Journal of Organometallic Chemistry, 210 (1981) 1—8
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

DIMESITYLBORYL COMPOUNDS

VI *. ^{13}C DYNAMIC NUCLEAR MAGNETIC RESONANCE STUDIES

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(Received November 3rd, 1980)

Summary

Dynamic ^{13}C NMR data have been obtained for a series of dimesitylboryl compounds $Mes_2BX(Y)(Z)$ where X = O, S or N, Y = hydrocarbyl and Z = H or a lone pair of electrons. The data are interpreted in terms of a low temperature perpendicular structure in which one of the mesityl rings is assumed to be perpendicular to the plane containing the boron atom, the X(Y)(Z) ligand and the second mesityl ring. The barrier to internal rotation about the boron—mesityl bond is attributed to steric interactions and depends only slightly on the nature of X and Y. The rotation barriers about the B—X bonds are caused primarily by B—X π back-bonding which increases in the order N > S > O.

Introduction

For some time now dynamic nuclear magnetic resonance (DNMR) spectroscopy has been applied to the study of restricted rotation about the bonds formed between a trigonal boron atom and ligands capable of π back-bonding. Most such investigations have concerned aminoboranes and the barriers to internal rotation, as measured by the free energy of activation $\Delta G^{\ddagger}$ for the process, have been interpreted in terms of appreciable boron—nitrogen π bond orders and steric effects [2]. Of the other related studies, the two most pertinent to the present work concern alkoxyboranes. Meissner and Staab studied a series of substituted aryl-n-butoxy(2,4,6-tri-tert-butylphenyl)boranes and concluded that the barrier to rotation about the boron—aryl bond arises primarily from steric effects and that π bonding is only of minor significance [3]. They reported no evidence for restricted rotation of the butoxy group. Mislow et al.

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* For Part V see ref. 1.

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in a very thorough study of dimesitylmethoxyborane and related compounds [4] were able to characterise rotational barriers about the boron—mesityl and boron—methoxy bonds. Steric and π conjugative effects were invoked to explain the barrier about the boron—oxygen bond.

Recent ^{1}H and ^{13}C NMR data obtained for series of dimesitylboryl compounds $Mes_2BX(Y)(Z)$ ($X = O, S$, Y = hydrocarbyl, Z = lone pair; $X = N$, Y = hydrocarbyl, Z = hydrogen) have shown that these compounds are amenable to variable temperature studies [5]. The availability of a range of these closely related compounds offered a rare opportunity to study, in the absence of any other variables, the properties of such ligands when bonded to boron. Of particular interest was the attractive possibility that $\Delta G^\ddagger$ values for rotational barriers about the B—X bonds could be measured. The resultant data would then provide information on the relative ability of single nitrogen, oxygen or sulphur ligands to act as π electron donors to the boron centre under circumstances where competing ligands of like or different donor ability are absent.

This paper presents the results of a ^{13}C DNMR study of a selected group of compounds from the series referred to above.

Results and discussion

The raw data were obtained by recording a spectrum of the system under study at as low a temperature as possible, usually 178 K, in order to obtain the non-exchanging chemical shift differences $\Delta\nu$ (Hz) between sets of signals that coalesced at a specific coalescence temperature T_c (°K) as the system was allowed to warm up. This information is all that is necessary for the calculation of $\Delta G^\ddagger$ values by the approximate method [6] based on the equation, $\Delta G_c^\ddagger = T_c\ [190.9 + 19.1 \log(T_c/\Delta\nu)]$ J mol^{-1}. While this method is susceptible to systematic errors it has been shown to give results of adequate precision when applied to simple two-site exchange processes [2c].

To verify this conclusion we carried out some preliminary ^{13}C DNMR measurements on Mes_2BOMe in carbon disulphide. The $\Delta G^\ddagger$ values for the two different barriers, 49.4 and 55.2 kJ mol^{-1}, obtained using the above equation, are identical to those calculated by Mislow et al. from a total line shape analysis [4] of their ^{1}H DNMR results.

In order to cover the whole temperature range of interest (170—470 K) it proved necessary to use two solvents. Low temperature spectra were recorded in CH_2Cl_2 and spectra recorded above 308 K were measured in hexachlorobutadiene. These solvents have the advantages that they contain carbon atoms which resonate outside the chemical shift ranges of interest and they are of reasonably similar chemical composition. The latter is desirable in order to minimise any variations in $\Delta G^\ddagger$ values due to solvent effects, if conclusions are to be drawn from data recorded in different solvents. As far as rotational barriers in *N,N*-disubstituted amides are concerned it has been shown that $\Delta G^\ddagger$ values are not significantly affected by changes in solvents [7].

Two factors are of crucial importance to the interpretation of the results reported here. These are the low temperature conformation of the systems in solution and the identification of the actual molecular processes which cause coalescence of signals.

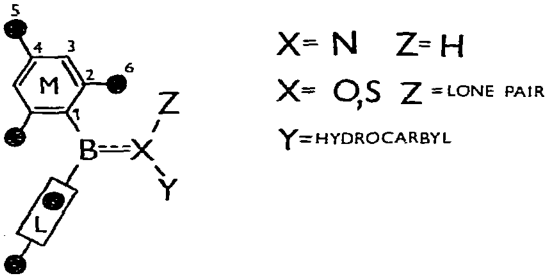


Fig. 1. The low temperature perpendicular structure for $Mes_2BX(Y)(Z)$ compounds.

Low temperature conformation of $Mes_2BX(Y)(Z)$ *systems*

Meissner and Staab [3] interpreted their results on substituted aryl-n-butoxy-(2,4,6-tri-t-butylphenyl)boranes in terms of a perpendicular structure in which the tri-tert-butylphenyl ring is assumed to be perpendicular to the plane containing the boron atom and the three atoms bonded to it. The substituted aryl ring and the butoxy group are considered to lie in this reference plane. The corresponding structure for the dimesityl compounds considered here is shown in Fig. 1.

The low temperature ^1H results of Mislow et al. [4] are consistent with three alternative explanations, two of which are based on a propeller conformation and the third on the perpendicular geometry shown in Fig. 1. On the basis of the data available they were unable to decide unambiguously which of the two alternative structures represented the low temperature geometry. It should be noted however, that one of the explanations based on the propeller conformation requires that two of the four *ortho*-methyl groups are accidentally isochronous and the other requires that one of the three ligands is undergoing a rapid flip at 180 K. Evidence in favour of the perpendicular conformation was obtained from a study of bis(2,6-dimethylphenyl)isopropoxyborane.

Since B—X back-bonding is maximised when the X ligand lies in the reference plane this geometry is to be favoured, particularly when the B—X π bond order is large as in mono-aminoboranes [2c]. There is theoretical and structural evidence to support this view. Ab initio molecular orbital calculations for H_2BOH [8], H_2BSH [9] and H_2BNH_2 [8a,10] predict that all three have planar geometries whilst X-ray analysis of $Me_2B—NMe_2$ at 178 K shows that the dimethylamino group lies in the reference plane with a calculated π bond order of 0.6 [11]. Electron diffraction data on Me_2BSMe and $(Me_2BS)_2$ [12] are also consistent with planar arrangements. If the maximisation of π-back-bonding is the dominant effect influencing the low temperature conformation of these molecules then to minimise unfavourable steric interactions the two mesityl groups have to be perpendicular to each other, as shown in Fig. 1.

From the ^{13}C data already published for dimesitylboryl compounds it is possible to draw an idealised fully proton noise-decoupled ^{13}C spectrum for the carbons of the two mesityl ligands with the geometry shown in Fig. 1. This spectrum is given in Fig. 2. It assumes perfect relative intensities and a chemical shift pattern free from overlapping signals. In this idealised spectrum the signals for the C(2), C(3) and C(6) carbons appear as three sets of three lines with rela-

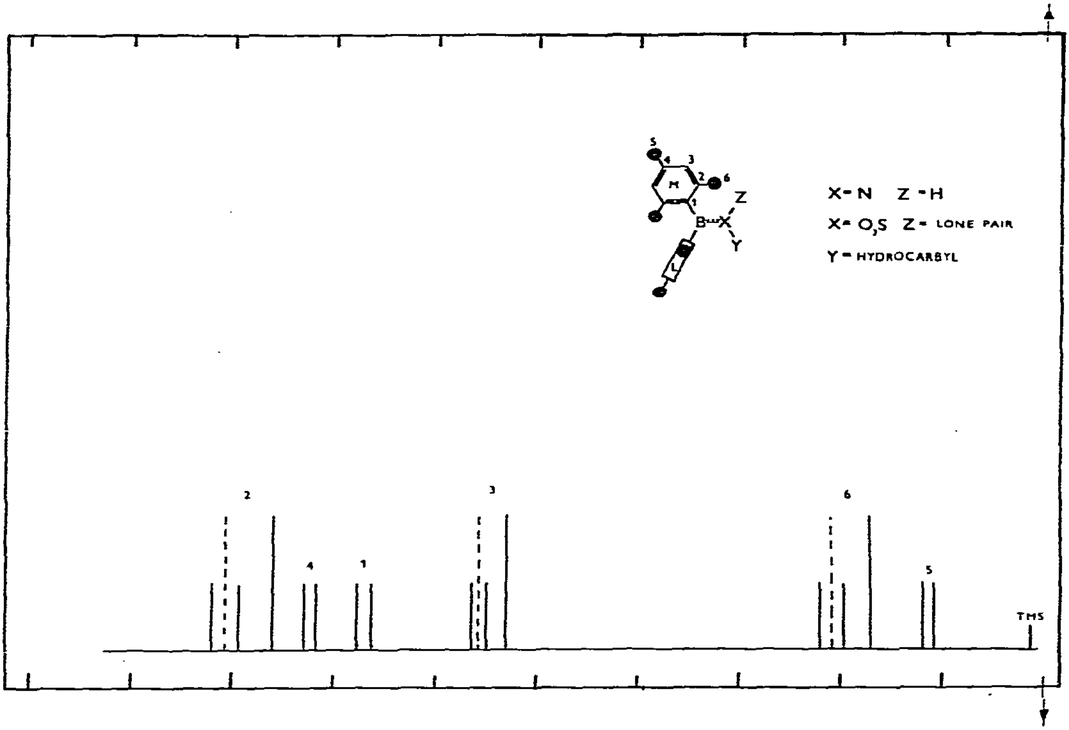


Fig. 2. An idealised fully ^1H noise-decoupled ^{13}C NMR spectrum of the mesityl carbons in dimesitylboryl compounds $Mes_2BX(Y)(Z)$ with the conformation shown.

tive intensity ratios of 1 : 1 : 2. It is possible to deduce the fact that the ring M carbons will be deshielded with respect to the corresponding carbons in ring L, from the results obtained for aminodimesitylboranes $Mes_2BNH(R)$ where it is observed that the carbons of the ring *cis* to the hydrogen are more deshielded than those of the *trans* ring [5b]. The ^1H DNMR results of Mislow et al. on Mes_2BOMe make it possible to predict how the spectrum should behave on increasing the temperature. These workers were able to identify two distinct processes which cause coalescence of the ^1H mesityl methyl signals. A low energy process associated with rotational flipping of a mesityl ligand(s) and a higher energy process assumed to be caused by rotational flipping of the methoxy group. If the two processes also occur in this order for X = O, S or N then the behaviour of the spectrum as the temperature is raised from the low temperature limit should be the same irrespective of the nature of X. Rapid rotation of M should cause coalescence of the two most deshielded signals of the sets originating from the C(2), C(3) and C(6) carbons to give the dotted lines in Fig. 2. Because of the non-equivalent mesityl groups the spectrum should then consist of three sets of two lines each, for the C(2), C(3) and C(6) carbons and the same for the C(1), C(4) and C(5) carbons. The relative intensities of the two groups being 2 : 1. Removal of the non-equivalence should cause coalescence of the two line sets to give a six line spectrum at the high temperature limit.

Every compound studied in this work shows the behaviour outlined above.

TABLE 1

FREE ENERGIES OF ACTIVATION $\Delta G^{\ddagger}$ FOR THE ROTATIONAL PROCESSES IN COMPOUNDS $Mes_2BX(Y)(Z)$

	Rotation of ring M			Rotation about B—X bond		
Compounds X(Y)(Z)	No. of data sets (maximum poss. = 3)	mean T_c (K)	mean[a] $\Delta G_c^{\ddagger}$ (kJ mol^{-1})	No. of data sets (maximum poss. = 6)	mean T_c (K)	mean[a] $\Delta G_c^{\ddagger}$ (kJ mol^{-1})
OMe	2	225	48.5	4	263	55.5
OPr^i	1	235	48.1	4	272	58.2
OPh	2	213	45.5	4	226	47.2
OC_6H_4OMe-*p*	1	227	47.2	4	231	48.5
OC_6H_4Cl-*p*	2	220	46.7	3	226	47.1
$OC_6H_4Bu^t$-*p*	1	223	46.0	4	224	47.0
SMe	2	185	38.1	3[c]	390	82.5
SEt	1	188	37.8	3[c]	392	82.9
SBz[b]	—	—	—	1[c]	398	84.3
SPh	2	200	41.1	4[c]	355	76.2
SC_6H_4-Me-*p*	1	203	40.9	3[c]	359	76.9
N(Me)(H)	1	193	39.7	1[c]	~450[d]	~105
$N(Pr^i)(H)$	3	192	40.7	—	—	—
N(Bz[a])(H)	1	201	41.4	—	—	—
N(Ph)(H)	3	208	44.9	1[c]	~420[d]	~105

[a] Values are considered to be precise to ±1.0 kJ mol^{-1}. [b] Bz = benzyl. [c] $\Delta\nu$ values obtained from the spectrum recorded in hexachlorobutadiene at 308 K. [d] Because of relatively poor signal: noise ratios at these high temperatures and incipient sample decomposition it proved impossible to assign precise T_c values.

In the case of the aminoboranes the high temperature limit lies well above the upper temperature limit of the instrument used i.e. it is >473 K, and so, for only two of these compounds the coalescence of just one set of signals is observed. These correspond to the C(4) carbons which have the smallest $\Delta\nu$ values and hence coalesce first (see Table 1). All the compounds show most but not all of the details of the idealised low temperature spectrum. In the main, discrepancies arise from incomplete resolution of the splitting patterns due either to the inability to attain temperatures low enough to maximise the expected splittings or from overlapping signals arising from carbon atoms in Y. In addition, in all cases studied, the C(5) carbons appear as a single line due to their very similar chemical shifts. In fact, of all the compounds studied so far in this series, in only three aminodimesitylboranes has the chemical shift difference of the C(5) carbons been sufficiently large to be detectable [5b].

Of the systems reported here, the one that corresponds most completely to the idealised spectrum is Mes_2BOPh whose low temperature spectrum is shown in Fig. 3. As can be seen, the spectrum shows all the expected features except that for the C(3) carbons the most deshielded pair of singlets are not quite resolved at 183 K, the lowest temperature at which a reasonable spectrum could be obtained. The C(5) carbon signals appear as a single line and the C(1) carbons as broad, low intensity signals due primarily to the boron quadrupole.

The symmetry of the mesityl ligands make it possible to obtain $\Delta G^{\ddagger}$ values for the two different molecular processes with good precision in most cases because there are, in principle, three ways of observing the rotation of ring M

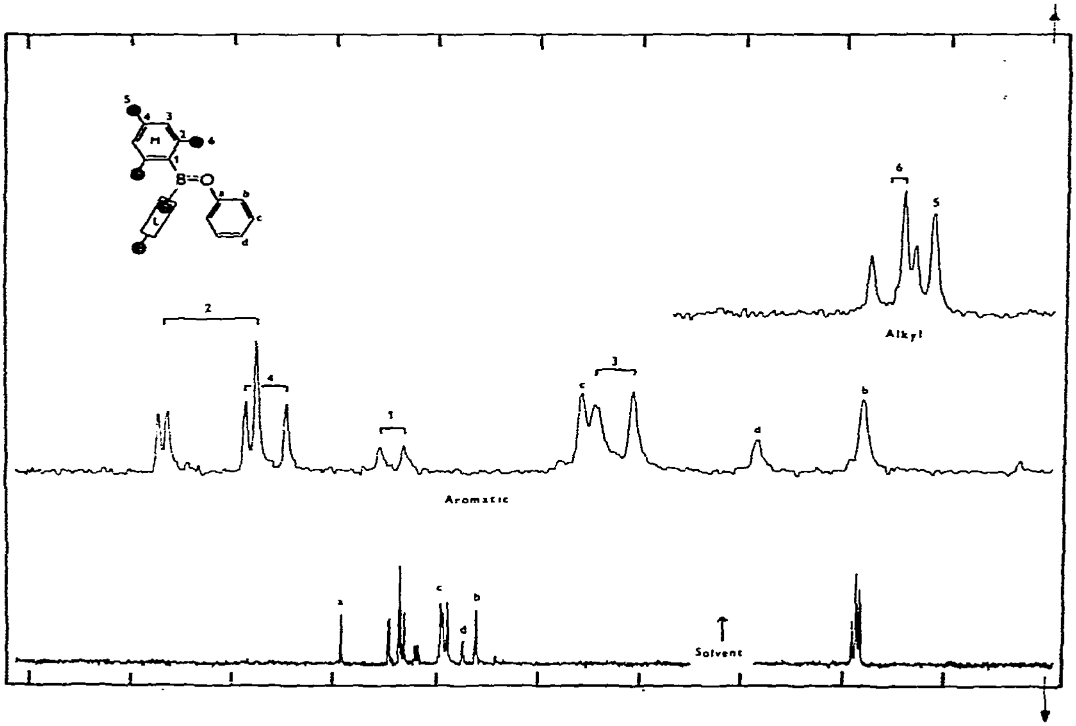


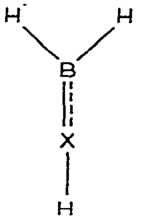
Fig. 3. The fully ^1H noise-decoupled ^{13}C NMR spectrum of dimesitylphenoxyborane at 183 K in CH_2Cl_2.

and six ways to observe the process causing the removal of the mesityl non-equivalence (vide supra). The results are given in Table 1. For any one compound the $\Delta G^{\ddagger}$ values obtained for each process varied only slightly with T_c and usually in an irregular manner. This implies that the corresponding $\Delta S^{\ddagger}$ values are very small and consequently the $\Delta G^{\ddagger}$ values are not significantly temperature dependent. Relevant values can therefore be compared with confidence.

Identification of the molecular processes causing coalescence

The low energy process associated with the restricted rotation of ring M is attributed, as indicated above and elsewhere [1,13], primarily to steric interaction between rings M and L. The values are all very similar as is to be expected. Differences can be explained in terms of the variation in B—X bond lengths, (B—O) ~ 1.36 Å [14], (B—N) ~ 1.42 Å [11,15] and (B—S) ~ 1.80 Å [12,16], and the steric demands of Y. These variables serve to restrict the space available for the oscillation of ring L in the vertical plane and hence will cause small variations in the rotational barrier.

Since the high energy process makes the two mesityl groups equivalent it must be associated with the motion of the third ligand. When X = N there is only one possible mechanism that can account for the observed behaviour i.e. rotation about the B—N bond. When X = O or S however, there are two possible limiting mechanisms. Rotation about the B—X bond or a lateral shift of Y to give the linear conformation (I). The experimental data do not allow a distinction to be made between these alternatives. However ab initio calculations on the parent compounds H_2BXH all show that rotation from the C_s planar conformer to conformation II is more favourable than a lateral shift to give I. In the case of oxygen, II is more favoured than I by 20 kJ mol^{-1} [8a] and in the case of sulphur it is favoured by ~120 kJ mol^{-1} [9b]. The rotational barriers are calculated to be ~65 kJ mol^{-1} for H_2BOH [8] and ~77 kJ mol^{-1} for H_2BSH [9]. These are in reasonable agreement with the corresponding experimental $\Delta G^{\ddagger}$ values reported here. The experimental value of ~105 kJ mol^{-1} for rotation about the B—N bond is somewhat lower (by 16 to 40 kJ mol^{-1}) than that calculated for H_2BNH_2 [8a,10] but is close to experimental values obtained for other monoaminoboranes [2].



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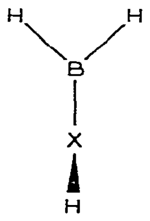

(II)

It would appear therefore, that in the absence of any evidence to the contrary, the rotational mechanism operates in all these systems.

Consideration of scale models indicate that in order to achieve simultaneous rapid rotation about all three bonds, the rotations of the ligands have to be correlated. This is readily achieved if, from the point of view of the boron atom, ring M rotates clockwise and ring L rotates anti-clockwise as Y rotates clockwise about the B—X bond. It is expected that any steric interaction between the ligands will be inversely proportional to the B—X bond length if Y is kept constant. Such interaction should therefore be greatest when X = O. Consequently steric effects due to variation in the size of Y should be seen most readily in the oxygen series as is indeed found to be the case. The fact that when Y = aryl the rotation barriers are less then when Y = alkyl, even though the former are bulkier, indicates that the major cause of the rotational barriers is electronic rather than steric in origin. Further indication that steric effects play a minor role in inhibiting the correlated motion comes from ^{13}C chemical shift data for these compounds. Studies on alkyldimesitylboranes Mes_2BR show that the ^{13}C chemical shifts of the C(6) carbons are sensitive to the size of R. When R is a primary or secondary group δ ^{13}C for the C(6) carbons is 23.0 ± 0.4 ppm. When R is tertiary the value increases and for R = t-butyl it is 30.2 ppm [17]. All the $Mes_2BX(Y)(Z)$ compounds studied in this work have values of δ $^{13}C = 22.7 \pm 0.3$ ppm for the C(6) carbons [5,13] which points to the absence of large steric effects. This being the case, the rotational barriers are due primarily to B—X π back-bonding which changes with X according to the order N > S > O. These are perhaps the first experimental data that show sulphur is clearly a better π donor than oxygen towards boron. This is also the case when the isoelectronic positively charged carbon atom is the π acceptor involved [18]. The decrease in the rotational barrier when Y changes from alkyl to aryl is attributed to the electron-withdrawing properties of the aryl groups which make the X atom less effective in back-donating π electron density to boron. Furthermore the apparent absence of a significant *para*-substituent effect in the aryloxy series implies that electron withdrawal takes place via an inductive mechanism. It is recognised, however, that a rather narrow range of *para*-substituents have been studied and further work is necessary before the origin of this effect can be unambiguously identified. In this regard the *para*-nitrophenoxy compound is readily synthesised but its low solubility in suitable solvents prevents the measurement of DNMR data.

Experimental

Spectra were recorded in 10 mm tubes on a Jeol FX90Q FT spectrometer using the ^{7}Li external lock facility from ca. 30% (w/v) solutions in dry redistilled methylene chloride or hexachlorobutadiene. A 10 μs pulse (α = 30°) with a pulse delay of 0.5 s and an acquisition time of 0.682 s was used in all cases. 8K → 4K transforms of 6000 Hz width were utilised with accumulation times more than sufficient to give satisfactory signal : noise ratio, typically 250 scans at low temperatures and 1000—2000 scans when above ambient.

Sample temperatures were controlled and monitored with a Jeol control unit calibrated against methanol and ethylene glycol in the usual way. Checks were made periodically by inserting N.P.L. calibrated thermometers into a dummy sample held in the probe. After each change in temperature the sample was allowed to equilibrate for 15 min before commencing data collection.

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