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Preliminary communication

PREPARATION AND X-RAY CRYSTAL STRUCTURES OF THE DIMERIC ALDIMINOBORANE $(PhCH{=}NBMe_2)_2$ AND MONOMERIC PADDLE-WHEEL SHAPED TRIS(KETIMINO)BORANE $B(N{=}CBu^t_2)_3$ *

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Summary

The aldiminoborane $(PhCH{=}NBMe_2)_2$, prepared from benzonitrile and tetramethyldiborane in 2/1 molar proportions, crystallizes in the form of centrosymmetric dimeric molecules with an *anti* arrangement of its bridging aldimino groups. Its planar $(BN)_2$ 4-membered ring has d(B—N) 1.59 Å angle NBN 87°. The tris(ketimino)borane, $B(N{=}CBu^t_2)_3$, prepared via $BF(N{=}CBu^t_2)_2$ from BF_3, OEt_2 and $3LiN{=}CBu^t_2$, contains paddle-wheel shaped trigonal monomeric molecules in which the $B(NC)_3$ and NCC_2 planes are mutually perpendicular, as appropriate for maximum $N \rightharpoonup B$ dative π-bonding and minimum $Bu^t \cdots Bu^t$ repulsions: d(B—N) 1.39 Å, angle BNC 166°. Features of these structures are compared with those of related compounds, and infrared and ^1H and ^{11}B NMR spectroscopic details are given.

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*Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June 1983. K.W.'s interest in imino derivatives arose from his postdoctoral studies (1957—1959) of nitrile hydroboration reactions [1] under the supervision of Professor H.J. Emeléus.

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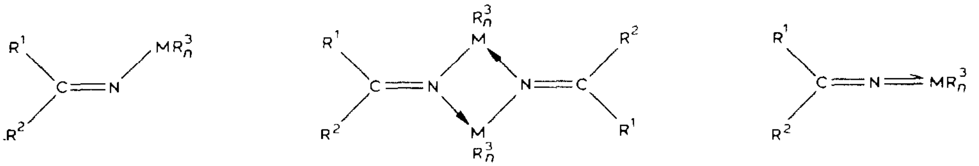
This paper gives a preliminary account of the structures of two key iminoboranes, the aldiminoborane $(PhCH{=}NBMe_2)_2$ and the ketiminoborane $B(N{=}CBu^t_2)_3$, which illustrate the two main bonding roles possible for an imino ligand $R^1R^2C{=}N$ attached to a coordinatively unsaturated metal or metalloid.

Imino ligands $R^1R^2C{=}N$, where R^1 and R^2 = alkyl, aryl or hydrogen, can bond to metals or metalloids in three main ways. When terminally attached as 1-electron ligands to coordinatively saturated metals (Fig. 1(a)), they adopt the angular $C{=}N{-}M$ geometry that is familiar in the parent imines $R^1R^2C{=}NH$, in oximes $R^1R^2C{=}NOH$, and in related systems, and that reflects the presence on the nitrogen atom of a stereochemically active lone pair of electrons. The Group IV derivatives $M(N{=}CPh_2)_4$ (where M = Si, Ge or Sn) are of this type [2,3]. However, when attached to coordinatively unsaturated metals, imino ligands can function as sources of three electrons, notably for bridging one metal atom to another (Fig. 1(b)) as in the case of dimeric Group III derivatives $(R^1R^2C{=}NM^{III}R^3_2)_2$ [4,5] or Group II derivatives $(R^1R^2C{=}NM^{II}R^3)_2$ [6,7]. If association is prevented, as it can be when the substituents R are bulky, dative $N \rightleftharpoons M$ π-bonding between the terminally-attached ligand and the metal atom will be strongest when the $C{=}N \rightleftharpoons M$ skeleton is linear (Fig. 1(c)), as in the case of the allene-like dimesitylborane $Ph_2C{=}N \rightleftharpoons Bmesityl_2$ [8].


(a) Terminal 1-electron ligand

(b) Bridging 3-electron ligand

(c) Terminal 3-electron ligand

Fig. 1. Possible bonding modes for an aldimino or ketimino ligand.

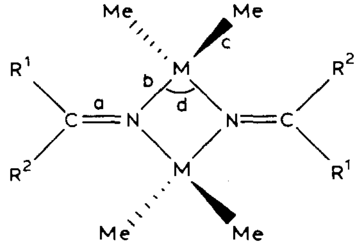
Although some structures have been established by X-ray crystallographic studies [3,4,6—11], our knowledge of the structures of most imino derivatives, and particularly of iminoboranes [12], has been derived from spectroscopic studies that have rarely been unambiguous. Although molecular mass measurements have allowed the degree of association in vapour and solution phases to be established, and so bonding of type 1(b) to be distinguished from 1(a) or 1(c), the question of whether the $C{=}N{-}M$ unit in a particular compound is linear or bent has not proved easy to resolve, even though two helpful pointers are available: the substituents R in derivatives $R_2C{=}NMX_n$ should in principle be distinguishable in the NMR spectrum if the $C{=}N{-}M$ unit is bent, and coupling of the $C{=}N$ and $N \rightleftharpoons M$ stretching vibrations in linear systems should be revealed by an increase in $\nu(C{=}N)$ in the infrared [12,13]. In practice non-equivalent substituents R may appear equivalent in the NMR if the $C{=}N{-}M$ unit is floppy, inverting rapidly at the nitrogen atom, and the shift in $\nu(C{=}N)$ in the infrared relative to a non-linear system may be slight, particularly if the $N \rightleftharpoons M$ bond is relatively weak. We accordingly sought further firm evidence of the structures of iminoboranes by preparing and structurally characterising the title compounds.

The aldiminoborane $(PhCH{=}NBMe_2)_2$

This was prepared from benzonitrile and tetramethyldiborane in 2/1 molar ratio in the absence of solvent:

$$2PhC{\equiv}N + B_2H_2Me_4 \rightarrow (PhCH{=}NBMe_2)_2$$

It crystallised from cyclohexane as colourless, air-stable plates which on X-ray study were found to be orthorhombic, with a 9.15(1), b 18.26(2), c 10.37(1) Å, space group $Pbca$, $Z = 4$, $R = 0.063$ for 1052 reflections for which $I > 3\sigma(I)$. The centrosymmetric molecular structure and selected bond distances and angles are shown in Fig. 2 together with related data for the compounds $(MeCH{=}NBMe_2)_2$ and $(Bu^tCMe{=}NAlMe_2)_2$ which were the subjects of earlier investigations [4]. A clear pattern emerges for all three compounds, which have C=N bond lengths 1.27—1.28 Å, consistent with a full C=N double bond, ring M—N distances (B—N 1.59 Å, Al—N 1.96 Å) virtually identical to the M—C distances to the terminal methyl groups, and ring angles of ca. 85—87° and 93—95°, the smaller at the Group III element, as expected in view of its higher coordination number and more electropositive character than nitrogen. Also as expected, the four atoms directly linked to each C=N unit are coplanar.



R^1	R^2	M	a(Å)	b(Å)	c(Å)	d
Ph	H	B	1.28	1.59	1.59	87°
Me	H	B	1.27	1.59	1.61	87°
Bu^t	Me	Al	1.27	1.96	2.01	85°

Fig. 2. Centrosymmetric structure of $(PhCH{=}NBMe_2)_2$ and related species. (Data for $(MeCH{=}NBMe_2)_2$ and $(Bu^tCMe{=}NAlMe_2)_2$ from ref. 4.)

All three compounds have an *anti* arrangement of their imino residues, and so equivalent MMe_2 units. Consistent with the retention of this structure in solution, the benzaldimino compound $(PhCH{=}NBMe_2)_2$ gives rise to a singlet absorption at δ + 0.21 ppm due to the BMe_2 protons in the ^1H NMR spectrum and a singlet at δ + 5.3 ppm (appropriate for four-coordinate boron) relative to BF_3, OEt_2 in the ^{11}B NMR spectrum (C_6D_6 solution). The azomethine stretching absorption, $\nu(C{=}N)$, in the infrared is at 1654 cm^{-1} which is only slightly above the $\nu(C{=}N)$ value in the parent aldimine.

The tris(ketimino)borane, $B(N{=}CBu^t_2)_3$

Earlier studies [7,13] had shown the bulk of the t-butyl groups to be sufficient to restrict association of derivatives containing di-t-butylketimino ligands, and indeed the ligands are so bulky that three can be attached to one boron atom only with difficulty. The boron trifluoride-ether complex in hexane reacts readily enough with an excess of $(LiN{=}CBu^t_2)_6$ [11] at room temperature to afford the bis(ketimino)boron fluoride $BF(N{=}CBu^t_2)_2$, which in turn reacts slowly (48 h) with the lithioimine at 120°C in petroleum ether to afford

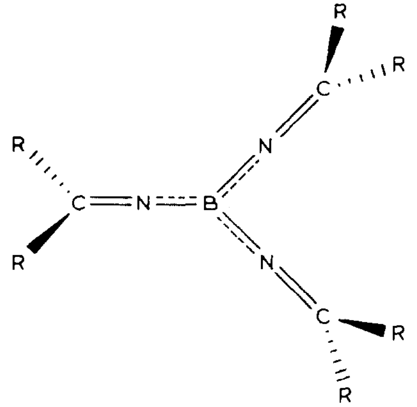


Fig. 3. "Paddle-wheel" structure of B(N=CBu$^t_2$)$_3$. R = Bu^t; B—N, 1.39 Å; C=N, 1.23 Å; angle NBN 118°; angle BNC 166°; angle between R$_2$CN and BN$_3$ planes 90°.

B(N=CBu$^t_2$)$_3$. The air-stable product can be recrystallised from hexane as colourless chunky crystals, m.p. 183—185°C, which absorb at 1735 cm^{-1} (ν(C=N)) in the infrared (KBr disc), at δ 1.20 ppm (singlet, in C$_6$D$_6$) in the ^{1}H NMR, and at δ +22.8 (relative to BF$_3$, OEt$_2$, in C$_6$D$_6$) in the ^{11}B NMR spectrum. Such spectroscopic data predict a monomeric, 3-coordinate boron species of type 1(c), and X-ray studies have now confirmed such a structure. The crystals of B(N=CBu$^t_2$)$_3$, i.e., C$_{27}$H$_{54}$BN$_3$, are trigonal, with a 10.70(1), c 45.41(2) Å, space group $R3c$, $Z = 6$, $R = 0.093$ for 596 reflections for which $I > 2\sigma(I)$.

The "paddle-wheel" molecular structure of B(N=CBu$^t_2$)$_3$ based on an essentially planar B(N=C)$_3$ skeleton, with the t-butyl ligands projecting above and below that plane, is shown in Fig. 3, which also indicates selected bond distances and angles. The molecule has a 3-fold symmetry axis through the boron atom. The C=N$\equiv$B units are slightly bent (angle CNB 166°), not linear as would be expected for maximum π-bonding. A similar slight bending is shown by the terminal ligands in LiAl(N=CBu$^t_2$)$_4$ [9]. Nevertheless, the planes in which the bonds to the butyl substituents lie, being perpendicular to the B(NC)$_3$ skeletal plane, generate a pseudo-allene geometry for each R$_2$C=N$\equiv$BN$_2$ unit, underlining the importance of N$\overset{\rightarrow}{-}$B dative π-bonding in this compound, a point reflected also in the short N$\overset{\rightarrow}{\equiv}$B distance of 1.39(1) Å (cf. 1.38 Å in Ph$_2$C=N$\overset{\rightarrow}{-}$B-mesityl$_2$ [8] and in Ph$_2$NBCl$_2$ [14], 1.41 Å in B-trichloroborazine [15], and 1.43 Å typically found in tris(amino)borane BN$_3$ systems such as B(NMe$_2$)$_3$ [16], the tricyclic compound B[N(CH$_2$)$_3$N(CH$_2$)$_3$N(CH$_2$)$_3$] [17] and the tetraazadiborine [Me$_2$NBNMeNMe]$_2$ [18]).

This "paddle wheel" shape of B(N=CBu$^t_2$)$_3$ may be contrasted with the "propeller" shape adopted by monomeric tris(amino)boranes and alanes M(NR$_2$)$_3$ such as B(NMe$_2$)$_3$ [16] and Al[N(SiMe$_3$)$_2$]$_3$ [19] in which the C$_2$N/Si$_2$N planes are twisted (by 32.8 and 50°, respectively) out of the MN$_3$ planes; a similar arrangement around the B atoms was also found in [Me$_2$NBNMeNMe]$_2$ [18] (dihedral angle 39° between the C$_2$N and BN$_3$ planes). Such atomic arrangements represent a compromise between the planar shape (with the R_2N units in the MN_3 plane) that would allow maximum $\mathrm{N}\dashrightarrow\mathrm{M}$ dative π-bonding, and the extreme non-planar shape (with the R_2N units perpendicular to the MN_3 plane) that would minimise non-bonding repulsive interactions between the substituents R on neighbouring R_2N units; calculations indicate that the loss in π-bonding energy resulting from such distortions is significant, e.g., 16% for $B(NMe_2)_3$, 22% for $[Me_2NBNMeNMe]_2$ [18]. However, with ketimino derivatives $M(N{=}CR_2)_3$, the "paddle-wheel" structure minimises non-bonding repulsions while maximizing $\mathrm{N}\dashrightarrow\mathrm{M}$ dative π-bonding; the bulk of the substituents R helps rather than hinders the adoption of the structure most appropriate for $\mathrm{N}\dashrightarrow\mathrm{M}$ π-bonding.

Satisfactory analytical data were obtained for $(PhCH{=}NBMe_2)_2$ and $B(N{=}CBu^t_2)_3$. Full analytical, structural and spectroscopic details will be published in a later paper.

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