Monomeric Phosphinoboranes: The Role of the B- and P-Substituents for P=B Multiple Bonding

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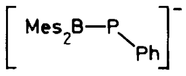
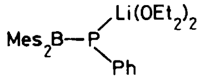
The influence of the boron substituents on the structures of the first fully characterized monomeric diphosphinoboranes $[(2,4,6\text{-}Me_3C_6H_2)_2P]B\text{-}X$ (X = OEt, Br) has been established; especially for X = Br, P–B multiple bonding may be clearly inferred from the molecular structure.

A large number of phosphinoboranes have been prepared and were initially claimed to be 'monomeric,'[1] but only recently have the first structurally characterized, monomeric phosphinoboranes (**1**)—(**3**) been established by the elegant work of Power *et al.*[2] Since they are isoelectronic with silenes (**4**),[3] monomeric phosphinoboranes (**5**) should exhibit some degree of multiple bonding and, indeed, in the two 'phosphido'-type phosphinoboranes (**1**) and (**2**) a nearly planar phosphorus atom [sum of the angles at P for (**2**): 350.9°] and a short P–B bond [(**1**), 1.835 Å; (**2**), 1.823 Å] were interpreted as having 'double-bond' character.[2] A similar bonding situation was ascribed to (**3**), but the higher degree of pyramidality at the phosphorus atom [sum of the angles at P for (**3**), 339.4°] and a slightly longer P–B distance (1.859 Å) are indicative of less



(1)



(2)

$Mes_2B{-}PPh_2$

(3)

$R^1_2C{=}SiR^2_2$

(4)

$R^1_2B{=}PR^2_2 \longleftrightarrow R^1_2B{-}\ddot{P}R^2_2$

(5)

Mes = $2,4,6\text{-}Me_3C_6H_2$

effective multiple bonding. Objectively, an electron donating ('pushing') effect at the P atom (+*I*), as in (**1**) and (**2**), promotes multiple bonding. In our own approach, we applied the opposite strategy: electron withdrawing ('pulling') substituents X at boron likewise should promote multiple bonding. Since the −*I* substituents OEt and Br employed in our study are also p-donors to a varying degree, this approach seems to be more versatile than the former in tuning the degree of $P \rightleftharpoons B$ multiple bonding. Furthermore, we turned to the previously unknown monomeric diphosphinoborane compounds[4]† to study the competitive effects of P=B/X=B *vs.* P=B/P=B multiple bonding.

The new compounds $(Mes_2P)_2B{-}X$ (X = Br, OEt) were synthesized according to equation (1).‡

$$BX_3 + 2\,LiPMes_2 \xrightarrow{-2LiX} \underset{(\mathbf{6})}{(Mes_2P)_2B{-}X} \qquad (1)$$

a; X = Br, toluene, −40 °C
b; X = OEt, Et_2O, −40 °C

The ^{11}B n.m.r. spectral data confirm the presence of three-co-ordinate boron and hence the monomeric nature of (**6a, b**). Taking a low-field shift of the ^{31}P nucleus as indicative of multiple bonding, in (**6a**) (X = Br) P=B multiple bonding is more pronounced than in (**6b**) (X = OEt). Obviously, the ethoxy group itself takes part in supplying electrons to the electron-deficient three-co-ordinate boron atom. The ^{31}P signal of (**6b**) at low temperatures splits up, giving rise to an AB pattern and thus indicates inequivalence of the two phosphorus atoms. This might also imply inequivalence of the amount of multiple bonding to the boron atom.

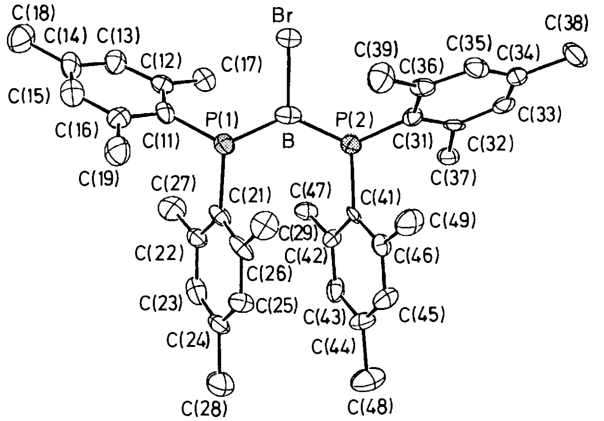
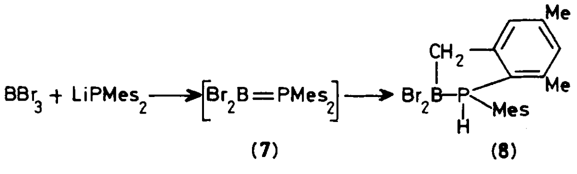


Figure 1. Molecular structure of $(Mes_2P)_2BBr$ (**6a**). (ORTEP, displacement parameters at the 50% probability level, without H-atoms). Important bond distances (Å) and torsion angles (°): B–Br 2.00(1), B–P(1) 1.82(1), B–P(2) 1.84(1), P(1)–C(11) 1.810(9), P(1)–C(21) 1.835(9), P(2)–C(31) 1.796(9), P(2)–C(41) 1.830(8); Br–B–P(1)–C(11) 36.1, Br–B–P(1)–C(21) 174.2, Br–B–P(2)–C(31) 39.4, Br–B–P(2)–C(41) 176.5.

This interpretation is fully consistent with the structural features as determined by *X*-ray diffraction.§ As Figure 1 shows, (**6a**) has approximate C_2 symmetry. Both phosphorus atoms are equivalent and essentially in one plane with the trigonal B atom, the bromine atom, and the C_{ipso} atoms of two of the mesityl substituents [deviation of C(21)/C(41) from the plane through Br, B, P(1), P(2): 0.17/−0.10 Å]. The two remaining mesityl groups deviate by 0.93/−0.98 Å from this plane, pointing in opposite directions. Thus both P atoms approach planarity [sum of the angles at P(1) 347.1°; P(2) 346.7°]. The P–B distances [1.82(1), 1.84(1) Å] are the shortest phosphorus–boron distances observed as yet, but very close to those of (**1**) and (**2**). This means that owing to the inefficient multiple bonding from the Br substituent[5] *both* phosphorus atoms are effectively involved in multiple bonding. This leads to the conclusion that a P–B distance of *ca.* 1.82 Å is not the minimum: with only *one* phosphino substituent and even more effective electron withdrawing properties of the X substituent(s), further increase of the double bond character for compounds of type (**5**) may be envisaged. First attempts to verify this concept were directed to the synthesis of $Br_2B{-}PMes_2$ (**7**). However, the novel heterocycle (**8**) was isolated instead of (**7**) (Scheme 1).

An entirely different situation may be inferred from the structure of (**6b**) (Figure 2). Both P atoms of (**6b**) differ considerably in their pyramidality [sum of the angles at P(1): 337.0, at P(2) 314.0°] and conformation: at P(1), the position of the substituents resembles roughly that in (**6a**) (with one C_{ipso} atom being approximately antiperiplanar to the B–O bond), whereas the torsion angles for the mesityl substituents at P(2) indicate an almost eclipsed conformation of C(41). Both P–B distances are much longer than in (**6a**) [P(1)–B: 1.913(3) Å, P(2)–B: 1.951(3) Å] thus indicating substantially



Scheme 1

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† *Note added in proof.* After submission of this manuscript, two papers relevant to this topic have appeared: (a) R. A. Bartlett, H. V. R. Dias, and P. P. Power, *Inorg. Chem.*, 1988, **27**, 3979; (b) H. V. R. Dias and P. P. Power, *J. Am. Chem. Soc.*, 1989, **111**, 144.

‡ (**6a**), orange crystals, m.p. 159 °C (decomp.); (**6b**): colourless crystals, m.p. 163 °C; (**8**): pale yellow crystals.

^{31}P N.m.r. data (p.p.m. referred to external 85% H_3PO_4): (**6a**) (C_6D_6, +20 °C): δ −31.25; (**6b**) ($C_6D_5CD_3$, +20 °C): δ −65.38; (**6b**) ($C_6D_5CD_3$, −100 °C): $\delta_{P(1)}$ −62.26, $\delta_{P(2)}$ −68.28 [AB system, ^2J(PP) 182.7 Hz]; (**8**) (C_6D_6, +20 °C): δ −31.55 [^1J(BP) 133.2 Hz, ^1J(PH) 423.4 Hz]. ^{11}B N.m.r. data (p.p.m. referred to external $BF_3{\cdot}Et_2O$, C_6D_6, +20 °C): (**6a**): δ +51.5; (**6b**): δ +55.0; (**8**): δ −5.33 [^1J(BP) 133.2 Hz].

§ *Crystal data:* (**6a**): $C_{36}H_{44}BBrP_2$, *M* = 629.42, triclinic, space group $P\bar{1}$ with *a* = 8.426(2), *b* = 11.954(2), *c* = 17.532(4) Å, α = 93.83(2), β = 89.09(2), γ = 109.40(2)°, *U* = 1661.9 Å^3, D_c = 1.258 g cm^{-3} for *Z* = 2 at −40 °C, μ(Mo-K_α) = 13.4 cm^{-1}, *F*(000) = 660. Lorentz-polarization and empirical absorption corrections were applied (rel. transm.: 0.76—1.00). The structure was solved by automated Patterson methods (SHELXS-86) from 3567 unique reflections [$(\sin\theta/\lambda)_{max.}$ = 0.504 Å^{-1}, Syntex-P2$_1$ diffractometer] and refined to $R(R_w)$ = 0.065(0.050), $w = 1/\sigma^2(F_o)$ for 2405 'observed' reflections with $F_o \geqslant 4.0\sigma(F_o)$ (anisotropic, H constant, 361 refined parameters, SHELX-76). $\Delta\rho_{fin.}$ (max./min.) = 0.55/−0.46 e/Å^3.

(**6b**): $C_{38}H_{49}BOP_2$, *M* = 594.57, triclinic, space group $P\bar{1}$ with *a* = 9.642(2), *b* = 12.059(2), *c* = 15.278(2) Å, α = 90.97(1), β = 105.17(1), γ = 93.30(1)°, *U* = 1710.7 Å^3, D_c = 1.154 g cm^{-3} for Z = 2, *T* = −35 °C, μ(Mo-K_α) = 1.5 cm^{-1}, *F*(000) = 640. Lorentz-polarization, but no absorption, corrections were applied. The structure was solved by direct methods (SHELXS-86) and refined to $R(R_w)$ = 0.059(0.053), $w = 1/\sigma^2(F_o)$ for all unique reflections up to $(\sin\theta/\lambda)_{max.}$ = 0.572 Å^{-1} (anisotropic, CH_3 as rigid groups, other H atoms constant, 418 refined parameters, 5330 reflections). $\Delta\rho_{fin.}$ (max./min.) = 0.30/−0.36 e/Å^3. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Date Centre. See Notice to Authors, Issue No. 1.

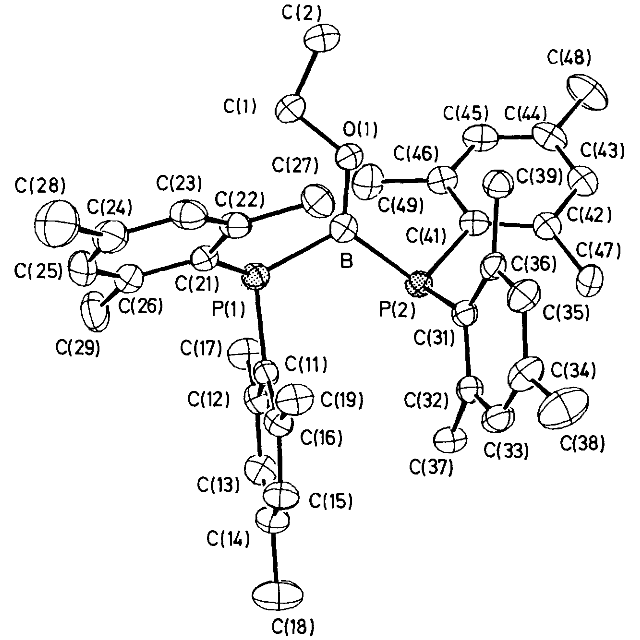

Figure 2. Molecular structure of $(Mes_2P)_2BOEt$ (**6b**). Important bond distances (Å) and torsion angles (°): B–O 1.349(3), B–P(1) 1.913(3), B–P(2) 1.951(3), P(1)–C(11) 1.838(2), P(1)–C(21) 1.837(2), P(2)–C(31) 1.865(2), P(2)–C(41) 1.846(2); O–B–P(1)–C(11) 178.4, O–B–P(1)–C(21) −56.5, O–B–P(2)–C(31) 102.4, O–B–P(2)–C(41) −11.2.

less P–B multiple bonding. In line with this is a short B–O bond [1.349(3) Å] and a conformation of the ethoxy group [torsion angle C(1)–O(1)–B(1)–P(1) 0.0°] which optimizes B–O double bonding. Remarkably, both the shorter P(1)–B bond length and lesser pyramidality at P(1) point to some additional P–B interaction for this phosphino substituent compared with P(2), thus corroborating the low temperature n.m.r. spectroscopy results.

The P–C(aryl) bond lengths clearly reflect the varying degree of P–B multiple bonding, shorter P–C bonds being indicative of more nearly planar geometries at P.

In summary, the structures of the first fully characterized monomeric diphosphinoboranes (**6a, b**) demonstrate that the multiple bonding ability of phosphorus in monomeric phosphinoboranes is dominated not only by the electron donating properties of the P substituents but also by the electronic properties (*−I*, *+M* effects) of the cosubstituent(s) at boron. Finally, (**6a**) is unique in being the first bis-arene ligand with parallel arene rings even in the uncomplexed state and having an 'ideal' ring–ring distance of 3.24 Å for the formation of bis-arene complexes of first row d-block elements [*cf.* the ring–ring distance of 3.22 Å in $(C_6H_6)_2Cr$[6]].

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