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DIMESITYLBORYL COMPOUNDS. PART II.* NITROGEN DERIVATIVES

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Summary

A series of nine aminodimesitylboranes (Mes_2BNRR') have been synthesised and their ^1H, ^{11}B and ^{13}C NMR data recorded. The restricted rotation about the B-N bond is clearly demonstrated in the ^{13}C spectra of compounds where $R \neq R'$ in that two sets of signals are observed for the mesityl group resonances. The mesityl ^{13}C chemical shift data for the series vary only slightly with change in size and electronic character of R and R' in the nitrogen substituents.

Introduction

The recent synthesis and characterisation of stable alkyldimesitylboranes [2] suggested that the dimesitylboryl group (Mes_2B) may impart unusual stability to the series of compounds Mes_2BX (where X = NR_2, OR, SR, unsaturated hydrocarbon, pseudohalogen etc.). This stability in turn would provide an opportunity to study, by multinuclear N.M.R. spectroscopy, the electronic and perhaps steric effects of the group X when attached to boron. Furthermore results of such a study on

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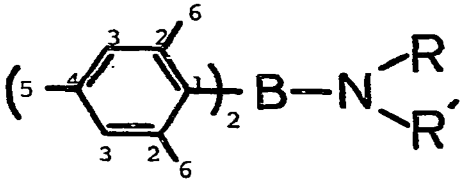
* For Part I see ref.1

** Author to whom correspondence should be addressed on alkyldimesitylboranes [1] suggested that the two mesityl groups are not involved to any great extent in π electron delocalisation onto the boron because of the steric requirements of the orthomethyl groups. If this is indeed the case then the interpretation of results obtained from Mes_2BX systems would be greatly simplified.

This paper reports the results of a systematic study of a series of aminodimesitylboranes (I). Earlier workers have reported on the synthesis and photochemistry of anilinodimesitylboranes [3].



(I)

Results and Discussion

The compounds were made by the literature methods [3-5]. They are all white crystalline materials, soluble in most organic solvents. Compound (1) is moisture sensitive. Of the remainder only (2) showed appreciable moisture sensitivity being ~25% hydrolysed in three days on standing in air.

It has been shown that whilst aminodiphenylborane is dimeric, compound (1) is monomeric in benzene. Furthermore, substitution of one of the amino hydrogens by anything other than a methyl group or the presence of one orthomethyl group per ring in the diarylboryl moiety is sufficient to prevent dimerisation [4]. It has been assumed therefore that all the compounds reported here are monomeric. The ^{11}B chemical shift values observed indicate that this is a safe assumption.

^{1}H Spectra

The proton spectra of these compounds are not particularly informative. The resonances associated with the mesityl ligands usually consisted of a broad singlet in the aromatic region (in the range δ 6.60-6.77 in CCl_4) due to the meta hydrogens and a signal ca. δ 2.10, due to the methyl groups whose precise appearance is solvent and substituent dependent. In most cases it consists of the expected two relatively broad singlets (ratio 2:1) but in certain instances a broad singlet or a complex multiplet is observed. The one significant exception to this pattern of behaviour is the benzylamine derivative (6). This showed a (1:1) doublet in CCl_4 due to the mesityl meta protons indicating non-equivalence due to restricted rotation about the B-N bond. Such effects are well documented [3,6] and are even more dramatically demonstrated in the ^{13}C spectra due to larger chemical shift differences vide infra. The ^1H spectrum of (6) did not change significantly on heating to 140°C in hexachlorobutadiene and hence frustrated attempts to obtain thermodynamic data for the rotational barrier in this compound [6].

^{11}B Spectra

All the compounds gave well defined signals with the exception of (10) where the signal was so broad that a meaningful assignment of a chemical shift value was impossible. The chemical shift values of the remainder indicate a somewhat shielded boron atom as would be expected in the presence of π back donation from nitrogen. These shifts lie within the range observed for aminodialkyl and aminodiarylboranes [7] and are given in Table 1.

^{13}C Spectra

Assignment of resonances in the fully proton noise-decoupled spectra was usually straightforward. The results for the mesityl groups are given in Table 1. For compounds in which R=R' the expected spectra are observed with the C_1 carbons appearing as relatively broad low intensity signals. When $R \neq R'$ two sets of mesityl carbon resonances are observed. These observations are a manifestation of the restricted rotation about the B-N bond mentioned above and clearly demonstrate the diagnostic power of ^{13}C over ^1H measurements in such studies.

Table 1. The chemical shifts[a] $\delta^{13}C$ and $\delta^{11}B$ of compounds (I)

Amine			$\delta^{13}C$						$\delta^{11}B$
No.	R	R^1	1	2	3	4	5	6	
1	H	H	– [b]	140.5	128.1	137.3	21.1	22.7	44.5
2	H	CH_3	138.8[c]	141.0 140.4	128.3 127.6	137.2 136.8	21.0	22.7 22.1	44.0
3	CH_3	CH_3	138.8	140.7	127.6	136.6	21.0	22.2	44.5
4	H	$CH(CH_3)_2$	138.7[c]	141.1 139.9	128.4 127.5	137.2 136.5	21.0 20.9	22.8 22.4	43.0
5	H	$C(CH_3)_3$	140.1[c]	141.2 139.4	128.6 127.2	137.0 136.1	21.0 20.9	23.7 23.2	42.5
6	H	CH_2Ph	– [b]	141.1 140.3	128.5 127.7	137.3 137.0	21.1 21.0	22.8 22.4	43.5
7	H	Ph	138.7[c]	141.2 140.1	128.8 128.0	137.9 137.5	21.1	22.6 22.1	45.0
8	Ph	Ph	139.0	140.1	127.8	137.0	21.0	22.4	49.5
9	piperidine		138.5	140.7	127.6	136.3	20.9	23.0	43.0
10	$=C(Ph)_2$		– [b]	141.2	128.0	137.0	21.0	23.0	–

[a] Spectra were recorded on ca. 30% (w/v) solutions in $CDCl_3$ which also provided the deuterium lock. $\delta^{13}C$ vs. TMS as internal standard, $\delta^{11}B$ vs. external BF_3 etherate. Downfield chemical shifts from the reference are positive.

[b] Not observed under the conditions of the experiment (10μs pulse, angle of tip ~30° with a 2-3s pulse interval at ~25°C).

[c] No splitting discernable because the signals are too broad and of too low intensity.

A detailed discussion of the ^{13}C chemical shift effects is to be given in Part III of this series when results for Mes_2BX (X = OR, F) systems will be reported. It is worth noting here that when R≠R' and R=H it appears that the carbon atoms of the mesityl ring cis to hydrogen resonate at lower fields than those of the trans mesityl ring. It is not unexpected that the R' groups exert such effects which may possibly reflect their steric requirements. What is perhaps surprising is the remarkably narrow chemical shift range for each mesityl carbon atom throughout the series, especially when the variation in size and electronic properties of R' are considered. This holds even when the nitrogen atom is involved in an allene type structure as in (10) [8].

Experimental

Syntheses involving n-butyllithium were carried out under a dry nitrogen atmosphere using dry solvents, as were manipulations involving compounds (1) and (2). The compounds were characterised by ^{1}H and ^{11}B N.M.R. and precise mass spectrometric measurements. The crude products, which were obtained in good yields, were recrystallised once from the specified solvents to give the yields quoted in Table 2. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 457 grating spectrophotometer.

Table 2. Experimental and physical data for aminodimesitylboranes (I)

No.	1	2	3	4	5	6	7	8	9	10
Product yield (%)	30[a]	89[a]	68[b]	57[c]	65[a]	63[c]	74[d]	30[e]	65[a]	38[f]
M.p. (°C)	158-62	131-4	104-6	83-5	81-3	88-90	151-2	220-1	130-2	162-4
ν(N-H) (cm^{-1})	3362 3442	3470	-	3401	3355	3380	3340	-	-	-

a. from hexane; b. from CH$_3$OH; c. from pentane; d. from hexane/Et$_2$O;
e. from hexane/THF; f. from light petroleum (B.p.80-100°).

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