APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 377–382
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.434

Synthesis of bipyridine-linked dimers of azanonaborane: electronic absorption and molecular-orbital calculations†

Mohamed E. El-Zaria, Tobias Borrmann and Detlef Gabel*

Department of Chemistry, University of Bremen, PO Box 330440, D-28334 Bremen, Germany

Received 12 December 2002; Revised 6 January 2003; Accepted 15 January 2003

A new class of azanonaborane–bipyridine derivatives was synthesized from the reaction of bidentate nitrogen ligands with the azanonaborane cluster $[(RNH_2)B_8H_{11}NHR]$ in benzene under reflux. The exchange of the *exo*-amino ligand by bipyridine derivatives is a convenient route to yield a dimer of the azanonaborane cluster in good yield. Thus, 4,4′-bipyridine (PyPy) and *trans*-1,2-di-(4-pyridyl)-ethene (Py=Py) replace the *exo*-NH_2R unit to give $[(PyPy)B_8H_{11}NHR]$ or $[RHNH_{11}B_8{-}PyPy{-}B_8H_{11}NHR]$ and $[(Py{=}Py)B_8H_{11}NHR]$ or $[RHNH_{11}B_8{-}Py{=}Py{-}B_8H_{11}NHR]$ respectively as colored products due to electronic interaction between the $\{B_8N\}$ unit and the bonded bipyridine units. This interaction has been investigated by UV–vis spectroscopy and by AM-1 molecular-orbital calculations. In the case of $[(Py{=}Py)B_8H_{11}NHR]$, the ^1H and ^{13}C NMR analysis of the products revealed two isomeric forms (*cis* and *trans*). This is attributed to thermal *cis*–*trans* isomerization. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: azanonaborane; borane; boron; cluster compounds; bidentate ligand; isomerization; NMR spectroscopy; MO calculations

INTRODUCTION

The azanonaboranes $[(RH_2N)B_8H_{11}NHR]$ are easily synthesized by the reaction of 1 mol of dimethyl sulfide-*arachno*-nonaborane $(Me_2S)B_9H_{13}$ with 3 mol of primary amino ligand (RNH_2) in refluxing benzene,[1,2] and the determination of their structures and unequivocal constitution has been reported (Fig. 1).[3,4] In the transition of $(Me_2S)B_9H_{13}$ to $[(RH_2N)B_8H_{11}NHR]$, one boron atom is lost and a pathway for the conversion is proposed.[5] The azanonaborane clusters have been shown to constitute a good entry into azacarbaborane[6] and azametallaborane chemistry[7] and may be useful as a new class of boron clusters in neutron capture therapy.[8,9] The azanonaborane cluster also undergoes several other interesting reactions, such as: (i) ligand-exchange reaction in which the *exo*-(NH_2R) group (Fig. 1) is replaced by other donor ligands; (ii) *N*-deprotonation followed by subsequent *N*-alkylation; (iii) halogenation reaction giving 8-exohalogen-substituted derivatives of $[(RNH_2)B_8H_{10}XNHR]$; (iv) hydrolytic decomposition to the new 5-*vertex* compound $[B_5H_{10}(\mu\text{-}NH^iPr)]$ of *hypho*-type structure.[10,11] The molecular structure of the azanonaborane cluster is based on eight boron atoms with one nitrogen bridge $\{B_8N\}$ and one *exo*-amine ligand. The necessary conditions for a ligand-exchange reaction of the azanonaborane, in which the *exo*-NH_2R group is replaced by other nitrogen donor ligands, have been reported.[9] Recently, Bauer *et al.*[12] synthesized new colored azanonaborane–pyridine $[(R'C_5H_4N)B_8H_{11}NHR'']$ derivatives, contrasting with the colorless nature of the starting materials. The electronic interaction of these compounds has been investigated by using UV–vis spectroscopy and by AM-1 molecular-orbital calculations.[12]

The exciting results with the ligand-exchange reaction stimulated us to explore new species of azanonaborane by the reaction of $[(^iPrH_2N)B_8H_{11}NH^iPr]$ with bidentate ligands. In this case, the use of bidentate ligands such as 4,4′-bipyridine (PyPy) and *trans*-1,2-di-(4-pyridyl)-ethene (Py=Py) might lead to compounds with two boron clusters as well as monomers. The azanonaborane cluster $[(Py{=}Py)B_8H_{11}NH^iPr]$ shows the occurrence of two products resulting from E/Z (i.e. *cis*–*trans*) isomerization. In this

---

*Correspondence to: Detlef Gabel, Department of Chemistry, University of Bremen, PO Box 330440, D-28334 Bremen, Germany.
E-mail: gabel@chemie.uni-bremen.de

†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

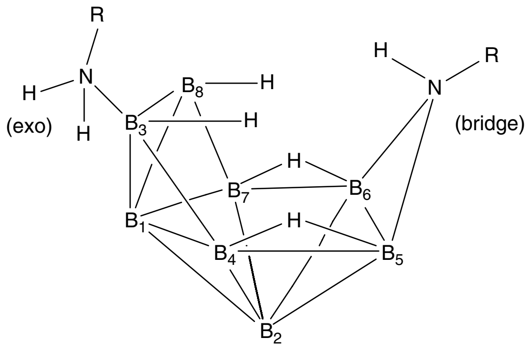


Figure 1. Schematic structure of azanonaborane cluster (*exo*-H atoms are omitted for clarity).

paper, therefore, we wish to report the synthesis of these kinds of novel azanonaborane–bipyridine derivatives. These compounds are colored, therefore, we investigated their spectroscopic properties by UV–vis spectroscopy and AM-1 molecular-orbital calculations.

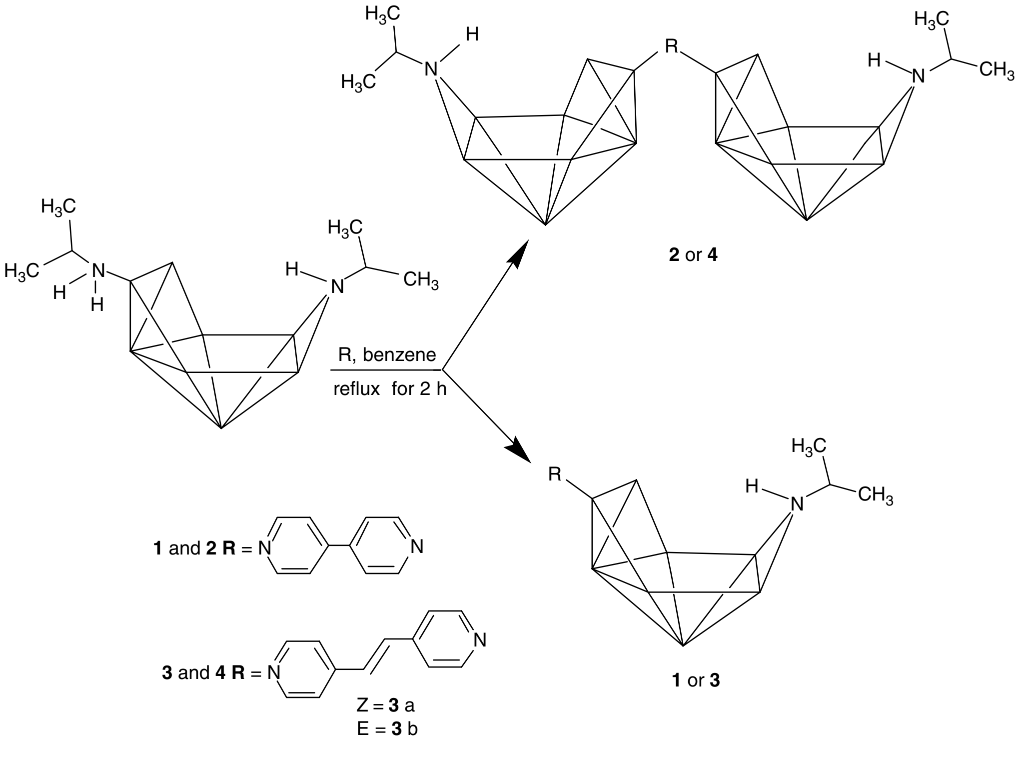
RESULTS AND DISCUSSION

Preparation

In initial experiments, we investigated the synthesis of azanonaborane dimers in two ways. The first one is the reaction of $(Me_2S)B_9H_{13}$ with diamines $H_2N(CH_2)_nNH_2$, where $n = 2$–6 and 12 in ratio (1 : 1) to give $B_9H_{13}NH_2(CH_2)_nNH_2$[8] followed by the reaction with another 1 mol of $(Me_2S)B_9H_{13}$ in tetrahydrofuran (THF) at 60 °C for 2 days to yield $B_9H_{13}NH_2(CH_2)_nH_2NB_9H_{13}$ as a colorless solid substance. However, it is not possible to obtain a dimeric form of azanonaborane by the reaction of $B_9H_{13}NH_2(CH_2)_nH_2NB_9H_{13}$ with excess of amino ligands. The reason for this might be attributed to the mechanistic pathway of the reaction[4] in the transition from the B_9 cluster to the B_8N cluster. The second approach involves the ligand-exchange reaction in which the *exo*-(NH_2R) group (Fig. 1) is replaced by amino ligands. According to our previous work, the *exo*-primary amine group ($^iPrH_2N$) of the boron cluster of the type $[(^iPrH_2N)B_8H_{11}NH^iPr]$ can be replaced by 1,4-diaminobutane to give $[(H_2N(CH_2)_4H_2N)B_8H_{11}NH^iPr]$ and the reaction showed no definitive evidence of any dimer or polymer of the azanonaborane cluster.[9] Therefore, it is necessary to choose a different type of ligand in order to obtain the desired dimeric form of the azanonaborane cluster.

We investigated pyrazine, 4,4′-bipyridine, and *trans*-1,2-di-(4-pyridyl)-ethene as bidentate ligands, for use in the ligand-exchange reaction. The monitoring by NMR spectroscopy of the reaction mixture of pyrazine and $[(^iPrH_2N)B_8H_{11}NH^iPr]$ showed the progressive loss of boron cluster exclusively to give boric acid.

Successful syntheses were obtained with 4,4′-bipyridine and *trans*-1,2-di-(4-pyridyl)-ethene, which have a free lone pair on the nitrogen atoms, bridging two boron clusters



Scheme 1.

Table 1. Selected NMR parameters for $[(PyPy)B_8H_{11}NH^iPr]$ (**1**), $[^iPrHNH_{11}B_8{-}PyPy{-}B_8H_{11}NH^iPr]$ (**2**), $[(Py{=}Py)B_8H_{11}NH^iPr]$ (**3**) in $CDCl_3$ and $[^iPrHNH_{11}B_8{-}Py{=}Py{-}B_8H_{11}NH^iPr]$ (**4**) in CD_2Cl_2 at 20 °C

	δ (^{11}B) [δ (^1H)] (ppm)								
Compound	B1	B2	B3	B4	B5,6	B7	B8	μH(4,5) μH(6,7)	NH
1	1.85 [+2.97]	−54.88 [−0.52]	−15.04 [+2.09]	−28.95 [+0.96]	−11.60 [+2.42] [+2.62]	−32.10 [+0.96]	−28.95 [+0.77] [−0.17]	[−1.76] [−1.76]	[−1.35]
2	1.94 [+2.87]	−54.97 [−0.6]	−15.13 [+2.2]	−29.09 [+0.8]	−11.14 [+2.48] [+2.59]	−31.80 [+0.82]	−29.09 [+0.78] [−0.11]	[−1.92] [−1.85]	[−1.25]
3	1.44 [+2.95]	−55.00 [−0.47]	−14.05 [+2.25]	−29.27 [+0.9]	−11.64 [+2.58] [+2.62]	−31.95 [+0.96]	−29.27 [+0.79] [−0.16]	[−1.75] [−1.75]	[−1.36]
4	1.75 [+2.92]	−54.91 [−0.5]	−15.63 [+2.26]	−28.92 [+0.92]	−11.37 [+2.44] [+2.55]	−32.12 [+0.92]	−28.92 [+0.81] [−0.11]	[−1.76] [−1.66]	[−1.30]

by one 4,4′-bipyridine or *trans*-1,2-di-(4-pyridyl)-ethene unit (Scheme 1). The ligand-exchange reaction of 4,4′-bipyridine with $[(^iPrH_2N)B_8H_{11}NH^iPr]$ in 1 : 2 ratio in refluxing benzene for 2 h, followed by chromatography, resulted in the isolation of $[(PyPy)B_8H_{11}NH^iPr]$ (**1**, 36%) and $[^iPrHNH_{11}B_8{-}PyPy{-}B_8H_{11}NH^iPr]$ (**2**, 31%) as brown and red solid substances respectively (Scheme 1). *trans*-1,2-Di-(4-pyridyl)-ethene reacted with $[(^iPrH_2N)B_8H_{11}NH^iPr]$ under the same conditions to form $[(Py{=}Py)NB_8H_{11}NH^iPr]$ (**3**, 53%) and $[^iPrHNH_{11}B_8{-}Py{=}Py{-}B_8H_{11}NH^iPr]$ (**4**, 35%) as brown and red solid substances respectively (Scheme 1). The constitution and purity of each of these compounds were established by NMR spectrometry (Table 1), elemental analysis, and mass spectrometry. The NMR spectroscopic data of the series of compounds among all the family number (**1**, **2**, **3**, and **4**) are very similar (see Experimental section), although there are some minor variations in the proton shielding as the organobipyridine group changes.

The NMR spectrum of **3** with one boron cluster showed clearly that the compound is found in two forms, *cis* (**3a**, 30%) and *trans* (**3b**, 70%), which could not be separated. The *cis–trans* isomerization occurred thermally in the dark. The standard free energy change associated with this *cis–trans* isomerization is $\Delta G = 2.1$ kJ mol^{-1}, which is smaller than the energy reported for stilbene (14.65 kJ mol^{-1}).[13] Compound **4**, however, with two boron clusters was found only as *trans*.

The coloration of these compounds might be due to the electronic interaction between the boron cluster unit and the bonded bipyridine units, as has been found for the monopyridine compounds.[11] This phenomenon may be related to that found for other borane–pyridine complexes, particularly those of the $[6,9\text{-}L_2\text{-}arachno\text{-}B_{10}H_{12}]$ constitution.[14–16] The color variation in solution from yellow–orange (compounds **1** and **3**) to a deep red (compounds **2** and **4**) can be attributed to the complexation of the bipyridine unit with one boron unit in the case of compounds **1** and **3** in (i.e. 1 : 1) or two boron units in the case of compounds **2** and **4** (i.e. 1 : 2), as indicated by NMR spectroscopy and elemental analysis.

Molecular-orbital calculations

Ground-state calculation at the semi-empirical AM-1 level[17] were used to obtain the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies. The orbital energies for the LUMO and

Table 2. Observed wavelength of main absorbance and orbital energies after geometry optimization for the HOMO and the LUMO for pyridine–, substituted pyridine–, and bipyridine–azanonaborane complexes

Compound	$1/\lambda_{max}$ (10^{-4} cm^{-1})	HOMO (eV)	LUMO (eV)	$\Delta E_{(LUMO-HOMO)}$ (eV)
1	2.49	−8.08	−1.52	6.56
2	2.18	−8.25	−2.15	6.10
3 *Z*	2.46	−8.00	−1.50	6.50
3 *E*	2.46	−8.05	−1.70	6.35
4	2.15	−8.39	−2.41	5.98
5[a]	2.75	−7.97	−1.05	6.92
6[a]	2.32	−8.08	−1.69	6.39
7[a]	2.41	−7.92	−1.46	6.46
8[a]	2.56	−7.91	−1.29	6.62
9[a]	2.60	−8.07	−1.30	6.77
10[a]	2.08	−8.34	−2.32	6.02
11[a]	3.13	−7.70	−0.63	7.07

[a] Data taken from Ref. 12.

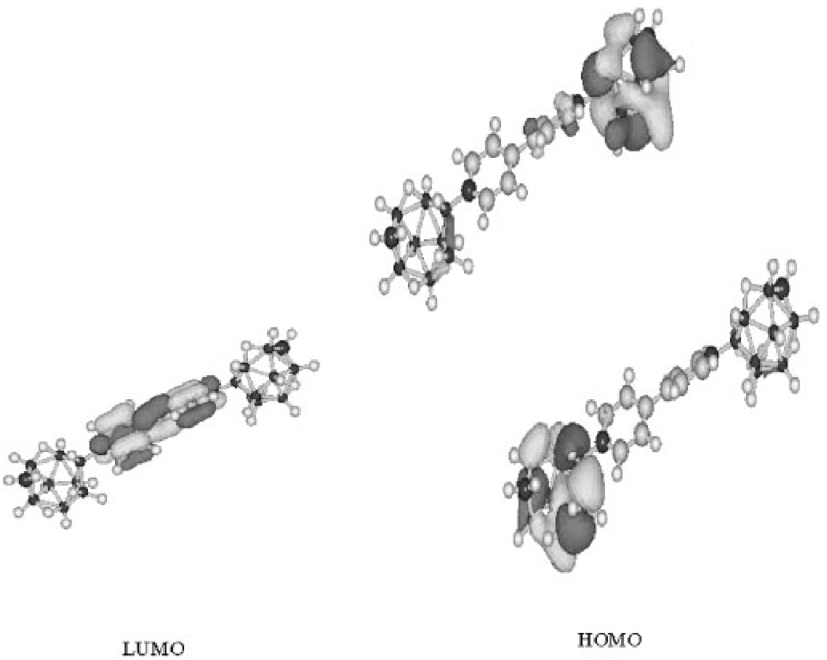


Figure 2. AM-1 calculated molecular orbitals of $[^{i}PrHNH_{11}B_8{-}PyPy{-}B_8H_{11}NH^{i}Pr]$ (**2**).

the HOMO of the bipyridine–azanonaborane compounds (**1**–**4**) are summarized in Table 2. These values have been calculated after total geometry optimization,[12] as indicated in Fig. 2 and compared with that obtained from pyridine–azanonaborane,[12] e.g. $[(C_5H_5N)B_8H_{11}NHMe]$ (**5**), and substituted pyridine–azanonaborane,[12] e.g. $[(4\text{-}MeCO{-}C_5H_4N)B_8H_{11}NHMe]$ (**6**), $[(C_9H_7N)B_8H_{11}NH^{i}Pr]$ (**7**), $[(4\text{-}Ph{-}C_5H_4N)B_8H_{11}NHMe]$ (**8**), $[(3\text{-}Br{-}C_5H_4N)B_8H_{11}{-}NH^{i}Pr]$ (**9**), $[(4\text{-}NO_2{-}C_5H_4N)B_8H_{11}NHMe]$ (**10**), $[(4\text{-}NMe_2{-}C_5H_4N)B_8H_{11}NHMe]$ (**11**) (Table 2). It was found that there is a linear correlation between the orbital energy differences $\Delta E_{\text{LUMO-HOMO}}$ and the experimental values of $1/\lambda_{\max}$ for the bipyridine–, pyridine– and substituted pyridine–azanonaborane complexes (Fig. 3). The observed wavelength range of bipyridine–azanonaborane compounds was between 400 and 465 nm, whereas for pyridine–azanonaborane compounds it was between 320 and 480 nm.[12]

In pyridine–azanonaborane complexes, the color was attributed to the combinations of HOMO of the azanonaborane and π-LUMO of pyridine.[12] The resulting energy of the HOMO of bipyridine–azanonaborane complexes is higher than that of the HOMO of the B_8N fragment, and localized completely around the framework of the cluster. On the other hand, the energy of the LUMO is lower than the LUMO in pure bipyridine. The LUMO is extensively delocalized in the bipyridine fragment (Fig. 2).

The orbital energy differences between the LUMO and HOMO for aliphatic azanonaboranes calculated with AM-1 were between 9 and 10 eV, whereas for pyridine–azanonaborane complexes they were between 6 and 7 eV.[12] These smaller orbital-energy differences are responsible for the absorption of pyridine–azanonaborane complexes in the visible region. The calculated LUMO–HOMO energy differences of bipyridine–azanonaborane compounds **1** and **2** are 6.56 eV and 6.1 eV respectively. Compared with the unsubstituted pyridine compound **5**, the orbital-energy differences of compounds **1** and **2** are clearly much lower than that of compound **5** (Table 2). However, the 4-phenylpyridine compound **8** has an orbital-energy difference very similar to compound **1**. When two clusters are present (compound

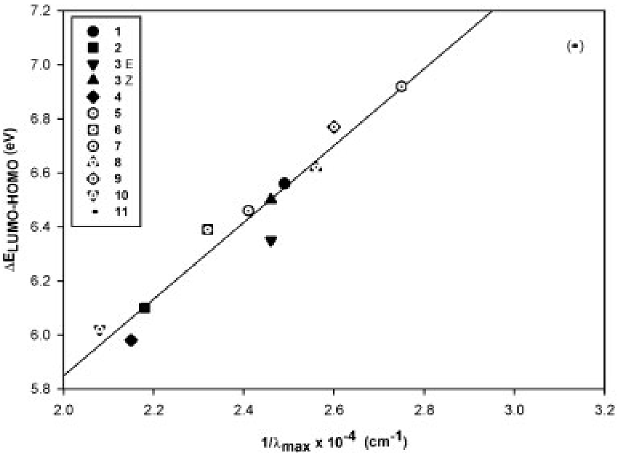


Figure 3. The relation of $\Delta E_{\text{LUMO-HOMO}}$ against $1/\lambda_{\max}$ for pyridine– and bipyridine–azanonaborane complexes. The linear regression curve is shown. Compound (**11**) was excluded from the regression analysis.

Table 3. Maximum absorption wavelength λ_{max}, molar absorption coefficients ε, bandwidth ν_{max}, half bandwidth $\Delta\nu$ 1/2, oscillator strength f, and transition dipole moment μ, of azanonaborane–bipyridine derivatives at 20 °C

Compound	λ_{max} (nm)	ε (10^2 l mol^{-1} cm^{-1})	ν_{max} (cm^{-1})	$\Delta\nu$ 1/2 (cm^{-1})	$f \times 10^{-2}$	μ (debye)
1	402	50	24875.62	3034.78	6.55	2.37
2	459	240	21786.49	3065.18	31.78	5.57
3	406	74	24630.54	3093.43	9.88	2.92
4	465	144	21505.37	2772.37	17.25	4.13

2) the orbital-energy difference is much smaller. Also, as reported in the literature,[12,13] a π-donor leads to a blue shift and a π-acceptor leads to a red shift. Both **1** and **3** show approximately the same red shift as **7**. This means that the substitution of the phenyl group in **7** by a pyridine ring in **1** or the ethene–pyridine moiety in **3** has the same effect on the LUMO energy of pyridine–azanonaborane **5**. However, **2** and **4**, with two {B_8N}, units are red shifted compared with **1** and **3**, which contain only one {B_8N} unit. The connection of two {B_8N} units to bipyridine rings increases the cationic character of the bipyridine, which is responsible for the reduction of the LUMO energies of the **2** and **4** compared with **1** and **3**.

It had been shown previously by others that there is no significant influence on the color of pyridine–decaborane or –azanonaborane complexes by the differences of cluster-structure character between ten-vertex {B_{10}}[14] and nine vertex {B_8N}.[12] We found that the results of bipyridine–azanonaborane compounds are in accordance with these previously results.

The oscillator strength f, which is a measure of the integrated intensity of the band, and the transition dipole moments μ were calculated on the basis of the approximate equations of Tsubomura and Lang.[18] The estimated values are given in Table 3. It was observed that the values of the oscillator strength of these compounds reflect the strong interaction of the molecular orbitals of the bipyridine derivatives with that of the {B_8N} unit.

In conclusion, we have explored new compounds of 4,4′-bipyridine and 1,2-di-(4-pyridyl)-ethene containing one or two azanonaborane clusters. The spectroscopic data of the azanonaborane–bipyridine derivatives and the molecular-orbital calculations were obtained. The presence of two {B_8N} clusters with bipyridine ligands led to a red shift in UV–vis spectra compared with that containing only one {B_8N} cluster. The mono adduct of B_8N with 1,2-di-(4-pyridyl)-ethene was found in two forms: *cis* (**3a**, 30%) and *trans* (**3b**, 70%).

EXPERIMENTAL

General

The reagents, dry solvents THF, dichloromethane, methanol, ethanol and hexane, were used as presented directly without further purification. Pyrazine, 4,4′-bipyridine, and *trans*-1,2-di-(4-pyridyl)-ethene were purchased from Aldrich Co. Dimethyl sulfide-*arachno*-nonaborane and [$Pr^iNH_2B_8H_{11}NHPr^i$] were prepared as described in the literature.[1,2] The measurements for NMR (^{11}B, ^1H and ^{13}C) were carried out on a Bruker DPX 200 spectrometer. The chemical shifts δ (ppm) are given relative to $\Xi = 100$ MHz for δ (^1H) (nominally $SiMe_4$), and $\Xi = 32.083\,972$ MHz for δ (^{11}B) (nominally F_3BOEt_2) in $CDCl_3$ (**1** and **3**) and CD_2Cl_2 (**2** and **4**). IR (cm^{-1}) spectra were determined as KBr discs on a Biorad FTS-7 spectrometer. UV data were measured on a Varian Cary 50 Bio instrument. Molecular-orbital calculations[17] were carried with HYPERCHEM.[19] Plate chromatography was conducted on silica gel 60 (Fluka). Elemental analysis was performed on a Perkin–Elmer 2400 automatic elemental analyzer.

Preparation of [$(PyPy)B_8H_{11}NH^iPr$] (1) and [$^iPrHNH_{11}B_8$–PyPy–$B_8H_{11}NH^iPr$] (2)

A solution of 4,4′-bipyridine (0.07 g, 0.46 mmol) was added to a solution of [$^iPrH_2NB_8H_{11}NH^iPr$] (0.2 g, 0.93 mmol) in 20 ml dry benzene and the solution was then heated at reflux for 2 h. The more volatile components were removed in vacuum, the solid residue redissolved in CH_2Cl_2 and the products separated and purified by preparative thin-layer chromatography. Development in CH_2Cl_2 gave [$(PyPy)B_8H_{11}NH^iPr$] as solid dark brown substance **1** and [$^iPrHNH_{11}B_8$–PyPy–$B_8H_{11}NH^iPr$] as a red solid substance **2**. For compound **1** recrystallized from (CH_2Cl_2–hexane) (0.1 g, 36%, $R_f = 0.22$): MS (FAB$^+$) $m/z = 312$ [M$^+$, 30%]; IR 2966w ν(CH), 2523m ν(BH), 1627s ν(C=C), 1597s ν(NH), 1462m ν(BN), 1406s ν(CH_3), 1147s ν(CN). ^1H NMR ($CDCl_3$), 1.08 (q, 6H, $(CH_3)_2$), 2.62 (hept, 1H, CH), 7.55 (d, 2H), 7.33 (d, 2H), 8.71 (d, 2H), 8.99 (d, 2H). ^{13}C NMR ($CDCl_3$) 21.7, 21.8 $(CH_3)_2$, 53.41 (CH), 121.69, 123.4, 142.94, 148.44, 151.61 (PyPy). Anal. Found: C, 50.01; H, 8.62; N, 13.36; $B_8H_{27}C_{13}N_3$ requires: C, 50.09; H, 8.67; N, 13.48%.

For compound **2** recrystallized from (CH_2Cl_2–hexane) (0.085 g, 31%, $R_f = 0.73$): MS (FAB$^+$) $m/z = 467$ [M$^+$, 5%]; IR 2985w ν(CH), 2520s ν(BH), 1627s ν(C=C), 1624s ν(NH), 1461m ν(BN), 1424s ν(CH_3), 1151s ν(CN). ^1H NMR (CD_2Cl_2) 1.05 (q, 6H, $(CH_3)_2$), 2.48 (hept, 1H, CH), 8.01 (d, 4H, CH) 9.05 (d, 4H, CH). ^{13}C NMR (CD_2Cl_2) 27.99, 28.21 $(CH_3)_2$, 51.48 (CH), 121.95, 126.6, 145.37, 146.68 (PyPy). Anal. Found: C, 41.03; H, 9.78; N, 11.76; $B_{16}H_{46}C_{16}N_4$ requires: C, 41.13; H, 9.85; N, 11.99%.

Preparation of [(Py=Py)$B_8H_{11}NH^iPr$] (3) and [$^iPrHNH_{11}B_8$–Py=Py–$B_8H_{11}NH^iPr$] (4)

These compounds were synthesized in the same manner as **1** and **2**, yielding **3** as a dark brown solid and **4** as a red solid.

For compound **3** recrystallized from (CH_2Cl_2–hexane) (0.15 g, 53%, $R_f = 0.25$): MS (FAB$^+$) $m/z = 337$ [M$^+$, 25%]; IR 2968w ν(CH), 2532m ν(BH), 1622s ν(C=C), 1594s ν(NH), 1440m ν(BN), 1395s ν(CH_3), 1144s ν(CN). ^{1}H NMR ($CDCl_3$) 1.09 (q, 6H, $(CH_3)_2$), 2.62 (hept, 1H, CH), (*Z*: 6.96), (*E*: 7.12) (s, 1H, CH=CH), (**3b**: 7.35), (**3a**: 7.39) (s, 1H, CH=CH), 7.41 (d, 2H), 7.51 (d, 2H), 8.62 (d, 2H), 8.83 (d, 2H). ^{13}C NMR ($CDCl_3$) 21.82 $(CH_3)_2$, 53.52 (CH); (**3a**): 121.75, 122.98, 128.76, 128.89, 136.38, 143.89, 148.4, 150.95; (**3b**): 122.07, 126.08, 128.22, 131.07, 135.72, 142.76, 147.91, 151.17 (Py=Py). Anal. Found: C, 53.02; H, 8.39; N, 12.31; $B_8H_{29}C_{15}N_3$ requires: C, 53.34; H, 8.59; N, 12.44%.

For compound **4** recrystallized from (CH_2Cl_2–hexane) (0.1 g, 35%, $R_f = 0.68$): MS (FAB$^+$) $m/z = 484$ [M$^+$, 12%]; IR 2985w ν(CH), 2520s ν(BH), 1627s ν(C=C), 1623s ν(NH), 1441m ν(BN), 1424s ν(CH_3), 1151s ν(CN). ^{1}H NMR (CD_2Cl_2) 1.14 (q, 6H, $(CH_3)_2$), 2.55 (hept, 1H, CH), 6.98 (s, 1H, CH=CH) 7.44 (s, 1H, CH=CH), 7.62 (d, 4H) 8.92 (d, 4H). ^{13}C NMR (CD_2Cl_2) 21.25, 21.46, $(CH_3)_2$, 52.77 (CH), 123.3, 125.81, 128.69, 132.22, 136.22, 147.13, 147.99, 151.86 (Py=Py). Anal. Found: C, 43.76; H, 9.69; N, 11.18; $B_{16}H_{48}C_{18}N_4$ requires: C, 43.83; H, 9.74; N, 11.36%.

REFERENCES

1. Graybill BM, Pitochelli AR, Hawthorne MF. *Inorg. Chem.* 1962; **1**: 626.
2. Dörfler U, Thornton-Pett M, Kennedy JD. *J. Chem. Soc. Dalton Trans.* 1997; 2547.
3. Lewin R, Simpson PG, Lipscomb WN. *J. Chem. Phys.* 1963; **39**: 1532.
4. MacKinnon P, Fontaine XLR, Kennedy JD, Salter PA. *Collect. Czech. Chem. Commun.* 1996; **61**: 1773.
5. El-Zaria ME, Dörfler U, Gabel D. *Angew. Chem. Int. Ed. Engl.* 2002; **41**: 4498.
6. Dörfler U, Ormsby DL, Greatrex R, Kennedy JD. *Inorg. Chim. Acta* 2000; **304**: 268.
7. Dörfler U, Salter PA, Fontaine XLR, Greenwood NN, Kennedy JD, Thornton-Pett M. *Collect. Czech. Chem. Commun.* 1999; **64**: 947.
8. Bauer C, Dörfler U, Gabel D. *Eur. J. Med. Chem.* 2002; **37**: 649.
9. El-Zaria ME, Dörfler U, Gabel D. *J. Med. Chem.* 2002; **45**: 5817.
10. Dörfler U, Bauer C, Gabel D, Rath NP, Barton L, Kennedy JD. *J. Organometal. Chem.* 2000; **614–615**: 215.
11. Bauer C, Gabel D, McGrath TD, Dörfler U. *Inorg. Chim. Acta.* 2002; **332**: 181.
12. Bauer C, Gabel D, Borrmann T, Kennedy JD, Kilner CA, Thornton-Pett M, Dörfler U. *J. Organometal. Chem.* 2002; **657**: 205.
13. Graybill BM, Hawthorne MF. *J. Am. Chem. Soc.* 1961; **83**: 2673.
14. Dutt GB, Konitsky W, Waldeck DH. *Chem. Phys. Lett.* 1995; **245**: 437.
15. Schaefer T, Sebastian R, Salman R. *Can. J. Chem.* 1981; **59**: 3026.
16. Londesborough MGS, Price C, Thornton-Pett M, Clegg W, Kennedy JD. *Inorg. Chem. Commun.* 1999; **2**: 298.
17. Stewart JJP. *J. Comput. Aided Mol. Des.* 1990; **4**: 1.
18. Tsubomura H, Lang R. *J. Am. Chem. Soc.* 1961; **83**: 2085.
19. HYPERCHEM 5.1, HyperCube Inc., Waterloo, Ontario, Canada.