Topographical Analyses of Homonuclear Multiple Bonds between Main Group Elements

Hansjörg Grützmacher* and Thomas F. Fässler*[a]

Abstract: Recent experiments have resulted in the completion of the series of Group 14 and Group 15 element double-bond systems, $R_nE=ER_n$ ($E = C-Pb$, $n = 2$; $E = N-Bi$, $n = 1$). Furthermore, new families of multiple-bonded species have been discovered, such as the radical anion $[RSnSnR]^-$, the close ion pairs $[RE(\mu_2Na)_2\text{-}ER]$ ($E = Ge,Sn$), and a digallyne $[RGa(\mu_2Na)_2GaR]$ for which a $Ga\equiv Ga$ triple bond was formulated. Some of these compounds show classical multiple bond features (i.e. the dipnictogens $RE=ER$, $E = N-Bi$) in the sense that planar structures with short $E-E$ distances are observed. However, many (i.e. $R_2E=ER_2$, $E = Si-Pb$) do not behave as expected for compounds with multiple bonds. They have *trans* bent structures, show enormous variation in their $E-E$ distances, and some dissociate easily under $E-E$ bond cleavage in solution. These properties raised doubts as to whether these compounds can be formulated as multiple-bonded systems. Using the electron localization function (ELF) it is possible to clearly show the topographical similarities between classical and nonclassical multiple bonds; ELF divides these systems into *unslipped* (classical) and *slipped* (nonclassical) systems. ELF can also be employed to confirm the nonexistence of multiple bonds. Therefore, topographical analyses using ELF are useful to categorize a bonding system. In particular, the bonds in the heavier Group 14 double systems and the Ga–Ga bond in digallyne are clearly shown by this method as slipped double and triple bonds, respectively.

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Some Historical Remarks

Controversy surrounding the chemical bond and its graphical representation are not new.[1a] In 1865, S. Couper and C. Brown introduced dashes "-" as "bonds" to represent the topography of molecules and the valency of their atomic centers (Scheme 1, **B–E**).[1b] Other descriptions were in
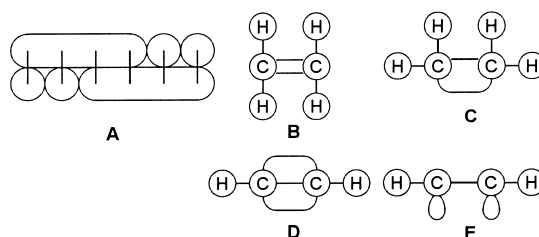
Scheme 1. Historical graphical representations of C_2H_4 (**A–C**) and C_2H_2 (**D, E**).

common use at that time already and most of them were not designed to reflect the three-dimensional structure of molecules.[2a–d] Kekulé found Brown's and Couper's formulae "exasperating to draw, impossible to print except from plates and capable of ambiguity". In Scheme 1, **A** as the depiction of the ethylene molecule preferred by Kekulé is compared with the ones, **B** or **C**, proposed by Brown.

Noteworthy is also the representation of acetylene as shown with a "triple bond" in **D** and with "self-neutralizing atoms" in **E**. (These descriptions resemble the approximation of electronic ground states by resonance structures—which **D** and **E** were not meant to be!—that came into use about 60 years later.) The "dash" model was rapidly accepted by other chemists[3] and it is interesting to note that *the representation of a double bond or a triple bond by double or triple dashes was a consequence of valence theory* ("type theory") and was used long before the structures and physical properties of molecules were known (i.e., precise bond lengths and angles, force constants, dissociation or rotation energies, even electrons were unknown).

The introduction of quantum-mechanical equations changed the meaning of these dashes. In Lewis structures each dash is interpreted as a pair of electrons (an α- and a β-electron).[4] Following work by Siedwick, Heitler, and Lon-

don, filled orbitals were identified with electron pairs. Subsequently, two major approaches for the description of electronic states of molecules were developed: molecular orbital (MO) theory, which uses delocalized orbitals, and valence bond (VB) theory, which is based on the formation of electron pairs starting from atomic orbitals.

In the more common MO theory, the set of four (six) valence electrons in a double (triple) bond is described by a symmetry-separated set of one σ- and one π- (one σ- and two π-) molecular orbitals. Strictly by definition, the terms σ- and π-bond are restricted by symmetry to linear molecules but are commonly used for bond descriptions in planar molecules as well. Alternatively, multiple bonds are described by bent bonds or banana bonds.[5] Both approaches are equally legitimate[6] and as approximate descriptions neither of these can be proven to be right or wrong.

Experiments directed towards the synthesis of unsaturated main group element compounds date back to the last century. In accord with the picture of chemical bonding and the valence concepts of their time, Michaelis et al. described "phospho-" and "arsenobenzene", PhE=EPh (E = P, As), and explicitly applied the term double bond to characterize the arsenic – arsenic bond.[7] Ehrlich used a related formula for "Salvarsan" $[(3\text{-}H_3N^+\text{-}4\text{-}HO\text{-}C_6H_3)As{=}As(C_6H_3\text{-}3\text{-}NH_3^+\text{-}4\text{-}OH)] \cdot 2\,Cl^-$. Later advances in spectroscopic methods proved these formulations to be wrong and these compounds correspond to oligomeric $(RE)_n$ compounds.

Short bond lengths, planar or linear arrangements of the substituents around the multiple bond, rotational barriers, and enhanced bond energies were introduced as classical indicators for multiple bonds. It is important to remember that these indicators evolved from the studies of bonding systems in which elements of the second row, that is C, N, O, are incorporated. In 1976 Lappert and co-workers isolated the first distannene, $R_2Sn{=}SnR_2$ (**1**) (R = CH(SiMe$_3$)$_2$) as an example for a homonuclear heavier analogue of an olefin and determined its structure (Scheme 2).[8] This true milestone

in main group element chemistry created serious problems for the classical valence concepts: The skeleton of **1** is not planar but *trans* bent ($\Theta = 41°$); the Sn=Sn bond (2.77 Å) is not significantly shorter than a single bond (2.81 Å), and the molecule dissociates easily in solution into two stannanediyl (stannylene) fragments (SnR$_2$). Five years later West et al. succeeded in the isolation of the first stable disilene, Mes$_2$Si=SiMes$_2$ (**2**) (Mes = 2,4,6-Me$_3$C$_6$H$_2$) which was formed by dimerization of two silanediyl (silylene) fragments, SiMes$_2$, generated by photolysis of a polysilane precursor (Scheme 2).[9]

In the same year 1981, Yoshifuji and co-workers prepared the first "true phosphabenzene", Mes*P=PMes* (**3**) (Mes* = 2,4,6-(tBu)$_3$C$_6$H$_2$) (Scheme 2).[10] Both compounds, **2** and **3**, were characterized by X-ray structure analyses. The Si=Si bond in **2** and the P=P bond in **3** are significantly shorter (9%) than corresponding single bond lengths. While diphosphene **3** is planar, **2** shows a slightly *trans*-folded structure. The fold angle which is defined by the intersection of the R-Si-R plane and the Si–Si vector is 18°.

Recent Experimental Advances

Only recently the series compounds containing homonuclear double-bond systems $R_nE{=}ER_n$[11] between elements of Group 14 (E = C – Pb, $n = 2$)[12] or Group 15 (E = N – Bi, $n = 1$)[13] was completed (Scheme 3). Table 1 contains a compilation of geometrical and thermodynamical data for Group 14 double-bond systems.

Even in the sterically most crowded olefin, Z-[(tBuMe$_2$-Si)(Me$_3$Si)C=C(SiMe$_2$tBu)(SiMe$_3$)],[12a] the C=C bond is only slightly elongated by 2%, although both RR^{1}C halves are twisted by 60°. The heavier homologues of olefins become increasingly more flexible with increasing principle quantum number N. They show large deviations in bond lengths and fold angles, and the dimerization energy E_{dim}, which can be taken as an approximation of the $E_{\sigma+\pi}$ bond energy, dramatically drops to values typical for van der Waals interactions. Consequently, most digermenes, distannenes, and all diplumbenes easily dissociate into the ER$_2$ monomers (E = Ge, Sn, Pb) in solution. Among Group 14 element double-bond systems, only C=C bonds are considered "hard double bonds" and it is only these for which the traditional indicators of double-bonded systems like bond lengths, planarity, high dissociation energies, and isomerization by bond rotation can be applied.

On the other hand, all Group 15 element double-bond systems,[13] such as the dibismuthene **5**, show a classical planar molecular framework in which the E=E distance is shorter than that of a single bond (about 6% for E = Bi).[13d] Furthermore, there are no indications that dibismuthene **5** dissociates into BiR (bismuthanediyl) fragments in solution. In the search for stable triple bond systems, an instructive series of anionic compounds **6 – 8** became available.[14–16] All contain the sterically very demanding substituent, C$_6$H$_3$-2,6-Trip$_2$ (Trip = triisopropylphenyl), which shields the central bond from further reactions (kinetic stabilization).
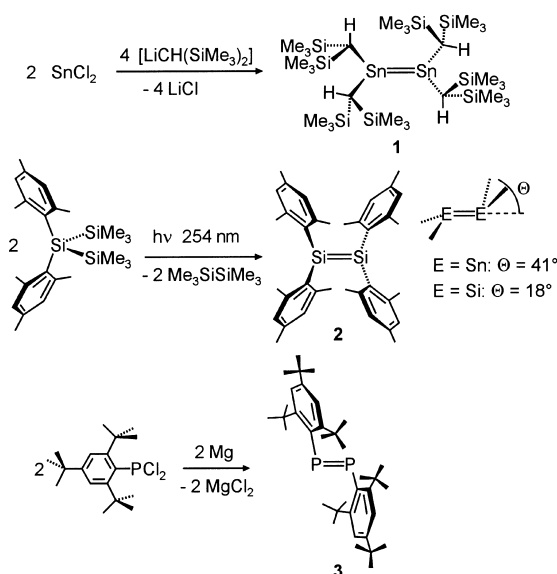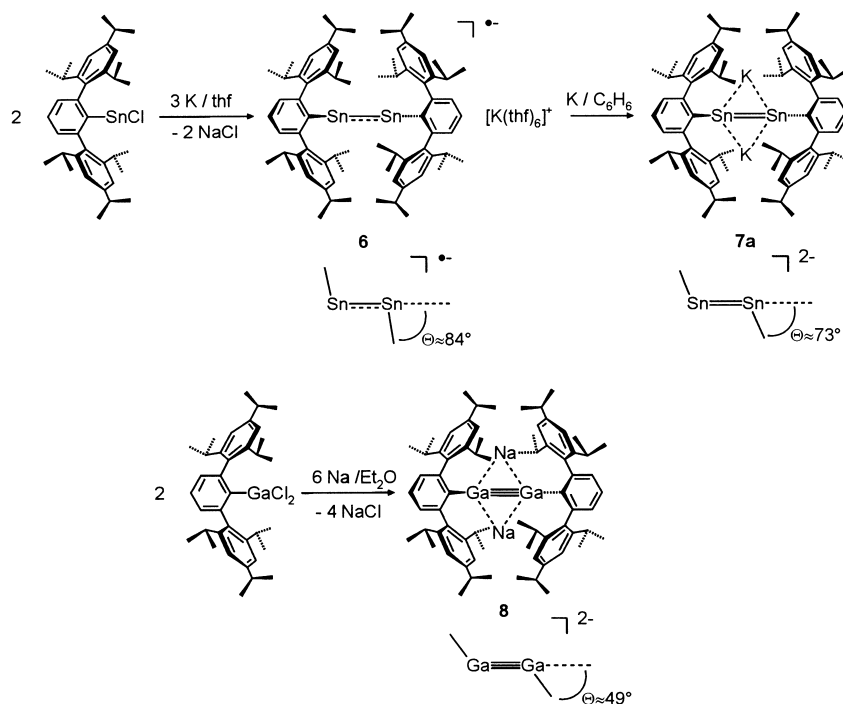

Scheme 2. Syntheses of the first distannene **1**, disilene **2**, and diphosphene **3**.
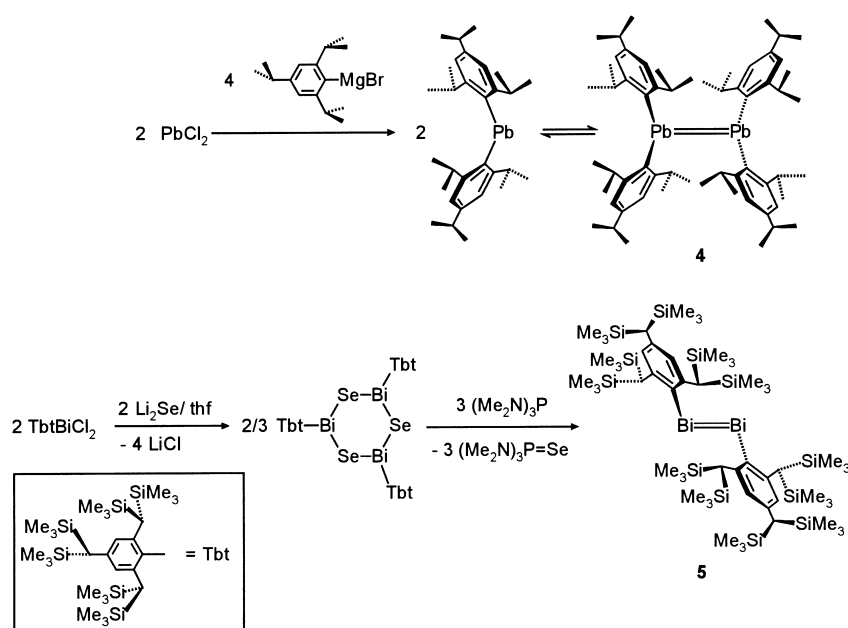
Scheme 3. Syntheses of diplumbene **4** and dibismuthene **5**.

Table 1. Range of experimental bond lengths, $d_{(E-E)}$ [Å], fold angles Θ [°], calculated distances, angles, and dimerization energies, E_{dim} [kJ mol^{-1}] for Group 14 double-bond systems $R_2E=ER_2$.

	$d_{(E-E)}$ exp.	$d_{(E-E)}$ calcd	Θ exp.	Θ calcd	ΔE_{dim}[12d]	Ref.
C	1.34–1.37	1.35	0	0	739	[12a]
Si	2.14–2.25	2.16	0–18	29.0	250	[11b]
Ge	2.21–2.35	2.34	12–36	43.7	180	[11a, b]
Sn	2.77–3.63	2.68	41–46	48	96	[11a, b]
Pb	2.99–3.53	2.95	41–51	54.6	24	[11a, b, 12c]

In compounds **6–8** the central R−E=E−R units (E = Ge, Sn, Ga) differ by one valence electron (VE) if ionic interactions are assumed with the alkali metal centers (i.e. complete transfer of one electron from the metal to the anion). In the radical anion **6** (11 VE taking [HSnSnH]$^{\cdot-}$ as the parent system), the unpaired electron is equally delocalized over the Sn−Sn bond as indicated by EPR studies (A(^{117}Sn) = 8.3 G; A(^{119}Sn) = 8.5 G) and is thought to be in a pp(π) orbital perpendicular to the R_2Sn_2 skeleton. Further reduction of **6** in benzene leads to the close contact ion pair **7a** in which both potassium ions are complexed by the Trip units. The structural differences between diamagnetic **7a** in which the perpendicular pp(π) orbital is filled by two electrons (12 VE with respect to [HSnSnH]$^{2-}$) and its radical precursor **6** are small; a slight shortening of the

Sn−Sn distance is observed in **7a** (0.04 Å) and the fold angle Θ closes by about 10° (see Scheme 4). The germanium analogue [Na$_2$Ge$_2$(C$_6$H$_3$-2,6-Trip$_2$)] (**7b**) has been prepared by the same method (Ge−Ge 2.394 Å, Θ = 77.6°). These dianionic species may be best compared to the neutral isoelectronic dipnictogenes RE=ER (E = As, Sb) which have very similar forms. Note that in these planar molecules, Θ corresponds to an ordinary E-E-R bond angle and not to a deviation of a π system from planarity.

The digallyne **8** has been prepared by the same synthetic approach to that applied for **6** and **7a, b**, that is simple Wurtz type coupling of an element dichloride. This species (10 VE with respect to [HGaGaH]$^{2-}$) has two valence electrons less than **7b**. Formally the pairs **7a, b/8** correspond to the system [HC=CH]$^{2-}$/HCCH. Consequently, **8** was formulated with a Ga≡Ga triple bond. However, **8** shows a nonclassical *trans* bent structure (Θ = 49°) and the Ga−Ga bond is not significantly shorter than a single bond. These structural features in particular led to a vivid debate on whether this dianion is not better represented by a resonance form showing a Ga−Ga single bond and a lone pair on each Ga center (see also **D** and **E** in Scheme 1 and **K** and **L** in Scheme 8).[17] In this discussion not only the question of "to π or not to π" was

Scheme 4. Syntheses of novel multiple-bonded tin (**6**, **7a**) and gallium (**8**) compounds.

brought up again but furthermore, it became evident that there was a lack of methods available to graphically visualize the electronic nature of main group element multiple bond systems.

Recent Theoretical Investigations

When double-bond systems $R_2E=ER_2$ are homolytically cleaved, the resulting two carbene-analogous fragments ER_2 may either exist in a triplet state **F** or singlet state **H**. In an analogous way, triple-bond systems either fall apart into two quartet ER fragments **G** or into two doublet fragments **I** (Scheme 5).
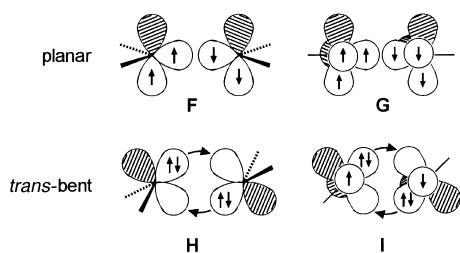
Scheme 5. Interaction of triplet ER_2 (**F**), quartet ER (**G**), singlet (ER_2) (**H**), an doublet ER (**I**) fragments.

Only for the elements from the second period are the high-spin states **F** and **G** energetically low lying. The elements from the higher periods prefer low-spin ground states **H** and **I**.[11c] Each of these low-spin fragments donates a pair of electrons from an occupied sp hybrid orbital to an empty p orbital of its bonding partner to form double donor–acceptor bonds.[8c] By this approach bent double bonds in Group 13 species RE=ER (E = Ga, In, Tl)[18a] and Group 14 species $R_2E=ER_2$ (E = Si, Ge, Sn, Pb),[8c, 18b–d] and bent triple bonds RE≡ER (E = Ga⁻ or Si)[19a,c] can be rationalized. Furthermore, since dative bonds are much weaker than σ and π bonds, very low binding energies are expected for nonclassical double or triple bonds.

In the Carter, Goddard III, Malrieu, and Trinquier model[20, 21] (CGMT model[11c]) the criterion for a nonplanar *trans* bent form of a multiple bond system in $R_nE=ER_n$ is given by: $\Sigma\Delta E_{(S\rightarrow T)} > \frac{1}{2}E_{\sigma+\pi}$. Here $\Delta E_{(S\rightarrow T)}$ corresponds to the singlet–triplet excitation energy of the fragment ER_2 and is positive when the singlet state is the ground state, and $E_{\sigma+\pi}$ denotes the E=E bond energy.[22] Classical planar forms should be observed when $\Sigma\Delta E_{(S\rightarrow T)}$ is smaller than $\frac{1}{2}E_{\sigma+\pi}$: $\Sigma\Delta E_{(S\rightarrow T)} < \frac{1}{2}E_{\sigma+\pi}$. The planar forms of Group 15 double-bond systems RE=ER (E = N–Bi)[18e–g] are within this model simply due to the fact that all ER fragments have triplet ground states (i.e. $\Delta E_{(S\rightarrow T)}$ is negative).

The long E–E distances for the heavier Group 13 to 15 elements are caused by increasing interatomic repulsion ΔE_{Pauli}, as was pointed out by Ziegler and Jacobsen.[18b] The energy ΔE_{Pauli} results from repulsive two-center, three-electron (2c–3e) and two-center, four-electron (2c–4e) interactions between occupied orbitals on both fragments. This unfavorable interaction will increase with increasing orbital overlap, that is upon shortening of any bond. Especially, for

the heavier elements, ΔE_{Pauli} becomes dominant already at quite long E–E distances because the valence np-orbitals of one fragment, which are rather extended in space, underlie a repulsive 2c–3e interaction with (n − 1)p-core orbitals on the other fragment. In contrast, elements of the second period have only core electrons in the 1s level.[18h]

Finally, one needs to ask whether a double-bond system—be it classical or nonclassical—is the only possible stable structure one can imagine (guided by the valence theory). Within the GCMT model, the requirement for the existence of a planar or *trans* bent ground state double-bond system is given by $\Sigma\Delta E_{(S\rightarrow T)} \leq E_{\sigma+\pi}$. As a consequence, doubly H-bridged structures **V** and **VI** (Scheme 6) represent the global

E	energy of isomers $\Longrightarrow$				
C	I				
Si, Ge	II	<	IV	<	V, VI
Sn, Pb	V, VI	<	III	<	IV	<	II
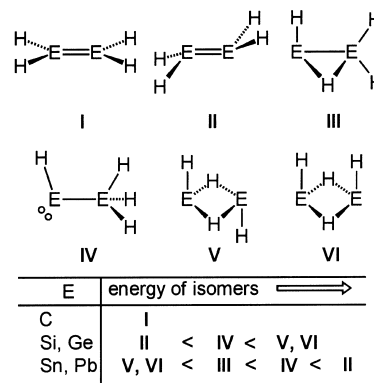
Scheme 6. The various possible E_2H_4 (E = C–Pb) isomers **I – VI** and their relative energy ordering.

minima on the Sn_2H_4 and Pb_2H_4 energy surfaces because SnH_2 or PbH_2 have very stable singlet states and $E_{\sigma+\pi}$ becomes even smaller than $\Delta E_{(S\rightarrow T)}$.[21c,d] The *trans* bent double-bond forms **II** are the least stable isomers!

Ethylene exists only in form of one isomer **I**; however five different isomers **II – VI** in a narrow energy band are found as local minima on the energy surfaces of the homologues. This may explain the facile ligand scrambling reactions that are experimentally observed when the homoleptic fragments ER_2 and $E^1R^1_2$ (E, E^1 = Sn, Pb) are mixed and heteroleptic double-bond systems $RR^1E=ERR^1$ and $RR^1E^1=E^1RR^1$ are obtained as products.[12d]

Summarizing the experimental and theoretical findings leads to the following conclusion: *The classical multiple bond indicators—bond lengths and bond strengths—have no meaning for multiple bonds in which elements from the higher periods are involved. However, they are valid for an exceptional element: carbon.*

A Topographical Analysis of Main Group Element Multiple Bonds

However, the questions still remain: Are the bonds in the higher homologues of ethylene correctly represented as double bonds? Is the Ga–Ga bond in digallyne **8** a real triple bond? In order to find more general answers, we suggest here a description based on the electron localization function (ELF).[23–25] In a very simplistic way, ELF represents the

probability of finding two electrons with the same spin α in a given space (Pauli repulsion). In regions where this probability is small, electrons are localized. Since the same considerations are valid for β-electrons, ELF divides the valence electron density of a closed-shell system into regions of (bonding and nonbonding) *electron pairs*. The definition of ELF is chosen such that at high values of ELF (close to 1, color-coded white) electron pairs are localized. It is very important to keep in mind that high electron density does not necessarily coincide with large ELF values. For example, although the uniform electron density of an atom shows only *one* maximum at the position of the nucleus, ELF reveals the shell structure of atoms, that is several local maxima are found. The same holds for molecules where the electron density is highest at the position of the nuclei, from which it monotonically decreases towards the bond centers.[25] However, again the ELF can show maxima at these latter positions. As such, ELF is a projection of properties of the electron density and coincides in many cases with chemist's ideas of electron pairs when they draw chemical formulae. Furthermore, as long as no specific quantitative values shall be obtained for a given structure, ELF is widely independent of the quantum mechanical method as well as of the basis sets chosen to calculate the electron densities and reliably reproduces trends. This is an advantage over any MO description, which relies on well-defined but arbitrarily chosen wavefunctions.[32]
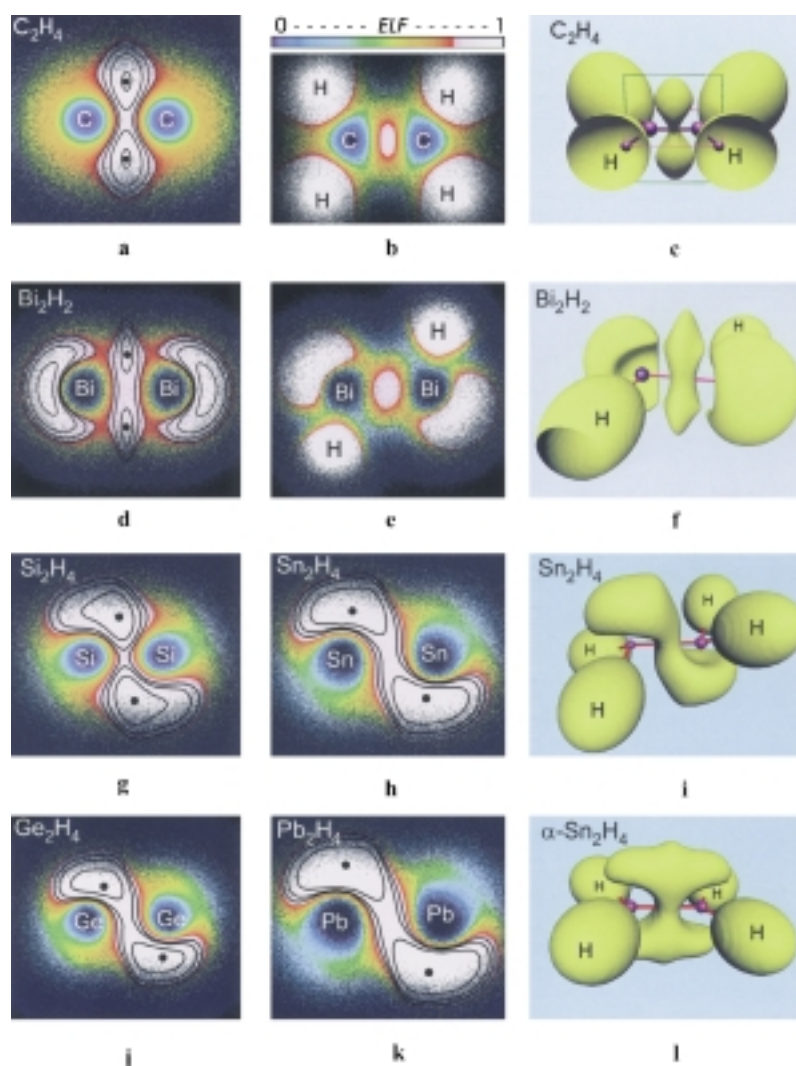

Figure 1. Two-dimensional (2D) cross sections through the molecules (left two columns) and three-dimensional (3D) representations (right column) of the electron localization function (ELF). In all 2D pictures the density of points measures the electron density. Regions of low-electron density appear instead of the atom cores, because valence electron calculations were performed. The color of ELF at each point corresponds to the values given in the color bar on top of Figure 1b. The contour lines of the 2D images correspond to ELF = 0.80, 0.85, 0.90, and 0.95 with higher values towards the maximum shown as black dot. All 3D surfaces correspond to the ELF = 0.80. a)–c) C_2H_4, d)–f) Bi_2H_2, g) *trans* bent Si_2H_4, h)–i) *trans* bent Sn_2H_4, j) *trans* bent Ge_2H_4, k) *trans* bent Pb_2H_4, and l) hypothetical planar Sn_2H_4.

In Figure 1 we show various plots of ELF based on calculated electron densities for classical (**a**–**f**) and non-classical (**g**–**k**) double-bond systems.

In **a** and **b** color-coded two-dimensional contour line plots of the ELF of C_2H_4 are shown. The molecule lies either with the E–E axis in the plane of the paper and the hydrogen atoms above and below that plane (**a**) or the molecular plane coincides with the paper plane (**b**). In all molecules, the local ELF maxima (bond attractors[24]), M^1 and M^2, of the ELF of the E–E bond regions are indicated by a dot.

In C_2H_4, the C=C bonding domains are characterized by a dumb-bell shaped region of localized electrons (ELF > 0.8).

The bond attractors M^1 and M^2 lie above and below the molecular plane on a line m perpendicular to the molecular plane intersecting the midpoint of the E–E distance (see Scheme 7). Note also that ELF shows a local minimum at this point of intersection. This is nicely seen as well in **c** in which an isosurface of ELF = 0.8 is shown. As was mentioned above, large ELF values within the double-bond region do not

unslipped double bond   slipped double bond
E = Si, Ge, Sn, Pb
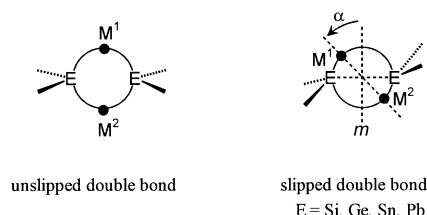
Scheme 7. Placement of local ELF maxima M^1, M^2 in unslipped and slipped double bonds.

coincide with high electron density, which is given by the pixel density in the two dimensional (2D) plots. The particular form of ELF for a double bond can be understood by using the arguments given above: In double-bond domains, two α and two β electrons have to be hosted. The Pauli repulsion will force the electrons with the same spin to localize in separate regions. Or in other words: although the electron density is higher on the C−C connecting line, the electrons formally assigned to the double bond do not localize here due to the Pauli repulsion. The relation of the observed distribution of bonding domains—projected from the electron density by the ELF—to the VSEPR model is evident: Electron pairs try to keep a maximum distance to each other![26] In **d** to **f**, the ELF of HBi=BiH as a model for dibismuthene **5** is shown. The resemblance between these plots and the ones for ethylene is striking, the only difference being the lone pairs on each Bi center shown as closed spheres in **f**. Hence dibismuthene **5** like all dipnictogenes RE=ER (E = N – Bi) falls within the category of classical double bonds.

In **g** – **k** color-coded ELF plots based on the nonclassical *trans* bent structures of the parent compounds $H_2E=EH_2$ (E = Si, Ge, Sn,[25b] Pb) are depicted (see Table 1 for structural details). As the fold angle Θ increases with increasing atomic number of E, the maxima M^1 and M^2 are increasingly slipped away from the line *m* as is described by the deviation angle α: $\alpha(C) = 0°$, $\alpha(Si) = 9°$, $\alpha(Ge) = 40°$, $\alpha(Sn) = 41°$, $\alpha(Pb) = 43°$ (Scheme 7).

However, the principle characteristics of a double-bond system, that is the finding of M^1 and M^2 above and below the E−E axis are retained. Therefore, this property of ELF, that is two weakly separated maxima M^1 and M^2 and a local minimum on the E−E vector is proposed as double-bond criterion.[27] This analysis describes *all* E=E bonds as *double bonds* even in nonplanar molecules and tolerates a wide range of bond lengths and fold angles Θ. Double bonds can be divided into *unslipped double bonds* which is the classical case of planar molecules and *slipped double bonds* in molecules of lower symmetry.[28]

At this point it is interesting to examine the form of the ELF of a *hypothetical* planar distannene (Figure 1l). In contrast to planar C_2H_4 or Bi_2H_2, where both double-bond domains take a rather contracted space above and below the midpoint of the E−E bond, in planar α-Sn_2H_4 the double-bond

domains are considerably localized over the two Sn centers. Since, as we stated above, bonding domains tend to keep apart from each other as far as possible, it is not difficult to imagine that a distribution for the double-bond domains in a *trans* bent structure as shown in Figure 1i is more favorable.[29]

As was seen from the comparison of ethylene and bibismuthene in Figures 1c and 1f, respectively, ELF shows nicely the relationship between bonding and nonbonding electron pairs. ELF can also be used to demonstrate the *topographical* relationship between the double bond in ethylene and the three-center, two-electron BHB bonds in the isoelectronic diborane B_2H_6.[24, 25c] ELF plots of B_2H_6 using the same orientations as were chosen for C_2H_4 are shown in Figures 2a – c.
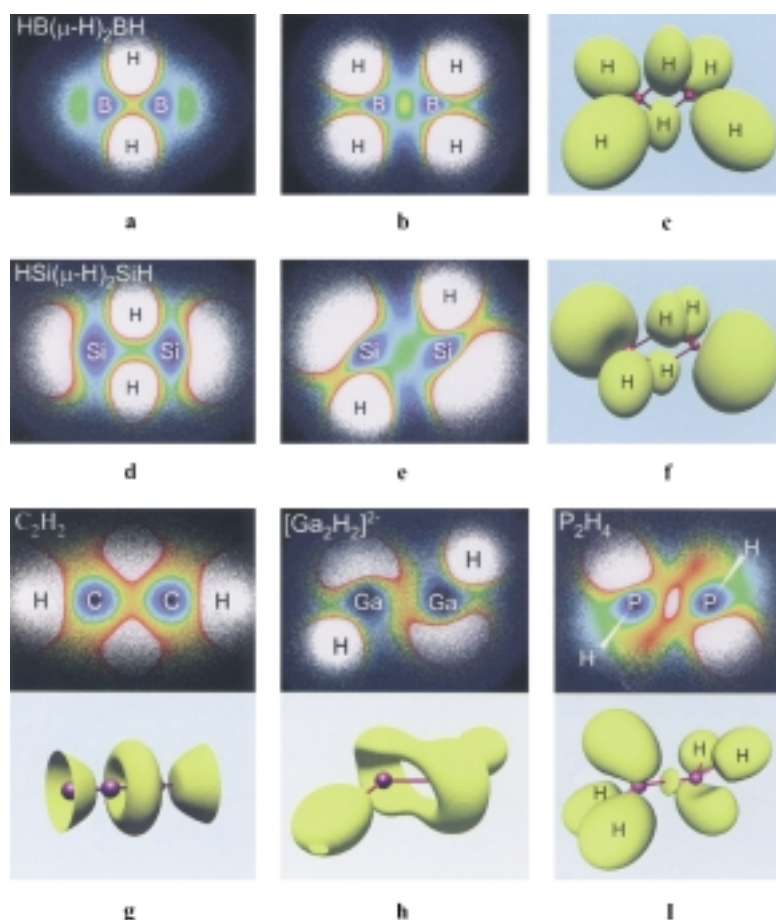

Figure 2. Two-dimensional (2D) cross sections through the molecules and 3D representations of the ELF. For further details see caption of Figure 1. a) – c) doubly H-bridged B_2H_6, d) – f) doubly H-bridged Si_2H_4, g) C_2H_2, h) Ga_2H_2, and i) P_2H_4.

Clearly, the ELF regions of the two bridging hydrogen atoms in B_2H_6 (Figure 2a – c) are closely related to the double-bond domains of ethylene in Figures 1a – c. However, the two maxima M^1 and M^2, which coincide with the positions of the protons are strongly separated in this case. In Figures 2d – f, the same topographical relationship is seen for the domains for the hydrogen atoms of the doubly hydrogen-bridged disilene isomer $HSi(\mu_2\text{-}H)_2SiH$ (**V**; see Scheme 6) and the Bi=Bi double-bond domains shown in Figure 1d – f. Again, the only difference is the stronger separation of the ELF

maxima (i.e. proton positions) above and below the molecular plane. Generally, hydrogen cores (protons) show a preference to locate where electrons localize anyway, that is close to ELF maxima.[25a]

Finally classical and nonclassical triple bonds are discussed. In Figure 2g, the ELF of the classical triple bond system of HC≡CH is shown. No maximum is found on the C–C axis and the chemical bond is represented as a cylindrical torso following the D_h symmetry of the molecule. In this case, the ELF maxima of triple bonds are represented by ring attractors as was proposed earlier (Scheme 8).[24] When a triple bond is
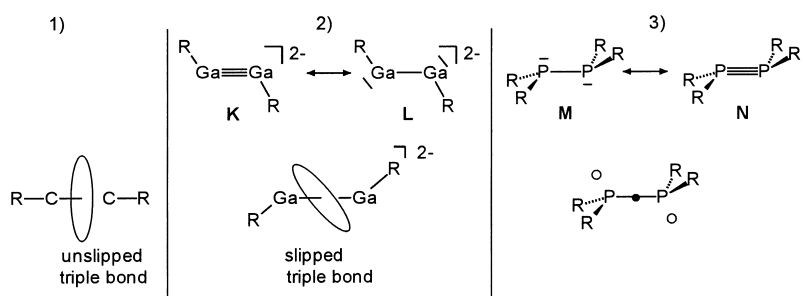
Scheme 8. 1) Unslipped and 2) slipped ring attractors in acetylene and digallyne, respectively. 3) The bond attractor in P_2H_4 is shown as filled dot, lone pair attractors are shown as unfilled circles.

treated as a six-electron problem, this ELF shape is expected to be the best compromise to host three α and three β electrons. Most remarkably, the torso-type shape of the triple-bond domain is retained in the nonclassical digallyne dianion $[HGa \equiv GaH]^{2-}$ as is shown in Figure 2h. *Clearly this compound has a triple bond!* Using the terminology introduced above, this bond corresponds to a *slipped triple bond* system and acetylene is shown with an *unslipped triple bond* in Scheme 8. The tilted torus can also be interpreted as a consequence of mixing in a small contribution of resonance structure L into resonance structure **K**.

In order to confirm our analysis of the triple bond in digallyne **8** and to rule out a description with two lone pairs at the Ga centers and a Ga–Ga single bond, we inspected the chemical bonds in diphosphene $H_2P–PH_2$. Considering the E–H bonds as localized two-electron, two-center bonds, in both cases three electron pairs are left for bonding between the E centers. As shown in Figure 2i, clearly a maximum on the P–P vector and two further maxima at each P centre are found. The interpretation as σ-P-P bond and two lone pairs on each phosphorus center is straightforward, and the contribution of the resonance structure $H_2P \equiv PH_2$ **N** to the electronic ground state is certainly negligible. Therefore $H_2P–PH_2$ may be represented with a bond attractor on the P–P connection line (black dot) and two nonbonding attractors (unfilled circles) on each P center (Scheme 8).

Conclusion

Classical multiple bond indicators such as planar or linear structures, short bond lengths, and bond energies stem from concepts which were developed to identify the "chemical bonds" between a rather limited number of elements, namely carbon, nitrogen, and oxygen. Over the last 20 years refined experimental techniques have allowed the synthesis, isolation, and detailed study of many fascinating multiple-bonded main group element compounds; however, the classical indicators cannot be applied to many of these compounds. These nonclassical multiple-bonded systems have distorted structures, their bonds are not shortened and are even sometimes longer than single bonds, and they dissociate homolytically in solution. Although these differences to classical bonding systems can be rationalized by theoretical models, the question still remains whether they are correctly represented by the graphical methods, which are in common use. An analysis of classical and non-classical bonding systems by means of ELF permits a topographical classification of multiple bonds, which is free from restrictions imposed by the classical indicators. In particular, the distribution of local ELF maxima in the multiple-bond region allows one to distinguish between unslipped (i.e. classical) and slipped (i.e. nonclassical) multiple bonds. This leads to a very general classification, and a wide range of bond lengths and distortions is tolerated. Also, ELF shows the absence of multiple bonding. These topographical analyses reveal that the similarities between classical and nonclassical multiple bonds are much larger than one might have anticipated on the basis of the molecular structures alone (which are defined by the positions of the nuclei). Both, classical and nonclassical double bonds or triple bonds are characterized by two weakly separated domains or ring attractors, respectively, which are placed around the bond vector. Therefore they are, in our opinion, graphically adequately represented by the traditional Lewis formulae (i.e. *trans* bent distannenes such as $R_2Sn=SnR_2$ and digallynes such as $[RGa \equiv GaR]^{2-}$) keeping in mind that these graphical descriptions are unbeatable in their clearness and simplicity.

Methods

Acknowledgement

[1] a) E. Frankland was careful when he introduced his view of a chemical bond in 1866[1a]: "By the term bond I intend merely to give a more concrete expression to such names as 'an atomicity', 'an atomic power', or 'an equivalence'.... By this term I do not intend to convey the idea of any material connection." E. Frankland, *J. Chem. Soc.* **1866**, *19*, 372; b) For a review see: W. G. Palmer, *A History of the Concept of Valency*, University Press, Cambridge **1965**.

[2] a) A. C. Brown, *On the Use of Graphic Representations of Chemical Formula*, *Proc. Royal Soc. of Edinburgh*, Session **1864 – 65**, 429; b) A.-S. Couper, *Compt. Rend. Ann. Chim. Phys.* **1858**, *469*; c) A. Kekulé, *Ann.Chem. Pharm.* **1858**, *56*, 129; d) V. Meyer, *J. Liebigs. Ann. Chem.* **1876**, *180*, 192; e) A short but concise recent review is given by: E. Heilbronner, J. Jaques, *Chemie in unserer Zeit*, **1998**, *32*, 256.

[3] See for instance: E. Frankland, *Experimental Researches in Pure*, *Applied and Physical Chemistry*, London, **1877**.

[4] G. N. Lewis, *J. Am. Chem. Soc.* **1916**, *38*, 762.

[5] a) P. A. Schultz, R. P. Messmer, *J. Am. Chem. Soc.* **1991**, *113*, 433; b) P. A. Schultz, R. P. Messmer, *J. Am. Chem. Soc.* **1993**, *115*, 10925; c) P. A. Schultz, R. P. Messmer, *J. Am. Chem. Soc.* **1993**, *115*, 10938; d) P. A. Schultz, R. P. Messmer, *J. Am. Chem. Soc.* **1993**, *115*, 10945.

[6] See for example: F. Ogliaro, D. L. Cooper, P. B. Karadakov, *Int. J. Quant. Chem.* **1999**, *74*, 223.

[7] a) PhP=PPh: H. Köhler, A. Michaelis, *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 897; b) PhAs=AsPh A. Michaelis, C. Schulte, *Ber. Dtsch. Chem. Ges.* **1881**, 912.

[8] a) D. E. Goldberg, D. H. Harris, M. F. Lappert, K. M. Thomas, *J. Chem. Soc. Chem. Commun.* **1976**, 261; b) P. J. Davidson, D. Harris, M. F. Lappert, *J. Chem. Soc. Dalton Trans.* **1976**, 2268; c) D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, A. J. Thorne, T. Fjeldberg, A. Haaland, B. E. R. Schilling, *J. Chem. Soc. Dalton Trans.* **1986**, 2387.

[9] a) R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343; b) M. J. Fink, M. J. Michalczyk, K. J. Haller, R. West, J. Michl, *Organometallics* **1984**, *3*, 793.

[10] M. Yoshifuji, I. Shima, N. Inamoto, *J. Am. Chem. Soc.* **1981**, *103*, 4587.

[11] For some reviews see: a) M. Weidenbruch, *Eur. J. Inorg. Chem.* **1999**, 373; b) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463; c) M. Driess, H. Grützmacher, *Angew. Chem.* **1996**, *108*, 900; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 829; d) Special issue *Adv. Organomet. Chem.* **1996**, 39; e) M. F. Lappert, *Main Group Met. Chem.* **1994**, *117*, 183; f) T. Tsumaraya, S. A. Batcheller, S. Masamune, *Angew. Chem.* **1991**, *103*, 916; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 902; g) J. Barrau, J. Esudié, J. Satgé, *Chem Rev.* **1990**, *90*, 283; h) M. Yoshifuji in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, 321; i) R. West, *Angew. Chem.* **1987**, *99*, 1231; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1201; j) A. G. Brook, K. M. Baines, *Adv. Organomet. Chem.* **1986**, *25*, 1; k) G. Raabe, J. Michl, *Chem. Rev.* **1985**, *85*, 419; l) A. H. Cowley, *Acc. Chem. Res.* **1984**, *17*, 386.

[12] Group 14: a) For a discussion of C=C bond lengths see: H.Sakurai, K. Ebata, C. Kabuto, Y. Nakadaria, *Chem. Lett.* **1987**, 301; b) For a discussion of Si=Si bond lengths see refs. [11a,f]; c) For a general discussion of Ge=Ge, Sn=Sn and Pb=Pb bond lengths see refs [11a,b] and: M. Stürmann, W. Saak, M. Weidenbruch, K. W. Klinkhammer, *Eur. J. Inorg. Chem.* **1999**, 579; d) recent calculations: K. W. Klink-hammer, T. F. Fässler, H. Grützmacher, *Angew. Chem.* **1998**, *110*, 114; *Angew. Chem. Int. Ed.* **1998**, *37*, 124 and references therein.

[13] For a general discussion see ref. [11b]. a) Group 15: P=P: refs. [10, 11h]; b) As=As: A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski, *J. Am. Chem. Soc.* **1983**, *105*, 5506; c) Sb=Sb: N. Tokitoh, T. Arai, T. Sasamori, R. Okazaki, S.Nagase, H. Uekusa, Y. Ohashi, *J. Am. Chem. Soc.* **1998**, *120*, 433; d) Bi=Bi: N. Tokitoh, Y. Arai, R. Okazaki, S. Nagase, *Science* **1997**, *277*, 78; B. Twamley, C. D. Sofield, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1999**, *121*, 3357.

[14] M. M. Olmstead, R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **1997**, *119*, 11 705.

[15] L. Pu, M. O. Senge, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1998**, *120*, 12 682.

[16] J. Su, X.-W. Li, R. C. Crittendon, G. H. Robinson, *J. Am. Chem. Soc.* **1997**, *119*, 5471.

[17] a) See the "hot article": *Gallium Triple Bonds Under Fire* by R. Dagani in *Chem. Eng. News* **1998**, March 16. b) Note that the ambiguity of the graphical representation of acetylene as HC≡CH or HC:−C:H was already recognized in the middle of the last century (see ref. [2b]). c) Note also that whenever resonance structures are used for the approximation of the "true" electronic ground state, the position of the nuclei must be kept unchanged; that is resonance of linear [RGa≡GaR]$^{2-}$ with bent [RGa:−Ga:R]$^{2-}$ is incorrect (see. L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, **1960**.

[18] a) For Group 13 double-bond systems see: G. Treboux, J.-C. Barthelat, *J. Am. Chem. Soc.* **1993**, *115*, 4870; b) For a rather complete listing of work devoted to Group 14 double bonds see: H. Jacobsen, T. Ziegler, *J. Am. Chem. Soc.* **1994**, *116*, 3667; c) P. von Ragué Schleyer, D. Kost, *J. Am. Chem. Soc.* **1988**, *110*, 2105; d) T. L. Windus, M. S. Gordon, *J. Am. Chem. Soc.* **1992**, *114*, 9559; e) For Group 15 double-bond systems see: M. W. Schmidt, P. N. Truong, M. S. Gordon, *J. Am. Chem. Soc.* **1987**, *109*, 5217; f) W. W. Schoeller in *Multiple bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 5; g) S. Nagase, S. Suzuki, T. Kurakeke, *J. Chem. Soc. Chem. Commun.* **1990**, 1724. For a discussion of the effect of *intra* atomic repulsion on the bonding in main group elements see: h) W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272.

[19] a) Recent work on group triple-bond systems: K. Kobayashi, S. Nagase, *Organometallics* **1997**, *16*, 2489; b) F. A. Cotton, A. H. Cowley, X. Feng, *J. Am. Chem. Soc.* **1998**, *120*, 1795; c) Y. Xie, R. S. Grev, J. Gu, H. F. Schaefer III, P. von R. Schleyer, J. Su, X.-W. Li, G. H. Robinson, *J. Am. Chem. Soc.* **1998**, *120*, 3773.

[20] E. A. Carter, W. A. Goddard III, *J. Chem. Phys.* **1986**, *90*, 998.

[21] a) G. Trinquier, J.-P. Malrieu, *J. Am. Chem. Soc.* **1987**, *109*, 5303; b) G. Trinquier, J.-P. Malrieu in *The chemistry of functional groups, Suppl. A*: *The chemistry of double bonded functional groups, Vol. 2, Part 1* (Ed. S. Patai), Wiley, Chichester, **1989**, p. 1; c) G. Trinquier, *J. Am. Chem. Soc.* **1990**, *112*, 2130; d) G. Trinquier, *J. Am. Chem. Soc.* **1991**, *113*, 144.

[22] According to Ziegler et al.,[18b] the dissociation energy, $E_{\sigma+\pi}$, may be de-convoluted as: $\Delta E_{\sigma+\pi} = \Delta E_{snap} - \Delta E^{g}_{prep} - \Delta E^{e}_{prep}$, where ΔE^{g}_{prep} and ΔE^{e}_{prep} are energies required to prepare the fragments structurally (ΔE^{g}_{prep}) and electronically (ΔE^{e}_{prep}) for bonding. Furthermore the interaction energy ΔE_{snap} which is gained upon reacting two prepared ER_n and $E^1R^1_m$ fragments may be expressed as: $\Delta E_{snap} = \Delta E_{elstat} + \Delta E_{Pauli} + \Sigma \Delta E^{r}_{int}$. The term ΔE_{elstat} corresponds to the mutual attractive electrostatic interaction of the nuclear charge of E of one fragment with the unmodified charge density of the other. As discussed above, ΔE_{Pauli} is repulsive and counterbalances ΔE_{elstat}, while $\Sigma \Delta E^{r}_{int}$ represents attractive orbital interactions. These authors proposed to identify $E_{\sigma+\pi}$ with ΔE_{snap} instead of using the total bond energy which contains already contributions from $\Delta E_{(S \rightarrow T)}$.

[23] A. D. Becke, E. Edgecombe, *J. Chem. Phys.* **1990**, *92(9)*, 5397.

[24] B. Silvi, A. Savin, *Nature* **1994**, *371*, 683.

[25] a) A. Savin, R. Nesper, S. Wengert, T. F. Fässler, *Angew. Chem.* **1997**, *109*, 1892; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1808; b) A. Savin, A. D. Becke, J. Flad, R. Nesper, H. G. von Schnering, *Angew. Chem.* **1991**, *103*, 421; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 409; c) T. F. Fässler, A. Savin, *Chemie in unserer Zeit* **1997**, *31*, 110.

[26] a) R. J. Gillespie, E. A. Robinson, *Angew. Chem.* **1996**, *108*, 539; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 495; b) R. F. W. Bader, R. J. Gillespie, P. J. MacDougall in *From Atoms to Polymers* (Eds.: J. F. Liebman, A. Greenberg), VCH, **1989**, 1 – 51.

[27] To fulfil the chosen double-bond criterion, M^1 and M^2 must lie within one region with ELF ≥ 0.8. This value might depend on the theoretical method or basis set used. In order to obtain comparable results, extended Hückel (EH) calculations were performed even when the structures were optimized with advanced methods. For a further discussion of the separation of attractors and related bifurcation diagrams see: D. Marx, A. Savin, *Angew. Chem.* **1997**, *109*, 2168; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2077.

[28] This term has been used by us in a manuscript describing the synthesis and structure of a diplumbene[12d] where we intended to include a topographical analysis of classical and nonclassical double bonds. However, this part was excluded in the refereeing process but subsequently used by K. W. Klinkhammer in a commentary on ref. [16] see: K. W. Klinkhammer, *Angew. Chem.* **1997**, *109*, 2414; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2320.

[29] Actually the ELF plot in Figure 1l is a visualization of the interatomic Pauli repulsion which decisively influences the structures of Group 14 double-bond systems as was discussed before. It is evident that in the planar arrangement of α-Sn_2H_4 the repulsive 2c-3e interactions are more severe than in the *trans* bent form. Within the MO approximation, the *trans* bent structures become energetically stabilized by orbital mixing of the π-HOMO with the σ*-LUMO upon distortion from planar D_{2h} to *trans* bent C_{2v} symmetry. Since in the heavier homologues the π–σ* gap becomes smaller, this mixing becomes more efficient and the stabilization of the π-HOMO overcompensates eventually the destabilization of the bonding E–E σ-orbital (see refs. [8c, 18b] for a more thorough discussion).

[30] U. Häußermann, S. Wengert, R. Nesper, T. F. Fässler, Zürich, **1993**. Programm MEHMACC is based on the QCPE-Extended-Hückel-Program EHMACC.[31] The program is available under: mehmacc@inorg.chem.ethz.ch

[31] M.-H. Whangbo, M. Evain, T. Hughbanks, M. Kertes, S. Wijeyesekera, C. Wilker, C. Zheng, R. Hoffmann, *Program EHMACC*, **1990**.

[32] For attempts to visualize localized chemical bonds in digermene by re-localization of the delocalized MOs according to Boy's criterion see: G. Tinquier, J.-P. Malrieu, P. Riviere, *J. Am. Chem. Soc.* **1982**, *104*, 4529.