Ab initio study of Arduengo-type group 13 carbene analogues

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L e t t e r

An *ab initio* study on anions $[L_HE]^-$ (L_H = 1,4-diaza-buta-1,3-diene, E = B, Al) and the corresponding neutral radicals L_HE has been carried out. Both $[L_HB]^-$ [**1(B)**] and $[L_HAl]^-$ [**1(Al)**] are predicted to be thermodynamically and kinetically stable species. However, the rearrangement to the isomeric amides **4(B)** and **4(Al)** is endothermic only for **1(Al)**. This and a better stabilized lone pair appear to make **1(Al)** the more promising preparative target.

Recently, spectacular progress has been made in the synthesis of two-coordinate main-group compounds. In particular, use of the 1,4-diazabuta-1,3-diene ligand (DAB, herein abbreviated L_X, where X denotes the substituents on the nitrogen atoms) has resulted in the synthesis of carbenes L_XC[1] (extreme variety of X),[2] silylenes L_XSi[3] and germylenes[4] (several X, mostly Bu^t). Although phosphenium cations are well-known, $[L_{Bu^t}P]^+$ has been synthesized only recently[5,6] and the isolation of two stable nitrenium ions $[L_XN]^+$ certainly presents a milestone in this chemistry.[7] On the other hand, there is only scarce information in the literature on the isolobal group 13 analogues of Arduengo's carbene $[L_XE]^-$ (E = B, Al, Ga), possibly a consequence of difficulties in their preparation or isolation due to subsequent decomposition. These compounds may be perceived as 'umpoled' boranes or alanes and may thus be valuable synthons in preparative main-group chemistry.[8] *Ab initio* molecular orbital theory has furnished a wealth of detailed information on carbenes and their analogues, including the factors contributing to their stability.[9–12] We have adapted these methods to gain insight into the electronic structure and reactivity of borane and alane anions $[L_HB]^-$ and $[L_HAl]^-$. The aim of this study is to direct further synthetic efforts.

Since the appropriate computational treatment of anions requires large basis sets with diffuse functions, the RHF/6-311 + G* level of theory was used throughout this study. All structures were computed with the highest reasonable symmetry and were subsequently confirmed to be local minima (except for transition states **6**) on the energy surface by a frequency calculation. The suitability of the approach was confirmed by verifying a positive electron affinity for the corresponding neutral radicals (optimized at UHF/6-311 + G*, geometrical parameters are summarized in Table 1), which also increased smoothly from UHF to MP2 to MP4. Reaction energies were calculated with inclusion of electron correlation up to fourth order (MP4/6-311 + G*//6-311 + G*) and zero-point energy. All calculations were carried out with the GAUSSIAN 94 program package[22] on Silicon Graphics workstations.

Compounds **1** are local minima on the energy surface. The electron affinities (EA) for the corresponding neutral radicals **2(B)** and **2(Al)** (Table 1) are 0.16 eV (**B**) and 1.34 eV (**Al**), the positive values indicating the anions to be thermodynamically stable (EA = $-\Delta H$ for: $\mathbf{2} + e^- \rightarrow \mathbf{1}^-$).[13] Thirdly, there are no low-lying breathing modes (below 1000 cm^{-1}) of the heavy atom skeleton. Therefore, anions of this structural type are located in a reasonably deep potential well and should be stable species. Calculated structures of **1(B)** and **1(Al)** as well as **3(B)**, **3(Al)** (with methyl groups on one of the nitrogen atoms, Fig. 1) are summarized in Table 1. The N—E bond distances in **1(B)** and **1(Al)** are longer by more than 0.1 Å than the experimental values in carbene $L_{tBu}C$,[11] **1(C)** and silylene $L_{tBu}Si$,[3] **1(Si)**. Also, the N—E—N angle in **1(B)** and **1(Al)** is significantly more acute [**1(C)**: 1.362 Å and 102.2° (X-ray); **1(Si)**: 1.753 Å, 90.5° (GED, gas phase electron diffraction)]. Compared with group 14 and 15 analogues the N—E—N angle is smaller for the heavier congeners as a consequence of the longer N—E bonds. Methyl group substitution shortens the N(Me)—B bond length, but elongates the
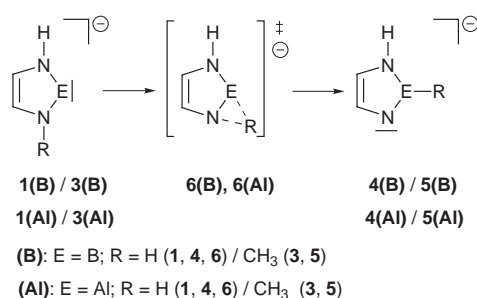

1(B) / **3(B)**   **6(B)**, **6(Al)**   **4(B)** / **5(B)**
1(Al) / **3(Al)**   **4(Al)** / **5(Al)**

(B): E = B; R = H (**1**, **4**, **6**) / CH$_3$ (**3**, **5**)

(Al): E = Al; R = H (**1**, **4**, **6**) / CH$_3$ (**3**, **5**)

Fig. 1   Rearrangement of carbene analogues **1**, **3** to amides **4**, **5**

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Table 1   Selected structural parameters of neutral radicals **2** and anions **1** and **3** (Å and degrees); magnetic susceptibility anisotropy χ_{Anis} (IGAIM/RHF/6-311 + G*, sign reversed) and NICS (GIAO/RHF/6-311 + G*), both (ppm cgs) for **1(B)** and **1(Al)**

	1(B)/2(B)	**3(B)**	**1(Al)/2(Al)**	**3(Al)**
N(H)—E (/N(Me)—E)	1.475/1.417	1.478 (/1.474)	1.891/2.001	1.888 (/1.901)
N(H)—C (/N(Me)—C)	1.388/1.397	1.385 (/1.388)	1.390/1.317	1.387 (/1.389)
C—C	1.338/1.334	1.338	1.340/1.401	1.340
N—E—N	97.72/105.09	98.39	83.32/78.27	83.95
χ_{Anis}	28.86		19.3	
NICS	−10.4		−5.9	

N(Me)—Al bond length with respect to the respective N(H)—E bonds. We conclude that the N—C—C—N skeleton of the ring system in L_XE is largely invariant towards the electronic or steric effects of *N*-substitution or even different elements E of the same row of the periodic table.

The stabilizing effect of cyclic electron delocalization on carbene analogues with the diazabutadiene backbone has been evaluated theoretically by several groups.[14-16] In this study we have applied two magnetic criteria to investigate whether such 'aromaticity' plays a significant role in 1(B) and 1(Al), namely the anisotropy of the magnetic susceptibility χ_{Anis}[17] and the nucleus-independent chemical shift (NICS).[18] The results are shown in Table 1. Both criteria indicate that there is an appreciable aromatic stabilization, albeit less than in the corresponding carbene for which $\chi_{Anis} = 38.1$ ppm and $\delta(NICS) = -12.5$ ppm are calculated to be at the same level of theory. Evidently, both criteria indicate less aromatic ring current for the alane anion 1(Al). In search for a molecular basis of this effect we have investigated the molecular orbital situation, of which the totally delocalized π orbital is plotted in Fig. 2 [b_1, HOMO-4 for both 1(B) and 1(Al)]. As can be seen very nicely, the empty orbital on boron is fully included in the delocalized π system, whereas there is little overlap with the empty orbital on Al in 1(Al). In line with this orbital picture, an analysis of the Löwdin bond order matrix yields a bond order of 1.51 [1(B)] and 1.12 [1(Al)] for the N—E bond (Table 2). Consequently, it appears comprehensible that there is less cyclic delocalization in 1(Al).

One of the textbook reactions of carbenes is the insertion into (neighbouring) X—H bonds. Although this does not seem to be a problem in Arduengo's carbenes in general, compounds 1(B) and 1(Al) are expected to be more reactive in this respect owing to their negative charge. We have therefore investigated the rearrangement of 1(B), 1(Al) and 3(B), 3(Al) to the amide anions 4 and 5(B), 5(Al), respectively (Table 3). Most notably, the rearrangement reaction is highly exothermic for boranes but endothermic for alane anions 1, 3(Al). A negative charge is well accommodated on the nitrogen atom in amides 4 and 5, and little difference is expected between (B) and (Al) in this respect. The lone pair in 1 and 3, however, should be stabilized to a higher degree in the alane anions owing to its higher s character. This reasoning is in line with photo-electron spectroscopy of the carbene/silylene/germylene series[11,12] and is confirmed computationally by the HOMO energy of 1(B) (−0.84 eV) and 1(Al) (−1.67 eV). A plot of the HOMO of 1(B), 1(Al) (Fig. 2) demonstrates that it has mainly lone pair character.

It is interesting to note the structural changes between anions 1 and the corresponding neutral radicals 2 (Table 1). In the case of 1(B) and 2(B) the N—B and C—C bonds are shortened and correspondingly the N—B—N angle increases. These changes are anticipated because a removal of negative charge from the lone pair of 1(B) will lead to reduced electronic repulsion. At first glance, the situation for aluminium compounds 1(Al) and 2(Al) appears contradictory since the N—Al and C—C bonds are elongated, while the N—C bonds are drastically shortened. Inspection of the frontier orbitals of 2 provides a rational for this differing behaviour. For radical 2(B), the singly occupied orbital (SOMO) is the totally symmetric lone pair at the boron centre, while the first doubly occupied orbital has π character. This order is reversed for 2(Al). While the first doubly occupied orbital is the lone pair on Al, the SOMO of 2(Al) has mainly π character around the five-membered ring with nodal planes orthogonal to the C—N bond vector. The consequence of this different π electron configuration is illustrated by a comparison of the Löwdin bond orders in 2(B) and 2(Al) (Table 2) which are in line with a half-filled π orbital and the observed bond lengths in 2(Al).

Since we assume that steric shielding by large substituents on the nitrogen atoms will be an important factor for stabilizing the compounds under investigation we have included the methyl-substituted derivatives 3 and 5 (Table 3). Methyl group migration is energetically more favourable than H migration for both B and Al, yet the rearrangement 3(Al) to 5(Al) is still endothermic. We have located and optimized the transition states 6(B), 6(Al) for the rearrangements 1 → 4 (Fig. 3). The activation energy for 1 to 4 *via* these transition states is 63.8 (MP4: 47.2) kcal mol^{-1} (B) and 114.2 (MP4: 83.4) kcal mol^{-1} (Al, 6-31G* only), respectively. Hence, an intramolecular rearrangement of the anions is kinetically hindered.
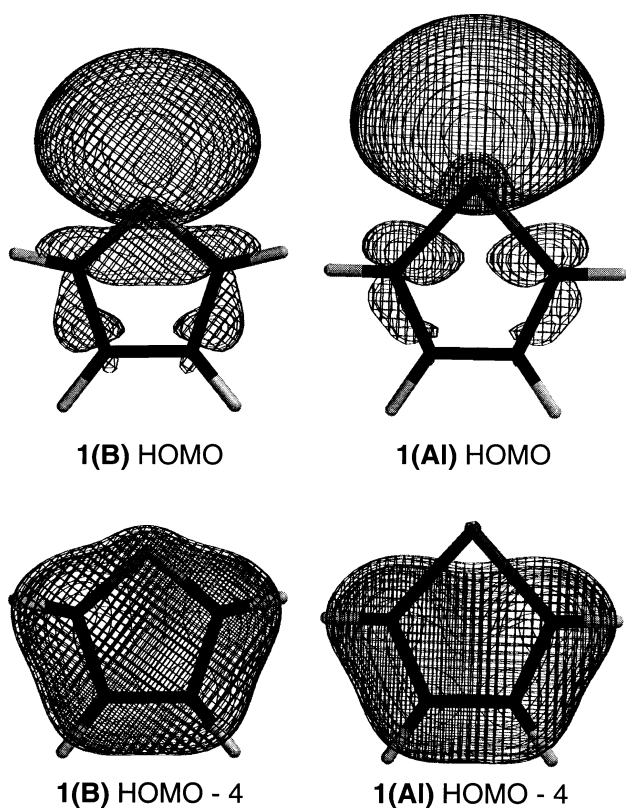

1(B) HOMO   1(Al) HOMO

1(B) HOMO - 4   1(Al) HOMO - 4

Fig. 2 Orbital plots of the HOMO and HOMO-4 for 1(B), 1(Al)[23]

Table 2 Löwdin bond orders in 1 (HF/6-311+G*) and 2 (ROHF/6-311+G*) and change of bond order ΔBO in % relative to 1

	1(B)	2(B)	ΔBO	1(Al)	2(Al)	ΔBO
N—E	1.51	1.44	−5	1.12	0.9	−22
N—C	1.30	1.25	−4	1.37	1.71	+25
C—C	1.85	1.86	+1	1.87	1.35	−28

Table 3 Energy of the rearrangement of borane/alane anions to their corresponding amides (Fig. 1)

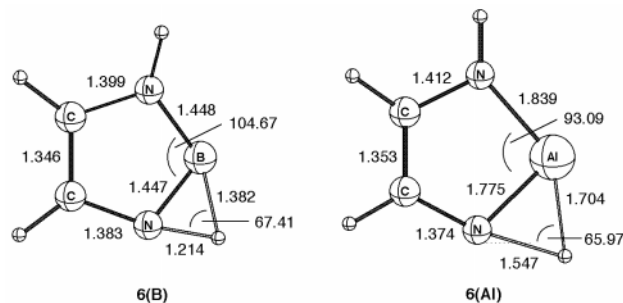|	1(B) → 4(B)	3(B) → 5(B)	1(Al) → 4(Al)	3(Al) → 5(Al)
6-311+G*//6-311+G*	−42.1	−53.3	20.1	10.2
MP4/6-311+G*//6-311+G*	−41.8	−52.7	14.9	4.5

Fig. 3 Structural parameters for the transition states **6(B)** and **6(Al)** (Å and degrees)

The following predictions emerge from this computational study: (a) borane and alane anions of the 'Arduengo' type are thermodynamically stable species; (b) the lone pair is the HOMO in both compounds and high in energy, thus making them very reactive towards electrophiles; (c) alane anions of type **1(Al)** are expected to be more stable than their corresponding borane analogues **1(B)**. Very recently, a related conclusion has been published by Schoeller and coworkers.[19] This view is further substantiated by the fact that a 1,2 hydrogen or methyl group migration to the anionic centre in **1(Al)** and **3(Al)** is endothermic and kinetically slow. Summarizing, the problems some groups experienced in preparing these 'umpoled' group 13 compounds are most likely due to the as yet inappropriate synthetic routes used rather than to an inherent instability of the products. Further synthetic efforts are certainly called for which should invoke alternative methods of preparation.[20,21]

Acknowledgements

References

1 A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
2 W. A. Herrmann and C. Köcher, *Angew. Chem.*, 1997, **109**, 2256.
3 M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691.
4 W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F-R. Klingan, H. Bock, B. Solouki and M. Wagner, *Angew. Chem.*, 1992, **104**, 1489.
5 M. K. Denk, S. Gupta and R. Ramachandran, *Tetrahedron Lett.*, 1996, **37**, 9025.
6 C. Carmalt, V. Lomeli, B. G. McBurnett and A. H. Cowley, *J. Chem. Soc., Chem. Commun.*, 1997, 2095.
7 G. Boche, P. Andrews, K. Harms, M. Marsch, K. S. Rangappa, M. Schimeczek and C. Willeke, *J. Am. Chem. Soc.*, 1996, **118**, 4925.
8 M. Wagner, N. J. R. van Eikema Hommes, H. Nöth and P. v. R. Schleyer, *Inorg. Chem.*, 1995, **34**, 607.
9 D. A. Dixon and A. J. Arduengo III, *J. Phys. Chem.*, 1991, **95**, 4180.
10 A. J. Arduengo III, H. V. R. Dias, D. A. Dixon, R. L. Harlow, W. T. Klooster and T. F. Koetzle, *J. Am. Chem. Soc.*, 1994, **116**, 6812.
11 A. J. Arduengo III, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner and R. West, *J. Am. Chem. Soc.*, 1994, **116**, 6641.
12 M. Denk, J. C. Green, N. Metzler and M. Wagner, *J. Chem. Soc., Dalton Trans.*, 1994, 2405.
13 P. W. Atkins, *Physical Chemistry*, Oxford University Press, Oxford, 1990.
14 C. Heinemann, T. Müller, Y. Apeloig and H. Schwarz, *J. Am. Chem. Soc.*, 1996, **118**, 2023.
15 C. Boehme and G. Frenking, *J. Am. Chem. Soc.*, 1996, **118**, 2039.
16 R. West, J. J. Buffy, M. Haaf, T. Müller, B. Gehrhus, M. F. Lappert and Y. Apeloig, *J. Am. Chem. Soc.*, 1998, **120**, 1639.
17 V. I. Minkin, M. N. Glukhovtsev and B. Y. Simkin, *Aromaticity and Antiaromaticity*, Wiley, New York, 1994.
18 P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. v. E. Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317.
19 A. Sundermann, M. Reiher and W. Schoeller, *Eur. J. Inorg. Chem.*, 1998, 305.
20 F. G. N. Cloke, C. I. Dalby, M. J. Henderson, P. B. Hitchcock, C. H. L. Kennard, R. N. Lamb and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1990, 1394.
21 F. G. N. Cloke, C. I. Dalby, P. J. Daff and J. C. Green, *J. Chem. Soc., Dalton Trans.*, 1991, 181.
22 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, 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. Ayala, 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 and J. A. Pople, *Gaussian 94, Revision D. 4*, Gaussian Inc., Pittsburgh PA, 1995.
23 *Spartan version 5.0*, Wavefunction Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA, 1997.