On the electronic structure of main group diazadiene complexes, with boron, aluminium, gallium and indium, a density functional evaluation

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Homoleptic diazabutadiene complexes with the Group 13 elements boron, aluminium, gallium and indium are studied by means of density functional calculations. For the homologues with aluminium and gallium they are in accord with experiment and predict tetrahedrally shaped complexes with C_{2v} symmetry. For the boron compound the complexes are also tetrahedral, but the nitrogens in one ring system are slightly pyramidalised. For the indium homologue a totally different geometry is obtained from the calculations. Both rings are almost in one plane, slightly twisted towards each other. As a consequence the spin density of the unpaired electron in the doublet system for E = B, Al, Ga is located in one ring system while it is equally spread over both rings for E = In, with concomitant strong spin polarisation for the overall structure. The formal oxidation state of the central atom is compared with the results of a charge density analysis.

Introduction

Main group elements of Group 13 of the Periodic Table of elements are predicted to form stable anions of type I which are isovalent electronically with the Arduengo type carbenes [1,2] (Scheme 1). For E = Ga [3] and Al [4] stable species of this type were
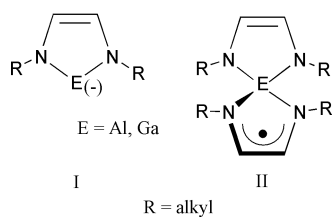
Scheme 1

recently synthesised and spectroscopically characterised. In these compounds the element E is chelated by a diazabutadiene ligand. A related type of compound is presented in II. The central atom is surrounded by two diazabutadiene ligands and the system is a radical. The homoleptic gallium complex was obtained by co-condensation of gallium vapour with an excess of 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene at low temperature.[5] Also the aluminium compound has been prepared.[6] For both compounds the X-ray structures show different ligands with different geometries and spin density is located within one ring system which is spanned by the ligand with the central atom. The photoelectron spectrum of the gallium compound was recently reported.[7] The original assignment of the central atom as Ga(+2) was debated on the basis of an ESR investigation.[8] These authors stated that the central atom should be better assigned to an oxidation state +3.

Here we report density functional calculations on the homologous series of type II compounds with E = B, Al, Ga and In. Our investigations will also include structural predictions on the hitherto experimentally unknown homologues with boron and indium. Details of the quantum chemical calculations are presented in the Theoretical section of this paper.

Theoretical section

Qualitative considerations were deduced from EH calculations,[9] the density functional calculations supported them quantitatively.[10] For the latter we used an all-valence electron basis set of double-ζ quality for the elements B, Al and Ga (6-31++g(d,p)).[11] For E = In a corresponding basis set does not exist, hence alternatively a relativistically corrected effective core potential basis set described by Stevens and co-workers[12] was utilised. This type of basis set is denoted as SBK++g**. Both types of basis sets are of similar quality. All atoms were augmented by one single set of polarisation[13] as well as a single set of diffuse functions.[14] In order to allow comparison of the type I with the type II structures the basis sets were chosen to be the same as those used in ref. 1. The density functional calculations[15] were performed with Becke's three-parameter function,[16] with local and non-local electron correlation contributions of the Lee–Yang–Parr correlation functional[17] (B3LYP). The structures were fully optimised and characterised by vibrational analyses, using analytic first and second derivatives. The population analysis was obtained according to the Weinhold–Reed partitioning scheme.[18] In addition the method of "atoms in molecules" developed by Bader[19] was employed.

Results and discussion

a. Qualitative considerations

In structures of type II the central atom is surrounded by two ligands (RNCHCHNR, R = alkyl), with a total of four coordinating positions. Consequently it is logical to first analyse various possible structures on the basis of ligand field considerations[20] (Scheme 2).

Scheme 2

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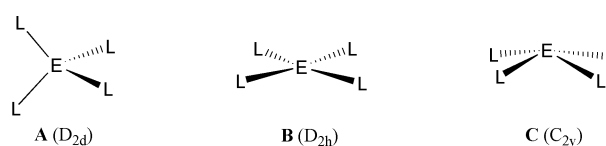
In the diazabutadiene ligand each nitrogen atom is bound to the central atom, each of them denoted here as a ligand L. The most relevant conformations refer to a distorted tetrahedral **A** (D_{2d}), a planar **B** (D_{2h}) or a pyramidalised **C** (C_{2v}) arrangement of ligands. We note that a more detailed analysis of these aspects was already presented recently in an analysis of bonding in the bis(amidinate) complex formation.[21] It is expected that for the higher element homologue indium the inert s-pair effect comes to the fore[22–24] and for this element a chelate structure of type **C** is most likely.

The diazabutadiene ligand possesses the molecular orbital system shown in Scheme 3.
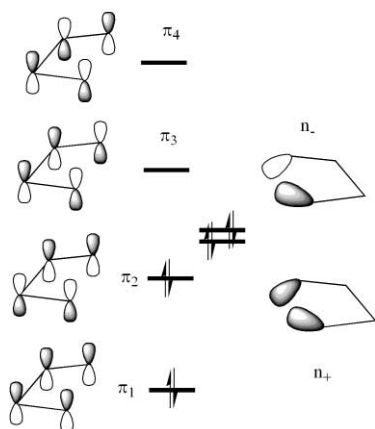
Scheme 3

The structure comprises of a set of π_1 to π_4 molecular orbitals, and two combinations of lone pair orbitals at the nitrogens, n_+ and n_-. In general lone pair orbitals are better suited for complexation with E than the set of π-orbitals.[21]

The system of frontier orbitals for the various ligand arrangements **A** to **C** were first evaluated by the EH calculations. The two rings, here denoted as ring L (left) and ring R (right), constitute two mutual weakly interacting molecular orbital systems (of each ligand L). In accordance with the previous considerations[7] they also interact weakly with the orbitals at the central atom E. For **A** the resulting five lowest energy molecular orbitals are as shown in Scheme 4.
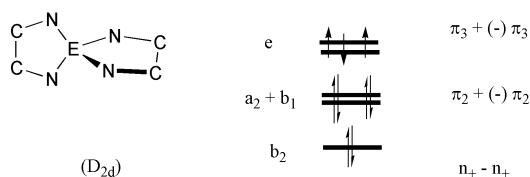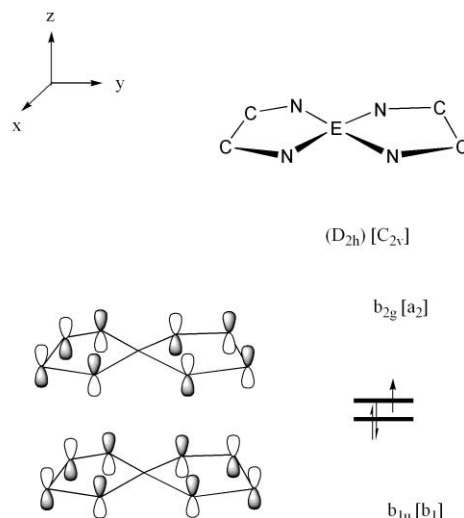

Scheme 4

The molecular orbitals of both rings (D_{2d} symmetry imposed) form either a degenerate ($\pi_3(L) \pm \pi_3(R)$) or an energetically weakly split ($\pi_2(L) \pm \pi_2(R)$) set. Below the π-orbitals is the antibonding combination of lone pair orbitals, $n_+ - n_+$.

Since the degenerate e-set of orbitals is occupied by three electrons the degeneracy is broken due to Jahn–Teller distortion. The vibrational modes which lead to lower symmetry are given[25] by the cross product $e \otimes e = a_1 + b_1 + b_2$. The distortion which preserves the tetrahedral shaping of the complex structure II leads to C_{2v} symmetry. In this case the experimentally observed structural types with two different ring geometries for E = Al and Ga are obtained and only one ring takes up the unpaired electron.

Alternatively to **A** one may consider the structural type **B**. The degenerate set of π_3 orbitals is now weakly split into $b_{2g} + b_{1u}$ (D_{2h} symmetry) (Scheme 5).

For the unpaired electron a different bonding situation results. It becomes delocalised, equally over both ring
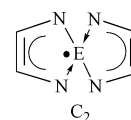

Scheme 5

systems. Simultanously the E–N bonds are weakened. A further geometrical relaxation may be achieved in the structural type **C**, here the central atom E can form an inert, stereochemically active s-electron. It requires pyramidalisation at E. The bonding situation of type **C** comes to the fore for weak overlap of E with the ligands. For the C_{2v} symmetrical case (type **C**) the frontier orbitals refer to a_2 and b_1.

The electronic states of the doublet configurations are given as follows: (i) for type **A** conformation $^2B_1$ (within C_{2v} symmetry).[7] (ii) For type **C** conformations two possibilities are feasible. The unpaired electron resides in the a_2 or b_1 molecular orbital (see Scheme 5). It has the consequence that a $^2A_2$ and a $^2B_1$ state exist which are close in energy. The energetic levelling of the quasi-degenerate molecular orbitals depends on (a) the ligand–ligand orbital overlap, (b) the weak mixing of suitable orbitals (p_z) with the central atom E and (c) on the electronegativity of E.

Because of the small energy difference between the $^2A_2$ and $^2B_1$ states, deformation to a lower symmetry (*e.g.* favoured by steric factors) is easy. This distortion will be along the $a_2 \otimes b_1 = b_2$ mode and causes a lowering to C_2 symmetry (Scheme 6).

Scheme 6

The E–N bonds become unsymmetrical and the unpaired electron is delocalised over both the ligands and the central atom. We note this view of bonding is only operative in the case of a very weak ligand field of L, according to the numerical calculation it is the ground state for E = In (see below).

b. Equilibrium geometries

In order to examine these aspects more closely we performed for the parent systems (R = H) density functional calculations on the complete series of compounds (E = B, Al, Ga, In) of type II. All structures were subjected to vibrational analyses, in order to ensure that they were energy minima. Plots of the three typical equilibrium geometries with C_s, C_{2v} and C_2 symmetry were obtained with the Molden program[26] and are shown in Fig. 1 (from top to bottom E = B, Al, In). The most relevant bonding parameters are collected in Table 1. Thus the calculations predict tetrahedrally shaped (type **A**) structures for E = B to Ga.

The boron compound preferentially adopts C_s symmetry, with the ligands arranged in a distorted tetrahedron. Both rings
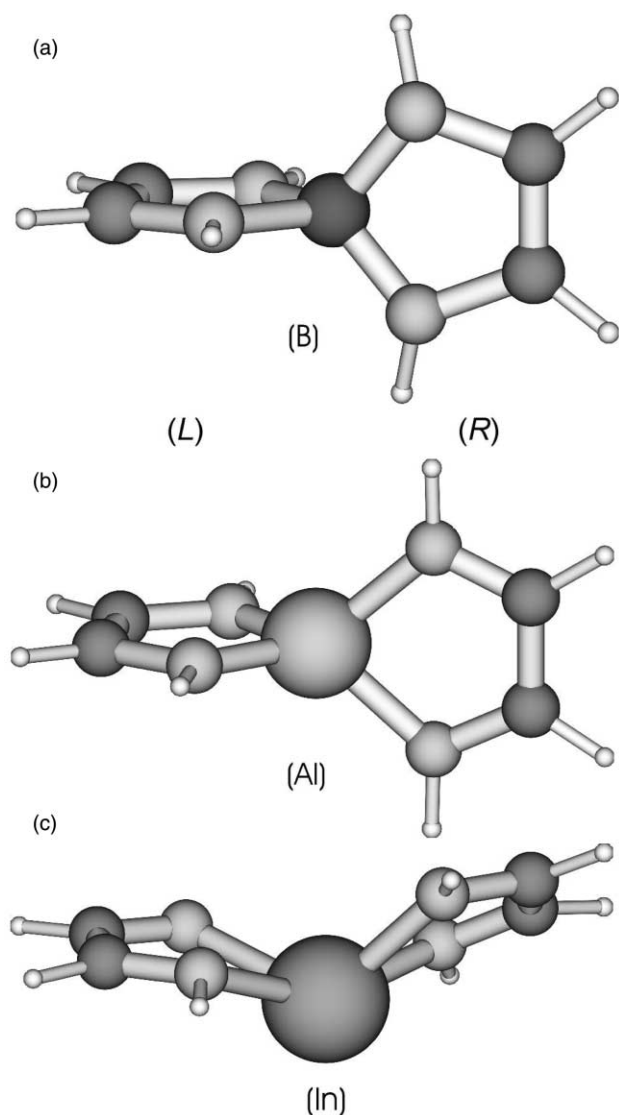
(a)

(B)

(L)   (R)

(b)

(Al)

(c)

(In)

Fig. 1 Molden plots of the equilibrium geometries of homoleptic compounds II, from top to bottom E = B, Al, In.

Table 1 Equilibrium parameters (bond lengths in Å, bond angles in degrees) for parent II (R^1 = R^2 = H), first entry ring L, second entry ring R, at B3LYP/6-31++g** (B3LYP/SBK++g**) level of sophistication

E	Symmetry	E–N	C–N	C–C	N–E–N
B	C_s	1.606; 1.623	1.333; 1.336	1.411	92.6
		1.503; 1.503	1.412; 1.412	1.351	100.7
	C_{2v} ($^2B_1$)^a	1.630	1.352	1.381	87.8
Al	C_{2v}	1.945	1.338	1.414	82.5
		1.826	1.416	1.355	90.8
	C_{2v} ($^2B_1$)^a	1.897	1.366	1.384	83.0
Ga	C_{2v}	1.984	1.335	1.413	81.7
		1.871	1.409	1.356	89.2
	C_{2v} ($^2B_1$)^a	1.945	1.359	1.385	82.1
In^b	C_{2v}^{c}	2.207	1.347	1.432	75.7
		2.069	1.418	1.379	83.6
	C_{2v} ($^2B_1$)^d	2.265	1.349	1.429	72.8
	C_2	2.236; 2.311	1.347; 1.348	1.430	72.8

^{a} Type **C** conformation. ^{b} Values obtained at effective core potential level. ^{c} Type **A** conformation. ^{d} Type **C** conformation, 0.4 kcal mol^{-1} less stable than the C_2 conformation.

have different bond lengths, in one ring (R) the nitrogens appear slightly pyramidalised while in the other (L) they are in plane with the residual ring atoms. The Al and Ga systems are of C_{2v} symmetry, the nitrogens are in plane with the corresponding ligand system. Since both cases are similar, only one case is shown in Fig. 1.

On the contrary, a peculiar bonding situation is achieved for E = In. The central atom is slightly pyramidalised and the two ring systems are now almost identical. Hence, all the homologues indicate different structures. They range from C_s symmetry (for E = B) to C_2 symmetry (for E = In), meeting an intermediate bonding situation (C_{2v} symmetry) for E = Al and Ga. Experimentally only the cases with E = Al and Ga have been published.[5–8] The reported bonding parameters agree well with the calculated data. The ring R refers to the ligand which hosts the unpaired electron. In comparison with ring L it possesses a shorter C–C bond, but elongated C–N bonds. Furthermore the E–N distances are decreased. These considerations only hold true for the case E = B to Ga and the unpaired electron is placed into the π_3 molecular orbital of one ligand. It weakens the C–N bonds and strengthens the C–C bond. Consequently the E–N bonds become stronger.

For further information on the conformational rigidity of the complexes we have also investigated the C_{2v} symmetrical alternatives of type **C**. These geometries do not refer to energy minima on the electronic hypersurfaces, but yield valuable information on the various possible structures **A** to **C**. For these cases one expects identical geometries of both ring systems and weaker E–N bonds, as compared with type **A** conformation. The C–N and C–C bonds are intermediate in lengths, with respect to **A**. The energy differences between type **A** and type **C** conformations decrease with increasing size of the central atom E. Schematically the situation can be depicted as shown in Scheme 7.

|	E = B	Al Ga	In
ΔE (kcal/mol)	38.0	1.5 8.0	-6.1
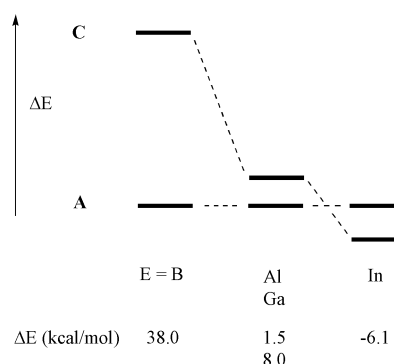
Scheme 7

In other words the tetrahedral shape is most inherent in the boron compound and less inherent in the aluminium and gallium species. Finally for indium a type **C** conformation is preferred. Experimentally, however, the ligands are substituted by bulky groups at the nitrogens. Consequently the sterically less hindered tetrahedral type **A** structures are preferred. Overall, the calculations reveal highly flexible structures for the chelate complexes of the Group 13 elements Ga to In with diazabutadiene ligands.

It is interesting to compare the resulting bonding parameters with those in the corresponding Arduengo-type homologues, type **I**. They were evaluated at the same quantum chemical level[1] and are given in Table 2.

The type **I** compounds are best described by the canonical structures[1] shown in Scheme 8.

Table 2 Relevant bonding parameters for the type **I** anionic carbene homologues, taken from ref. 1 (bond lengths in Å, bond angles in degrees, C_{2v} symmetry)

E	E–N	C–N	C–C
B	1.481	1.400	1.364
Al	1.924	1.395	1.367
Ga	1.983	1.388	1.368
In	2.143	1.414	1.371
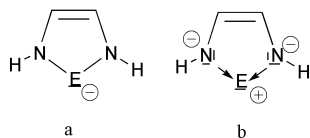
Scheme 8

In **a** the element E is covalently bound to the coordinating nitrogens, the negative charge residing preferentially at E. Alternatively in **b** the ligand is formally doubly reduced by the atom E. By this we mean that predominantly p-electrons of the electropositive element E are shifted towards the more electronegative nitrogens. The canonical structure **a** comes to the fore at boron while **b** is predominant for the higher element homologues Al to In.[1] The geometry of the ligand structure does not essentially change, whether the element E is coordinated as in **a**, or by donor–acceptor interaction, as in **b**. Apart from the longer E–N bonds, in type I *versus* type II structures the ligand bonding parameters appear very similar. The shortening of the E–N bonds by homoleptic bond formation can be attributed to enhanced bond ionicity. It indicates that the central atom in the type II structures has a stronger positive charge than in the type I structures.

A rather different bonding situation is obtained for E = In. Both rings possess almost identical geometries, but are slightly twisted towards each other. The central atom is slightly pyramidalised (see Fig. 1). Again, experimentally the bulky substitutents attached to the nitrogens should enforce a stronger twisting of both ring planes. The adoption of lower symmetry is in accord with the qualitative considerations (see also Scheme 6).

c. Population analysis, spin densities

It is of interest to analyse the charge densities and the spin density distributions in the various structures of type II. The most important quantities are collected in Table 3.

We will first discuss the spin densities. For the series E = B, Al and Ga which adopt a type **A** structure the spin of the unpaired electron is mainly located in one ring system, no sizable contribution of spin density is apparent at the central atom E. The situation is different for E = In. Here a type **C** structure is found with a strong contribution of negative spin density. It is compensated for by equal, but enlarged positive spin densities within the ligand rings. This confirms that the latter electronic structure differs essentially from the others. The tetrahedral shape of the equilibrium structure is broken (C_2 symmetry) and the ligands tend to adopt planarity.

The NPA charges (Table 3) on the other hand complete the understanding of bonding within these systems. The positive charge at the central atom E increases strongly from E = B to the much more electropositive higher element homologues Al and to a lesser extent to Ga and In. Concomitantly negative charge is shifted into the ring systems. Interestingly, the negative charge is more strongly concentrated on the ring system without spin density. Finally for the indium compound both rings possess equal charge distributions. Overall, the charges at E are more positive than in the corresponding Arduengo-type compounds of type I; *e.g.*, for the latter they result[1] in E = B −0.022, Al +0.420.

Table 3 Spin densities ρ (Mulliken) and NPA charges q in compounds of type II

E	ρ (E)	$\Sigma \rho$ (L)	$\Sigma \rho$ (R)	q (E)	Σq (L)	Σq (R)
B	−0.011	0.988	0.024	0.965	−0.155	−0.809
Al	0.011	0.978	0.010	1.853	−0.548	−1.305
Ga	−0.044	1.006	0.038	1.655	−0.475	−1.181
In	−0.401	0.700	0.700	1.140	−0.570	−0.570

The NBO population analysis (Wiberg bond indices) indicates a partial bonding character between E and the surrounding nitrogens. The matter is better substantiated by an analysis of the Laplacian of the electron density of the gallium compound (Fig. 2).
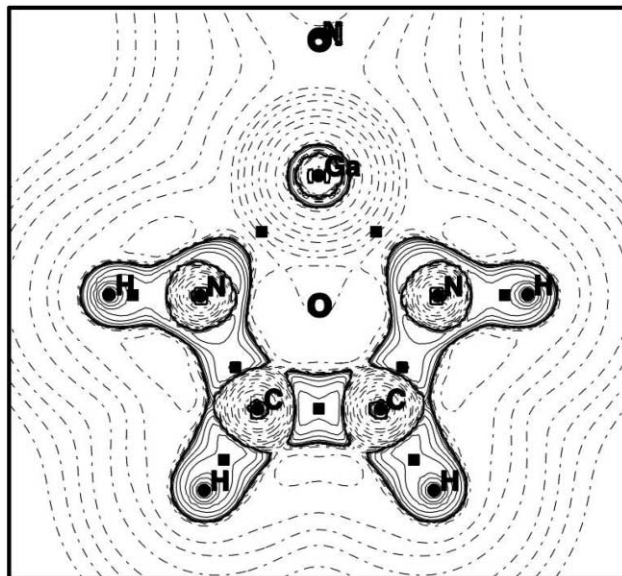

Fig. 2 Laplacian of the electron density of ring L for E = Ga. The bond critical points are indicated by a square.

The values are determined in the plane spanned by the ligand L. However, both rings, L and R, show similar features. Electron density is predominantly located at the electronegative nitrogen atoms, indicating the strong donor–acceptor character for the homoleptic compound II, E = Ga. Similar trends are also observed for the other homologues, but to a lesser extent for E = B.

Based on the population analysis it is tempting to assign formal oxidation states for the various compounds. In fact this has been the subject of discussion between two research groups.[5–8] For the compounds E = B, Al, Ga the absence of spin density at the central atom requires a formal charge of +1 or +3, with concomitant accumulation of negative charge in the ligands. Population analysis cannot provide a clear cut distinction between both alternatives. Overall the central element E is more positive in the type II than in the type I structures. The latter are considered as the Arduengo-type homologues of Group 13 elements.[1]

Summary

The conclusions of our study are as follows: (1) in accordance with previous considerations of the homoleptic diazabutadienyl complexes of aluminium and gallium the two rings constituted from the ligands are different. In the energy lowest doublet states the unpaired electron is located in one ring. This principle is also followed in the experimentally hitherto unknown boron compound. (2) The E–N bonds for the boron case are of stronger covalent character, with the necessary consequence of pyramidalisation of two nitrogens in one ring system. A distorted tetrahedral environment of the central atom with respect to the coordinating nitrogen atoms is preferred. (3) The energy differences between type **A** and type **C** conformations are rather small for the higher element homologues E = Al and Ga. Thus the conformational rigidity of these species should be mainly determined by the bulky substituents at the nitrogens which tend to lock the structures in a tetrahedral geometry. (4) The rotation of bound ligands should occur in a concerted manner, accompanied by a change in symmetry from C_{2v} (type **A**) to C_2 (type **C**). (5) We may add here a further aspect. Our

calculations were carried out on the parent compounds, *i.e.*, with R = H. Alkyl substituents at the nitrogens in general exert a +I effect on the neighbouring atoms. It increases the p-character of the chelating lone pairs at the nitrogens. This again induces a strengthening of the ligand field exerted towards the central atom. (6) The bonding situation is entirely different for the indium homologue. Here the E–N bonds for formation of a tetrahedron are essentially weaker. Furthermore, the inert s-pair effect of the central atom comes to the fore and a weak pyramidalisation at E = In is enforced. A twisted arrangement of the two ligand systems is intended. In this case the unpaired electron is distributed equally over both rings and a strong spin polarisation will be induced.

Acknowledgements

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