An Alternative Way of Characterising the Bonding in Compounds Featuring Main-Group Elements and with the Potential for Multiple Bonding: On the Dissociation of Binary Main-Group Hydrides

Hans-Jörg Himmel* and Hansgeorg Schnöckel[a]

Dedicated to Prof. Dr. Hartmut Bärnighausen on the occasion of his 70th birthday

Abstract: Herein the bonding in compounds featuring main-group elements and with the potential for multiple bonding is studied theoretically by examination of their fragmentation into two fragments that still exhibit the same structure as they had in the molecule prior to dissociation. The fragments were calculated both in their electronic ground state and in an excited electronic state, in which the number of unpaired electrons is equal to the maximal number of bonds in the compounds before dissociation. The energies of the fragmentation processes (ΔE_{frag}) can be more directly linked to the bond strengths than the dissociation energies (ΔE_{diss}), because of the absence of any secondary effects like relaxation of the electronic state or of the geometry of the fragments. These relaxation energies of the fragments (ΔE_{frag}) are also studied herein. The energies derived in this work allow for an accurate comparison of the bonding properties in main-group-element hydrides. The trends of the fragmentation and relaxation energies are discussed in detail. It will be shown that the relaxation energies allow for a classification of the bonds ("classical" σ and π bonds or donor–acceptor interactions), while the fragmentation energies are good quantitative measures for the total bond strength. Similar calculations are on the way to explore the bonding in systems in which the hydrogen atoms are replaced by organic groups or halogen atoms.

Keywords: bond energy · dissociation energy · fragmentation · main-group elements · multiple bonds

Introduction

In recent years several new compounds containing heavier main-group elements and with the potential for multiple bonding between these elements were characterized.[1] The increasing accessibility of experimental information about these species gave the incentive to explore in more depth the possibility of multiple bonding between heavier main-group elements.[1] However, the simple concept of single, double, or triple bonds proved to be difficult if not impossible to apply to most of these compounds. Thus an analysis of compounds such as $Na_2[Ga_2R_2]^{2-}$ ($[Ga_2R_2]^{2-}$ is formally valence-isolelectronic to acetylene),[2] R_2NGaR_2, or R_2PBR_2 (being formally valence-isoelectronic to ethylene),[1] which have all been recently synthesized and characterized (R being a sterically demanding organic group), reveals that the bonding between the main-group elements in these compounds is not as straightforward to describe. For example, recent studies suggest that the alkali-metal ions in $Na_2[Ga_2R_2]$ are involved to a large extent in the bonding and, therefore, these compounds are better described as "Na_2Ga_2 cluster" compounds.[3, 4] The presence of the Na ions in $Na_2[Ga_2R_2]$ also has consequences on the reactivity. This is evident when the heat of hydrogenation for this compound is compared with that of the hypothetical free $[RGaGaR]^{2-}$ ion. Calculations predict an enthalpy of 116 kJ mol^{-1} for Equation (1), but only 67 kJ mol^{-1} for Equation (2), indicating that the Na^+ ions modify the reactivity of these species. Thus the expression "triple bond", which has been used for the Ga–Ga interaction, is somewhat misleading. Recently we have suggested to use the expression $[(6-x)e\,2c]$ bond for these kind of systems.[4] In this notation $(6-x)$ electrons are engaged in a two-center bond and x is a parameter that has to be specified for each molecule.

Another example is provided by compounds of the type R_2NGaR_2, which feature a strong, short Ga–N bond, but with a significant ionic contribution so that the expression double bond does not describe the bond accurately.[1, 5, 6] The same holds for the P–B bond in R_2BPR_2 compounds.[1, 6, 7] The structures of these compounds deviate also from the ones of linear HCCH or planar H_2CCH_2, and the change of structures might already decrease the chances for optimal π–π interaction.

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[a] Dr. H.-J. Himmel, Prof. Dr. H. Schnöckel
Institut für Anorganische Chemie der Universität Karlsruhe
Engesserstr., Geb. 30.45, 76128 Karlsruhe (Germany)
Fax: (+49) 721-608-4854
E-mail: himmel@chemie.uni-karlsruhe.de

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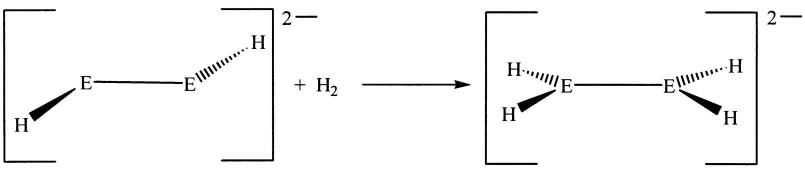

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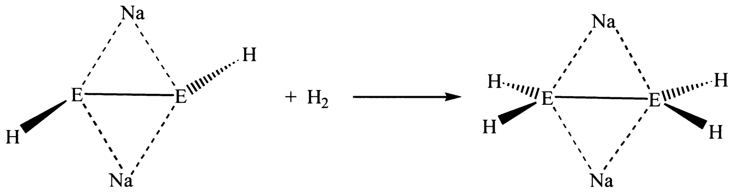

(2)

Finally, very lately several new compounds formally valence isoelectronic to ethylene or even acetylene of the heavier Group 14 elements have been reported for the first time experimentally. Power et al. have synthesized and characterized by x-ray crystallography the germanium[8] and tin[9] analogues of an alkyne containing sterically demanding aryl groups. Wiberg et al. accumulated NMR (and mass spectrometric) evidence for the formation of the disilyne $R^{*}_{2}HSi\text{-}SiSi\text{-}SiHR^{*}_{2}$, R* being Si*t*Bu$_3$.[10]

In the past, the homolytic dissociation energies were used as one possible and, most importantly, experimentally verifiable route to probe the bond strengths.[11] However, the comparison of experimentally determined dissociation energies of homologues is severed by relaxation effects (electronic states and/or geometries) of the fragments formed in these processes. These relaxation energies are negative quantities and, therefore, estimates on the basis of dissociation energies tend to underestimate the actual bond strengths. Herein, we have studied fragmentation into two fragments that exhibit the same structure which they had in the compound prior to fragmentation. Although our theoretically derived fragmentation energies (ΔE_{frag}) appear at first glance to be difficult to verify experimentally, there can be no doubt that experiments can be realized, in principle, in which the fragmentation occurs on such a short timescale such that the fragments do not have the chance to relax into their favored geometry and electronic state. In fact electronic quenching is sometimes so inefficient (being often spin-forbidden) that there is already a whole range of known fragmentation processes which result in the formation of fragments in excited electronic states.[12]

Our approach has some similarities to the ones described in previous works, especially of Jacobsen and Ziegler.[13] These authors differed between the preparation energy (ΔE_{prep}) of the two fragments, and the "bond snapping" energy (ΔE_{snap}). The term ΔE_{prep} contains an electronic and a geometric component, and can be compared with the relaxation energy ($\Delta E_{\mathrm{relax}}$) defined and discussed herein. Then ΔE_{snap} can be compared with the fragmentation energy (ΔE_{frag}) of our work. The authors also analyzed ΔE_{snap} in detail, which can be expressed as the sum of electrostatic, exchange, or "Pauli" repulsion, and attractive orbital interaction energies. However, Jacobsen and Ziegler restrict themselves to a discussion of Group 14 element composites. In contrast, our discussion includes molecules of Group 13, 14, and 15 elements. The differences in the trends found for the groups will be compared and discussed herein. Especially an analysis of the Group 13 element compounds is of considerable interest in the light of the newly synthesized species. Additionally, the CCSD(T) method applied in our studies is generally believed to give more accurate energies than the methods used in previous studies of this kind.

Although most of the hydrides addressed in this work have been characterized experimentally in one way or another, some of them are extremely unstable and can only be stabilized in inert gas matrices. Otherwise, the replacement of hydrogen atoms by bulky organic groups is the only way to get access to similar species on a preparative scale. In these compounds the bonding certainly can be different to the one in the hydrides. Therefore calculations are on the way to explore the bonding in systems in which the hydrogen atoms are replaced by organic groups or halogen atoms. However, herein, as a first step, we concentrate on the hydrides. The results will show that the fragmentation energies calculated for the hydrides are good quantitative measures of the bond strength, which deviates significantly from the dissociation energy.

Computational Methods

Calculations by means of the CCSD(T) and hybrid-DFT (B3LYP) methods in combination with a 6-311 + G(df,p)-type basis set were performed with the aid of the GAUSSIAN 98 program package.[14] The molecules were firstly optimized by using the B3LYP method. In a second step single-point calculations for the molecules in their optimized geometries were performed by using the CCSD(T) method to get more accurate energies. Then, the molecules were divided into two fragments and the energies of these fragments calculated again by using CCSD(T) and B3LYP methods. In these calculations, the geometry was kept as it was prior to fragmentation. Calculations were performed for the fragments in their electronic ground state and in the excited state in which the number of unpaired electrons corresponded to the maximum number of bonds between the two fragments prior to fragmentation. Finally, the fragments were allowed to relax into their electronic ground state and energy-minimum geometry and the energies of these structures were again calculated by using B3LYP and CCSD(T) methods.

Results and Discussion

Scheme 1 is designed to illustrate the difference between the fragmentation energies (ΔE_{frag}) studied herein and the homolytic dissociation energies (ΔE_{diss}), which have been generally determined previously. Note that ΔE_{diss} is defined here as an energy and *not* as an enthalpy.[11] The homolytic fragmentation energy (ΔE_{frag}) as defined herein, is the energy that is needed to separate the two groups "Frag" without

$$\begin{tikzcd}
& \mathrm{Frag} + \mathrm{Frag} \arrow[dr, "2\,\Delta E_{\mathrm{relax}}"] & \\
(\mathrm{Frag})_2 \arrow[ur, "\Delta E_{\mathrm{frag}}"] \arrow[rr, "\Delta E_{\mathrm{diss}}"'] & & 2\ \mathrm{Frag}_{\mathrm{relax}}
\end{tikzcd}$$

Scheme 1.

changing their structure and with a number of unpaired electrons equal or less than the expected number of bondlike interactions ["classical" bonds (meaning that both fragments contribute one electron to the bonding interaction) or donor–acceptor bonds] between the two "Frag" groups in the compound $(\mathrm{Frag})_2$. The homolytic dissociation energy (ΔE_{diss}) is here defined as the energy difference between the $(\mathrm{Frag})_2$ molecule in its global energy minimum structure and the two "Frag" groups, also in their electronic ground state and in their global energy minimum. The relaxation energy ($\Delta E_{\mathrm{relax}}$) then is half of the difference between the fragmentation and the dissociation energy.

$$\Delta E_{\mathrm{frag}} = \Delta E_{\mathrm{diss}} - 2\,\Delta E_{\mathrm{relax}}$$

It is clear that $\Delta E_{\mathrm{relax}}$ should generally be a negative quantity, since the fragmentation energy is expected to be larger than the dissociation energy. The ΔE_{frag} term should be a much better quantitative measure of the bond strength in Frag–Frag than ΔE_{diss}. The term $\Delta E_{\mathrm{relax}}$ is informative if the reasons for differences in the bonding between homologues should be analyzed, because it is the energy that is needed to "prepare" the two fragments for bonding (see below). Our approach has some similarities with the Carter–Goddard–Malrieu–Trinquier (CGMT) model,[15] which also links the singlet–triplet energy difference of the fragments with the interaction between the two fragments prior to fragmentation. However, this model considers the fragments in their energy minimum structure, and not in a structure similar to the one they had prior to fragmentation. We will see that this is an important difference. It will be shown in the following that the geometry relaxation can be associated with energies as high as $2 \times 56 = 112\ \mathrm{kJ\,mol^{-1}}$ and, therefore, cannot be ignored. For example, the difference between triplet GeH_2 in its non-optimized geometry and singlet GeH_2 in its global energy minimum structure amounts to as much as $116.8/98.8\ \mathrm{kJ\,mol^{-1}}$. These energy differences are included in the relaxation energies, $\Delta E_{\mathrm{relax}}$, in which relaxation means optimization of the geometry or of both the electronic state and the geometry. Figure 1 shows as example the fragmentation, relaxation and dissociation energies for Si_2H_4. From this representation, it is clearly visible that there is a significant difference between the fragmentation and the dissociation energies, and that relaxation of the geometry is a process that has to be taken account of.

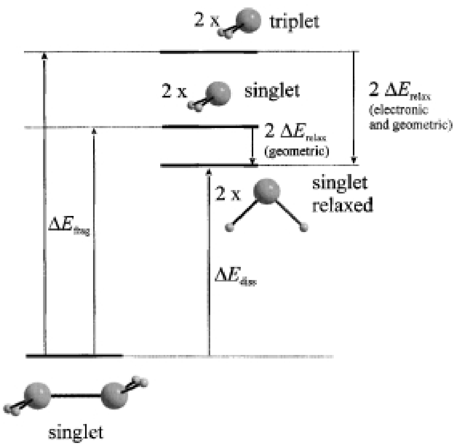

Figure 1. Energy scheme for the fragmentation of Si_2H_4 into two singlet or two triplet SiH_2 fragments, which are relaxing afterwards into the global energy minimum structure of SiH_2 (singlet).

In some cases the molecules, the fragmentation of which are studied here, are not the lowest energy isomers. Thus, of the compounds of Group 13 elements, Al_2H_2 and Ga_2H_2 prefer the doubly-hydrogen-bridged isomers $\mathrm{Al}(\mu\text{-H})_2\mathrm{Al}$, $\mathrm{Ga}(\mu\text{-H})_2\mathrm{Ga}$, which were recently generated and characterized in matrix isolation experiments.[16, 17] However, it is questionable whether these isomers exhibit significant E–E interactions (E = Al or Ga). Therefore we concentrate herein on the *trans*-bent isomers HEEH and, for comparison with HBBH, the linear HEEH species, the latter exhibiting triplet electronic ground states, like HBBH.[18, 19] REER species (E = Al or Ga, R being a sterically demanding organic group) should, however, have their global energy minimum in the *trans*-bent form. The energy differences between the *trans*-bent singlet isomer and the linear triplet form amount to 49.6 and $72.7\ \mathrm{kJ\,mol^{-1}}$ for E = Al and Ga, respectively (for calculations with B3LYP). As to E_2H_4 (E = Al or Ga), several isomers were calculated to lie very close in energy. The most stable isomers seem to have the saltlike structures $\mathrm{Al^+[AlH_4]^-}$ and $\mathrm{Ga^+[GaH_4]^-}$,[20, 21] but there is no hope for a covalent Ga–Ga interaction in these compounds. In these compounds, the E^+ ion is placed close to one of the faces of the EH_4^- tetrahedron (E = Al or Ga). Therefore we have considered herein only the H_2AlAlH_2 and H_2GaGaH_2 isomers with D_{2d} symmetry. In the case of B_2H_4, the D_{2d} symmetric isomer apparently is the global energy minimum structure, although the planar D_{2h} symmetric structure has an energy very close by.[22] However, up till now the isomers of Al_2H_4 and Ga_2H_4 have eluded detection in experiments. In the case of Group 14 compounds,[23] for Si_2H_4 and Ge_2H_4 both the global energy minimum isomer with C_{2h} symmetry and the planar D_{2h} symmetric forms were considered. The D_{2h} form, being a saddle point rather than a local energy minimum on the potential energy curve (and therefore being not an isomer), has an energy 2.7/7.6 and $16.7/36.2\ \mathrm{kJ\,mol^{-1}}$ [values quoted in the order B3LYP/CCSD(T)] higher than the C_{2h} isomer for Si_2H_4 and Ge_2H_4, respectively. The change of symmetry from C_2H_4 to Si_2H_4 and Ge_2H_4 can also be explained by a second-order Jahn–Teller effect, which allows orbital mixing for a nonplanar geometry. In the case of Si_2H_2 and Ge_2H_2, the lowest energy isomers exhibit a "butterfly" shape with C_{2v} symmetry. However, we have only looked at the fragmentation of the *trans*-bent isomers (C_{2h} symmetry)[24] and the linear forms ($D_{\infty h}$ symmetry), the latter one being a saddle point rather than a local minimum on the potential-energy curve.

For these two forms, we have calculated energy differences of as much as 85.4/97.9 and 130.1/121.1 kJ mol^{-1} [values quoted in the order B3LYP/CCSD(T)] for Si_2H_2 and Ge_2H_2, respectively. Finally, for the hydrides of Group 15 elements, we have considered in all cases the global energy minimum structures, since they all exhibit a direct and covalent E–E bond (E = N, P or As).

Tables 1 and 2 (below) include the fragmentation and relaxation energies for several main-group hydrides of Group 13, 14, and 15 elements. In the following, the trends of both the fragmentation energy and the relaxation energy will be discussed in turn.

Table 1. Fragmentation energies ΔE_{frag} [kJ mol^{-1}] for the compounds considered in this work.

Compound optimized	Symmetry	d(E–E) [Å]	Fragment nonoptimized	ΔE_{frag} B3LYP	ΔE_{frag} CCSD(T)
H_3CCH_3 (GM)	D_{3d}	1.5287	H_3C (doublet)	461.7	476.1
H_3SiSiH_3 (GM)	D_{3d}	2.3531	H_3Si (doublet)	308.2	329.3
H_3GeGeH_3 (GM)	D_{3d}	2.4390	H_3Ge (doublet)	286.5	295.4
H_2CCH_2 (GM)	D_{2h}	1.3263	H_2C (triplet)	774.5	762.8
	D_{2h}	1.3263	H_2C (singlet)	875.4	864.9
H_2SiSiH_2 (GM)	C_{2h}	2.1685	H_2Si (triplet)	427.7	441.0
	C_{2h}	2.1685	H_2Si (singlet)	313.9	331.8
H_2SiSiH_2	D_{2h}	2.1385	H_2Si (triplet)	422.3	430.2
	D_{2h}	2.1385	H_2Si (singlet)	332.2	343.9
H_2GeGeH_2 (GM)	C_{2h}	2.2976	H_2Ge (triplet)	420.9	405.1
	C_{2h}	2.2976	H_2Ge (singlet)	227.6	243.2
H_2GeGeH_2	D_{2h}	2.2208	H_2Ge (triplet)	409.5	375.4
	D_{2h}	2.2208	H_2Ge (singlet)	282.4	277.0
HCCH (GM)	$D_{\infty h}$	1.1981	CH (doublet)	985.5	974.7
	$D_{\infty h}$	1.1981	CH (quartet)	1149.6	1087.5
HSiSiH	C_{2h}	2.1045	SiH (doublet)	244.6	282.4
	C_{2h}	2.1045	SiH (quartet)	602.5	588.8
HSiSiH	$D_{\infty h}$	1.9705	SiH (doublet)	165.1	189.2
	$D_{\infty h}$	1.9705	SiH (quartet)	520.1	492.5
HGeGeH	C_{2h}	2.2176	GeH (doublet)	200.1	219.7
	C_{2h}	2.2176	GeH (quartet)	611.7	554.7
HGeGeH	$D_{\infty h}$	2.0522	GeH (doublet)	84.0	112.6
	$D_{\infty h}$	2.0522	GeH (quartet)	491.1	440.7
H_2BBH_2 (GM)	D_{2d}	1.6269	H_2B (doublet)	466.1	461.8
H_2BBH_2	D_{2h}	1.7418	H_2B (doublet)	400.8	409.4
H_2AlAlH_2	D_{2d}	2.5916	H_2Al (doublet)	248.8	271.2
H_2AlAlH_2	D_{2h}	2.6185	H_2Al (doublet)	241.7	263.5
H_2GaGaH_2	D_{2d}	2.4695	H_2Ga (doublet)	260.0	261.7
H_2GaGaH_2	D_{2h}	2.5194	H_2Ga (doublet)	247.0	252.9
HBBH (triplet, GM)	$D_{\infty h}$	1.5068	HB (singlet)	511.0	449.6
	$D_{\infty h}$	1.5068	HB (triplet)	719.2	691.5
HAlAlH	C_{2h}	2.6726	HAl (singlet)	64.9	–[a]
	C_{2h}	2.6726	HAl (triplet)	427.1	–[a]
HAlAlH (triplet)	$D_{\infty h}$	2.3034	HAl (singlet)	24.3	27.0
	$D_{\infty h}$	2.3034	HAl (triplet)	378.8	380.9
HGaGaH	C_{2h}	2.6197	HGa (singlet)	56.5	57.3
	C_{2h}	2.6197	HGa (triplet)	476.4	440.8
HGaGaH (triplet)	$D_{\infty h}$	2.2282	HGa (singlet)	4.9	–[a]
	$D_{\infty h}$	2.2282	HGa (triplet)	410.3	388.9
H_2NNH_2	C_2	1.4786	H_2N (doublet)	277.8	289.4
H_2PPH_2	C_2	2.2692	H_2P (doublet)	223.7	232.5
H_2AsAsH_2	C_2	2.4897	H_2As (doublet)	202.0	204.4
HNNH	C_{2h}	1.2369	HN (singlet)	940.5	894.5
	C_{2h}	1.2369	HN (triplet)	521.1	519.3
HPPH	C_{2h}	2.0409	HP (singlet)	592.1	574.6
	C_{2h}	2.0409	HP (triplet)	327.0	330.3
HAsAsH	C_{2h}	2.2567	HAs (singlet)	532.7	493.5
	C_{2h}	2.2567	HAs (triplet)	283.7	267.7

[a] CCSD(T) calculation failed.

Table 2. Relaxation energies ΔE_{relax} [kJ mol^{-1}] (negative values) and structural details (bond lengths in Å, bond angles in °) for the fragments formed from fragmentation of the hydrides considered in this work and with the potential for two bonds between the elements under consideration

Fragment	Optimized species	ΔE_{relax} B3LYP	ΔE_{relax} CCSD(T)
CH_3 (doublet)	CH_3 (doublet)	39.4	37.6
C–H 1.0935, H-C-H 107.5°	C–H 1.0803, H-C-H 120°		
SiH_3 (doublet)	SiH_3 (doublet)	19.3	20.0
Si–H 1.4870, H-Si-H 108.5°	Si–H 1.4710, H-Si-H 120°		
GeH_3 (doublet)	GeH_3 (doublet)	20.5	20.7
Ge–H 1.5382, H-Ge-H 108.4°	Ge–H 1.5173, H-Ge-H 120°		
CH_2 (singlet)	CH_2 (triplet)	63.8	62.4
C–H 1.0848, H-C-H 116.4°	C–H 1.0795, H-C-H 135.3°		
CH_2 (triplet)	CH_2 (triplet)	13.4	11.3
SiH_2 (singlet, from C_{2h} Si_2H_4)	SiH_2 (singlet)	29.2	25.4
Si–H 1.4821, H-Si-H 112.3°	Si–H 1.5271, H-Si-H 91.5°		
SiH_2 (triplet, from C_{2h} Si_2H_4)	SiH_2 (singlet)	86.1	80.0
SiH_2 (singlet, from D_{2h} Si_2H_4)	SiH_2 (singlet)	39.7	35.2
Si–H 1.4763, H-Si-H 115.7°	Si–H 1.5271, H-Si-H 91.5°		
SiH_2 (triplet, from D_{2h} Si_2H_4)	SiH_2 (singlet)	84.7	78.4
GeH_2 (singlet)	GeH_2 (singlet)	20.2	17.9
Ge–H 1.5445, H-Ge-H 108.0°	Ge–H 1.5973, H-Ge-H 90.8°		
GeH_2 (triplet)	GeH_2 (singlet)	116.8	98.8
GeH_2 (singlet, from D_{2h} Ge_2H_4)	GeH_2 (singlet)	55.9	52.8
Ge–H 1.5243 , H-Ge-H 116.1	Ge–H 1.5973, H-Ge-H 90.8°		
GeH_2 (triplet, from D_{2h} Ge_2H_4)	GeH_2 (singlet)	119.5	102.0
BH_2 (doublet, for D_{2d} B_2H_4)	BH_2 (doublet)	7.2	6.5
B–H 1.1971, H-B-H 115.7°	B–H 1.1872, H-B-H 129.7°		
AlH_2 (doublet, for D_{2d} Al_2H_4)	AlH_2 (doublet)	0.4	0.3
Al–H 1.5940, H-Al-H 116.0°	Al–H 1.6025, H-Al-H 118.2°		
GaH_2 (doublet, for D_{2d} Ga_2H_4)	GaH_2 (doublet)	1.4	1.8
Ga–H 1.5785, H-Ga-H 115.9°	Ga–H 1.5965, H-Ga-H 120.1°		
BH (singlet)	BH (singlet)	5.2	5.4
B–H 1.1721	B–H 1.2345		
BH (triplet)	BH (singlet)	109.3	126.3
AlH (singlet)	AlH (singlet)	0.7	0.1
Al–H 1.6247	Al–H 1.6657		
AlH (triplet)	AlH (singlet)	181.8	180.4
GaH (singlet)	GaH (singlet)	1.4	1.1
Ga–H 1.6299	Ga–H 1.6872		
GaH (triplet)	GaH (singlet)	211.4	192.8
NH_2 (doublet)	NH_2 (doublet)	0.5	0.4
N–H 1.0178, H-N-H 103.8°	N–H 1.0292, H-N-H 103.3°		
PH_2 (doublet)	PH_2 (doublet)	0.1	0.1
P–H 1.4239, H-P-H 92.6°	P–H 1.4275, H-P-H 91.7°		
AsH_2 (doublet)	AsH_2 (doublet)	0.03	0.03
As–H 1.5284, H-As-H 91.3°	As–H 1.5305, H-As-H 90.9°		
NH (triplet)	NH (triplet)	0.1	0.1
N–H 1.0341	N–H 1.0426		
NH (singlet)	NH (triplet)	209.8	187.7
PH (triplet)	PH (triplet)	0.03	0.03
P–H 1.4284	P–H 1.4330		
PH (singlet)	PH (triplet)	132.6	122.1
AsH (triplet)	AsH (triplet)	0.1	0.02
As–H 1.5336	As–H 1.5361		
As (singlet)	As-H (triplet)	124.5	112.9

Fragmentation energy (ΔE_{frag}): The energy values derived from our hybrid-DFT (B3LYP) and CCSD(T) calculations are given in Table 1. The fragmentation energies cover a large range from only 4 up to as much as 1000 kJ mol^{-1}. The lowest fragmentation energies are found for the linear HEEH species, in which E = Al or Ga, and, therefore, we start with Group 13 element compounds. Compounds like RGaGaR and $[RGaGaR]^{2-}$ (R being an organic group) have stirred

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intense discussions about the possibility of "multiple" bonding between Ga atoms. Thus it has been claimed that species like $Na_2[R_2GaGaR_2]$ exhibit Ga–Ga "triple" bonds.[2] However, as already mentioned in the introduction, a detailed analysis indicates that the compound is most adequately described as a "Na_2Ga_2 cluster" compound.[3, 4] The fragmentation energies of HAlAlH and HGaGaH amount to only 24.3 and 4.9 kJ mol^{-1}, respectively. As the energies are so low, there can be no real E–E bond present in these species. Somewhat stronger is the E–E bond in the *trans*-bent HEEH isomers (E = Al or Ga). Here the interactions amount to 64.9 and 56.5 kJ mol^{-1} according to B3LYP calculations. On the basis of these numbers, it is clear that the Al–Al and Ga–Ga bonds cannot be described as "double" bonds. Presumably the best description is a donor–acceptor interaction between two Al^I or Ga^I species. Furthermore, the change of geometry before and after relaxation of the EH fragment (see Table 2 and the next paragraph) is very small. There is a very clear difference between HBBH and its heavier homologues HAlAlH and HGaGaH. In the case of HBBH, fragmentation into two singlet HB fragments is associated with as much as 511/449.6 kJ mol^{-1}, and fragmentation into two triplet HB fragments requires 719.2/691.5 kJ mol^{-1} (values quoted in the order B3LYP/CCSD(T)). For the E_2H_4 species, one can see that the bond strength of the Al–Al bond in H_2AlAlH_2 is almost equal to that of the Ga–Ga bond in the homologue H_2GaGaH_2 (around 260 kJ mol^{-1} for the D_{2d} symmetric isomers), while there is again a large increase to the boron homologue (fragmentation energy of slightly more than 460 kJ mol^{-1}). Figure 2 illustrates some of the trends. It is clearly visible that the biggest changes between homologues happen from B to Al.

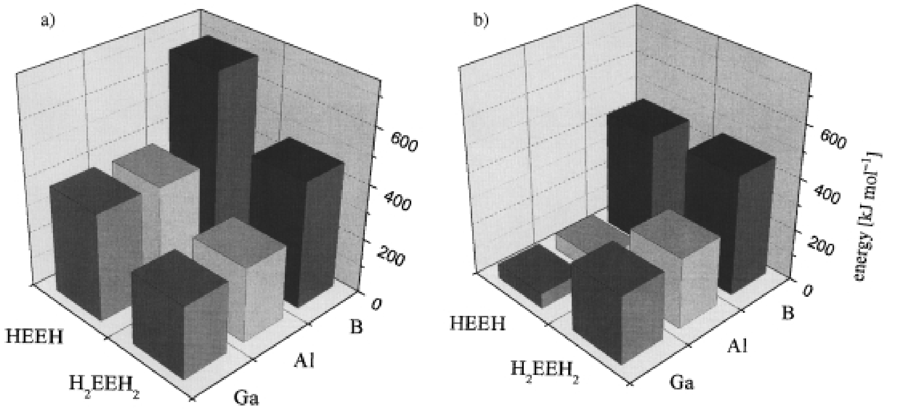

Figure 2. Fragmentation energies (ΔE_{Frag}) as derived from CCSD(T) calculations for binary Group 13 element hydrides (see text for the definition of ΔE_{Frag}). a) Fragmentation leading to EH fragments with triplet electronic states; b) fragmentation leading to EH fragments with lowest energy electronic state (singlet).

Turning our attention to Group 14 hydrides, the fragmentation energies increase in general. With 286.5/295.4 kJ mol^{-1} (values quoted in the order B3LYP/CCSD(T)), the single bond in H_3GeGeH_3 is slightly stronger than the single bond in H_2AlAlH_2 or H_2GaGaH_2. The fragmentation energy increases for the lighter homologues, with again a large difference between H_3CCH_3 and its heavier homologues (about 470 kJ mol^{-1} for E = C, 320 kJ mol^{-1} for E = Si, and 290 kJ mol^{-1} for E = Ge). For species bearing the formula E_2H_4, the difference between the species with E = Si and the one with E = Ge is about 90 kJ mol^{-1}. C_2H_4 has more than twice the fragmentation energy than Si_2H_4. Some of the trends are visible from Figure 3. Again, the largest changes are monitored by replacement of C by Si in homologous compounds.

It might come as a surprise that with 277.8/2889.4 kJ mol^{-1} (values quoted in the order B3LYP/CCSD(T)), the single bond strength in H_2NNH_2 is only slightly higher (by about 20 kJ mol^{-1}) than the one of H_2AlAlH_2 (see Figure 4).

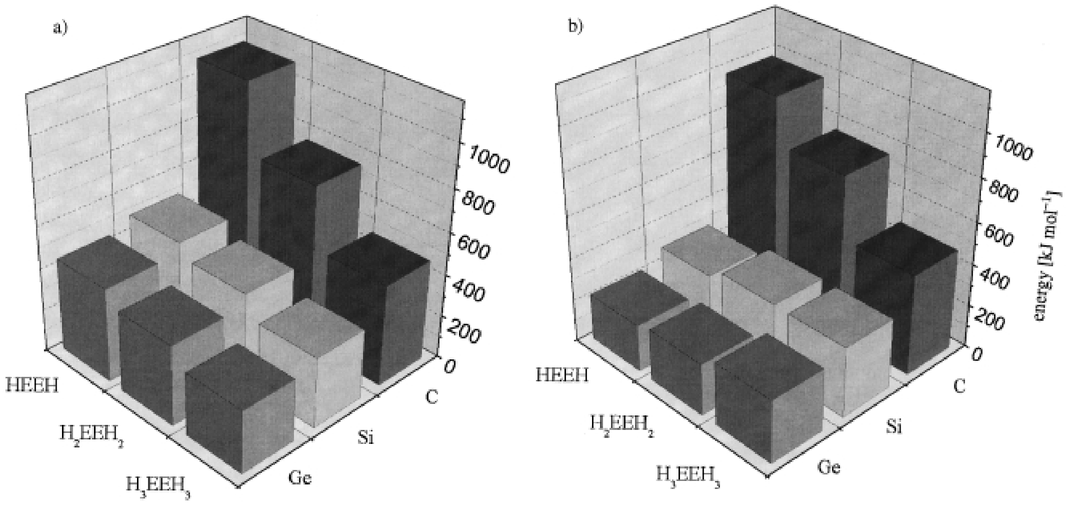

Figure 3. Fragmentation energies (ΔE_{Frag}) as derived from CCSD(T) calculations for binary Group 14 element hydrides (see text for the definition of ΔE_{Frag}). a) Fragmentation leading to EH_2 fragments with triplet and EH fragments with quartet electronic states; b) fragmentation leading to fragments with lowest energy electronic states.

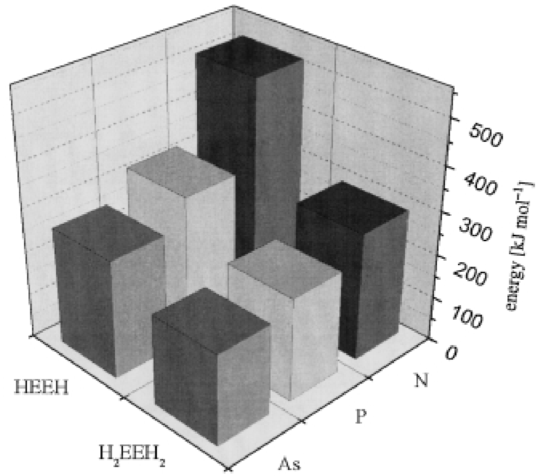

Figure 4. Fragmentation energies (ΔE_{Frag}) as derived from CCSD(T) calculations for binary Group 15 element hydrides (see text for the definition of ΔE_{Frag}).

Hydrazine (H_2NNH_2) has been known for a long time as a stable compound, while H_2AlAlH_2 has not yet been observed. In H_2PPH_2, the P–P bond is already weaker than the Al–Al and Ga–Ga bonds in H_2AlAlH_2 and H_2GaGaH_2, respectively. As to compounds with the potential for "double" bonds, HAsAsH has a fragmentation energy (283.7/267.7 kJ mol^{-1} for fragmentation into two triplet HAs fragments) that is comparable to that found for H_2GeGeH_2 (282.4/277.0 kJ mol^{-1} for fragmentation into two singlet H_2Ge fragments). While in HAsAsH two "classical" bonds ("classical should mean here that each fragment contributes one electron to the bonding molecular orbital) are present, H_2GeGeH_2 is believed to contain two donor–acceptor interactions. The result that both species have nearly the same bond strength indicates that two donor–acceptor interactions can be as strong as two "classical" bonds. Of course, one also has to be aware of lone–lone pair repulsion in molecules such as HAsAsH. Nevertheless, the comparison shows that both classes of bonds can lead to the same total interaction. In the case of HPPH, the fragmentation energy is even slightly smaller than that calculated for H_2SiSiH_2 (327.0/330.3 kJ mol^{-1} for fragmentation of HPPH into two triplet HP fragments vs 332.2/343.9 kJ mol^{-1} for fragmentation of H_2SiSiH_2 into two singlet H_2Si fragments). Thus it might be concluded that donor–acceptor interactions can be as strong as or, in some special cases, even stronger than "classical" bonds. Only in the case of Group 13 element hydrides, the donor–acceptor interactions, where present, loose out against "classical" bonds. It is also noteworthy that the bond strength of HNNH (521.1/519.3 kJ mol^{-1} for fragmentation into two triplet HN fragments) is not very much larger than the one of HBBH, although a comparison is questioned by a large deviation between B3LYP and CCSD(T) calculations for HBBH (511.0/449.6 kJ mol^{-1} for fragmentation into two singlet HB fragments).

Relaxation energy ($\Delta E_{\mathrm{relax}}$): The relaxation energies (see Table 2) include either relaxation of only the geometry or relaxation of both the electronic state and the geometry. It does not come as a surprise that $\Delta E_{\mathrm{relax}}$ is generally large if a change of the electronic state is involved and smaller if only the geometry changes. Relaxation of only the geometry is associated with an energy gain in the range $2 \times (0.02-56) = 0.04-112$ kJ mol^{-1}. Therefore, at least in some cases, the geometry relaxation effect cannot be ignored. For compounds featuring Group 15 elements the relaxation of the geometry is close to zero (less than 1 kJ mol^{-1} according to our calculations). This implies that the differences between the relaxation energies and the dissociation energies are very small. For example, the standard enthalpy for the dissociation of H_2NH_2 was experimentally determined to be 275.3 kJ mol^{-1}.[25] This value is very close to that calculated herein for the fragmentation energy (277.8 and 289.4 kJ mol^{-1} according to B3LYP and CCSD(T), respectively). The fragments NH, PH, and AsH all exhibit triplet electronic ground states; thus, these species are already in their global energy minimum structure and their electronic ground states almost perfectly able to establish the interactions they adopt in N_2H_2, P_2H_2, or As_2H_2. On this basis one might also expect that the barriers to dimerization of the NH, PH, and AsH fragments are very small, although this still has to be proved.

The relaxation of the geometry is much larger for Group 14 hydrides, being here in the range 11–56 kJ mol^{-1}. This mainly is caused by change of hybridization of the fragments. Hence the E–H bond lengths in the fragments are already close to their optimal values before relaxation, while the bond angles undergo significant alterations. For example, CH_3 has an H-C-H angle of 107.5° (C_{3v} symmetry) before and 120° (D_{3h} symmetry) after relaxation. The energy difference amounts to 39.4 or 37.6 kJ mol^{-1} according to calculations at the B3LYP and CCSD(T) level of theory, respectively. Therefore relaxation of the fragments is associated with an energy of 78.8 or 75.2 kJ mol^{-1} (B3LYP or CCSD(T) values) and as a consequence the estimates based on the dissociation energies heavily underestimate the actual bond strength. In fact the standard enthalpy for dissociation was determined to be 376.0 ± 2.1 kJ mol^{-1} for H_3CCH_3,[26] while we get a value of 461.7/476.1 kJ mol^{-1} (B3LYP/CCSD(T)) for the fragmentation energy. In the case of hydrides of Si and Ge, the largest structural relaxation energies are calculated for the ethylene-like planar structures. Hence GeH_2, as a fragment of planar Ge_2H_4, has a relaxation energy of 55.9 or 52.8 kJ mol^{-1}, according to B3LYP or CCSD(T) calculations, respectively. Thus, for Group 14 hydrides, the dissociation and fragmentation energies differ substantially; this shows that the bond strength is not adequately described by the dissociation energies. The relaxation energies of EH fragments (E = C, Si or Ge) were not considered herein, since we restrict ourselves on candidates for two bonds between the elements under consideration.

Finally, in the case of fragments of Group 13 hydrides, the geometry relaxation energies are but small, being in the range 0.1–7 kJ mol^{-1}. The only larger effect with respect to the geometry is an increase of the H-B-H bond angle of BH_2 from 115.7° to 129.7°.

As already mentioned, the relaxation energies are much bigger if a change of the electronic state is involved, ranging then between 62 and 210 kJ mol^{-1}. As to the fragments containing Group 13 elements, all EH fragments (E = B, Al or Ga) formed from *trans*-bent or linear HEEH species prefer a singlet electronic state, and the energy differences between the singlet ground state and the first triplet excited state can be derived easily from the fragmentation energies given in Table 1. In the case of Group 14 element hydrides, CH_2 prefers a triplet electronic ground state, whereas SiH_2 and GeH_2 prefer a singlet state, mirroring the trend well known for the species in their global energy minimum structures. Finally, it does not come as a surprise that the Group 15 element fragments EH (E = N, P and As) all prefer triplet electronic ground states.

In Figure 5, the effect the relaxation energy has is illustrated for the Group 14 compounds. The contributions from the relaxation energies to the fragmentation energies are marked in light gray, and those from the dissociation energies are marked in dark gray.

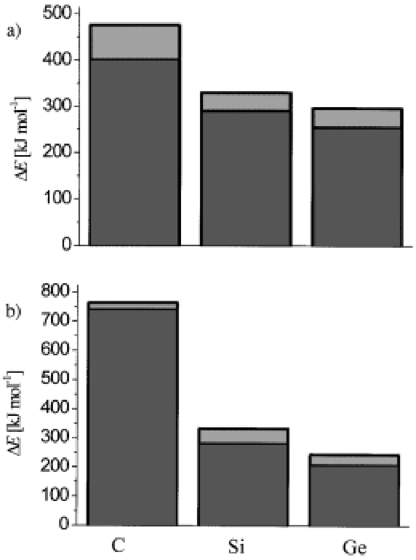

Figure 5. Plot showing the fragmentation energies for a) C_2H_6, Si_2H_6, and Ge_2H_6 and b) C_2H_4 (fragmentation leading to two triplet CH_2 fragments), Si_2H_4, and Ge_2H_4 (fragmentation leading to two singlet SiH_2 or GeH_2 fragments), with contributions from the dissociation energies marked in dark gray and contributions from the relaxation energies (only relaxation of the geometry) marked in light gray.

Conclusion

The dissociation process of main-group-element hydrides with the potential for multiple bonding is considered herein as the sum of two processes: the first process is a fragmentation leading to fragments that retain the structure they had before fragmentation and with a number of unpaired electrons equal or smaller than the expected number of attractive bond interactions ["classical" bonds (where each fragment contributes one electron to the MO) or donor–acceptor interactions]. The second process is relaxation of the fragments into their global energy minimum structure and, if necessary, electronic ground state. The fragmentation energy should be a good quantitative measure of the bond strength, and the relaxation energy can be used to classify the bond. The Carter–Goddard–Malrieu–Trinquier (CGMT) model[15] also links the singlet–triplet energy difference of the fragments with the interaction between the two fragments prior to fragmentation. However, this model considers the fragments in their energy minimum structure, and not in a structure similar to the one they had prior to fragmentation. Our results clearly show that the geometric relaxation cannot be ignored. In summary, the following two rules for the relaxation energy can be established for candidates for two bonds:

- "Classical" bonds (each fragment contributes one electron) are present if the relaxation energy of the triplet fragment is smaller than the one of the singlet fragment.
- Donor–acceptor interactions apply if the relaxation energy of the singlet fragment is smaller than the one of the triplet fragment.

We have found no system in which these two rules do not apply. This implies that generally and on a qualitative level, our results are in agreement with those of the CGMT model. The rules are valid simply because generally the energy difference between the singlet and triplet lowest energy electronic state of the fragment is quite high, apparently at least higher than the difference between the energies of "classical" bonds on the one hand and donor–acceptor interactions on the other hand. In fact we have seen that there are some species for which donor–acceptor interactions are associated with an even larger energy than "classical" bonds (H_2SiSiH_2 vs HPPH, see discussion of the fragmentation energies). On the basis of this rule it can be said that:

- All Group 15 element hydrides are perfectly able to form "classical" bonds.
- In Group 14, only C_2H_4 forms "classical" bonds. Si_2H_4 and Ge_2H_4 form donor–acceptor interactions, but these interactions can rival "classical" bonds in terms of their strength.
- None of the hydrides of Group 13 elements forms classical, ethylene-like bonds. Weak or very weak donor–acceptor interactions govern the scene, the only exception being B_2H_2.

The only molecule that is more difficult to describe is HBBH, which exhibits a linear energy minimum structure with a triplet electronic ground state. The relaxation energy for the singlet fragment is much larger than that for the triplet fragment, and, therefore, if the rules are correct, this species features no classical σ and π bonds. In fact, the unpaired electrons are found in perpendicular p orbitals at each B center. Therefore it can be argued that two donor–acceptor bonds are present, this time with only one electron residing in each of the donor orbitals.

The analysis of the fragmentation energies indicates that the donor–acceptor interactions that are present in compounds of the heavier Group 14 elements (Si and Ge) are comparable in strengths to the "classical" bonds, which are found in the hydrides of the heavier Group 15 elements (P and As). On the other hand, the donor–acceptor interactions in HAlAlH and HGaGaH are much weaker.

The results reported herein should be of significant importance for a better understanding of the bonding in binary main-group-element compounds. Similar calculations are on the way for related systems, for example, ones that contain organic groups in place for the hydrogen atoms.

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[1] See, for example: a) W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272; b) A. H. Cowley, *Acc. Chem. Res.* **1984**, *17*, 386; c) R. T. Paine, H. Nöth, *Chem. Rev.* **1995**, *95*, 343. d) M. Driess, H. Grützmacher, *Angew. Chem.* **1996**, *108*, 900; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 828; e) K. W. Klinkhammer, *Angew. Chem.* **1997**, *109*, 2414; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2320; f) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463; g) A. J. Downs, *Coord. Chem. Rev.* **1999**, *189*, 59; h) R. Köppe, H. Schnöckel, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1095; i) H. Grützmacher, T. F. Fässler *Chem. Eur. J.* **2000**, *6*, 2317; j) A. J. Downs, H.-J. Himmel, L. Manceron, *Polyhedron* **2002**, *21*, 473.

[2] a) J. Su, X.-W. Li, R. C. Crittendon, G. H. Robinson, *J. Am. Chem. Soc.* **1997**, *119*, 5471; b) Y. Xie, R. S. Grev, J. Ga, H. F. Schaefer III, P. von R. Schleyer, J. Su, X.-W. Li, G. H. Robinson, *J. Am. Chem. Soc.* **1998**, *120*, 3773; c) G. H. Robinson, *Acc. Chem. Res.* **1999**, *32*, 773.

[3] N. Takagi, M. W. Schmidt, S. Nagase, *Organometallics* **2001**, *20*, 1646.

[4] H.-J. Himmel, H. Schnöckel, *Chem. Eur. J.* **2002**, *8*, 2397.

[5] a) H.-J. Himmel, A. J. Downs, T. M. Greene, *Chem. Commun.* **2000**, 871; b) H.-J. Himmel, A. J. Downs, T. M. Greene, *J. Am. Chem. Soc.* **2000**, *122*, 9793.

[6] H.-J. Himmel, A. J. Downs, J. C. Green, T. M. Greene, *J. Chem. Soc. Dalton Trans.* **2001**, 5, 535.

[7] H.-J. Himmel, A. J. Downs, T. M. Greene, *Inorg. Chem.* **2001**, *40*, 396.

[8] a) M. Stender, A. D. Phillips, R. J. Wright, P. P. Power, *Angew. Chem.* **2002**, *114*, 1863; *Angew. Chem. Int. Ed.* **2002**, *41*, 1785; b) M. Stender, A. D. Phillips, P. P. Power, *Chem. Commun.* **2002**, 1312

[9] A. D. Phillips, R. J. Wright, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 5930.

[10] N. Wiberg, W. Niedermayer, G. Fischer, H. Nöth, M. Suter, *Eur. J. Inorg. Chem.* **2002**, 1066.

[11] The dissociation energy in fact is an enthalpy and is generally defined as the difference between the enthalpies of the compound under consideration, in its global energy minimum structure and electronic ground state, and the enthalpies of the two fragments resulting from dissociation, also in their global energy minimum structure and electronic ground state.

[12] For example, photolytically induced decomposition of HN_3 leads to N_2 and HN, the latter in its singlet electronic state, which is preserved for some time in the gas phase (over a period of several seconds) before relaxation into the triplet electronic ground state occurs. See: H.-J. Himmel, M. Junker, H. Schnöckel, *J. Chem. Phys.* **2002**, 117, 3321, and references therein.

[13] H. Jacobsen, T. Ziegler, *J. Am. Chem. Soc.* **1994**, *116*, 3667.

[14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrewski, 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. Lui, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, 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, J. A. Pople, Gaussian 98, Revision A.3, Gaussian Inc., Pittsburgh PA, **1998**.

[15] See, for example: a) E. A. Carter, W. A. Goddard III, *J. Phys. Chem.* **1986**, *90*, 998; b) G. Trinquier, J.-P. Malrieu, *J. Am. Chem. Soc.* **1987**, *109*, 5303; c) J.-P. Malrieu, G. Trinquier, *J. Am. Chem. Soc.* **1989**, *111*, 5916; d) G. Trinquier, *J. Am. Chem. Soc.* **1990**, *112*, 2130; e) G. Trinquier, *J. Am. Chem. Soc.* **1991**, *113*, 144.

[16] G. V. Chertihin, L. Andrews, *J. Phys. Chem.* **1993**, *97*, 10295.

[17] a) H.-J. Himmel, L. Manceron, A. J. Downs, P. Pullumbi, *Angew. Chem.* **2002**, *41*, 796; *Angew. Chem. Int. Ed.* **2002**, *114*, 829; b) H.-J. Himmel, L. Manceron, A. J. Downs, P. Pullumbi, *J. Am. Chem. Soc.* **2002**, *124*, 4448.

[18] T. J. Tague, Jr., L. Andrews, *J. Am. Chem. Soc.* **1994**, *116*, 4970.

[19] G. Treboux, J. C. Barthelat, *J. Am. Chem. Soc.* **1993**, *115*, 4870.

[20] K. Lammertsma, O. F. Güner, R. M. Drewes, A. E. Reed, P. von R. Schleyer, *Inorg. Chem.* **1989**, *28*, 313.

[21] K. Lammertsma, J. Leszczynski, *J. Phys. Chem.* **1990**, *94*, 5543.

[22] L. A. Curtiss, J. A. Pople, *J. Chem. Phys.* **1989**, *90*, 4314.

[23] For further details (also for substituted derivatives) see, for example: a) R. West, *Angew. Chem.* **1987**, *99*, 1231; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1202; b) T. Tsumaraya, S. A. Batcheller, S. Masamune, *Angew. Chem.* **1991**, *103*, 916; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 902; c) M. Weidenbruch, *Coord. Chem. Rev.* **1994**, *130*, 275.

[24] D. Danovich, F. Ogliaro, M. Karni, Y. Apeloig, D. L. Cooper, S. Shaik, *Angew. Chem.* **2001**, *113*, 4146; *Angew. Chem. Int. Ed.* **2001**, *40*, 4023.

[25] D. F. McMillen, D. M. Golden, *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

[26] J. A. Seetula, J. J. Russell, D. Gutman, *J. Am. Chem. Soc.* **1990**, *112*, 1347, and references therein.

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