

Azacarborane chemistry. Butyl nitrite synthesis of the new eight-, nine- and ten-vertex azacarboranes *exo*- and *endo*-7-CH₃-*hypho*-7,8-NCB₆H₁₁, *nido*-6,8,9-NC₂B₇H₁₀, *arachno*-6,5,9-NC₂B₇H₁₂ and *arachno*-6,5,10-C₂NB₇H₁₂ †

Tomáš Jelínek,^a Bohumil Štibr,^{*a} John D. Kennedy,^b Drahomír Hnyk,^a Michael Bühl^c and Matthias Hofmann^d

^a Institute of Inorganic Chemistry of The Academy of Sciences of the Czech Republic, 250 68 Řež, The Czech Republic. E-mail: stibr@iic.cas.cz

^b The Department of Chemistry of The University of Leeds, Leeds, UK LS2 9JT

^c Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45740 Mülheim an der Ruhr, Germany

^d Anorganisch-Chemisches Institut, Ruprecht-Karls Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received 3rd January 2003, Accepted 20th February 2003

First published as an Advance Article on the web 4th March 2003

The reaction between excess *n*-C₄H₉ONO and *arachno*-4,5-C₂B₇H₁₃ (**1**) in diethyl ether at room temperature results in the formation of the first representatives of the *arachno* ten-vertex azadiborane family, *arachno*-6,5,9-NC₂B₇H₁₂ (**2**) and *arachno*-6,5,10-NC₂B₇H₁₂ (**3**) in yields of 6 and 20%, respectively. The reaction also generates *exo*-8-CH₃-*hypho*-7,8-NCB₆H₁₁ (**4**) (yield 5%) as a result of the extrusion of the CH₂ group from the cluster of the starting dicarbaborane to generate a terminal methyl unit. The reaction between 8,9-μ-NH₂-*arachno*-5,6-C₂B₈H₁₁ (**5**) and NaH, followed by treatment with iodine and water, produced the unique *endo* isomer of **4**, *endo*-8-CH₃-*hypho*-7,8-NCB₆H₁₁ (**6**) (yield 22%). The reaction between *n*-C₄H₉ONO and *nido*-5,6-C₂B₈H₁₂ (**7**) in hexane at reflux generates the first compound of the ten-vertex *nido* azadiborane family, *nido*-6,8,9-C₂NB₇H₁₀ (**8**), in 13% yield. The structures of all the compounds isolated are proposed on the basis of NMR spectroscopy, the geometries optimized at the RMP2(fc)/6-31G* level and their correctness was supported on the basis of GIAO-SCF NMR calculations.

Introduction

An area of chemistry currently undergoing development is that of the heterodiboranes, *i.e.* boron-cluster compounds that also contain two carbon atoms and one atom of another main-group element in the cluster. These can be exemplified by the *arachno* compounds 4,6,8-SC₂B₆H₁₀¹ and 6,8,9-SC₂B₇H₁₁,² *nido*-7,9,10-SC₂B₈H₁₀,³ and the alkylated phosphadiborane isomers *arachno*-RPC₂B₇H₁₁⁴ and 7-*R*-*nido*-7,8,9-PC₂B₈H₁₀⁵ (*R* = CH₃ and C₆H₅), together with several isomeric eleven-vertex *nido* phosphadiboranes (phosphadiborollides) of formulations PC₂B₈H₁₁ or [PC₂B₈H₁₀]⁻.⁶ The last anion is a cluster analogue of the cyclopentadienide anion and is capable of forming *closo* complexes of formulation [CpFePC₂B₈H₁₀], analogues of ferrocene.⁷ The related area of azadiborane chemistry has so far been represented by the eleven-vertex compounds, *nido*-10,7,8-NC₂B₈H₁₁, μ-8,9-NH₂-*arachno*-5,6-C₂B₈H₁₁,⁸ and *t*-C₄H₉-*arachno*-NC₂B₈H₁₂.⁹ We now report an extension of the *n*-C₄H₉ONO method, which we have previously reported in a preliminary fashion,¹⁰ to the preparation of three new representatives of families of ten-vertex azadiboranes, *viz.* *nido*-6,8,9-NC₂B₇H₁₀, *arachno*-6,5,9-NC₂B₇H₁₂ and *arachno*-6,5,10-NC₂B₇H₁₂. We also report two mutually isomeric azamonocarboranes of the eight-vertex *hypho* series, *endo*-8-CH₃-*hypho*-7,8-NCB₆H₁₁ and *exo*-8-CH₃-*hypho*-7,8-NCB₆H₁₁. The numbering schemes for the ten-vertex *nido* and *arachno*, nine-vertex *arachno*, and eight-vertex *hypho* frameworks used in this paper are in Scheme 1.

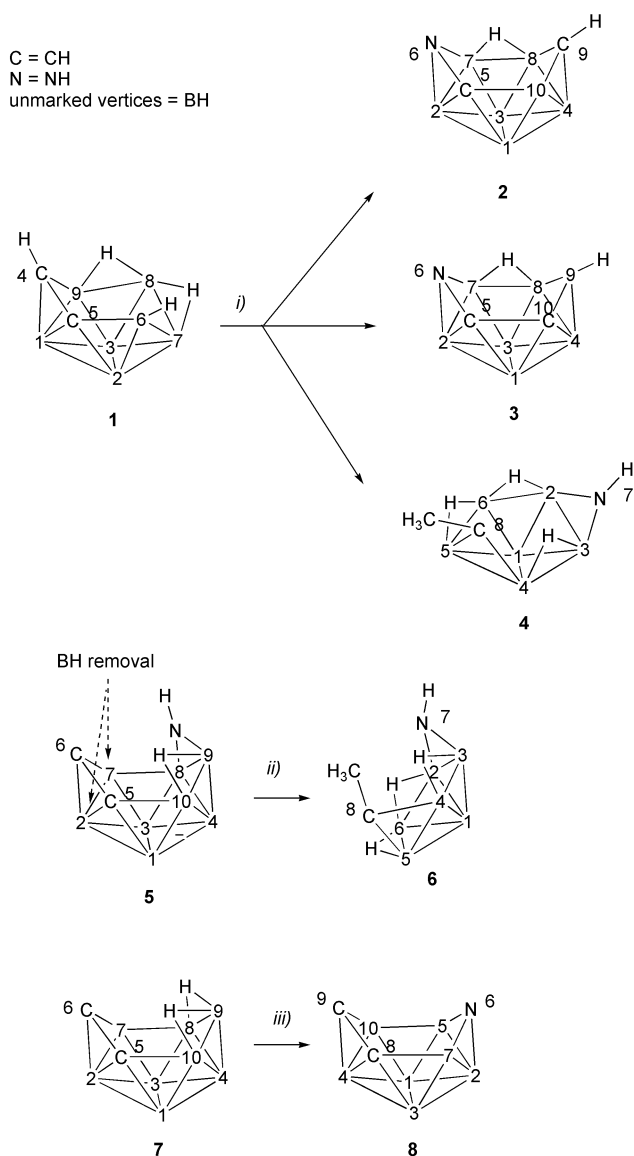
Results and discussion

Syntheses

As shown in path (i) of Scheme 1, treatment of the nine-vertex *arachno* dicarbaborane 4,5-C₂B₇H₁₃ (**1**) with an approximately two-and-a-half fold excess of *n*-butyl nitrite in diethyl ether at room temperature for 48 h, followed by the separation of the reaction products by column chromatography on silica gel, resulted in the isolation of three main fractions, of *R*_f 0.4, 0.2 and 0.15 in benzene. From these, after evaporation and vacuum sublimation at *ca.* 50 °C, were isolated three azacarboranes which were identified as *arachno*-6,5,9-NC₂B₇H₁₂ (**2**) (yield 6%), *arachno*-6,5,10-NC₂B₇H₁₂ (**3**) (yield 20%), and *exo*-8-CH₃-*hypho*-7,8-NCB₆H₁₁ (**4**) (yield 5%). All these compounds are white crystalline air-sensitive compounds which should be stored under nitrogen. Scheme 1 suggests that compound **3** may be reasonably formed *via* direct insertion of the *n*-C₄H₉ONO nitrogen atom into the C(4), B(8) and B(9) region of compound **1**. The formation of the *hypho* compound **4** would seem to be compatible with the elimination of the B(6) atom, scission of the B(1)–C(4) and B(1)–C(5) connectivities, and a concomitant movement of the C(4) centre into the exocenter region to generate the C-methyl substituent. The formation of the other azacarborane **2** seems to be associated with a more complex reorganisation of the skeletal carbons during the N-insertion process.

Path (ii) of Scheme 1 shows that a compound structurally very similar to the *hypho* azamonocarborane **4** was obtained upon treatment of the eleven-vertex *arachno* azadiborane μ-8,9-NH₂-5,6-C₂B₈H₁₁ (**5**)⁸ with sodium hydride in diethyl ether at room temperature for 1 h, followed by the addition of one molar equivalent of iodine and treatment of the mixture with water. Column chromatography on silica thence led into the

† Electronic supplementary information (ESI) available: calculated coordinates for all compounds. See <http://www.rsc.org/suppdata/dt/b3/3300088e/>



Scheme 1 Reagents and conditions: (i) $n\text{-C}_4\text{H}_9\text{ONO}/\text{Et}_2\text{O}$, r.t., 48 h; (ii) NaH, then I_2 and H_2O ; (iii) $n\text{-C}_4\text{H}_9\text{ONO}$ –hexane, reflux, 5 days.

isolation of *endo*-8- CH_3 -*hypho*-7,8- $\text{NCB}_6\text{H}_{11}$ (**6**) in 22% yield. No rearrangement to the *exo* isomer **4** was observed over a period of several months at room temperature. As shown in Scheme 1, the formation of compound **6** would be consistent with the hydrolytic elimination of two boron vertices B(2) and B(7) adjacent to the C(6) atom in structure **5**, the C(6) vertex being a source of the *endo*- CH_3 substituent in structure **6**.

Path (iii) of Scheme 1 shows that the ten-vertex *nido* dicarbaborane 5,6- $\text{C}_2\text{B}_8\text{H}_{12}$ (**7**)¹¹ is also a suitable synthon for the preparation of azadiboraboranes. Treatment of compound **7** with excess $n\text{-C}_4\text{H}_9\text{ONO}$ in hexane under reflux for 5 days generates *nido*-6,8,9- $\text{NC}_2\text{B}_7\text{H}_{10}$ (**8**) in a yield of 13%. The compound was separated from unreacted **7** by column chromatography on silica gel using a CH_2Cl_2 –hexane mixture as liquid phase and was purified by vacuum sublimation. As shown in Scheme 1, the formation of the azadiboraborane **8** is in agreement with a degradative replacement of the B(9) vertex in structure **7** by the $n\text{-C}_4\text{H}_9\text{ONO}$ nitrogen atom.

The stoichiometry of the $n\text{-C}_4\text{H}_9\text{ONO}$ reactions outlined above is not clear and the only certain observation in this regard is that they result in the incorporation of the butyl nitrite nitrogen into the cluster framework. The formation of the azadiboraboranes in these reactions is accompanied by the formation of large amounts of boric acid [presumably from the atmospheric hydrolysis of $\text{B}(\text{On-}\text{C}_4\text{H}_9)_3$] that must result from

more complete degradation of the starting carboranes. This finding would also account for the observed modest yields of the azadiboraborane products. Nevertheless, in spite of these modest yields, this synthetic approach does constitute a viable source of structurally interesting azadiboraborane compounds.

Structural studies

General. All the azadiboraborane compounds reported here are volatile materials, mostly very soluble in organic solvents such as dichloromethane and hexane. For these reasons we have so far not succeeded in growing crystals suitable for single-crystal X-ray diffraction analyses. The constitutions of the products were however established using NMR spectroscopy. All cluster BH and CH, ^{11}B and ^1H resonances were interrelated by $[^{11}\text{B}\text{--}^{11}\text{B}]$ -COSY¹² and $^1\text{H}\text{--}\{^{11}\text{B}(\text{selective})\}$ ¹³ experiments, which permitted complete assignments after comparison with congener species as discussed for individual species below. Additionally, the structures of all these new azadiboraboranes were geometry-optimized using *ab initio* RMP2(fc)/6-31G* calculations and the ^{11}B chemical shifts for these calculated geometries thence were calculated using the GIAO-SCF NMR approach. These calculated chemical shifts are summarized in Table 1 together with the experimental NMR data. Inspection of these data shows a satisfactory agreement between the experimental and calculated $\delta(^{11}\text{B})$ values, thereby supporting the overall structural conclusions.

NMR spectroscopy. The ^{11}B NMR spectrum of *arachno*-6,5,9- $\text{NC}_2\text{B}_7\text{H}_{12}$ (compound **2**) consists of seven doublets of relative intensity 1 and its ^1H NMR spectrum indicates the presence of three CH resonances together with one broad singlet attributable to a bridging hydrogen atom. The two high-field CH resonances at $\delta(^1\text{H})$ +0.20 and –0.02 ppm can be reasonably assigned to the *exo* and *endo* components of the cage CH_2 unit¹⁴ and the third CH resonance at $\delta(^1\text{H})$ +2.78 ppm can be attributed to a normal *exo* CH cluster unit. As shown in Fig. 1, the ^{11}B NMR data for **2** correlate approximately with those for the isostructural tricarbaborane *arachno*-5,6,9- $\text{C}_3\text{B}_7\text{H}_{13}$ (**9**).¹⁵ Therefore the *arachno*-6,5,9- $\text{NC}_2\text{B}_7\text{H}_{12}$ constitution, which is also in agreement with the results of mass spectrometry (m/z_{max} 127), is strongly indicated.

Of similar character are the NMR patterns for the 6,5,10-isomer (compound **3**) except that the ^1H NMR data demonstrate the presence of two different CH cluster units [at $\delta(^1\text{H})$ +1.51 and +3.85 ppm], and the triplet [at $\delta(^{11}\text{B})$ –28.1 ppm] in the ^{11}B NMR spectrum clearly shows the presence of one BH_2 unit. As also shown in Fig. 1, the NMR data correlate marginally with those for the structurally related *t*- C_4H_9 -*arachno*- $\text{NC}_2\text{B}_8\text{H}_{12}$ (**10**).⁹ The principal differences, at B(7,8), are consistent with recognized α -effects¹⁶ arising from the cluster NH(6) and BH_2 (9) units in the azadiboraborane. The *arachno*-6,5,10- $\text{NC}_2\text{B}_7\text{H}_{12}$ formulation is therefore reasonably supposed for compound **3**, this being additionally consistent with the results of mass spectrometry (m/z_{max} 127).

The experimentally observed NMR data and the results of mass spectrometry (m/z_{max} 119) for the eight-vertex *hypho* compounds **4** and **6** are in good agreement with their formulation as two isomeric compounds of the eight-vertex constitution 8- CH_3 -*hypho*-7,8- $\text{NC}_6\text{BH}_{11}$. As seen in Fig. 1, the observed ^{11}B NMR chemical shifts for both compounds excellently correlate, for example, with the corresponding patterns for the isostructural [*hypho*-7,8- $\text{C}_2\text{B}_6\text{H}_{13}$][–] anion (**11**).¹⁷ The patterns are also very similar to those of the isoelectronic [*7,8*- $\text{SCB}_6\text{H}_{11}$][–] anion¹⁸ and neutral 7,8- $\text{SNB}_6\text{H}_{11}$.^{10a} It can be seen that the NMR patterns for **4** and **6** (Table 1 and Fig. 1) are mutually very similar indeed. We attribute this to their having closely isomeric structures, specifically *exo*- and *endo*-8- CH_3 -*hypho*-7,8- $\text{NCB}_6\text{H}_{11}$ for **4** and **6**, respectively. Evidence for these *exo* and *endo* structural assignments resides in the resonance

Table 1 NMR Data

Compound	Nucleus	δ (multiplicity, assignment, J_{BH}/Hz)
<i>arachno</i> -6,5,9-NC ₂ B ₇ H ₁₂ (2)	¹¹ B ^a	-2.4 (d, B4, 159), -11.8 (d, B2, 179), -17.4 (d, B7, 146), -25.1 (d, B10, ~150 ^b), -25.5 (d, B8, ~150 ^b), -34.5 (d, B1, 157), -53.0 (d, B3, 148)
	¹¹ B- ¹¹ B ^c	All theoretical crosspeaks observed, except B2-B7
	¹ H ^d	3.20 (br, NH6), 2.78 (H5), 2.74 (H2), 2.71 (H4), 2.68 (H7), 1.83 (H8), 1.68 (H10), 1.25 (H1), 0.02 (<i>exo</i> -H9), -0.02 (<i>endo</i> -H9), -0.27 (H3), -0.38 ($\mu\text{H}7,8$)
<i>arachno</i> -6,5,10-NC ₂ B ₇ H ₁₂ (3)	¹¹ B (calc.)	2.1 (B4), -7.2 (B2), -13.4 (B7), -21.2 (B8), -22.0 (B10), -31.6 (B1), -53.2 (B3)
	¹¹ B ^a	-3.9 (d, B4, 159), -8.2 (d, B7, 149), -21.8 (d, B2, 186), -28.1 (d, B8, 127 ^b), -28.7 (t, B9, 127 ^b), -31.5 (d, B1, 175), -53.9 (d, B3, 152)
	¹¹ B- ¹¹ B ^c	All theoretical crosspeaks observed, except B2-B7
<i>exo</i> -8-CH ₃ - <i>hypho</i> -7,8-NCB ₆ H ₁₁ (4)	¹¹ B (calc.)	3.91 (br, H6), 3.80 (H5), 2.84 (H7), 2.76 (H4), 2.28 (H2), 1.84 (H1), 1.51 (H10), 1.28 (H8), 0.93 (<i>exo</i> -H9), 0.67 (<i>endo</i> -H9), -0.06 (H3), -0.58 ($\mu\text{H}7,8$), 0.6 (B4), -4.3 (B7), -18.5 (B2), -23.3 (B8), -26.9 (B9), -28.5 (B1), -54.6 (B3)
	¹¹ B ^a	-0.8 (d, B5, 149), -4.1 (d, B2, 140), -21.3 (d, B3, 133), -22.5 (d, B6 ~154 ^b), -28.5 (d, B4, ~164 ^b), -57.3 (d, B1, 143)
	¹¹ B- ¹¹ B ^c	All theoretical crosspeaks observed, except B2-B3
<i>endo</i> -8-CH ₃ - <i>hypho</i> -7,8-NCB ₆ H ₁₁ (6)	¹¹ B (calc.) ^f	2.92 (H5), 2.68 ^e (s, 3 H, <i>exo</i> -8-CH ₃), 2.58 (H2), 2.17 (H4), 2.11 (H6), 1.14 (H3), -0.95 (H1), -0.63 (br, $\mu\text{H}3,4$), -2.00 (br, 2 H, $\mu\text{H}2,6/5,6$), -2.18 (<i>endo</i> -H8)
	¹¹ B ^a	0.2 (B5), -1.2 (B2), -17.7 (B6), -18.7 (B3), -21.0 (B4), -58.7 (B1)
	¹¹ B- ¹¹ B ^c	All theoretical crosspeaks observed, except B2-B3
<i>nido</i> -6,8,9-NC ₂ B ₇ H ₁₀ (8)	¹¹ B (calc.) ^f	3.03 (H2), 2.46 (H5), 2.34 (H6), 2.17 (s, 3 H, <i>endo</i> -8-CH ₃), 2.06 (H4), 0.99 (H3), -0.57 (br, $\mu\text{H}3,4$), -0.92 (H1) -1.68 (<i>exo</i> -H8), -1.88 (br, 2 H, $\mu\text{H}2,6/5,6$)
	¹¹ B ^a	2.9 (B5), 0.6 (B2), -17.9 (B3), -17.3 (B6), -21.0 (B4), -58.5 (d, B1, 141)
	¹¹ B- ¹¹ B ^c	All theoretical crosspeaks observed
	¹ H ^d	14.7 (d, B5, 159), 4.7 (d, B10, 151), -4.6 (d, B3, 154), -7.0 (d, B7, ~160 ^b), -8.8 (d, B1, ~145 ^b), -15.6 (d, B4, 173), -32.8 (d, B2, 149)
	¹¹ B (calc.)	6.51 (H9), 5.73 (t, br, NH6), 3.70 (H8), 3.70 (H5), 3.20 (H10), 2.95 (H3), 2.92 (H7), 2.44 (H1), 1.65 (H4), 1.30 (H2)
		19.6 (B5), 8.9 (B10), 0.8 (B3), -5.3 (B7), -4.4 (B1), -14.3 (B4), -33.2 (d, B2, 141)

^a $\delta(^{11}\text{B})$ values in CDCl₃ [determined by ¹¹B-¹H(broadband)] measurements with assignments by [¹¹B-¹¹B]-COSY NMR spectroscopy/GIAO-SCF-calculated $\delta(^{11}\text{B})$ chem. shifts. ^b Value uncertain due to peak overlap. ^c Measured under the conditions of ¹H(broadband) decoupling. ^d Assignments by ¹H-¹¹B(broadband) and ¹H-¹¹B(selective) NMR spectroscopy; unless stated otherwise, all signals are singlets of relative intensity 1 in the ¹H-¹¹B(broadband) NMR spectrum. ^e Additional doublet splitting *ca.* 6 Hz. ^f The corresponding GIAO-MP2 results for **4** and **6** are (in ppm): B1 -59.7, B2 -4.0, B3 -24.5, B4 -28.1, B5 -2.9, B6 -25.1 and B1 -63.6, B2 -4.5, B3 -23.0, B4 -26.1, B5 -2.2, B6 -22.4, respectively.

positions observed for the 8-CH₃CH cluster units, specifically those attributable to the *exo* and *endo* 8-CH₃ group in these compounds [$\delta(^1\text{H})$ at -2.68 and -1.68 ppm for compounds **4** and **6**, respectively].

The mass spectrum of compound **8** (m/z_{max} 125) and also the pattern of its ¹¹B NMR spectrum (see upper diagrams in Fig. 1) correspond to a ten-vertex *nido* structured 5,6,9-NC₂B₇H₁₀ formulation. The ¹H NMR spectrum shows two different *exo* CH cluster units at $\delta(^1\text{H})$ +3.75 and +6.51 ppm. These values approximate to those found for *nido*-5,6-C₂B₈H₁₂.¹¹ There is also a broad ¹H triplet, of relative intensity 1, assignable to the NH cluster unit. As seen in Fig. 1, there is also a striking similarity between the ¹¹B NMR data of **8** and those for the tricarbaborane analogue, the [6-CH₃-*nido*-5,6,9-C₂B₇H₉]⁻ anion (**12**).¹⁹ This close similarity suggests a straightforward isostructurality for both compounds, and thence the proposed *nido*-5,6,9-NC₂B₇H₁₀ formulation for the azaborane **8** with all the heteroatoms on the open hexagonal face of the cage.

Geometry optimization and GIAO calculations. The geometry-optimized RMP2(fc)/6-31G* structures of the ten-vertex compounds **2**, **3** and **8** are in Fig. 2 and selected intracage distances are in Table 2. The calculated N-C distances for **2** and **3** (1.498 and 1.465 Å, respectively) are within expected ranges, the N-B(2) separations (1.754 and 1.582 Å, respectively) are longer than the open-face N-B(7) distances (1.550 and 1.555 Å, respectively). The C(5)-B(2) bond lengths in **2** and **3** (1.783 and 1.780 Å, respectively) are comparatively very long. The C-C separation in **3** (1.485 Å) is comparable to that found crystallographically for 6-Et₃N-*arachno*-5,10-C₂B₈H₁₂ (1.483 Å)²⁰ although the hydrogen-bridged B-B separations in **2** and **3** (1.811 and 1.794 Å) are shorter (*cf.* 1.844(3) Å). These are also shorter than those found crystallographically for 6-(CH₃)₃-

Si-arachno-6,9-C₂B₈H₁₃²¹ (mean 1.885 Å). For further comparisons, the calculated hydrogen-bridged B-B separations for *arachno* compounds 6,8,9-SC₂B₇H₁₁ and 5,6,9-C₃B₇H₁₃ are 1.826 and 1.852 Å, respectively.²

The calculated open-face N-B distances (mean 1.487 Å) for the *nido* azadiborane **8** are much shorter than the corresponding distances in the *arachno* compounds **2** and **3** (1.550 and 1.555 Å, respectively). The N(6)-B(2) distance (1.625 Å) in **8** is also much shorter than the corresponding separation in **2** (1.754 Å), but longer than that in **3** (1.582 Å). The calculated C-C distance in **8** (1.463 Å) is comparable to that found in the crystal of the *ortho*-carboranyl-substituted derivative of *nido*-5,6-C₂B₈H₁₂ (1.457 Å).²² The C(9)-B(4) and C(9)-B(10) distances (1.694 and 1.511 Å) calculated for **8** are shorter than the corresponding C(9)-B(4) and C(9)-B(open-face) separations in **2** (mean 1.677 and 1.701 Å, respectively). As a consequence, the apical N and C vertices in the *nido* species **8** are more compactly incorporated into the cluster than those in the *arachno* compound **2**.

The calculated N-B distances (mean 1.570 Å) in the *hypho* compounds **4** and **6** (Fig. 3) are a little longer than the N-B(open-face) separations in *arachno* compounds **2** and **3** (1.550 and 1.555 Å, respectively), and much longer than those calculated for the *nido* compound **8** (1.487 Å). The C(8)-B distances in **4** and **6** (mean 1.587 and 1.591 Å, respectively) are shorter than those calculated for C(9)-B(open-face) in **2** (mean 1.701 Å), but longer than the corresponding separation in **8** (1.511 Å). A notable feature of compounds **4** and **6** are the extremely long B-B distances calculated for borons spanned by the NH₂ and CH₂ vertices (1.979 and 1.989 Å, and 1.957 and 1.958 Å, respectively). These approach the limits of non-bonding distances and are the longest encountered within a large body of boron-cluster compounds structurally characterized

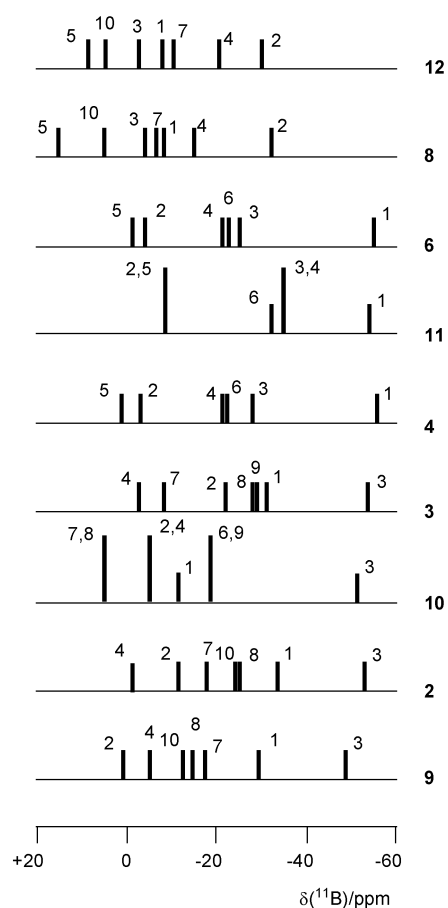


Fig. 1 Stick representations of the chemical shifts and relative intensities in the ^{11}B NMR spectra of the *arachno* compounds 5,6,9- $\text{C}_3\text{B}_7\text{H}_{13}$ (**9**) (data from ref. 15), 6,5,9- $\text{NC}_2\text{B}_7\text{H}_{12}$ (**2**), *t*- C_4H_9 -*arachno*- $\text{NC}_2\text{B}_8\text{H}_{12}$ (**10**) (data from ref. 9), 6,5,10- $\text{NC}_2\text{B}_7\text{H}_{12}$ (**3**), *hypho* compounds *exo*-8- CH_3 -7,8- $\text{NCB}_6\text{H}_{11}$ (**4**), [7,8- $\text{C}_2\text{B}_6\text{H}_{13}$] $^-$ (**11**) (data from ref. 17), *endo*-8- CH_3 -7,8- $\text{NCB}_6\text{H}_{11}$ (**6**), and *nido* compounds 6,8,9- $\text{NC}_2\text{B}_7\text{H}_{10}$ (**8**) and [6- CH_3 -5,6,9- $\text{C}_3\text{B}_7\text{H}_9$] $^-$ (**12**) (data from ref. 20).

thus far. Nevertheless, values of similar magnitude, 1.976 and 1.995 Å, were established, *e.g.*, in the microwave study of *closo*-1,6- $\text{C}_2\text{B}_7\text{H}_9$.²³

The GIAO-HF results for all molecules suggest that the corresponding MP2/6-31G* geometries can be deemed reasonably good representations of the geometries of relatively free molecules in solution. Comparison between theoretical and experimental ^{11}B chemical shifts in Table 1 generally reveals reasonable agreement, at least the calculated values follow the general trends in experimental shifts. The mean absolute deviation between computed and experimental ^{11}B shifts for compounds included in this study is 3.6 ppm, somewhat larger than found for boranes and carboranes at a comparable level.²⁴ It is to be expected that inclusion of electron correlation would improve the accord between theory and experiment for the azacarboranes of this study. This expectation was tested and borne out by performing GIAO-MP2 computations²⁵ for the two smallest molecules, namely *hypho*-species **4** and **6** for which the largest discrepancies between the GIAO-SCF and experimental ^{11}B NMR was noted. For this subset, the mean absolute error is reduced from 4.1 to 1.7 ppm on going from the GIAO-SCF to the GIAO-MP2 level (for individual values, see Table 1).

Conclusions

The reactions of butyl nitrite with *arachno*-4,5- $\text{C}_2\text{B}_7\text{H}_{13}$ **1** and *nido*-5,6- $\text{C}_2\text{B}_8\text{H}_{12}$ **7** reported here have generated the first examples of ten-vertex *nido*- and *arachno*-azadiboranes to be reported. These represent an interesting complementary

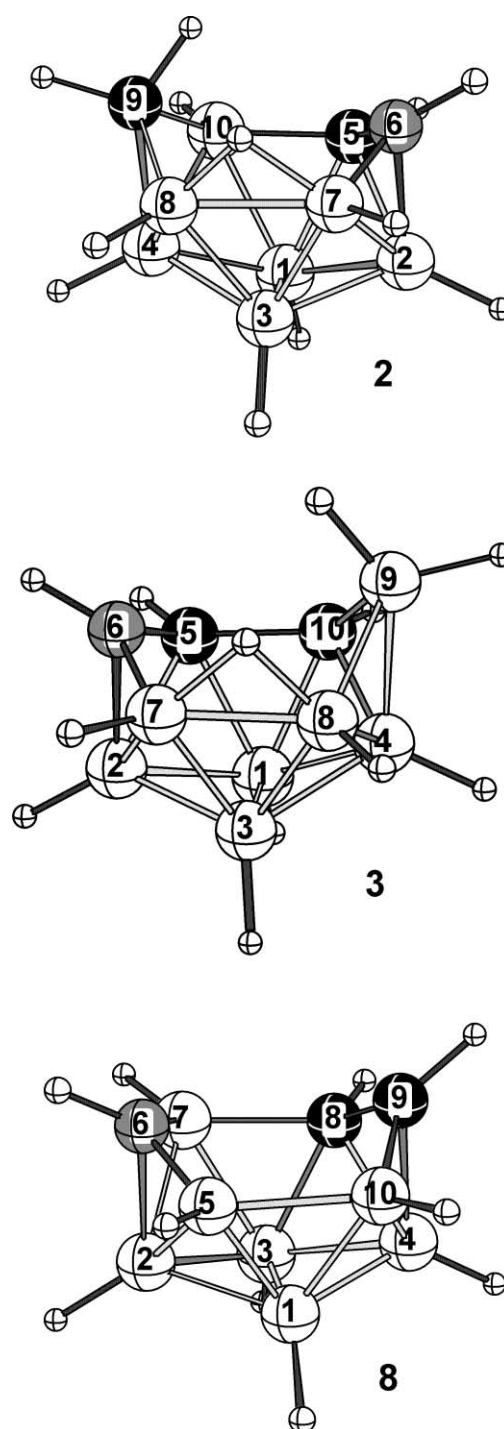


Fig. 2 Geometry-optimized structures of 6,5,9-*arachno*- $\text{NC}_2\text{B}_7\text{H}_{12}$ (**2**), 6,5,10-*arachno*- $\text{NC}_2\text{B}_7\text{H}_{12}$ (**3**) and *nido*-6,8,9- $\text{NC}_2\text{B}_7\text{H}_{10}$ (**8**).

contribution to contemporary developments in the area of ten-vertex heterodiborane chemistry.²⁶ The isolation of the two isomeric compounds **4** and **6** has extended the area of eight-vertex *hypho*-cluster chemistry by two novel azacarboranes, which are the first *hypho*-azamonocarborane species to be reported. These results, together with previously reported reactions,¹⁰ also indicate that the organic nitrite method may well be a quite general versatile and useful entry into azaborane and azaheteroborane chemistry, and can therefore be expected to be useful in producing further classes of new azaborane species, as well as new routes to known azaborane systems. Examination of these possibilities, together with work aimed at the generation of corresponding metallated derivatives, and the converse synthesis of metallazaboranes from the reaction of metallaboranes with nitrites, is ongoing.

Table 2 Selected geometrical parameters at the RMP2(fc)/6-31G* level

Bond lengths (Å)	2	3	4	6	8
1-2 ^a	1.747	1.759	1.800	1.798	1.784
1-3	1.784	1.775	1.777	1.778	1.829
1-4	1.710	1.759	1.844	1.845	1.776
1-5	1.731	1.720	—	—	1.768
1-6	—	—	1.727	1.724	—
1-10	1.804	1.707	—	—	1.786
2-3	1.779	1.766	1.979	1.989	1.747
2-5	1.783	1.780	—	—	1.821
2-6	1.574	1.582	1.764	1.765	1.625
2-7	1.887	1.891	1.563	1.561	1.827
3-4	1.790	1.813	1.785	1.787	1.759
3-7	—	—	1.577	1.578	1.796
3-8	1.823	1.801	—	—	1.686
4-5	—	—	1.957	1.958	—
4-8	—	—	1.591	1.595	1.717
4-9	1.677	1.782	—	—	1.694
4-10	1.748	1.671	—	—	1.803
5-6	1.498	1.465	1.787	1.791	1.487
5-8	—	—	1.582	1.586	—
5-10	1.580	1.485	—	—	1.861
6-7	1.550	1.555	—	—	1.488
7-8	1.811	1.794	—	—	1.687
8-9	1.715	1.971	—	—	1.463
9-10	1.696	1.685	—	—	1.511
8-C9	—	—	1.521	1.529	—
(B-H) _t , mean	1.189	1.191	1.192	1.192	1.189
7-H _b	1.351	1.372	—	—	—
8-H _b	1.290	1.266	—	—	—
(C-H) _{mean}	1.088	1.088	1.097	1.090	1.088
(C _{Me} -H) _{mean}	—	—	1.095	1.097	—
(N-H) _{mean}	1.017	1.017	1.019	1.019	1.018

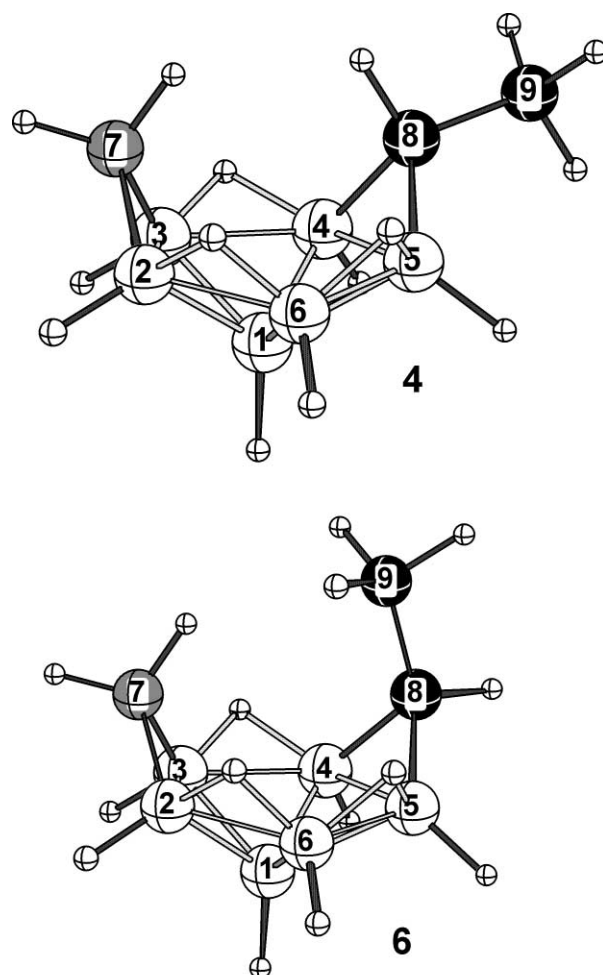
Bond angles (°)	2	3	4	6	8
5-6-7	119.8	119.2	—	—	119.8
8-9-10	111.8	97.8	—	—	115.2
4-8-5	—	—	76.1	76.0	—
2-7-3	—	—	78.2	78.6	—

^a For numbering schemes, see Figs. 2 and 3.

Experimental

General

The starting dicarbaborane compounds *arachno*-4,5-C₂B₇H₁₃ **1**,²⁷ *nido*-5,6-C₂B₈H₁₂**7**,¹¹ and nitrogen-bridged 8,9-μ-NH₂-*arachno*-5,6-C₂B₈H₁₁ **5**⁸ were prepared as reported previously and sublimed before use. Diethyl ether (Aldrich) was dried over Na/benzophenone, hexane and CH₂Cl₂ were dried over CaH₂, and all were freshly distilled before use. Reactions were carried out under dry nitrogen, with subsequent chromatographic separations being carried out in air. Column chromatography was performed using silica gel (Silpearl, Kavalier) and the purity of individual chromatographic fractions was checked by analytical TLC on Silufol (Kavalier, silica gel on aluminum foil; detection by UV 254 or iodine vapors, followed by 2% aqueous AgNO₃ spray). TLC R_F values are given for the same solvents as used in the column chromatography that is being monitored. Low-resolution mass spectra were obtained using a VG Autospec instrument and 70 eV electron-impact ionization. Proton (¹H) and boron (¹¹B) NMR spectroscopy was performed at 9.4 Tesla on a Bruker AM 400 instrument. The procedure for [¹¹B-¹¹B]-COSY¹² and ¹H-¹¹B(selective)¹³ NMR experiments were essentially as described in other recent papers from our laboratories.²⁸ NMR chemical shifts δ are given in ppm to high-frequency (low field) of ε = 32.083971 MHz (nominally F₃B·OEt₂ in CDCl₃) for ¹¹B (quoted ± 0.5 ppm) and ε = 100 MHz

**Fig. 3** Geometry-optimized structures of the *hypho* compounds *exo*-8-CH₃-7,8-NCB₆H₁₁ (**4**) and *endo*-8-CH₃-7,8-NCB₆H₁₁ (**6**).

(Si(CH₃)₄) for ¹H (quoted ± 0.05 ppm), ε being defined as in ref. 29. Solvent residual ¹H resonances were used as internal secondary standards. Coupling constants ¹J(¹¹B-¹H) are taken from resolution-enhanced ¹¹B spectra with digital resolution 8 Hz and are given in Hz.

arachno-6,5,9-NC₂B₇H₁₂ (**2**), *arachno*-6,5,10-C₂NB₇H₁₂ (**3**) and *exo*-8-CH₃-*hypho*-7,8-NCB₆H₁₁ (**4**). A solution of *arachno*-4,5-C₂B₇H₁₃ (compound **1**) (1.14 g, 10 mmol) in diethyl ether (50 cm³) was treated with *n*-C₄H₉ONO (3 cm³, 25.3 mmol) at ambient temperature for 48 h. The volatile materials were then evaporated and the solid residue extracted with benzene (20 cm³). The benzene extract was reduced in volume and subjected to column (30 × 2.5 cm) chromatography using benzene as the liquid phase. The three main fractions of R_f 0.4, 0.2 and 0.15 were isolated by evaporation and sublimation of the residual solid materials at ca. 50 °C (bath temperature). The white solid compounds thus obtained were respectively identified by NMR spectroscopy as compounds **2** (yield 75 mg, 6%), **4** (yield 60 mg, 5.0%) and **3** (yield 250 mg, 20%). For **2**: MS (70 eV, EI), *m/z* (%): 127 (15) [M]⁺, 122 (100) [M - 5H]⁺. Elemental analysis: calc. for C₂H₁₂B₇N (143.86): C 16.70, H 8.40; found: C 16.40, H 8.72%. For **3**: MS (70 eV, EI), *m/z* (%): 127 (5) [M]⁺, 123 (100) [M - 4H]⁺. Elemental analysis: calc. for C₂H₁₂B₇N (143.86): C 16.70, H 8.40; found: C 16.20, H 8.80%. For **4**: MS (70 eV, EI), *m/z* (%): 119 (65) [M]⁺, 118 (100) [M - H]⁺. Elemental analysis: calc. for C₂H₁₄B₆N (117.06): C 20.52, H 12.06; found: C 19.48, H 11.80%.

endo-8-CH₃-*hypho*-7,8-NCB₆H₁₁ (**6**). A suspension of NaH (500 mg, 60% suspension in mineral oil, 12.5 mmol) in thf

(20 cm³) was treated with a solution of 8,9- μ -NH₂-*arachno*-5,6-C₂B₈H₁₁ (compound **5**) (800 mg, 5.75 mmol) in thf (30 cm³) and the mixture was stirred for 1 h. This was followed by the addition of I₂ (2.4 g, 10 mmol) under cooling to 0 °C and the resulting mixture was stirred for additional 2 h. The mixture was then acidified with CF₃COOH (1.0 cm³), filtered and the thf removed by evaporation. The viscous residue thus obtained was extracted with CH₂Cl₂ (40 cm³) and the extract reduced in volume. Column chromatography on silica gel, using CH₂Cl₂–hexane (2 : 1, v/v) as the liquid phase, gave the main fraction of R_f 0.2. This was evaporated and the residual solid sublimed at ca. 50 °C (bath temperature) giving a white solid which was identified by NMR spectroscopy as compound **6** (yield 150 mg, 22%). For **6**: MS (70 eV, EI), *m/z* (%): 119 (65) [M]⁺, 118 (100) [M – H]⁺. Elemental analysis: calc. for C₂H₁₄B₆N (117.06): C 20.52, H 12.06; found: C 19.62, H 11.57%.

nido-6,8,9-NC₂B₇H₁₀ (**8**). A solution of *nido*-5,6-C₂B₈H₁₂ (compound **7**) (400 mg, 3.23 mmol) in hexane (10 cm³) was treated with *n*-C₄H₉ONO (5 cm³, 42.2 mmol) and the mixture was heated under reflux for 5 days. The volatile materials were then removed *in vacuo* and the viscous residue subjected to repeated column chromatography on silica gel, using CH₂Cl₂–hexane (1 : 4, v/v) as the liquid phase, ultimately to isolate two main components, of R_f 0.3 and 0.10. These were extracted with CH₂Cl₂, evaporated, and the residual solids sublimed at ca. 50 °C (bath temperature). The white solid compounds thus obtained were identified by NMR spectroscopy as compound **8** (yield 50 mg, 13 %) and the starting compound **7** (220 mg, 55 % recovery), respectively. For **8**: MS (70 eV, EI), *m/z* (%): 125 (15) [M]⁺, 123 (100) [M – 2H]⁺. Elemental analysis: calc. for C₂H₁₀B₇N (141.84): C 16.93, H 7.11; found: C 17.41, H 7.70%.

Computational details

All computations and were performed on the Power Challenge XL computer of the Supercomputing Centre of the Charles University in Prague using the Gaussian94 program package.³⁰ The geometries were fully optimized in C₁ symmetries by standard *ab initio* methods³¹ beginning at the SCF level with the 6-31G* basis set. Frequency calculations, carried out at the same level, determined the nature of the stationary points and gave the zero-point vibrational energies (ZPE).³² Minima on the respective potential energy hypersurfaces were characterized with zero imaginary frequency (NIMAG = 0). The final level of optimizations employed was second-order Moller–Pleset perturbation theory in the frozen-core approximation (RMP2(fc)/6-31G*) that includes the electron correlation effects and gave the relative energies. These geometries are reported. Selected geometry parameters are given in Table 2. The chemical shieldings were calculated at the SCF level using the GIAO (gauge-invariant atomic orbital) method incorporated in the Gaussian94 program and employed a II Huzinaga basis set³³ established well for calculations of magnetic properties.

Acknowledgements

We thank the Ministry of Education of the Czech Republic (project no. LN00A028), the Supercomputing Centre of the Charles University in Prague for granting computer time, and the EPSRC (United Kingdom) (Grant no. GR/F/43215) for support. M. B. wishes to thank Prof. W. Thiel and the Deutsche Forschungsgemeinschaft for support.

References

- 1 K. Baše, S. Heřmánek and F. Hanousek, *J. Chem. Soc., Chem. Commun.*, 1984, 299.
- 2 D. Hnyk and J. Holub, *Collect. Czech. Chem. Commun.*, 2002, **67**, 813.
- 3 V. A. Brattsev, S. P. Knyazev, G. N. Danilova and V. I. Stanko, *Zh. Obshch. Khim.*, 1975, **45**, 1393.
- 4 D. W. Hong, S. E. Rathmill, D. E. Kadlecck and L. G. Sneddon, *Inorg. Chem.*, 2000, **39**, 4996.
- 5 A. M. Shedlow and L. G. Sneddon, *Inorg. Chem.*, 1998, **37**, 5269.
- 6 J. Holub, D. L. Ormsby, J. D. Kennedy, R. Greatrex and B. Štíbr, *Inorg. Chem. Commun.*, 2000, **3**, 178; B. Štíbr, J. Holub, M. Bakardjiev, D. Hnyk, O. L. Tok, W. Milius and B. Wrackmeyer, *Eur. J. Inorg. Chem.*, 2002, 2320.
- 7 B. Štíbr, J. Holub, M. Bakardjiev, I. Pavlik, O. L. Tok, I. Císařová, B. Wrackmeyer and M. Herberhold, *Chem. Eur. J.*, in press.
- 8 J. Plešek, B. Štíbr and S. Heřmánek, *Chem. Ind. (London)*, 1974, 662; J. Plešek, S. Heřmánek, J. Huffman, P. Ragatz and R. Schaeffer, *J. Chem. Soc., Chem. Commun.*, 1991, 1389.
- 9 Z. Janoušek, J. Fusek and B. Štíbr, *J. Chem. Soc., Chem. Commun.*, 1992, 2649.
- 10 T. Jelínek, J. D. Kennedy and B. Štíbr, *J. Chem. Soc., Chem. Commun.*, 1993, 1628; T. Jelínek, J. D. Kennedy and B. Štíbr, *J. Chem. Soc., Chem. Commun.*, 1994, 677.
- 11 J. Plešek and S. Heřmánek, *Collect. Czech. Chem. Commun.*, 1974, **39**, 821.
- 12 W. C. Hutton, T. L. Venable and R. N. Grimes, *J. Am. Chem. Soc.*, 1984, **106**, 29.
- 13 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1987, 1573.
- 14 B. Štíbr, J. Plešek and S. Heřmánek, *Collect. Czech. Chem. Commun.*, 1974, **39**, 1805.
- 15 B. Štíbr, J. Holub, I. Císařová, F. Teixidor and C. Vinas, *Inorg. Chim. Acta.*, 1996, **245**, 129.
- 16 S. Heřmánek, *Chem. Rev.*, 1992, **92**, 325 and references therein.
- 17 T. Jelínek, J. Plešek, S. Heřmánek and B. Štíbr, *Main Group Met. Chem.*, 1987, **10**, 401.
- 18 J. Holub, J. D. Kennedy, T. Jelínek and B. Štíbr, *J. Chem. Soc., Dalton Trans.*, 1994, 1317.
- 19 S. O. Kang, G. T. Furst and L. G. Sneddon, *Inorg. Chem.*, 1989, **28**, 2339; C. A. Plumb, P. J. Carroll and L. G. Sneddon, *Organometallics*, 1992, **11**, 1665.
- 20 J. Holub, B. Štíbr, Z. Janoušek, J. D. Kennedy and M. Thornton-Pett, *Inorg. Chim. Acta.*, 1994, **221**, 5.
- 21 J. R. Wermher, N. S. Hosmane, J. J. Alexander, U. Siriwardane and S. G. Shore, *Inorg. Chem.*, 1986, **25**, 4351.
- 22 V. Šubrtová, A. Línek and V. Hašek, *Acta Crystallogr., Sect. B*, 1982, **38**, 3147.
- 23 K. Lau and R. A. Beaudet, *Inorg. Chem.*, 1976, **15**, 1059.
- 24 M. Bühl and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1992, **114**, 477.
- 25 M. Bühl, J. Gauss, M. Hofmann and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1993, **115**, 12385.
- 26 D. W. Hong, S. E. Rathmill, D. E. Kadlecck and L. G. Sneddon, *Inorg. Chem.*, 2000, **39**, 4996.
- 27 B. Štíbr, J. Plešek and S. Heřmánek, *Inorg. Synth.*, 1983, **22**, 237.
- 28 J. Plešek, B. Štíbr, X. L. R. Fontaine, J. D. Kennedy, S. Heřmánek and T. Jelínek, *Collect. Czech. Chem. Commun.*, 1991, **56**, 1618.
- 29 W. McFarlane, *Proc. R. Soc. London., Ser. A.*, 1968, **306**, 185.
- 30 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. Pettersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zahrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkra, M. Challacombe, C. Y. Peng, P. Y. Ayala, Y. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, L. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, Gaussian94, Revision B.2. Gaussian Inc., Pittsburg, PA, 1995.
- 31 W. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
- 32 A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502 and references therein.
- 33 S. Huzinaga, *Approximate Atomic Wave Functions*, University of Alberta, Edmonton, Canada, 1971.