X-Ray Crystallographic Evidence for a Boron–Nitrogen Analogue of an Allene: Diphenylmethyleneaminodimesitylborane

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Summary An *X*-ray crystallographic study of diphenylmethyleneaminodimesitylborane, $\mathrm{Ph_2C:NB(mesityl)_2}$, has established an allene-like geometry for the molecule.

MUCH attention has been paid recently[1–6] to the use of ketimino groups $\mathrm{R_2C{=}N{-}}$ as terminal substituents on co-ordinatively unsaturated metals or metalloids in the study of $\mathrm{N}\underline{\rightarrow}\mathrm{M}$ dative π-bonding. A linear $\mathrm{C{=}N}\underline{\rightarrow}\mathrm{M}$ group would be expected for maximum π-bonding, but a bent skeleton ($\angle$C–N–M *ca.* 120°) if π-bonding were unimportant. Whereas the i.r. and ^{1}H n.m.r. spectra of various derivatives have been interpreted as indicating linear $\mathrm{C{=}N}\underline{\rightarrow}\mathrm{M}$ skeletons in systems where, for example, M = 3-co-ordinate beryllium,[3] boron,[1,2,4] carbon,[5] or aluminium,[6] no definitive structural information on such systems has hitherto been available. We here describe the structure of the iminoborane $Ph_2C{=}N\underline{\rightarrow}B$ (mesityl)$_2$, which has the predicted[2,4] pseudo-allene geometry.

A sample of the iminoborane, prepared from (mesityl)$_2$BF and $Ph_2C{:}NLi$,[4] was crystallized from hexane–toluene. *Crystal data*: diphenylmethyleneaminodimesitylborane, $C_{31}H_{32}BN$, $M = 429{\cdot}41$, orthorhombic, $a = 17{\cdot}36$, $b = 29{\cdot}25$, $c = 10{\cdot}12$ Å, $U = 5139$ Å^3, $Z = 8$, $D_c = 1{\cdot}11$ g cm^{-3}, $D_m = 1{\cdot}08$ g cm^{-3}, space group *Pbca* (D_{2h}^{15}, No. 61). 608 X-ray reflexions with statistically significant intensities were measured on a Philips PAILRED diffractometer using Mo-K_α radiation. The structure was solved by using Σ_2 sign relationships to determine the signs of 144 reflexions whose $|E|$ values were larger than 1·5. An E map calculated with these signs revealed the nitrogen atom and 30 of the carbon atoms (of which three later proved to have been incorrectly placed). A subsequent electron density synthesis calculated with signs of 397 reflexions based on these atomic positions revealed the remaining carbon atom and the boron. Further Fourier and least-squares refinement reduced R to 0·092, individual isotropic temperature factors having been used and all hydrogen atoms included in the calculations.

The geometry of the central part of the molecule, shown in the Figure, closely resembles that of allene in the following respects: (i) the B–N–C link is very nearly linear, (ii) the B–N and N–C distances are both short, as expected for multiple bonds, and (iii) the C(1)–C(2)–C(3) and B–C(4)–C(5) planes are almost perpendicular (angle between planes 87°). These features confirm that there is π-bonding between the boron and nitrogen atoms producing a $C{=}N\underline{\rightarrow}B$ system. π-Bonding in other boron–nitrogen compounds such as $[(Me_2N)BCH_2]_3$,[7] Me_2NBMe_2,[8] and $(C_6H_4O_2B)_3N$,[9] is known to lead to a trigonal planar environment for the nitrogen atom but this is the first demonstration of a linear environment analogous to allene.

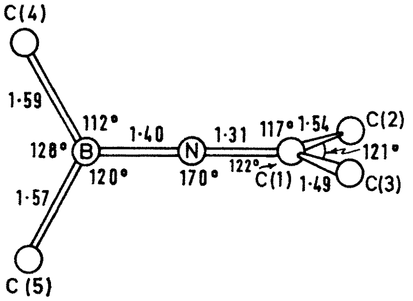

FIGURE. *Bond lengths in* Å (*estimated standard deviations* N–C 0·02 Å, *other bonds* 0·03 Å) *and bond angles* (*estimated standard deviations* 2°).

The slight deviation of the B–N–C angle from 180° results from atom C(1) lying 0·23 Å out of the plane N–B C(4)–C(5). Bond lengths and angles in the remainder of the molecule are similar to those usually found for aromatic rings. The benzene rings are not coplanar with the neighbouring C(1)–C(2)–C(3) or B–C(4)–C(5) planes, but are rotated through 29°—64°. By this means steric interference between methyl groups or hydrogen atoms attached to the rings is avoided.

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