Do Divalent [{HC(CR′NR″)$_2$}E] Compounds Contain E(I) or E(III) (E = B, Al, Ga, In)? On the Correspondence of Formal Oxidation Numbers, Lewis Structures, and Reactivity

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Dedicated to Professor Jürgen Hinze on the occasion of his 65th birthday

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Very recently, carbene-analogous aluminum and gallium compounds have been obtained in beautiful synthetic work giving rise to interesting theoretical questions in the framework of qualitative MO theory. We analyze the concept of oxidation numbers and the stabilities of these [{HC(CR′NR″)$_2$}E] compounds, **1(E)**, with E being boron, aluminum, gallium, and indium. Population analyses and the electron localization function are used as analytical tools for the elucidation of the electronic density distribution. Singlet-triplet splitting energies, and model reactions probing donor and acceptor properties of the atom E, yield criteria for the reactivity of the cyclic molecules. It is demonstrated that a unique class of Lewis structures can be selected from the large number of chemically reasonable Lewis structures in order to achieve a sufficiently good mapping of the quantum chemical results on simple chemical concepts. The analysis yields that **1(E)**, where E = In, is expected to have similar properties as the experimentally known compounds **1(Al)** and **1(Ga)**, while the boron homologue is expected to be highly reactive, such that its synthesis appears to be difficult.

1. Introduction

Recently, Cui et al.[1] synthesized a new cyclic compound **1(E)** = [{HC(CR′NR″)$_2$}E] containing an aluminum atom bound to two neighboring nitrogen atoms. At about the same time, the corresponding gallium compound was obtained.[2] The planarity of the ring resembles a benzene-like system. This observation led both groups of authors to the conclusion that the electronic structure of the molecule may be described as a carbene analog with Al and Ga, respectively, having the formal oxidation number +I. While **1(Al)** is the first carbene-analogous aluminum compound known, a carbene-analogous gallium compound has already been characterized[3] as predicted by quantum chemical calculations.[4] A divalent boron homologue has not yet been synthesized, and the question arises whether {HC(CR′NR″)$_2$}B might be sufficiently stable to be obtainable in bulk.

Since Cui et al. utilized quantum chemical calculations to support their conclusions,[5] the interesting problem has arisen of when and how numerical results of elaborate quantum chemical calculations can be mapped on simple qualitative chemical descriptors in order to gain transferable knowledge about the electronic structure of a new class of compounds. Is it, in particular, possible at all to determine the formal oxidation state from quantum chemical calculations? A positive answer to this question would in turn attribute substantial meaning to the concept of oxidation numbers.

Jørgensen already tried to settle this question in his book about oxidation numbers,[6] in which he introduced five different oxidation number concepts in order to account for many different chemical situations. Unfortunately, the definitions given[6] are mainly phenomenological, their number exceeds the acceptable degree, and they do not meet concepts of contemporary quantum chemical methods. For instance, Jørgensen defined a spectroscopic and a conditional oxidation state based on *atomic* orbital occupation numbers (atomic configurations). But the atomic occupation number is neither an observable property nor a decisive concept in the light of *molecular* orbitals and *configuration interaction* approaches. Atoms are no longer well-defined entities in molecules, because in all but the simplest cases molecules are treated as collections of electrons and atomic nuclei rather than as clusters of polarized atoms. Actually, this is the fundamental reason why the oxidation number concept can hardly be obtained directly as an atomic "property" in quantum chemical calculations.

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Some attempts have been made to circumvent this problem and to give a definition of the oxidation number concept based on quantum chemistry. Zhan et al. founded their definition on charge transfer within molecular orbital theory.[7] However, their approach appears useless since its ingredients are not well-defined quantities (from the viewpoint of the physical foundations) such as "charge in a local region of a given atom" or "charge in the bonding region". Additionally, some electronegativity values enter their definition neglecting the importance of using clearly defined electronegativity values for an atom in a particular valence state, which gives the best resemblance to its state in the molecule, as explicated in great detail 40 years ago by Hinze and Jaffe.[8−13]

In their analysis of the oxidation state and the possible carbene-analogous character of **1(Al)**, Cui et al. followed closely an earlier work on the electronic structure of Arduengo carbene analogs of group-13 elements.[4] Here, we extend and generalize the work of Cui et al. on the aluminum compound with respect to other group-13 elements to establish a thorough oxidation number classification and stability analysis of [{HC(CR′NR″)$_2$}E], **1(E)**, with E being boron, aluminum, gallium, and indium. This permits also an assessment of the possible stability of the divalent boron compound **1(B)**.

As we demonstrate in the sequel, it is difficult to assign a most suitable Lewis structure for **1(E)** on the grounds of (chemical) common sense. We will discuss possible candidates to conclude which class of Lewis structures is the best one for the representation of the electronic structure. These reasonable Lewis structures for **1(E)** are given in the following section and extended Hückel calculations are employed for a qualitative molecular orbital discussion of the electronic situation. The structures obtained from density functional calculations are discussed thereafter and the electronic density distribution is analyzed in terms of partial charges, the electron localization function, and the Laplacian of the electron density. A discussion of reactivity on the basis of singlet-triplet splitting energies and Lewis acid-base reactions follows in Section 5. Details on the quantum chemical methods employed are given in the Appendix.

2. Qualitative Picture

Nowadays, compounds of the size of **1(E)** can be analyzed on personal computers using quantum chemical methods with sufficiently large basis sets. The aim of a theoretical study should therefore be the gain of insight rather than a reproduction of experimentally obtained quantities. Consequently, the complete knowledge about the electronic density distribution obtained from the numerical calculation should be analyzed in order to assign a characteristic set of Lewis structures. The benefit is a simplified

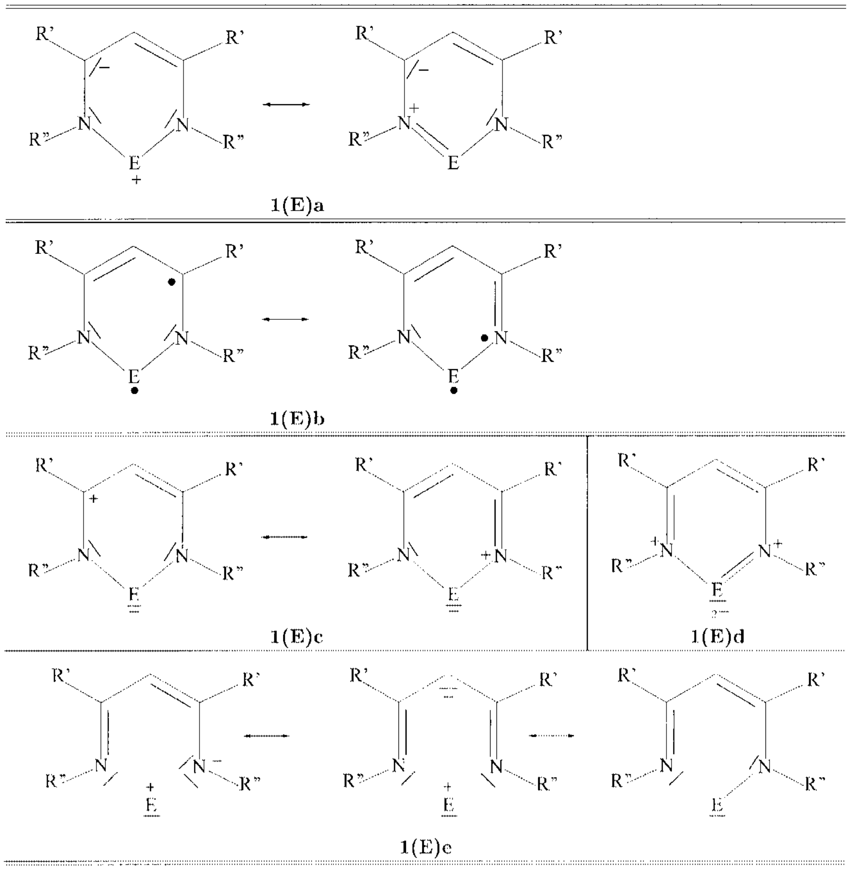

Figure 1. Three classes (the last one is subdivided into three sub-classes) of Lewis structures of [{HC(CR′NR″)$_2$E] compounds (E = B, Al, Ga, In); corresponding symmetric Lewis structures were omitted for the sake of brevity

graphical expression of the electronic structure with the most prominent features. Subsequent work should be possible on the back of an envelope rather than using large computer resources. Three different classes of Lewis structures can be constructed for **1(E)** (Figure 1).

- Class I: In **1(E)a** the element E bears a positive (formal) charge, while the corresponding negative charge is assigned to the ring carbon atoms resulting in an allyl-anion-type substructure. It is possible to delocalize the positive charge on the three-center N−E−N substructure by assuming an additional π interaction between E and the neighboring nitrogen atoms.
- Class II: The only possible electronic structure without charge separation is given by **1(E)b** yielding a diradical.
- Class III: This class is best discussed in terms of three subclasses. The structures in **1(E)c** show a similar bonding pattern like **1(E)a**, although the formal charges of the subsystems are reversed, i.e., a negatively charged atom E and an allyl cation substructure results or the positive charge is shifted towards the nitrogen atoms, respectively. Structure **1(E)d** builds up a separate subclass because a Hückel-aromatic 6π system can only be established at the cost of two negative charges localized on atom E and positive charges localized on the nitrogen atoms. Finally, the structures **1(E)e** generate the third subclass. A bidentate chelate ligand coordinates to the central atom E. Thus, **1(E)e** represents a donor-acceptor complex. This type of bonding has been extensively investigated by Schoeller and co-workers for group-13, -14, and -15 compounds with similar connectivities,[4,14−18] and others have also investigated this.[19−23]

All three classes of Lewis structures stress different qualitative aspects of the electronic structure and correspond to three different oxidation numbers. While Lewis structures and formal charges are well-defined concepts in the sense that they can be drawn without any arbitrariness, this does, in general, not hold for oxidation numbers as already discussed in the Introduction. However, in cases where electrons can be classified as "bonding" and "non-bonding" (such as in cases of lone pairs or non-bonding d electrons in transition metal complexes) the assignment of a formal oxidation number is possible. Since the Lewis structures suggest that we count 0 electron in **1(E)a**, 1 electron in **1(E)b**, and 2 electrons in **1(E)c−e** as non-bonding according to the lone-pair electrons at E [σ/π separation is possible (point group C_{2v})], we obtain the following oxidation number assignment: **1(E)c**, **1(E)d**, and **1(E)e** possess E in the formal oxidation number +I, while **1(E)b** contains E in the formal oxidation number +II and finally for **1(E)a** we have +III. This assignment is in accordance with the rules given by Pauling.[24] Pauling's rule no. 3, which states that the bonding electrons are assigned to the more electronegative atoms, leads to exactly the same oxidation number assignment. In our case, the nitrogen atoms are the more electronegative atoms when compared with E (in terms of Pauling's "averaged" electronegativity scale as well as in terms of the Mulliken−Jaffe electronegativity scale; see also ref.[8]).

The "oxidation number problem" has now been reduced to the analysis of the contribution of the Lewis structures in Figure 1 to the total electronic wavefunction. But a decision about which Lewis structure is most appropriate to describe the actual electronic structure is not straightforward. The standard textbook rules for the relative contribution of Lewis structures are difficult to apply because the stabilizing effect of several electronic and structural features (such as s−p separation in the valence shell of the isolated atom E, charge delocalization, and negative charge on electronegative atoms) is hard to estimate. Numerical results from quantum chemical calculations are needed to solve this puzzle and to achieve a better understanding and improvement of these formal concepts. It should be noted that counting the number of lone-pair electrons is complementary to counting the number of π electrons in the ring. We have 8π electrons in the case of **1(E)a** with oxidation number +III, and 6π electrons in the case of **1(E)c−d** with oxidation number +I. This gives a first hint, along the lines of Hückel's rule, which Lewis structures and thus which oxidation numbers are to be preferred.

The discussion of Lewis structures so far allows us to define descriptors for testing which of these structures are most appropriate. Firstly, we note that E^{III} always bears a positive charge while E^{II} is uncharged and E^{I} results in a more or less pronounced accumulation of negative charge on the group-13 atom. Therefore, population analyses yielding a formal separation of charges in areas of real or Hilbert space may be used to determine the partial charge on atom E.

Since a formal oxidation number of +I requires a lone-pair on atom E, approaches such as the electron localization function,[25] which are able to detect possible lone pairs, may contribute to the classification of the electronic structure in terms of the Lewis structures. Besides these methods for the direct analysis of the charge density, chemical measures for probing particular features of the electronic density distribution such as bond angles and distances, as well as reactivity-based approaches, can be considered. The latter appears to be promising because E^{I} and E^{III} compounds could be distinguished by their different affinity towards Lewis acids such as BF_3, and Lewis bases such as NH_3. Thus, the ability to form Lewis acid-base complexes could be utilized to probe for a lone-pair at the group-13 atom. Binding energies resulting from the analysis of such Lewis acid-base addition reactions are also accessible by quantum chemical calculations. A complication of this viewpoint comes from the so-called inert-pair effect: The larger the nuclear charge Z of atom E, the more important is this effect on reducing the donor property of E without changing the formal oxidation number.

To obtain a first qualitative picture of the electronic structure within molecular orbital theory, we performed Extended-Hückel Theory (EHT) calculations since they provide an *occupation number independent* view of the electronic structure. A representation of the molecular orbitals on the basis of fragment orbitals of cation E^+ and a negatively charged ligand $[HC(CR'NR'')_2]^-$ reveals some im-

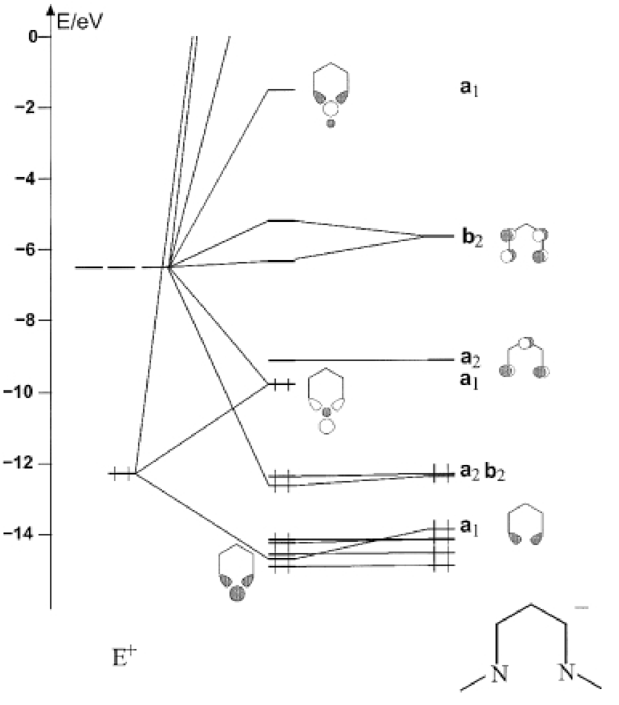

Figure 2. Simplified MO diagram from Extended-Hückel calculations; the left-hand side shows the valence atomic orbitals of the aluminum atom, whereby the highest occupied p-orbital is denoted by a small vertical line; the right-hand side gives the molecular orbitals of the remaining {HC(CR′NR′′)$_2$} chelate ligand; in the center the molecular orbitals for the total complex are depicted

portant aspects of the bonding situation (Figure 2). It should be noted that the ligand is σ- and weakly π-bonding, and element E^+ cannot back-donate.

The qualitative MO diagram from EHT calculations shows a rather small HOMO−LUMO energy splitting. The frontier orbitals can be classified as a metal−ligand nonbonding orbital of a_2 symmetry (point group C_{2v} assumed) being localized on the ligand and a weakly anti-bonding combination with nitrogen sp^2 and metal sp contributions. The latter MO has the character of a metal lone pair. Since the a_2 MO has no metal contributions for symmetry reasons, its energy is largely independent of the nature of E. The energy of the a_1 MO is expected to be the HOMO for the heavier group-13 elements, while at least for E = B a more pronounced antibonding character due to a larger π overlap may result in a_2 then becoming occupied. A decision about this ordering is beyond the scope of the qualitative EHT treatment.

3. Optimized Structures

The structures obtained with the pure density functional BP86 and the hybrid functional B3LYP are discussed in the following. For the sake of simplicity and computational efficiency and to arrive at substituent-independent conclusions we concentrate on generic models of **1(E)**. Therefore, we chose the model compound with R′ = R′′ = H. However, to test for substituent effects we also performed calculations for R′′ = Me. The most important structural parameters are depicted in Figure 3 and given in Table 1. All optimized structures **1(E)** are found to be minima on the potential energy surface.

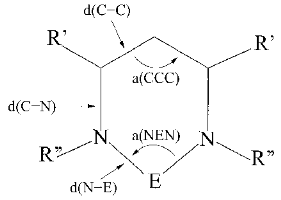

Figure 3. Definition of characteristic structural parameters

The optimized structures for the heavy elements of group-13 adopt C_{2v} symmetry in their singlet ground state, and they are thus planar. For the boron compound, a distortion to C_2 symmetry is observed, indicating a qualitatively different electronic structure of **1(B)** when compared to its higher homologues. In the triplet state, **1(Al)** and **1(B)** are planar, while the Ga and In atoms in **1(Ga)** and **1(In)**, respectively, may lie above the NCCN plane in an envelope-type structure (this depends on the density functional and on the R′′ substituent, indicating an electronic structure of the triplet state being too complicated to be accessible by density functional methods).

The C−C and N−C bond lengths deviate for Al to In slightly from the values found for the anionic $C_3H_5N_2^-$ ligand. These findings justify the fragmentation used in the qualitative EHT calculation and indicate that the Lewis structures **1(E)e** are a good representation for E = Al and an even better one for E = Ga and E = In. The heavier the group-13 element E is, the more the binding situation resembles a chelate complex.

In the case of E = B, the changes observed in the ligand are larger; the C−N bond is 5 pm longer while the C−C distance is shortened by 2.5 pm. It is interesting to note that similar values can be found for the lowest triplet states of the Al, Ga, and In complexes. This may be interpreted as an indicator for the orbital crossover discussed in the previous section.

In general, the substitution of hydrogen by a methyl group does not change the structure significantly and both compare very well with the experimental structures for E = Al and E = Ga, in which 2,6-iPr$_2$C$_6$H$_3$ substituents are present, Only the N−E bond lengths deviate by 5−6 pm from the calculated distances.

4. Analysis of the Electronic Density

According to the charge separation suggested by the different Lewis structures, we calculated partial charges from two different population analyses. One was suggested by Cioslowski,[26] which is defined in real space, and the other one by Heinzmann and Ahlrichs,[27] which is defined in the Hilbert space of (modified) atomic orbitals. The two conceptually different population analyses are used since the partial charge of an atom in a molecule is not a well-defined

Table 1. Selected structural parameters of [{HC(CR′NR″)$_2$}E] (R′ = H) for their singlet ground states (S = 0) and the lowest-lying triplet states (S = 1); the last data set contains structural parameters for the anionic ligand; distances d are given in pm and the angles a in °; the definition of parameters $a-d$ are given in Figure 3; the experimental bond lengths and angles for [{HC(CMeNAr)$_2$}E] (R″ = Ar = 2,6-iPr$_2$C$_6$H$_3$) with E =Al, Ga are given for comparison (PG is an acronym for "point group")

E	R"	parameter	BP86/RI		B3LYP	
			S=0	S=1	S=0	S=1
B	H	d(C–C)	139.1	138.9	138.6	138.3
		d(C–N)	137.7	141.8	135.9	141.3
		d(N–E)	145.6	142.1	146.5	141.4
		a(NEN)	112.4	118.4	110.0	118.6
		a(CCC)	120.5	122.5	119.7	122.4
		PG	C_2	C_{2v}	C_2	C_{2v}
	Me	d(C–C)	139.2	138.9	138.5	138.2
		d(C–N)	137.8	141.5	136.5	141.0
		d(N–E)	144.6	142.3	144.7	141.6
		a(NEN)	115.6	120.8	114.8	121.0
		a(CCC)	120.5	122.5	120.1	122.4
		PG	C_2	C_{2v}	C_2	C_{2v}
Al	H	d(C–C)	139.8	139.4	139.2	138.8
		d(C–N)	133.3	141.3	132.4	140.9
		d(N–E)	200.6	181.9	199.6	181.0
		a(NEN)	85.8	104.5	85.9	104.5
		a(CCC)	123.0	128.1	122.7	127.9
		PG	C_{2v}	C_{2v}	C_{2v}	C_{2v}
	Me	d(C–C)	139.8	139.4	139.3	138.8
		d(C–N)	133.0	141.1	132.0	140.6
		d(N–E)	201.7	182.9	200.7	181.9
		a(NEN)	89.2	107.9	89.4	107.9
		a(CCC)	124.2	128.9	124.0	128.7
		PG	C_{2v}	C_{2v}	C_{2v}	C_{2v}
exp. [1]	Ar	d(C–C)	139.1			
		d(C–N)	134.1			
		d(N–E)	195.7			
		a(NEN)	89.9			
		a(CCC)	126.8			
Ga	H	d(C–C)	140.0	139.7	139.4	138.8
		d(C–N)	133.0	140.5	132.1	140.5
		d(N–E)	209.7	190.7	209.5	187.0
		a(NEN)	84.1	99.3	84.0	102.6
		a(CCC)	124.2	128.5	124.0	128.7
		PG	C_{2v}	C_s	C_{2v}	C_{2v}
	Me	d(C–C)	140.0	139.4	139.5	139.0
		d(C–N)	132.6	140.8	131.6	139.4
		d(N–E)	210.7	188.1	210.6	191.0
		a(NEN)	87.5	106.7	87.4	101.5
		a(CCC)	125.5	129.7	125.3	129.1
		PG	C_{2v}	C_{2v}	C_{2v}	C_s
exp. [2]	Ar	d(C–C)	140.0			
		d(C–N)	133.8			
		d(N–E)	205.5			
		a(NEN)	87.5			
		a(CCC)	127.7			
In	H	d(C–C)	140.2	141.2	139.7	140.8
		d(C–N)	132.9	138.0	132.0	136.9
		d(N–E)	229.8	222.6	229.6	226.0
		a(NEN)	79.8	84.2	79.5	82.3
		a(CCC)	126.4	130.4	126.1	130.8
		PG	C_{2v}	C_s	C_{2v}	C_s
	Me	d(C–C)	140.3	140.7	139.8	140.0
		d(C–N)	132.4	132.2	131.5	131.2
		d(N–E)	231.1	218.2	231.0	218.7
		a(NEN)	83.1	92.6	82.9	92.1
		a(CCC)	127.9	129.5	127.6	129.1
		PG	C_{2v}	C_{2v}	C_{2v}	C_{2v}
ligand	H	d(C–C)	142.1	142.5	141.5	142.5
		d(C–N)	132.0	137.6	130.8	137.6
		a(CCC)	132.1	136.5	131.6	136.5
		PG	C_{2v}	C_{2v}	C_{2v}	C_{2v}
	Me	d(C–C)	142.1	141.9	141.5	141.9
		d(C–N)	132.0	136.3	130.8	136.3
		a(CCC)	131.6	136.1	131.2	136.1
		PG	C_{2v}	C_{2v}	C_{2v}	C_{2v}

quantum mechanical quantity. Any definition of this intuitive concept is affected by a certain degree of arbitrariness. However, we aim at qualitative results and these should be reproduced by both population analyses. The results of the calculations are given in Table 2.

Table 2. Partial charges q on atom E in fractions of the elementary charge in the singlet state of **1(E)** (R′ = H) according to population analyses by Cioslowski q_C[26] and by Ahlrichs and co-workers q_A[27] (q_A includes multi-center corrections); discrepancies occur for E = In, where the general trend is not maintained; this can be traced back to the use of the ECP for In

E	R"	BP86(/RI)		B3LYP	
		q_C	q_A	q_C	q_A
B	H	−1.37	−0.34	−1.75	−0.39
	Me	−1.16	−0.35	−1.45	−0.37
Al	H	1.21	0.36	1.29	0.37
	Me	1.13	0.41	1.25	0.42
Ga	H	1.66	0.45	1.75	0.46
	Me	1.54	0.45	1.65	0.47
In	H	0.64	0.94	0.67	0.95
	Me	0.60	0.95	0.64	0.95

While Al and its higher homologues carry positive partial charges, the boron compound exhibits negative partial charges indicating that reactions of **1(B)** will be different from those of the higher homologues. The N−E bonds have substantial ionic character.

In order to visualize a potential electron-pair on element E we utilize the electron localization function (ELF).[25] The ELF is a measure for the spherically averaged Fermi-hole around a reference electron at position $\vec{r}$. As introduced by Becke and Edgecombe,[25] the function can be mapped onto an interval 0 < ELF < 1. ELF ≈ 1 indicates areas of a localized exchange potential. Such areas are occupied by electron pairs. For ELF ≈ 0 the exchange hole is strongly delocalized. The ELF reveals the presence of a lone pair at atom E for all group-13 elements (Figure 4). A polar nature of the N−E bonds is present for all heavier atoms E, i.e., E = Al, Ga, In, which is typical for donor−acceptor complexes.

In addition to ELF, we also calculated the Laplacian of the electron density in the framework of the Atoms-In-Molecules theory[28] but refrain from giving plots of the result because of the mapping which connects ELF and the Laplacian of the density.[29,30] [An advantage of ELF is that the corresponding Laplacian of the density, $\nabla^2\rho(\vec{r})$, is unbound, while ELF is not; ELF is therefore more suitable for graphical representations.] Since the Laplacian field $\nabla^2\rho(\vec{r})$ is a measure for local charge concentrations [$\nabla^2\rho(\vec{r}) < 0$] and for charge depletion [$\nabla^2\rho(\vec{r}) > 0$] in the electron distribution of a molecule, we find for the elements Al to In the N−E bonding electrons assigned to the valence shell of the nitrogen atoms as witnessed by the convex nature of the area of charge concentration/electron localization. Only for E = B is the situation less clear. Here, the bond exhibits a more covalent character.

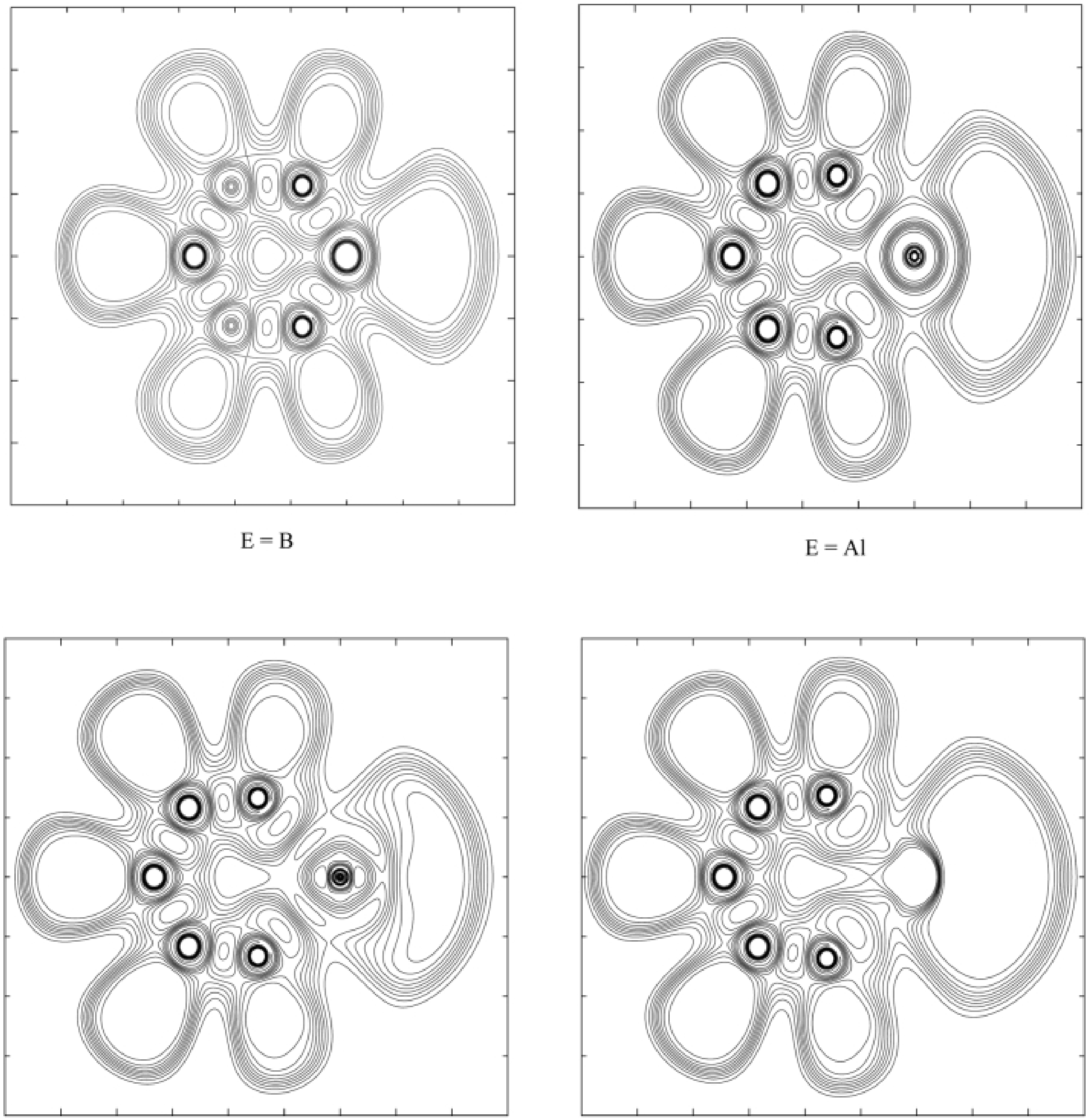

Figure 4. ELF plots for $[\{HC(CR'NR'')_2\}E]$, where $R' = R'' = H$; the contour lines give the increasing value for ELF in steps of 0.1 from 0.0 (no localization) outside the molecules to 1.0 (high localization) at the C−H and N−H bonds and at the lone pairs; the internal structure of the indium atom is not resolved because of the ECP

5. Reactivity − Singlet−Triplet Splittings and Addition of NH_3 and BF_3

We proceed by analyzing the singlet−triplet splitting energies given in Table 3. We find that for E = B and $R' = R'' = H$, the triplet state is almost as stable as the singlet state, indicating a high reactivity of **1(B)**. The B3LYP splitting energy favors the triplet state by about 20 kJ/mol, which is due to the fact that B3LYP always favors spin states of high multiplicities owing to the explicit consideration of Fermi correlation through exact exchange admixture.[31] If the hydrogen atoms on the ring nitrogen atoms are substituted by methyl groups, the situation becomes even less clear. DFT calculations are not sufficiently accurate to finally answer the question of the ground state multiplicity of **1(B)**. Since the knowledge of the ground state multiplicity is of minor importance to our study, we refrain from performing more elaborate calculations. The important result is that singlet and triplet states are energetically close for E = B, while this is not the case for the higher homologues, where the triplet states lie more than 150 kJ/mol above the singlet states.

This analysis of the singlet−triplet energy splittings reveals that the aluminum, gallium, and indium compounds have a similar electronic structure, while the boron compounds are different as they will exhibit a higher reactivity and are thus well represented by the Lewis structures of the biradical, **1(B)b**. This structure should also come to the fore in a plot of the spin polarization, which is the "excess density" of the unpaired electrons. It is plotted for the triplet state of **1(B)** in Figure 5 and clearly shows a single electron at atom E and a "delocalized" electron over the four ring atoms exactly corresponding to Lewis structure **1(B)b**. It is thus most likely that the boron compound **1(E)** is not sufficiently stable to be "accessible in a flask".

Table 3. Singlet−triplet splittings $\langle E\rangle_{\mathrm{ST}} = \langle E\rangle_{\mathrm{S=1}} - \langle E\rangle_{\mathrm{S=0}}$ in kJ/mol

E	R"	BP86(/RI)	B3LYP
B	H	−2	−18
	Me	12	−5
Al	H	144	148
	Me	160	164
Ga	H	217	227
	Me	233	224
In	H	245	257
	Me	271	282

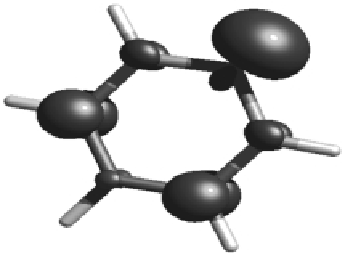

Figure 5. Spin polarization of the triplet state of **1(B)**

To analyze the electronic situation and reactivity of element E in **1(E)** further, we probe the potential lone pair or "electron-hole" on element E by addition reactions, in which an electron-pair donor such as NH_3 and an electron-pair acceptor such as BF_3 are added [Equations (1) and (2)].

$$\text{Reaction (I): } \mathbf{1(E)} + NH_3 \rightarrow \mathbf{1(E)}{-}NH_3 \qquad (1)$$

$$\text{Reaction (II): } \mathbf{1(E)} + BF_3 \rightarrow \mathbf{1(E)}{-}BF_3 \qquad (2)$$

Note that these addition reactions shall serve as model reactions to probe certain electronic features of **1(E)** rather than to find stable, experimentally accessible adducts. The addition of NH_3 occurs only perpendicular to the plane of the six-membered ring for E = Al, Ga, In, as one would expect for E bearing a lone-pair. An in-plane addition does not occur; the NH_3 is then rejected indicating that a lone-pair−lone-pair repulsion appears. In the case of E = B, the adduct rearranges to give a five-membered ring, where one N−H unit builds up an annulated B−C−N three-membered ring. Therefore, we restrict the discussion to the addition reactions for the higher homologues, which are all minimum structures on the potential energy surface. The general adduct structure is depicted for E = Al in Figure 6. Selected structural parameters are given in Table 4, and the reaction energetics can be found in Table 5.

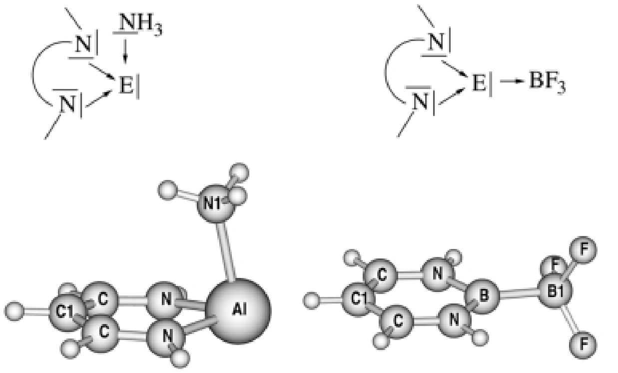

Figure 6. Structures for two possible adducts of NH_3 and BF_3 and the corresponding BP86/RI/TZVP-optimized structures for **1(Al)** + NH_3 and **1(B)** + BF_3

Table 4. Selected structural parameters of adducts $[\{HC(CR'NR'')_2\}E]NH_3$ (R′ = R″ = H) for their singlet ground state ($S = 0$): distances d are given in pm and the angles a in °; the definition of parameters $a-d$ are according to the definition for the basis systems in Figure 3; the labelling C1 and N1 is according to Figure 6; the bond lengths and angles for the boron adduct are not given since the structure rearranges drastically; all calculations have been performed with the TZVP basis set

E	parameter	BP86(/RI)	B3LYP
Al	d(C−C)	140.3	139.7
	d(C-N)	132.9	131.9
	d(N−E)	204.2	203.3
	d(E−N1)	231.1	234.1
	a(NEN)	85.6	85.7
	a(CCC)	123.2	123.0
	a(C1EN1)	79.3	79.6
Ga	d(C−C)	140.4	139.8
	d(C−N)	132.6	131.7
	d(N−E)	214.6	214.0
	d(E−N1)	252.4	260.3
	a(NEN)	83.3	83.2
	a(CCC)	124.6	124.3
	a(C1EN1)	77.6	77.5
In	d(C−C)	140.7	140.1
	d(C−N)	132.6	131.6
	d(N−E)	234.9	234.4
	d(E−N1)	266.6	271.1
	a(NEN)	79.1	78.8
	a(CCC)	126.8	126.5
	a(C1EN1)	71.4	72.1

Table 5. Energetics for the addition of NH_3 [Equation (1)]: reaction energy $\Delta\langle E\rangle$ at 0 K without zero-point vibrational energy correction (ZPVE), difference of zero point energies ΔZPVE, reaction enthalpy ΔH and free reaction enthalpy ΔG (both at 298.15 K and 1013.25 hPa) obtained for BP86/RI and B3LYP with the TZVP basis set; all energies are given in kJ/mol

	BP86(/RI)				B3LYP			
	$\Delta\langle E\rangle$	ΔZPVE	ΔH	ΔG	$\Delta\langle E\rangle$	ΔZPVE	ΔH	ΔG
Al	−20.9	5.4	−14.0	23.0	−15.1	5.3	−8.1	29.1
Ga	−13.6	4.6	−6.5	27.1	−10.2	5.3	−2.7	32.7
In	−23.5	5.5	7.9	23.4	−21.4	6.2	8.3	28.9

All three reactions are energetically very similar. They are exothermic by about 15 kJ/mol, but endergonic by about 20 kJ/mol because of the model-inherent increase of vibrational entropy from the quenching of translational and rotational degrees of freedom on adduct formation. These results are almost independent of the functional used and demonstrate that **1(E)** with E = Al, Ga, In react as Lewis acids if the Lewis base approaches from above the ring plane. Upon addition, the structure of the allyl system is not changed; the C−C and C−N bond lengths as well as the C−C−C angle do not change significantly. However, the donated lone-pair of ammonia lengthens the E−N bonds in the six-membered ring by 3.6 pm for E = Al and by about 5 pm for E = Ga, In. In all adducts, the E−NH_3 distances are 30 to 40 pm longer than the in-plane E−N distances, which may be an indication for a double-bond character of the E−N bond in the ring. However, the equatorial E−N distances should be shorter because of sp^2 hybridization and for steric reasons, while the axial E−NH_3 bond should be longer because of the larger repulsion in this position.

For reaction (II) [Equation (2)], i.e., the addition of the electron acceptor BF_3, stable addition products are found for all four molecules. The general structure of the adduct is shown for E = B in Figure 6 (selected parameters see Table 6). In contrast with the NH_3 addition, the addition of BF_3 occurs in the plane of the six-membered ring as would be expected in view of the Lewis base addition of **1(E)** to BF_3.

Table 6. Selected structural parameters of adducts $[\{HC(CR'NR'')_2\}E]BF_3$ (R′ = R″ = H) for their singlet ground state ($S = 0$): distances d are given in pm and the angles a in °; the definition of parameters $a-d$ are according to the definition for the basis systems in Figure 3; the labelling C1 and B1 is according to Figure 6; an asterisk, *, indicates that the BF_3 ligand tends to dissociate; all calculations have been performed with the TZVP basis set

E	parameter	BP86(/RI)	B3LYP
B	d(C–C)	139.7	138.9
	d(C-N)	133.6	132.8
	d(N–E)	147.1	146.5
	d(E–B1)	173.4	173.4
	a(NEN)	109.4	109.6
	a(CCC)	118.8	118.6
	a(C1EB1)	173.7	174.4
Al	d(C–C)	139.8	139.2
	d(C-N)	133.5	132.7
	d(N–E)	193.7	192.5
	d(E–B1)	232.6	233.9
	a(NEN)	90.6	90.8
	a(CCC)	123.5	123.2
	a(C1EB1)	177.1	179.1
Ga	d(C–C)	139.8	139.3
	d(C-N)	133.2	132.3
	d(N–E)	201.2	201.7
	d(E–B1)	237.6	250.3⋆
	a(NEN)	88.5	87.8
	a(CCC)	124.3	124.0
	a(C1EB1)	178.1	179.2
In	d(C–C)	140.2	139.6
	d(C-N)	132.9	132.0
	d(N–E)	226.9	227.5
	d(E–B1)	320.3⋆	356.4⋆
	a(NEN)	81.0	80.2
	a(CCC)	126.4	126.1
	a(C1EB1)	177.7	176.4

While the addition is about 140 kJ/mol exergonic for **1(B)** (Table 7) indicating that **1(B)** itself is unstable, reaction (II) is endergonic for the higher homologues, where the inert-pair effect becomes more and more important, such that the molecular orbital corresponding to the lone pair has an increased s character, which reduces the Lewis base character of the compound and reduces in turn the bond energy of the adduct. As a consequence, in the case of E = Ga and particularly for E = In, the Lewis acid BF_3 is rejected and thus does not build a donor−acceptor bond with the six-membered ring. In the case of E = B, Al, the allyl subsystem in the ring is again hardly distorted upon adduct formation, while the E−N bond lengths are shortened by about 7 pm, for aluminum it changes only little in the boron compound.

Table 7. Energetics for the addition of BF_3 [Equation (2)]: reaction energy $\Delta\langle E\rangle$ at 0 K without zero-point vibrational energy correction (ZPVE), difference of zero point energies ΔZPVE, reaction enthalpy ΔH and free reaction enthalpy ΔG (both at 298.15 K and 1013.25 hPa) obtained for BP86/RI and B3LYP with the TZVP basis set; ΔH and ΔG are not given in cases where the BF_3 tends to dissociate; all energies are given in kJ/mol

	BP86(/RI)				B3LYP			
	$\Delta\langle E\rangle$	ΔZPVE	ΔH	ΔG	$\Delta\langle E\rangle$	ΔZPVE	ΔH	ΔG
B	−196.7	8.3	−186.0	−141.5	−212.6	9.5	−201.4	−153.3
Al	−39.0	0.7	−34.3	5.03	−30.0	−0.6	−26.2	13.1
Ga	−23.7	3.4	−16.9	27.4	−13.3	1.6	—	—
In	−8.6	1.4	—	—	−8.1	2.5	—	—

6. Conclusion

To conclude, we were able to identify the formal oxidation number of atom E in **1(E)** through various descriptors and could correspond the electronic structure, stability, and reactivity with one particular class of Lewis structures for each molecule **1(E)**. This is remarkable in view of the many different classes of reasonable Lewis structures, which can be thought of for **1(E)**. All higher homologues of **1(E)** are best represented by the donor−acceptor Lewis structure **1(E)e**. For these cases we find a formal oxidation number of +I while boron is in its formal oxidation state +II in **1(B)**.

Furthermore, **1(B)** differs largely from the higher homologues: The electronic structure of **1(B)** can be characterized by the diradical Lewis structures **1(B)b**, symbolizing the low-lying triplet state, which is an indicator of high reactivity. This is supported by the finding that **1(B)** reacts with NH_3 under rearrangement, and with BF_3 to give a stable adduct with a boron−boron bond. Unfortunately, it also implies that **1(B)** with divalent boron is not a valuable synthetic target in contrast to the Arduengo-analoguous boron compound studied previously.[4]

Appendix

Quantum Chemical Methodology: For all calculations we used the density functional programs provided by the TUR-

BOMOLE 5.1 suite.[32] The Becke−Perdew functional dubbed BP86[33,34] and the hybrid functional B3LYP[35,36] were employed as implemented in TURBOMOLE. For all molecules that do not contain In, all-electron calculations have been performed. In these cases the resolution of the identity (RI) technique[37,38] was used in combination with the BP86 functional calculation. All results were obtained from fully optimized Kohn−Sham calculations using Ahlrichs' TZVP basis featuring a valence triple-zeta basis set with polarization functions on all atoms.[39] For all compounds containing indium, we tested the 46-electron effective core potential (ECP) from the Stuttgart−Bonn (SB) group,[40] which allowed us to treat only 3 electrons explicitly. It turned out that such a large-core ECP does not describe the In atom properly (i.e., the core polarization is drastically underestimated). Therefore, a 28-ECP from the SB group[41] was used, which leaves 16 electrons to be treated explicitly. The double-zeta basis set optimized for this ECP and distributed by the SB group has been employed.[42] Up to date, no optimized auxiliary basis exists for the small-core 28-ECP, therefore we did not apply the RI technique for the indium complexes. The addition reactions have not been corrected for the basis-set superposition error because it is less than 7 kJ/mol for the addition of NH_3, and less than 5 kJ/mol for the BF_3 addition, and would not change the qualitative picture. In order to analyze the electron density of the compounds, we use the population analysis by Ahlrichs and co-workers[27] as implemented in TURBOMOLE. For the vibrational analysis, the second derivatives of the total electronic energy were computed as numerical first derivatives[43,44] of analytical energy gradients (obtained from TURBOMOLE) within the harmonic approximation. The Cioslowski charges have been computed with SNF[43] as well as the thermochemical data, which were obtained in the standard way from the frequency analysis using the partition function of the harmonic oscillator in combination with the vibrational frequencies. Translational and rotational degrees of freedom were treated classically. For the EHT calculations we used YAEHMOP.[45] The ELF calculations and the analysis of the Laplacian of the electron density have been performed using the program ELF.[46] The program MOLDEN[47] has been used for the visualization of structures.

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