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Stereochemical Study of Imines and their *N*-Borane Adducts by ^{1}H, ^{11}B, ^{13}C and ^{15}N NMR

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The synthesis and NMR spectra of the *N*-borane adducts of two diimines, *N*-borane-bis(α-phenylethylidene)ethylenediamine and *N*-borane-bis(α-phenylbenzylidene)ethylenediamine, and four imines, *N*-borane-α-methylethylidene-2-phenylethylamine, two *N*-borane-α-phenylethylidene-*n*-butylamines and *N*-borane-α-phenylbenzylidene-*n*-butylamine, are reported. The NMR spectra of the *N*-borane adducts of these imines can be used to determine their configuration.

KEY WORDS ^{13}C, ^{1}H, ^{11}B, and ^{15}N NMR $^{1}J(^{13}C,^{13}C)$ coupling contants Configurational assignment *N*-Borane-imines

INTRODUCTION

We are interested in studying nitrogen stereochemistry by using *N*-borane adducts that function as stereochemical probes. The borane group has been shown to produce steric and electronic effects over its neighbouring atoms that allow the establishment of the nitrogen configuration.[1–5] In this context, we report here the use of chemical shift effects in *N*-borane adducts for the configurational assignment of imine groups. The unequivocal assignment of the imine configuration was confirmed by the analyses of ^{13}C and ^{1}H chemical shifts, a NOESY experiment and from the observed nitrogen lone pair effect on the $^{1}J(C,C)$ coupling constants in the imines.[6] The imine configuration is sufficiently stable to give two isolated geometric isomers when there are two different substituents on the imine carbon, the energy of this isomerization for *N*-alkylamines being *ca.* 84–126 kJ mol^{-1}.[7] The interconversion of the imine diastereoisomers has been explained by a planar inversion of the nitrogen atom, an imine–enamine tautomerization or a rotation about the C=N bond involving a dipolar transition state.[7–11] It was found that iminium salts have lower isomerization barriers than free imines, and hence it was of interest to establish the effect of borane on the stability of the imine configuration.

We prepared the *N*-borane adducts, **1b–6b**, of the six imines **1a–6a** (Scheme 1) and studied their spectra and stereochemistry in order to establish the effects of borane addition on the spectral properties of imines.

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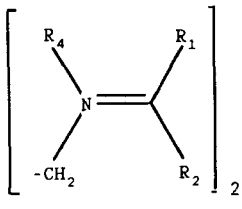
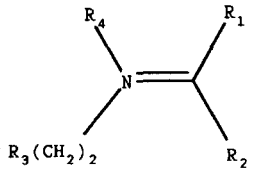
RESULTS

Imines

Imines **1a–6a** were prepared by conventional methods.[12] Two geometric isomers were expected in the reactions of ethylenediamine or butylamine with acetophenone. Only one isomer was detected (**1a**) using ethylenediamine, whereas a mixture of isomers (**4a** and **5a**) was obtained in a ratio of 93:7 from butylamine,



1 $R_1 = C_6H_5$; $R_2 = CH_3$
2 $R_1 = R_2 = C_6H_5$



3 $R_1 = R_2 = CH_3$; $R_3 = C_6H_5$
4 $R_1 = C_6H_5$; $R_2 = CH_3$; $R_3 = C_2H_5$
5 $R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = C_2H_5$
6 $R_1 = R_2 = C_6H_5$; $R_3 = C_2H_5$

a R_4 = lone pair
b $R_4 = BH_3$

Scheme 1

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similar to that found in the derivative from methylamine and acetophenone.[13]

The NMR spectroscopic data for the free imines and their *N*-borane adducts are summarized in Tables 1–3. The assignments of the free imines were achieved by comparison with literature data[13–17] and confirmed from the ^{1}J(C,C) coupling constants obtained using the double quantum coherence INADEQUATE method at natural isotopic abundance.[18] The quaternary imine carbons show ^{1}J(C,C) coupling constants which are approximately 10 Hz higher to the carbon atoms (from R_1) in the *syn* position to the lone pair than those in the *anti* position (in R_2); see the values in Scheme 2.

The configuration imine **1a** was also determined by a NOESY experiment, which showed an interaction between the methylene and the methyl groups. Comparison between the two isomeric compounds **4a** and **5a** allowed the assignment of the chemical shifts of both imine configurations.

^{13}C NMR spectroscopy shows that in symmetrically substituted imines (**2a**, **3a** and **6a**), the carbon atoms of R_1, which are *syn* to the lone pair, absorb at lower fields than those in the *anti* group R_2. The same trend was found for the isomeric compounds **4a** and **5a**. In the ^{1}H NMR spectra the methyl groups in **3a**, **4a** and **5a** reflect the same spectral feature, with a lower field signal for R_1.

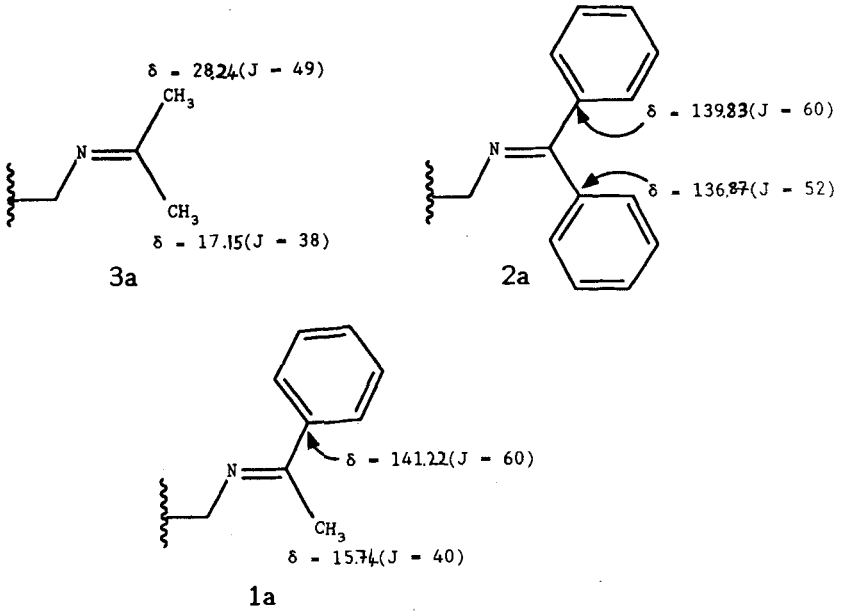
N-Borane-imines

The borane adducts **1b–6b** could be prepared, without hydroboration of the double bond, by borane–tetrahydrofuran addition under mild conditions. It was

Table 1. ^{1}H chemical shifts[a] and coupling constants (*J*, Hz)[b]

Compound	CH_2N	CH_2CH_2N	R_1	R_2	R_3
1a	3.96 (s)	3.96 (s)	7.86 (m), 7.36 (m)	2.33 (s)	
1b	4.33 (s)	4.33 (s)	7.56 (s)	2.7 (s)	
2a	3.7 (s)	3.7 (s)	7.0–7.9 (m)	7.0–7.9 (m)	
2b	4.3 (s)	4.3 (s)	7.0–7.9 (m)	7.0–79 (m)	
3a	3.5 (t)[c]	2.9 (t)[c]	2.0 (s)	1.7 (s)	7.32 (m)
3b	3.83 (t)[c]	3.06 (t)[c]	1.7 (s)	2.3 (s)	7.3 (m)
4a	3.47 (t)[c]	1.75 (m)	7.72, 7.28 (m)	2.18 (s)	1.47 (m), 0.95 (t)[d]
4b	3.75 (t)[c]	2.0 (m)	7.48 (s)	2.4 (br, s)	1.3 (m), 1.0 (t)[c]
5a	—[e]	—[e]	2.26 (s)	—[e]	—[e]
6a	3.4 (t)[f]	1.6 (m)	7.2–8.0 (m)	7.2–8.0 (m)	1.26 (m), 0.91 (t)[f]
6b	3.78 (t)[d]	1.86 (m)	7.1–7.9 (m)	7.1–7.9 (m)	1.26 (m), 0.85 (t)[d]

[a] Shifts given in ppm relative to TMS as internal reference in $CDCl_3$ as solvent.
[b] The spectra were recorded on a Jeol 270-GXS spectrometer at 270 MHz, with the exception of **6a** and **6b**; these were obtained on a Varian 390 and a Jeol FX-90 spectrometer at 90 MHz, respectively.
[c] J = 7.5 Hz.
[d] J = 7.0 Hz.
[e] Not assigned.
[f] J = 7.2 Hz.



Scheme 2 Selected values of ^{13}C chemical shifts (ppm) and $^{1}J(^{13}C,^{13}C)$ coupling constants (Hz) of compounds **1a–3a**.

Table 2. ^{13}C chemical shifts and $J(^{13}C,^{13}C)$ coupling constants[a]

Compound	C=N	CH_2N	CH_2CH_2N	R_1[b]	R_2[b]	R_3
1a[c]	165.77	53.37	53.37	141.22	15.74	
1b	179.53	55.21	55.21	138.68	24.60	
2a[d]	168.56	55.06	55.06	139.83	136.87	
2b	179.80	58.63	58.63	137.14	136.75	
3a[e]	166.06	52.50	36.53	28.24	17.15	
3b	177.45	57.60	33.54	22.04	25.62	
4a	164.61	51.94	33.15	141.53	15.32	20.84, 14.06
4b	175.47	57.39	30.39	139.34	23.77	20.40, 13.78
5a	164.49	53.05	33.34	29.14	139.36	20.29, 13.91
5b	175.49	57.22	30.15	19.57	137.80	19.39, 13.10
6a	166.58	52.90	32.88	139.41	136.51	20.05, 13.42
6b	179.93	59.81	31.53	137.87	137.11	19.93, 13.59

	R_1				R_2			
	C-*i*	C-*o*	C-*m*	C-*p*	C-*i*	C-*o*	C-*m*	C-*p*
1a[c]	141.22	126.51	128.08	129.27				
1b	138.68	128.12	127.05	130.36				
2a[d]	139.83	128.34	127.88	129.78	136.87	128.38	127.93	128.22
2b	137.14	128.82[f]	130.71[f]	130.79[f]	136.75	128.46[f]	127.50[f]	131.15[f]
4a	141.53	128.15	126.35	129.22				
4b	139.34	127.79	126.95	129.53				
5a					139.36	128.54	127.99	128.93
5b					137.80	128.09	126.45	128.99
6a	139.41	127.79[f]	127.10[f]	129.31[f]	136.51	127.58[f]	127.32[f]	127.49[f]
6b	137.87	128.72[f]	127.69[f]	129.96[f]	137.11	128.50[f]	128.18[f]	128.94

	R_3			
3a	139.64	127.94	127.38	125.07
3b	137.75	127.94	128.35	126.11

[a] Shifts given in ppm relative to TMS as internal reference, J in Hz, in $CDCl_3$ as solvent. The spectra were recorded on a Jeol 270-GXS spectrometer at 67.80 MHz, with exception of those of **6a** and **6b**, which were obtained on a Jeol FX-90 spectrometer at 22.49 MHz.
[b] *ipso* Carbon or methyl group.
[c] J(CN,C-*i*) = 60 Hz, J(CN,Me) = 40 Hz.
[d] R_1, J(CN,C-*i*) = 60 Hz, J(C-*i*,C-*o*) = 59 Hz, J(C-*m*,C-*p*) = 55.6 Hz; R_2, J(CN,C-*i*) = 52 Hz, J(C-*i*, C-*o*) = 57 Hz, J(C-*m*,C-*p*) = 53 Hz.
[e] J(CN,Me) = 49 Hz, J(CN,Me) = 38 Hz.
[f] Assignment could be exchanged.

established that the borane derivatives retain the free imine nitrogen atom configuration by the observation that the ratio of isomers (93:7) found in the free imines **4a** and **5a** remained the same in the corresponding boranes **4b** and **5b**.

We expected to observe two different types of effects in the ^{13}C and ^{1}H NMR spectra of the *N*-borane-imines: an important steric effect of the borane group on its *syn* substituent, which is normally shifted to higher field,[3,15,19] and a *trans* inductive effect[19,20] of the borane on its *anti* substituent, which is shifted to lower field. In fact, both effects were observed (Tables 1 and 2) in all adducts.

Table 3. ^{11}B and ^{15}N chemical shifts (in $CDCl_3$)[a]

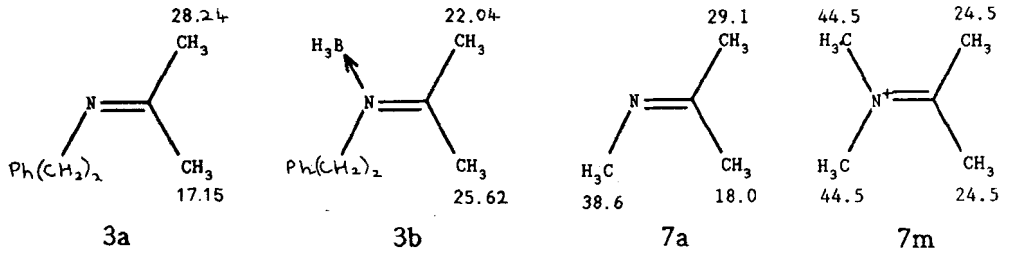
Compound	^{15}N[b]	Compound	^{11}B[c]	^{15}N[b]
1a	−60.9	**1b**	−15.8	—[d]
2a	−59.0	**2b**	−15.6	—[d]
3a	−58.8	**3b**	−17.2 [J(B,H) = 97 Hz]	—[d]
4a	−51.9	**4b**	−15.6	−133.6
5a	−52.8	**5b**	−17.9	—[e]
6a	−51.5	**6b**	−15.8	−133.3

[a] The spectra were recorded on a Jeol 270-GXS spectrometer at 86.55 MHz for ^{11}B and 27.25 MHz for ^{15}N.
[b] External reference nitromethane.
[c] External reference boron trifluoride etherate.
[d] Not sufficiently soluble to obtain a spectrum.
[e] No resonance observed.

DISCUSSION

Comparison between the ^{1}H and ^{13}C NMR chemical shifts of **3a**, **3b** or **7a** and **7m** shows that the borane in **3b** or the methyl groups in **7m** shields the *syn*-methyl and deshields the *anti*-methyl groups by an inductive effect. Comparison between **7a**[14] and **7m**[19] shows that methylation produces a similar effect in the iminium compound **7m** to that found upon borane coordination (Scheme 3).

The free phenylimine compounds **1a**, **2a** and **4a–6a** showed complex ^{1}H NMR signals characteristic of phenyl groups with restricted rotation. On the other hand, the *N*-borane adducts of the phenylimines show sharp signals for the phenyl protons, indicating free rotation of the aromatic ring. This phenomenon can be

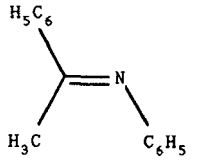


Scheme 3. ^{13}C chemical shifts of *N*-borane adduct **3b** compared with the related imines **3a** and **7a** and the *N*-methyliminium salt **7m**.

understood by examining the Dreiding models of the borane adducts, which show that the borane group creates a very strong steric effect on the phenyl group when it is coplanar with the imine; this steric interference produces a rotation of the bond between the imine carbon atom and the phenyl group, thus forcing the latter out of the plane of the imine group.

Coordination of borane decreases the bond strength of the C=N double bond by an inductive effect that favours the ionic resonance structure **b**[19,21] in Scheme 4. Information about the behaviour of the C=N bond on boration can be obtained by comparing the ^{13}C chemical shift of the imine carbon with those of *ipso* and *para* carbons in aromatic imines.

The imine carbon atom is shifted downfield by between 10.8 to 13.7 ppm on coordination; this is a very strong effect but it is smaller than that found on protonation of imines **8** (23.5 ppm) and **9** (16.0 ppm)[21] with trifluoroacetic acid.



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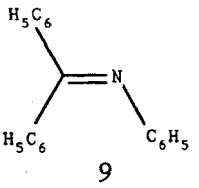

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As previously observed, proton coordination[21] to the nitrogen atom produces strong shifts to low field on the *para* and C=N carbons, and shielding of the *ipso* carbon. This was rationalized by an increase in the contribution of resonance structures **b** and **c** in Scheme 4. In borane adducts delocalization of the partial positive charge on the phenyl group (structure **c**) is impossible, because the planar system is hindered by the borane group and only the inductive effects can be observed in the phenyl group; the large shift of the imine carbon in the borane adducts implies that this carbon shows the effects of resonance structure **b**.

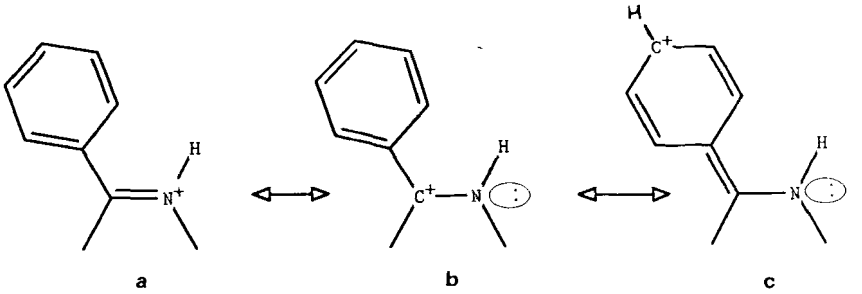
The chemical shifts of the aromatic *para* carbons[21,22] in **1a**, **2a**, **4a–6a**, **1b**, **2b** and **4b–6b** are indicative of the weak electronic effects produced by the borane imine substitution. Comparison between **4a** and **5a** shows that the *para* carbon atom of the phenyl groups is slightly different in the two isomers. The *para* carbon atom of the R_2 group *trans* to the borane group, shows the highest inductive effect. The same observation can be made in **2b** and **6b**.

By comparison of the chemical shift of the α-methylene group in **4a** and **5a**, it is apparent that the methyl group produces a greater steric effect on the methylene group than the phenyl group. The steric effects on both phenyl substituents of imines **2a** and **6a** are reflected in the chemical shifts of the *ipso* carbons, assigned by the INADEQUATE experiment. The carbon atom *syn* to the lone pair shows a small steric effect and absorbs at lower field. Borane addition shifts this carbon to higher field by the steric effect.

The ^{11}B NMR chemical shifts of **1b–6b** clearly reflect the nature of the group in a *cis* position with respect to the borane group; the values when the borane is in the proximity of a phenyl group, compounds **1b**, **2b**, **4b** and **6b**, lie in the range of −15.6 to −15.8 ppm, whereas when there is a nearby methyl group, compounds **3b** and **5b**, they are between −17.2 and −17.9 ppm.

It is known that steric crowding at the boron atoms is reflected by the ^{11}B chemical shifts, which are shifted to lower frequency.[2,3] The methyl group produces a stronger effect than the phenyl group; this can be explained by assuming that the plane of the phenyl group is perpendicular to the plane of the double bond. The ^{11}B chemical shifts in **1b**, **2b**, **4b** and **6b** are noteworthy because the phenyl shielding effect is not appreciable. Thus, boron chemical shifts can clearly indicate the configuration of the borane-imine adduct, confirming the other NMR observations.

The ^{15}N NMR chemical shifts of **1a–6a** show normal values for the imino groups, and are between −51 and −61 ppm (Table 3), similar to related compounds.[23,24] However, some interesting facts deserve mention. ^{15}N NMR can distinguish between geometric isomers, as in **4a** and **5a**, but it is less sensitive to the nature of the substituents on the carbon of the imine function, as



a b c

Scheme 4

shown by the small chemical shift difference bewteen **1a** and **2a** or between **4a** and **6a**. It is surprising that the resonances of diimines **1a** and **2a** are at higher field (−60.9 and −59.0 ppm) when compared with the similar imines **4a** and **6a** (−51.9 and −51.5 ppm). A similar phenomenon occurs when *n*-butylamine (−360.4 ppm) is compared with ethylenediamine (−366.1 ppm).[25] Careful examination of these and similar results seems to be desirable.

Borane *N*-coordination (**4a** and **6a**) produces a large ^{15}N NMR upfield shift on comparison with the free imines. This shift (82 ppm) can be interpreted in terms of a decrease in bond order and an increase in the electron density at the nitrogen atom.[25] It has a value intermediate between that produced by hydrogen bonding ($\Delta\delta$ = 20 ppm) and that for protonation ($\Delta\delta$ = 120–146 ppm)[24] and is similar to that found by rhodium coordination to bipyridines ($\Delta\delta$ = 94 ppm)[26] and in imidazole-triethylborane adducts ($\Delta\delta$ = 83 ppm).[27]

Infrared analysis

It has been reported that an increase in the imine C=N frequency on complexation with BF_3 can be connected with an increase in the bond order.[10,11,28] We found the opposite behaviour on complexation with borane, where the adducts show an unchanged frequency for the $\nu_{C=N}$ band or a slight shift to low frequencies. This can be attributed to the different electronegativity and mass at the nitrogen atom in the borane adducts compared with the BF_3 adducts. Based on these results, IR spectrometry cannot be used to give useful data on the nature of the C=N bond in these compounds.

CONCLUSIONS

The syntheses and subsequent NMR analysis of borane adducts provide an excellent method for the establishment of imine stereochemistry, and for the evaluation of the electronic and steric effects of the substituents. These data should provide a reference set for future identification of other more complex molecules.

EXPERIMENTAL

The infrared spectra were determined on a Nicolet MX-1-FT Fourier transform infrared spectrometer. ^1H and ^{13}C NMR spectra were measured on Varian EM-390, Jeol 90 FX-Q or Jeol GXS-270 spectrometers, in $CDCl_3$ solutions with TMS as internal reference. ^{11}B and ^{15}N NMR spectra were obtained on the Jeol GXS-270 spectrometer, using $BF_3 \cdot Et_2O$ or nitromethane as external references.

NMR experiments

The ^1H NMR spectra were recorded on a Jeol GXS-270 spectrometer at 270.05 MHz (spectral width 2700 Hz, acquisition time 1.516 s, pulse width 45°, number of repetitions 32, pulse delay 3 s) and on a Varian EM-390 spectrometer at 90 MHz.

The ^{13}C NMR spectra were recorded on a Jeol GXS-270 spectrometer at 67.80 MHz (spectral width 12 224.9 Hz, acquisition time 1.34 s, pulse width 30°, number of repetitions 128–16 000, pulse delay 1.8 s) and on a Jeol FX-90 spectrometer at 22.49 MHz (spectral width 5000 Hz, acquisition time 0.999 s, pulse width 45°, number of repetitions 500).

The ^1H and ^{13}C NMR chemical shifts are reported relative to internal tetramethylsilane (TMS), and the solvent was $CDCl_3$.

The 1D and 2D INADEQUATE spectra were obtained at 67.80 MHz on the Jeol GXS-270 spectrometer, for samples at natural abundance. The 1D INADEQUATE spectra were obtained using the pulse sequence given by Bax *et al.*,[29] using samples at natural isotopic abundance in $CDCl_3$ (200 mg of sample in 0.5 ml of solvent). The spectra were obtained in 5 mm diameter tubes at 24 °C. The delay was set to 5 ms [J(C,C) = 50 Hz] for **1a**, 4.55 ms [J(C,C) = 55 Hz] for **2a** and 5.55 ms [J(C,C) = 45 Hz] for **3a**. The number of data points was adjusted to give an acquisition time of 1.77 s and a digital resolution better than 0.5 Hz. The pulse delay was 20 s (the total measuring time was 16 h).

The 2D INADEQUATE spectrum was obtained using the pulse sequence provided by Jeol with a 32 transient phase cycle for *P*-type selection in ω_1. A τ value of 4.55 ms was taken for this sequence [$\tau = 2n + 1/4J$(C,C), $n = 0$ and $J = 55$ Hz], $\omega_1 = \pm 3315.6$ Hz, $\omega_2 = 3315.6$ Hz, pulse delay 25 s, with 256 increments and 4096 data points in 26 h of total measuring time.

The assignment of the ^{13}C NMR spectrum of **2a** was carried out using the INADEQUATE technique. The irradiation power was verified using the proton aromatic resonances. The imines **4a** and **5a** and the mixtures of **4b** and **5b** were analysed directly, and their ^{13}C NMR spectra were assigned using INEPT. For the INEPT, INADEQUATE and NOESY spectra the ^{13}C and ^1H pulses were calibrated prior to acquisition.

The NOESY spectrum was obtained for **1a** using 16 repetitions with a mixing time of 300 ms. The double Fourier transformation was carried out using a sine-bell function, and in the absolute value mode. A spectral width of 2500 Hz (270 MHz spectrometer) was used in both ω_1 and ω_2 dimensions; 1024 and 512 data points were used in the ω_2 and ω_1 dimensions, respectively. The pulse delay was maintained at 2.0 s. In order to eliminate the possibility of long-range couplings, the line width was verified and found to be similar to the digital resolution of the instrument measured from a one-dimensional ^1H NMR spectrum.

^{15}N NMR spectra were obtained at 27.25 MHz on a Jeol GXS-270 system, using a multinuclear 10 mm low-frequency probe. Approximately 0.8 mmol of each compound was dissolved in $CDCl_3$. The spectra were measured using INEPT with ^1H decoupling.[30] A $^3J(^{15}N,^1H) = 2$ Hz coupling constant was assumed for the natural abundance ^{15}N NMR spectra. A spectral width of 16 393 Hz with a digital resolution of 0.5 Hz was used; the pulse delay was 5 s with an acquisition time of 0.999 s and a 5 h total measuring time. The

chemical shifts are reported relative to CH_3NO_2 as external reference. The ^{11}B NMR spectra were recorded on a Jeol GXS-270 spectrometer at 86.55 MHz (spectral width 17 241.4 Hz, acquisition time 0.475 s, pulse width 75°, number of repetitions 64–600, pulse delay 1 s).

Reagents

Carbonyl compounds and amines (Aldrich) were used as received. $BH_3 \cdot THF$ was prepared as reported in Ref. 31.

Preparation of compounds

α-Methylketimines (1a, 3a, 4a, 5a). The imines were prepared by a standard method[12] from the amine and the corresponding methyl ketone in benzene as an azeotroping agent. The monoimines **3a–5a** were purified by vacuum distillation.

Bis(α-phenylethylidene)ethylenediamine (1a). The reaction of 5.56 ml of ethylenediamine (83.19 mmol) and 19.4 ml of acetophenone (166.4 mmol) gave a yellow solid, recrystallized from CH_2Cl_2–hexane, 65% yield, m.p. 98–100 °C; IR (KBr), $\nu_{C=N} = 1629$ cm^{-1}.

Bis(α-phenylbenzylidene)ethylenediamine (2a). This compound was obtained from 3 g of benzophenone (16.46 mmol) and 0.55 ml of ethylenediamine (8.23 mmol) in xylene, with *p*-toluenesulphonic acid as catalyst. The mixture was refluxed for 50 h, adding 2.99 mmol of ethylenediamine each 10 h. The reaction product is a white powder when recrystallized from CH_2Cl_2–hexane, 75% yield, m.p. 104–105 °C; IR (KBr), $\nu_{C=N} = 1625$ cm^{-1}.

α-Methylethylidene-2-phenylethylamine (3a). The reaction between 3.1 ml of 2-phenylethylamine (24.75 mmol) and 1.8 ml of acetone (24.75 mmol) gave a colourless liquid that was purified by distillation in vacuum, 76% (b.p. 70–75 °C, 2 mmHg); IR (CCl_4), $\nu_{C=N} = 1666$ cm^{-1}.

α-Phenylethylidene-*n*-butylamine (4a and 5a). A mixture of compounds (93 : 7) was obtained from the reaction of 5.4 ml of *n*-butylamine (54.68 mmol) and 6.38 ml of acetophenone (54.68 mmol). The mixture is a colourless liquid that was purified by distillation in vacuum, 80% yield (b.p. 45 °C, 2 mmHg); IR (CCl_4), $\nu_{C=N} = 1638$ cm^{-1}.

α-Phenylbenzylidene-*n*-butylamine (6a). The reaction was carried out with 2 g of benzophenone (10.97 mmol) and 1.2 ml of *n*-butylamine (12.07 mmol) in xylene, with *p*-toluenesulphonic acid as a catalyst. The mixture was heated under reflux for 50 h, adding 0.8 mmol of *n*-butylamine each 10 h. Examination of the reaction mixture by NMR showed a yield of 77% of the imine. After evaporation of the solvent the product was extracted with hexane, affording a clear brown oil (b.p. 103 °C, 0.15 mmHg); IR (CCl_4), $\nu_{C=N} = 1624$ cm^{-1}.

Borane adducts 1b–6b. The borane adducts were prepared from the reaction of borane–tetrahydrofuran and the imine in equimolar proportions at 0 °C under a nitrogen atmosphere. The solvent was evaporated under vacuum 3 min after the borane addition. For **2a** and **6a** the reaction was carried out at −80 °C in order to avoid hydroboration. The reactions gave quantitative yields.

***N*-Borane-*bis*(α-phenylethylidene)ethylenediamine (1b).** The reaction of 2 g of **1a** (7.57 mmol) and 6.4 ml (15.17 mmol) of $BH_3 \cdot THF$ (2.37 M) gave a white powder, m.p. 135–136 °C; IR (KBr), $\nu_{C=N} = 1630$, $\nu_{BH} = 2358$. $\nu_{BN} = 1150$ cm^{-1}.

***N*-Borane-bis(α-phenylbenzyliden)-ethylenediamine (2b).** The reaction of 400 mg of **2a** (1.03 mmol) and 1.81 ml (3.15 mmol) of $BH_3 \cdot THF$ (1.74 M) gave a white powder, m.p. 144–145 °C; IR (KBr), $\nu_{C=N} = 1611$, $\nu_{BH} = 2355$, $\nu_{BN} = 1145$ cm^{-1}.

***N*-Borane-α-methylethylidene-2-phenylethylamine (3b).** The reaction of 200 mg of **3a** (1.24 mmol) and 0.73 ml (1.24 mmol) of $BH_3 \cdot THF$ (1.7 M) gave a white powder; IR (CCl_4), $\nu_{C=N} = 1655$, $\nu_{BH} = 2348$, $\nu_{BN} = 1150$ cm^{-1}.

***N*-Borane-α-phenylethylidene-n-butylamine (4b and 5b).** The reaction of 235 mg of the mixture of **4a** and **5a** (1.34 mmol) and 0.5 ml (1.35 mmol) of $BH_3 \cdot THF$ (2.7 M) gave a white powder; IR (CCl_4), $\nu_{C=N} = 1639$, $\nu_{BH} = 1378, 1326$, $\nu_{BN} = 1185$ cm^{-1}.

***N*-Borane-α-phenylbenzylidene-n-butylamine (6b).** The reaction of 185 mg of **6a** (0.78 mmol) and 0.45 ml (0.78 mmol) of $BH_3 \cdot THF$ (1.74 M) afforded a white oil; IR (CCl_4), $\nu_{C=N} = 1602$, $\nu_{BH} = 2360$, $\nu_{BN} = 1186$ cm^{-1}.

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