Diphospha- and Diarsa-diboretanes. Four-membered Rings containing Boron and Phosphorus or Arsenic

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Diphospha- and diarsa-diboretanes, $(REBR')_2$, (E = P, As; R = mesityl, R' = 2,2,6,6-tetramethylpiperidino) have been prepared and the structure of the diphosphadiboretane and RP(H)B(Cl)R' have been established by X-ray crystallography.

Diazadiboretidines, (1a), constitute a well-known class of compounds.[1] However, no unequivocal examples of heavier congeneric diphospha- and diarsa-diboretanes, (1b) and (1c), have been reported previously.† Considerable interest is associated with the molecular and electronic structures of such compounds; moreover, they can be regarded as head-to-tail dimers of the unknown boraphosphenes (R–B=P–R') and bora-arsenes (R–B=As–R').

Treatment of MesPH$_2$ (Mes = mesityl) with a 1.5 mole ratio of Bu^{n}Li resulted in a 50:50 mixture of MesPHLi and MesPLi$_2$ (as estimated by ^{31}P n.m.r. spectroscopy). Treatment of this mixture with (tmp)BCl$_2$ (tmp = 2,2,6,6-tetramethylpiperidino),[2] followed by filtration, solvent evac-

uation, and extraction with n-hexane afforded pale yellow crystalline [MesPB(tmp)]$_2$ (2).‡

The structures of $(REBR')_2$ compounds (E = N, P) can be discussed in terms of canonical forms (3) and (4). Diazadi-


(1a) E = N
(1b) E = P
(1c) E = As

(3)

(4)

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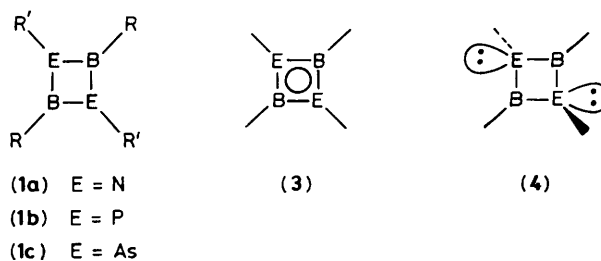
† Coates and Livingstone (*J. Chem. Soc.*, 1961, 5053) investigated the reaction of PhPH$_2$ and PhBCl$_2$ and suggested (PhPBPh)$_2$ and Ph(H)PB(Cl)Ph as two of the products. However, a subsequent reinvestigation of this reaction by Tevebaugh (*Inorg. Chem.*, 1964, 3, 302) indicated that the latter product is trimeric.

‡ All new compounds had satisfactory chemical analyses and spectroscopic characteristics.
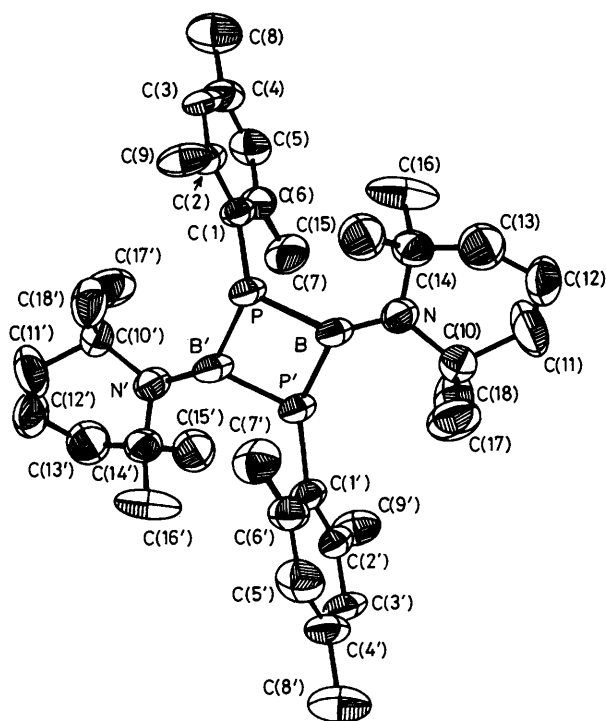
Figure 1. ORTEP view of (2) showing the atom numbering scheme. Important parameters: P–B 1.916(3), B–N 1.393(3), P–C(1) 1.844(2) Å; C(1)–P–B 119.5(1), B–P–B' 90.2(2), P–B–P' 89.8(2)°. The molecule resides on a centre of symmetry, the mesityl groups adopt a mutually *trans* orientation, and the P_2B_2 ring is planar.
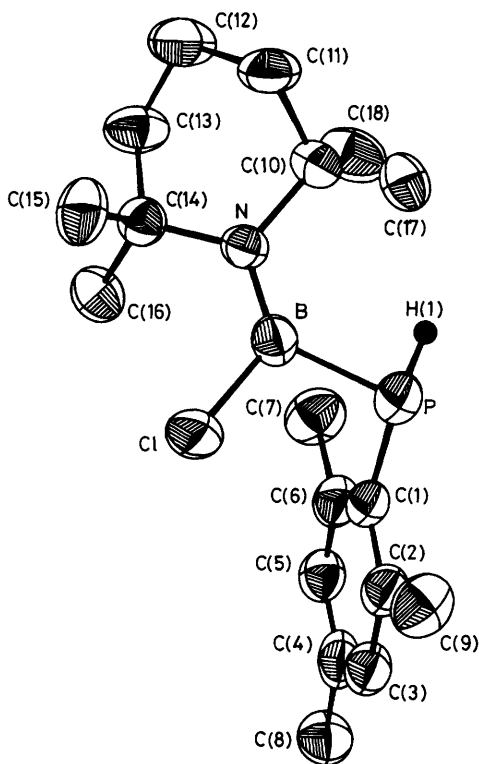
boretidines exhibit trigonal planar geometries at both N and B and N–B bond orders >1, hence their electronic structures are best represented by (3).[1] In sharp contrast, the X-ray structure of the diphosphadiboretane (2) (Figure 1)§ reveals pyramidal phosphorus geometries (sum of bond angles 329.0°) and a P–B bond length [1.916(3) Å] which is indicative of a bond order of unity. Clearly, there is no evidence for dative P → B π-bonding and the structure of (2) corresponds to canonical form (4). As indicated by the B–N(tmp) distances, the exocyclic N → B π-bonding in (2) [1.393(3) Å] is considerably stronger than that in [Bu^{t}NB(tmp)]$_2$ [1.465(3) Å].[1d] This is expected on the basis of competitive π-bonding between endo- and exo-cyclic nitrogens in the latter.

The arsenic analogue (1c) was prepared using a similar method to that employed for the preparation of (1b). Like (1b), (1c) exhibits a mass spectral parent peak; moreover, the fragmentation patterns of both molecules are very similar. One noteworthy feature in the mass spectra of (1b) and (1c) is the presence of peaks corresponding to the radical cations of MesP=B(tmp) and MesAs=B(tmp), respectively.

When MesPHLi was treated with (tmp)BCl$_2$, (*i.e.* in the absence of MesPLi$_2$) ^{31}P n.m.r. spectroscopy revealed the virtually quantitative formation of MesP(H)B(Cl)(tmp) (5). The monomeric nature of this compound was established by X-ray crystallography (Figure 2).§ As in the case of (2), the P–B bond is single [1.948(3) Å], the phosphorus atom adopts a tetrahedral geometry, and the B–N(tmp) bond length [1.380(3) Å] is indicative of a strong dative π-interaction.

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Figure 2. ORTEP view of (5) showing the atom numbering scheme. Important parameters: P–B 1.948(3), B–N 1.380(3), P–C(1) 1.843(2) Å, B–P–H(1) 102.(1), C(1)–P–B 103.1(1), C(1)–P–H(1) 102.(1)°.