Isoelectronic Arduengo-Type Carbene Analogues with the Group IIIa Elements Boron, Aluminum, Gallium, and Indium

Andreas Sundermann, Markus Reiher, and Wolfgang W. Schoeller*

Fakultät für Chemie, Universität Bielefeld,
Postfach 10 01 31, D-33501 Bielefeld, Germany

While Arduengo-type carbenes are now well established for the Group IVa elements carbon, silicon and germanium, they are experimentally unknown for the isoelectronic anions with the Group IIIa elements boron, aluminum, gallium, and indium. In the present quantum chemical investigations, the bonding features of this class of compounds are explored. As a result, they are predicted to be stable species with sizeable singlet-triplet energy separations and electron affinities. Hence, they may be considered as valid targets for experimental investigations. An analysis of the electron density distribution in the case of boron and aluminum reveals a strongly polar B—N bond for the former, and a half Al—N bond with positive charge at the aluminum, emphasizing the donor-acceptor formulation for the latter.

Introduction

Since the pioneering studies of Wanzlick on nucleophilic carbenes[1], their successful isolation as stable species became prominent in the reports of Arduengo et al.[2][3] on the imidazo-2-ylidene, **1** (E = C).
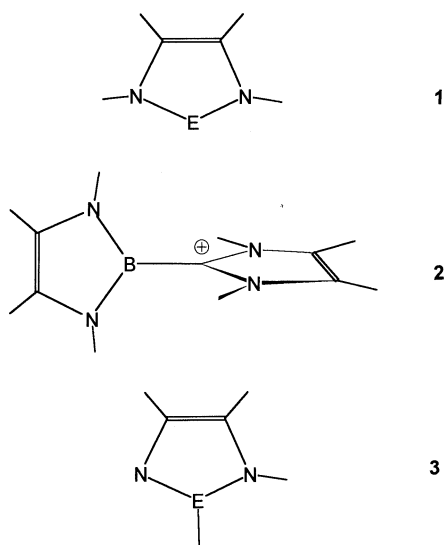
Subsequent experimental studies included the preparation of the analogous silylene[4], **1** (E = Si), and germylene[5], **1** (E = Ge), derivatives. In order to gain insight into the peculiar stability of the Arduengo-type carbenes, various quantum chemical calculations have been performed on **1**[6][7][8][9][10][11][12][13][14]. Furthermore, investigations of their photoelectron spectra[9] and a detailed analysis of their chemical shielding tensors have been reported[10].

Meanwhile, the enormous stability of the valence isoelectronic diaminophosphenium cation is a well established matter in phosphorus chemistry[15][16], in particular in ring systems analogous to **1**[17][18][19][20]. The halogen precursors of the latter dissociate spontaneously into the cyclic cation and a halide anion[17]. In contrast, Arduengo-type carbenes with Group IIIa elements are as yet unknown. If these compounds are considered as being isoelectronic with the Arduengo-type carbenes, they would bear a negative charge at the Group IIIa element. The capability of Group IIIa elements to stabilize a negative charge has nevertheless been demonstrated by experimental and theoretical studies on B—B and Al—Al bonded systems[21][22][23][24][25][26][27][28][29]. For boron, one-electron [24][25][26] as well as two-electron[21][22] reductions have been observed. In contrast, for the Al—Al bond, only one-electron reduction has been found[27][28][29]. These findings indicate that it might be feasible to prepare Arduengo-type carbenes in which E (= C, Si, Ge) is replaced by a valence isoelectronic Group IIIa element bearing a negative charge.

We report herein on an exploration of the bonding properties of Arduengo-type carbenes, **1**, with E = B(−), Al(−), Ga(−), In(−). A first experimental approach to this class of compounds has recently been undertaken in the synthesis and structural elucidation of **2**[30]. This structure is found to contain the diazaborolyl unit. In addition, we include in our investigations the 1,2-shifted structural isomers **3**.

Methodology

The geometries of the various molecular structures were energy optimized at the density functional theory level[31][32], utilizing Becke's three-parameter functional[33] with local and non-local electron correlation contributions. For the optimization of the geometries, the 6-31++g(d,p) basis set was used for carbon and hydrogen, as well as for boron, aluminum, and gallium[34]. One set of diffuse s,p-functions[35] and polarization functions[36] were added. Alterna-

tively, the relativistic pseudopotentials of Basch and Krauss[37], with a double-ζ description for the valence space, were employed for the evaluation of structures in the homologous series containing boron to indium. For these cases, the basis sets were again augmented by one set of polarization functions (at all atoms) and one set of diffuse sp-functions (at all atoms). The coefficients for the supplementary functions were chosen according to the recommendations made for the utilization of the Gamess program[38]. Single point calculations were additionally performed (for the cases of boron and aluminum) at a triple-ζ level, with the 6-311++g(d,p) basis set[39] and with the MP4SDTQ(fc) approximation[40] for the electron correlation correction treatment. For the evaluation of the energies in the open-shell cases (doublets), the spin-projection technique of Schlegel[41] was applied. Zero-point vibrational energies were included in the relative energies, unless noted otherwise. All stationary points were verified by calculation of the corresponding Hessian matrices. For the calculations, we used the Gaussian-94[42] and Gamess[43] programs. The electron distributions in the various molecular structures were examined within the natural bond orbital (NBO) partitioning scheme[44].

Results and Discussion

Qualitative Considerations: The stabilities of the carbene structures are determined by (a) the singlet-triplet energy separations, and (b) the electron affinities in **1** (E = B$^{(-)}$, Al$^{(-)}$, Ga$^{(-)}$, In$^{(-)}$). If the singlet-triplet energy separations are small, the carbene-type structures will not be stable and will be capable of facile radical reactions (with solvents, etc.). The electron affinities, on the other hand, give a quantitative measure of the anion stabilities. If the electron affinities are large, then the possibility of preparing the anion can be considered as being realistic. In practice, however, the anions are surrounded by cations (e.g. as lithium salts). Hence, their stabilities will be mediated by crystal effects[45].


4
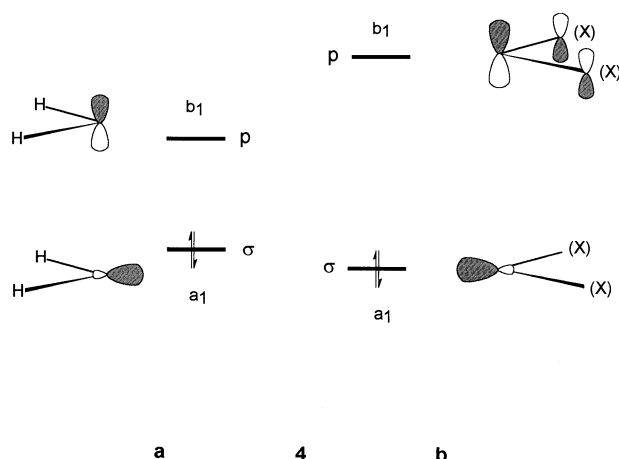
The frontier orbitals of methylene, **4a**, are given by the lone pair orbital at the central atom, σ, and the p-orbital[46]. Within C_{2v} symmetry they are confined to a_1 and b_1 representations. Both orbitals are energetically in close

proximity to each other, hence a triplet ground state $^3B_1$ is preferred[47]. In a stabilized carbene, **4b** (X = NH$_2$, halogens), a similar sequence of orbitals is present[48]. Since the energy splitting between HOMO (σ) and LUMO (p) becomes larger for these structures, a singlet ground state results[49].

The frontier orbital system of **1** can be viewed in a similar manner, as a mutual interaction between the orbitals of the diene unit (A) and the orbitals at E (B). The composition of the orbital system is given in (C) [= (A)−(B), Figure 1].

Figure 1. Diagram showing schematic interaction between a diene unit (A) and E (B), resulting in the cyclic compound (C) [= (A)−(B)]
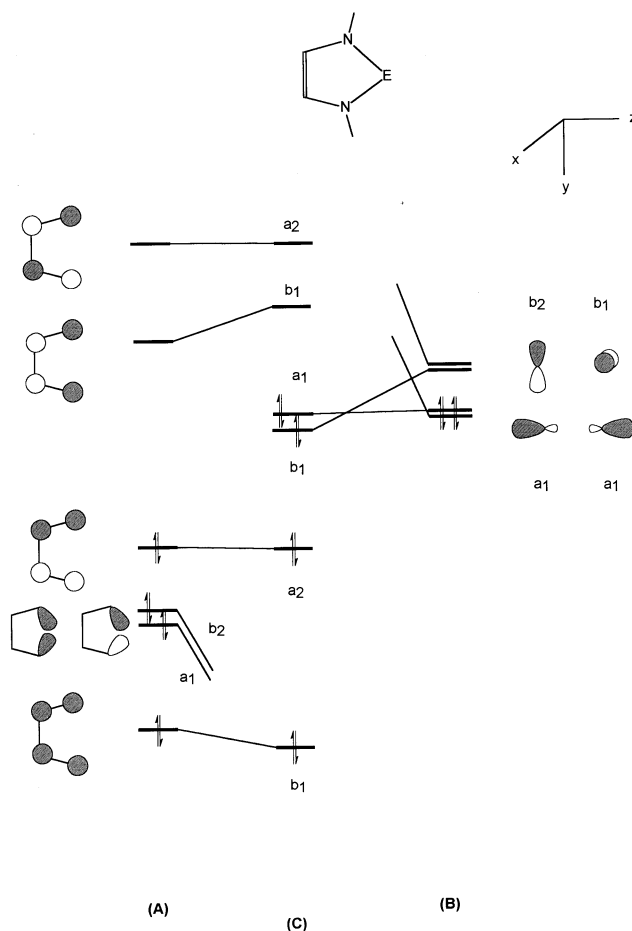
The p_y-orbital forms two linear combinations with the s-orbital (s ± p_y), of which one (s + p_y) remains non-bonding upon interaction with the corresponding orbitals at (A). On the other hand, the other combination (s − p_y) can strongly overlap with the a_1 orbitals at fragment (A). Similarly, the b_2 orbital at (B) strongly interacts with the antibonding lone pair combination b_2 at (A). In addition, π-type interaction occurs among the b_1 orbitals, between (A) and (B). Consequently, the relevant occupied frontier orbitals at (C) can be depicted as in formula **5**.

As mentioned above, the stabilities of the anions are determined by their electron affinities, i.e. the tendency to retain their negative charge. Consequently, it is necessary to examine the anions, the corresponding neutral doublet

a₁   5   b₁
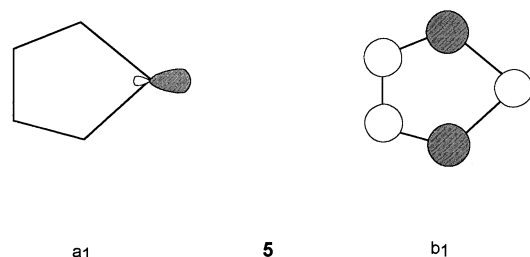
states, and the energy differences between the two species. The resulting Slater determinants for the singlet ground state of the anion and the two relevant doublet states are given as follows:

$\Psi(^1A_1) = ...(b_1)^2(a_1)^2 >$

$\Psi(^2A_1) = ...(b_1)^2(a_1)^1 >$

$\Psi(^2B_1) = ...(a_1)^2(b_1)^1 >$

The relevant triplet states for **1** are described by the following Slater determinants:

$\Psi(^3B_1) = ...(a_1)^1(b_1)^1 >$

$\Psi(^3A_1) = ...(b_1)^1(b_1)^1 >$

The first of these ($^3B_1$) refers to the lowest-energy triplet state, as has been evaluated for the classical Arduengo carbene[7]. All the states in question were examined by the quantum chemical calculations.

It should be noted that **1** is not the only feasible molecular structure. It might well be possible that it undergoes a 1,2-hydrogen shift with formation of species **3**. Consequently, we also included these possible structural isomers for the species in question in our evaluations.

Equilibrium Geometries: The equilibrium geometries of all these structures, **1** and **3**, (bond lengths in Å, bond angles in degrees) are collected in Figure 2.

Minimum-energy structures were established by (3N − 6) positive vibrations of each species. The geometries were obtained with (a) all-valence basis sets, or alternatively with (b) effective core potential methods (ECP's, values in parentheses) (for details, see the Methodology section). All structures were obtained at the DFT level.

The anions of **1** invariably adopt C_{2v} symmetry. The valence angle at E ranges from 97.8° [X = B$^{(-)}$] to 77° [X = In$^{(-)}$]. This indicates that the equilibrium geometries of these ring systems are largely determined by the angle strain due to the first-row atoms C and N.

The bonding situation is somewhat more complicated in the doublet states. Interestingly, the doublet states undergo a change in their electronic (ground) state in the sequence E = B to In. In the case E = B, a $^2A_1$ ground state is observed, while for E = In it becomes $^2B_1$. An intermediate case is **1**, E = Al. Here, both states, $^2A_1$ and $^2B_1$, mingle with each other with concomitant Jahn-Teller interactions[50]. Symmetry breaking occurs to give C_s symmetry, through induction of b₁ vibration within C_{2v} symmetry. For this case (E = Al), the five-membered ring is tilted out of the plane ($\angle$ CNNAl = 14.2° for $^2A'$). We acknowledge

Figure 2. Equilibrium geometries of lowest-energy singlets (first entry) and doublets (second entry) of **1** (E = B, Al, Ga, In) and **3** (E = B, Al, Ga), at all-valence electron (ECP) level
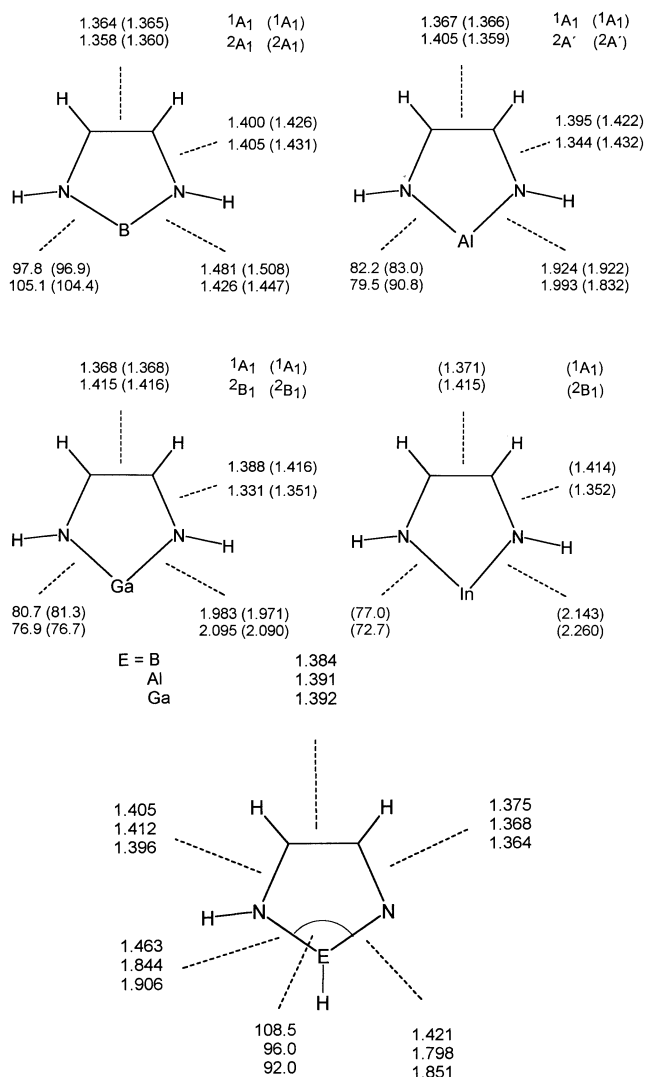
that a more rigorous approach for the study of the Jahn-Teller phenomena in the (neutral) doublet states would require elaborate MCSCF calculations with subsequent multi-reference CI calculations. For the case at hand, a detailed study of the crossing of the electronic hypersurfaces of the various doublet states was not attempted.

The rearranged structures **3** invariably adopt C_s symmetry. Again, all species possess (3N − 6) positive vibrations in their equilibrium geometries. Thus, they correspond to energy minima on the electronic hypersurfaces. In general, the E−N bonds in **3** are shorter than those in the structures **1**. Notably, the E−N bond to the twofold coordinated nitrogen atom is always shorter than that to the substituted nitrogen. This can be rationalized in terms of two prominent resonance structures, which contribute to bonding in the ground states.

In canonical structure **a**, the negative charge is localized at the nitrogen atom, while in **b** it is shifted towards E (= B, Al, Ga) with formation of a (partial) double bond. The

a   b
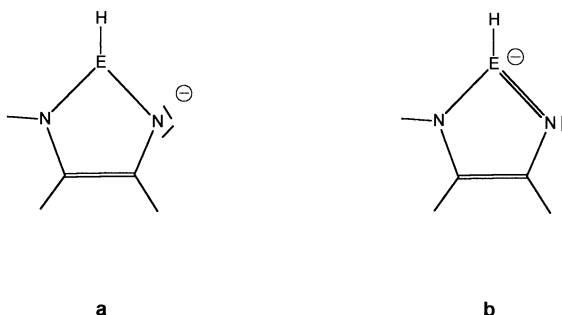
predominance of canonical structure **b** over **a** is determined by the electronegativity of E and the gain in π-energy. Although it is difficult to assess both factors quantitatively, one would expect that **3** becomes increasingly stabilized over (the singlet ground state) **1** in the order X = In < Ga < Al < B. As will be shown in the following section, this is indeed the case.

Energy Considerations: The electron affinities and singlet-triplet energy separations are the specific properties that determine the stabilities of the various species **1**. These are presented in Table 1.

Table 1. Electron affinities (in kcal/mol) [first entries] and singlet-triplet energy separations [second entries] for structure **1** (E = B to In); values in parentheses are derived from ECP calculations

Atom E		DZP[a]	DZP/ZPE[b]	TZP[c]	MP4[d]
B	($^1A_1\rightarrow^2A_1$)	7.0 (9.3)[e]	8.4	7.2	3.3 (2.8)
	($^1A_1\rightarrow^3A_1$)	20.2 (22.6)	20.9	20.4	23.1 (23.5)
Al	($^1A_1\rightarrow^2A'$)	32.5 (34.3)	33.1	33.4	34.5
	($^1A_1\rightarrow^3B_1$)	41.3 (50.5)	41.5	42.4	45.3
Ga	($^1A_1\rightarrow^2B_1$)	27.0 (32.1)	28.1	26.7	39.3
	($^1A_1\rightarrow^3A_1$)	52.0 (47.9)			
In	($^1A_1\rightarrow^2B_1$)	(27.0)			
	($^1A_1\rightarrow^3A_1$)	(38.8)			

[a] b3lyp/6-31++g(d,p). – [b] Method [a] plus zero-point vibrational energy correction (unscaled). – [c] b3lyp/6-311++g(d,p)//b3lyp(6-31++g(d,p). – [d] MP4SDTQ(fc)/6-31++g(d,p)//b3lyp/6-31++g(d,p). – [e] b3lyp/ECP-31++g(d,p).

For the cases X = B to Ga, they were explored with the all-valence electron basis set methods, and also with the ECP's (at times within the DFT procedure). For E = In, our considerations rely solely on the results of the ECP calculations. For the structures where the results of both quantum chemical procedures are available (all-valence electron basis sets and ECP's), the different approaches are seen to yield similar energy quantities. On closer inspection of the data, it can be seen that for E = B the electron affinity is found to be rather small. The value is only marginally changed by zero-point vibrational energy corrections or at an improved triplet-ζ basis set level. On the other hand, for all cases the singlet-triplet energy separations are sizeable. Thus, a singlet ground state of all structures is ensured. The electron affinity, and hence the stability of the anion, is increased for the higher element homologues. In essence, for all higher element homologues, the electron affinities are larger than those for the first-row element boron. Again, zero-point energy vibrational correction as well as explicit

CI methods, such as the MP4SDTQ approach, yield comparable energy quantities.

To evaluate the feasibility of the synthesis of **1**, it is necessary to have knowledge of the relative energetic ordering of **1** and **3**, given the same element E. Corresponding energy quantities were evaluated at various levels of sophistication for the cases E = B, Al and Ga, and are listed in Table 2.

Table 2. Energy differences (in kcal/mol) between **1** and **3**, at various levels of sophistication

Atom E	DZP[a]	DZP/ZPE[b]	TZP[c]
B	−40.8	−42.4	−40.7
Al	17.6	13.9	17.9
Ga	23.9		

[a] b3lyp/6-31++g(d,p). – [b] Method [a] plus zero-point vibrational energy correction. – [c] b3lyp/6-311++g(d,p)//b3lyp/6-31++g(d,p).

The trends in the energies are obvious. For E = B, the 1,2-hydrogen shifted structure is the lowest-energy alternative. In the other cases, **1** is more stable than **3**. It should be noted, however, that in the case of carbenes it has been recently demonstrated that although 1,2-hydrogen migrations are very exothermic, their occurrence is highly unlikely from a kinetic point of view[51].

Improvement of the basis set (level C) or the inclusion of zero-point vibrational energy contributions (level B) does not significantly alter the situation. There is a clear-cut tendency of enhanced stability of **1** over **3**, with increasing atomic number of E. The case E = In was not further explored, but it seems reasonable to assume that it is at least as stable as the case E = Ga (**1** in relation to **3**).

Electron Density Distributions: It is informative to analyze the electron distributions in **1** and **3**. The relevant values were computed within the natural bond orbital (NBO) scheme[44]. For the cases E = B and Al, these are displayed in Figure 3.

The electron distributions in E = B and E = Al reveal fundamental differences. For **1**, E = B, the E−N bond is almost a single bond, while it is almost a half bond for E = Al. Simultaneously, E releases electron density towards the neighbouring, more electronegative nitrogen atoms, with a concomitant strengthening of the E−N bonds. Similar trends are also observed in the Ga and In analogues, although detailed populations are not given here. Considering the data in more detail, the s/p ratio (atomic populations for the valence electrons) for the lone pair amounts to 1.378/0.918 for E = B and 1.660/0.536 for E = Al. (The corresponding π-populations of valence electrons are given in brackets in Figure 3).

Evidently, a fundamental change in the bonding is observed on going from E = B to E = Al. The Laplacians of the electron density for these two cases (as determined by the method of "atoms in molecules"[52], are shown in Figure 3b. For E = B, a non-bonding lone pair orbital (at E) is present. It is diminished in the case E = Al, in favour of an increased p-electron density at the neighbouring nitrogens. Furthermore, in the latter case (E = Al), the electron

Figure 3. (a) NBO analysis (natural atomic charges with π-occupancies in curly brackets), in parentheses Wiberg bond indices (in the NAO basis) and (b) Laplacians of the electron densities for **1**, E = B and Al

E = B

E = Al
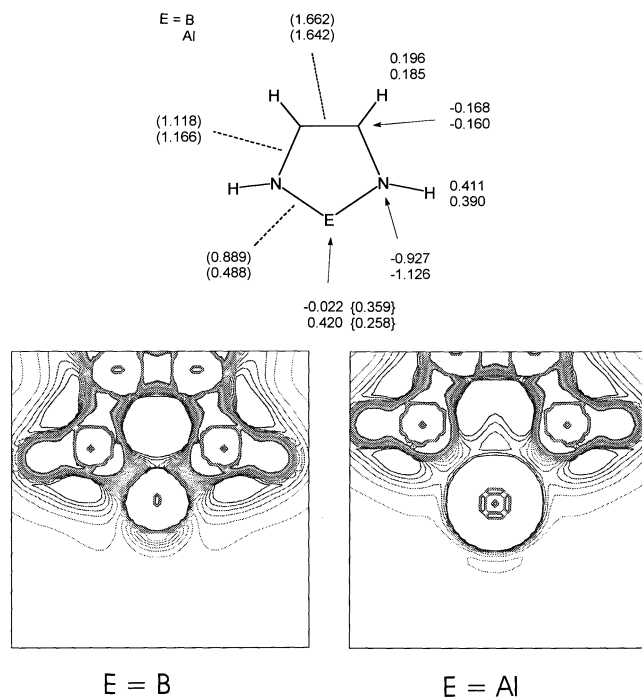
density is more concentrated at the nitrogens compared with the former (E = B). All these findings are in accord with the predominance of canonical structure **c** for E = B, and a donor-acceptor formulation **d** for E = Al. For the higher element homologue E = Al, a cyclic delocalization of electrons does not occur.

c   d
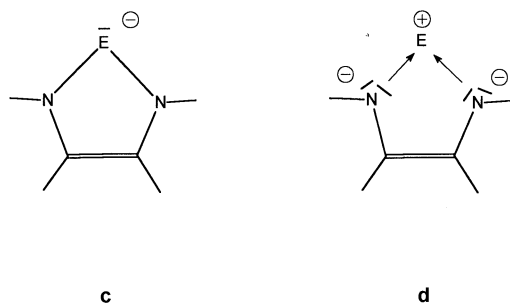
The structure **d** is dominant if E represents an electropositive element (as compared with nitrogen) and becomes increasingly so in the order X = Al < Ga < In.

Conclusions

The results of our quantum chemical study can be summarized as follows:

1. Arduengo-type carbene structures in which an isovalent electronic species E = $B^{(-)}$, $Al^{(-)}$, $Ga^{(-)}$, $In^{(-)}$ constitutes the divalent center are stable species. They possess singlet ground states and adopt C_{2v} symmetrical structures.

2. Although the central atom is relatively electropositive as compared with its neighbouring nitrogen atoms, the species possess bound states; i.e. they have a strong tendency to retain the negative charge. In other words, the corresponding doublet states have a strong electron affinity.

3. This is due to the enhancement of a chelate-type structure, in which the electropositive element E (In > Ga > Al) can release its formal negative charge to the more electronegative neighbouring nitrogen atoms.

4. Furthermore, with increasing atomic number of E, a possible 1,2-hydrogen rearrangement, which results in the formation of a "classical" structure becomes disfavored.

On the basis of our quantum chemical considerations, cyclic carbene structures of the Arduengo-type containing the Group IIIa elements should be interesting targets for synthetic verifications.

[1]   H. W. Wanzlick, *Angew. Chem.* **1960**, *72*, 494.
[2]   1,3-Adamantyl derivative: A. J. Arduengo, III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.
[3]   1,3-Dimethyl derivative: A. J. Arduengo, III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530.
[4]   M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691.
[5]   W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, *Angew. Chem.* **1992**, *104*, 1489; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1485.
[6]   D. A. Dixon, A. J. Arduengo, III, *J. Phys. Chem.* **1991**, *95*, 4180.
[7]   J. Cioslowski, *Int. J. Quantum Chem. Symp.* **1993**, *27*, 309.
[8]   A. J. Arduengo, III, H. V. R. Dias, D. A. Dixon, R. L. Harlow, W. T. Klooster, T. F. Koetzle, *J. Am. Chem. Soc.* **1994**, *116*, 6812.
[9]   A. J. Arduengo, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 6641.
[10] A. J. Arduengo, III, D. A. Dixon, K. K. Kumashiro, C. Lee, W. P. Power, K. W. Zilm, *J. Am. Chem. Soc.* **1994**, *116*, 6361.
[11] C. Heinemann, W. Thiel, *Chem. Phys. Lett.* **1994**, *217*, 11.
[12] C. Heinemann, W. A. Herrmann, W. Thiel, *J. Organomet. Chem.* **1994**, *475*, 73.
[13] C. Heinemann, T. Müller, Y. Apeloig, H. Schwarz, *J. Am. Chem. Soc.* **1996**, *118*, 2023.
[14] C. Boehme, G. Frenking, *J. Am. Chem. Soc.* **1996**, *118*, 2039.
[15] A. H. Cowley, R. Kemp, *Chem. Rev.* **1985**, *85*, 367.
[16] M. Sanchez, M. R. Mazieres, L. Lamande, R. Wolf, *Multiple Bonds and Low Coordination Chemistry in Phosphorus Chemistry* (Eds.: M. Regitz, O. Scherer), Georg Thieme Verlag, Stuttgart, **1990**.
[17] M. K. Denk, S. Gupta, R. Ramachandran, *Tetrahedron Lett.* **1996**, *37*, 9025.
[18] D. Gudat, *Coord. Chem. Rev.*, in press.
[19] I. A. Litvinov, V. A. Naumov, T. V. Gryazna, A. N. Pudovik, A. M. Kibardin, *Dokl. Akad. Nauk SSSR* **1990**, *312*, 623.
[20] For the analogous saturated system, see N. Burford, P. Losier, C. Macdonald, V. Kyrimis, P. K. Bakshi, T. S. Cameron, *Inorg. Chem.* **1994**, *33*, 1434.
[21] A. Moezzi, R. A. Bartlett, P. P. Power, *Angew. Chem.* **1992**, *104*, 1075; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1082.
[22] A. Moezzi, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1992**, *114*, 2715.
[23] M. A. Petrie, P. P. Power, H. V. R. Diaz, K. Ruhlandt-Senge, K. M. Waggoner, R. J. Wehmschulte, *Organometallics* **1993**, *12*, 1086.
[24] E. Kaufmann, P. v. R. Schleyer, *Inorg. Chem.* **1988**, *27*, 3987.
[25] J. E. Leffler. G. B. Watts, T. Tanigaki, E. Dolan, D. S. Miller, *J. Am. Chem. Soc.* **1970**, *92*, 6825.
[26] H. Klusik, A. Berndt, *Angew. Chem.* **1981**, *93*, 903; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 870.

[27] A. Berndt, H. Klusik, K. Schlüter, *J. Organomet. Chem.* **1981**, *C25*, 222.

[28] C. Pluta, K.-R. Pörschke, C. Krüger, K. Hildenbrand, *Angew. Chem.* **1993**, *105*, 451; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 388.

[29] W. Uhl, A. Vester, W. Kaim, J. Poppe, *J. Organomet. Chem.* **1993**, *454*, 9.

[30] L. Weber, E. Dobbert, H.-G. Stammler, B. Neumann, R. Boese, D. Bläser, *Chem. Ber./Recueil* **1997**, *130*, 705.

[31] P. Hohenberg, W. Kohn, *Phys. Rev.* **1964**, *136*, B864; W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140*, A1133.

[32] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, **1989**.

[33] A. D. Becke, *Phys. Rev.* **1988**, *A38*, 3098; A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[34] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724; W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257; P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213. See also *Gaussian 94 User's Reference Manual*, M. J. Frisch, A. Frisch, J. B. Foresman, Gaussian, Inc., Pittsburgh, PA 15106, and references cited therein.

[35] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294.

[36] M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265.

[37] W. J. Stevens, H. Basch, M. Krauss, *J. Chem. Phys.* **1984**, *81*, 6026; W. J. Stevens, H. Basch, M. Krauss, P. Jasien, *Can. J. Chem.* **1992**, *70*, 612; T. Cundari, W. J. Stevens, *J. Chem. Phys.* **1993**, *98*, 5555.

[38] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus, S. T. Elbert, *QCPE Bull.* **1990**, *10*, 52.

[39] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650; A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *92*, 5639.

[40] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618; R. Krishnan, J. A. Pople, *Int. J. Quantum Chem.* **1978**, *14*, 91.

[41] H. B. Schlegel, *J. Chem. Phys.* **1986**, *84*, 4530.

[42] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Peterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Avala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94 (Revision A.1)*, Gaussian, Inc., Pittsburgh, PA, **1995**.

[43] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347.

[44] A. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.

[45] W. W. Schoeller, T. Busch, *J. Mol. Struct. (THEOCHEM)* **1994**, *313*, 27. For the importance of solvation in determining carbenoid structures, see W. W. Schoeller, *Chem. Phys. Lett.* **1995**, *241*, 21.

[46] B. M. Gimarc, *Molecular Structure and Bonding*, Academic Press, New York, **1979**.

[47] E. R. Davidson, in *Diradicals* (Ed.: W. T. Bordon), Wiley-Interscience, New York, **1982**.

[48] G. Trinquier, *J. Am. Chem. Soc.* **1990**, *112*, 2130; for further references see therein.

[49] W. W. Schoeller, *J. Mol. Struct. (THEOCHEM)*, in press.

[50] F. L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, New York, **1968**.

[51] G. Maier, J. Endres, H. P. Reisenauer, *Angew. Chem.* **1997**, *109*, 1788; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1709.

[52] R. F. W. Bader, *Atoms in Molecules*, Clarendon Press, Oxford, **1994**.

[97214]