acceptor formation towards germylene and stannylene. Alternatively, the binding energies towards silylene correlate linear with those of germylene ($r^2 = 0.983$) and of stannylene ($r^2 = 0.804$). A plot for the former case is presented in Figure 6. These linear correlations indicate that the mechanism for donor-acceptor formation is similar in these species.

Figure 6. Binding energies of silylenes against binding energies of germylenes (in kcal/mol)



Throughout the donor-acceptor bonding in the investigated compounds may be best described as reaction of a Lewis base (AH_3, AH_2) with a Lewis acid (XH_2). For such a case the formation of a polar bond $A^{(+)}-X^{(-)}$ is determined by the following contributions[31]: (1) The covalent bond energy arises from electron sharing. It is maximum in a homopolar bond and decreases with ionicity. (2) The Madelung energy arises from the coulombic attraction of the partial charges in $A^{(+)}-X^{(-)}$. (3) Finally, the electronegativity energy is contributed from ionization energy by the donor molecule, *IE*, subtracted by the electron affinity, *EA*, of the acceptor molecule. In a more simplified manner these factors can be summarized in a Born-Haber cycle, as given by the reactions 3a and 3b (D = donor, AH_3, AH_2; A = acceptor, XH_2).

$$\mathrm{D} + \mathrm{A} \rightarrow \mathrm{D}^{(\overset{+}{\cdot})} + \mathrm{A}^{(\overset{-}{\cdot})} + IE - EA \tag{3a}$$

$$\mathrm{D}^{(\overset{+}{\cdot})} + \mathrm{A}^{(\overset{-}{\cdot})} \rightarrow \mathrm{D}^{(+)} \cdots \mathrm{A}^{(-)} + E_{\mathrm{cov}} \tag{3b}$$

Reaction 3a refers to ionization of the donor molecule followed by electron transfer to the acceptor molecule. Given the same acceptor molecule, this contribution depends on the donor ability, i.e., to a first order on its ionization potential. Within Koopman's theorem it is given by its HOMO energy. Reaction 3b corresponds to the covalent bond energy formation and can be approximated by the covalent bond energies[20]. We note that the Madelung energy is not explicitely considered here. However, the two leading terms, expressed by the reactions 3a and 3b refer to the nominator or deminator of the perturbational expression (eq. I). This arguments provides a rational for the dual parameter equation II.

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