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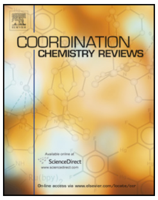

Review

Monomeric phosphinoboranes

Jonathan A. Bailey, Paul G. Pringle*

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Contents

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ABSTRACT

The key developments in the chemistry of $R_2PBR'_2$ over the last 20 years are reviewed. The categorization of phosphinoboranes as $R_2P{=}BR'_2$ species and borylphosphines as $R_2P—BR'_2$ species is suggested based on an analysis of the literature X-ray crystal structures. The chemistry of derivatives of the simplest borylphosphine $H_2P—BH_2$ is discussed. Six methods of preparation of $R_2PBR'_2$ are presented along with the reactions of the products with H_2, amine–boranes, elemental chalcogens, Me_3NO and compounds featuring C=O, C=C and C≡N functionalities. The two modes of coordination of $R_2PBR'_2$ to transition metals, κ^1 (P) and η^2 (P=B), are covered, along with the applications of borylphosphine complexes in homogeneous catalysis.

1. Introduction

Phosphinoboranes ($R_2PBR'_2$) contain trivalent and tricoordinate P and B atoms bonded together. They are valence isoelectronic with aminoboranes and alkenes and can be formulated containing a B=P double bond with a planar P as depicted in the Lewis structures for **A** shown in Fig. 1. The term borylphosphine has been used interchangeably with phosphinoborane but is more appropriate for the alternative structure **B** shown in Fig. 1 containing a B—P single bond with a pyramidal P. X-ray crystallography can be used to categorise the structures as phosphinoboranes (**A**-type) or borylphosphines (**B**-type) although there are structures which sit between these extremes. The stereoelectronic properties of the

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* Corresponding author. Tel.: +44 117 928 8114.
E-mail address: paul.pringle@bristol.ac.uk (P.G. Pringle).
URL: http://pringle.blogs.ilrt.org/ (P.G. Pringle).

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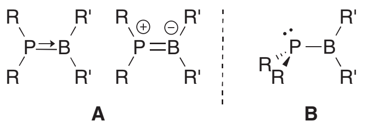

Fig. 1. The two structural extremes of $R_2PBR'_2$ compounds.

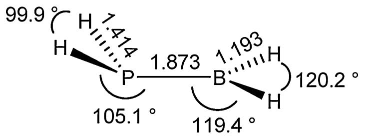

Fig. 3. Optimised computed structure of H_2P—BH_2.

substituents R and R′ determine the P—B bond order (as evidenced by the P—B bond lengths and geometry at P) and the chemistry of the P—B bond (see below). The name phosphinoboranes is used in this review to denote A-type structures as well as the generic term for $R_2PBR'_2$ and borylphosphine is reserved for **B**-type structures.

The chemistry of phosphinoboranes can be compared with that of their lighter congeners, the aminoboranes, which, along with the related amine–boranes $R_3N \cdot BR'_3$ have attracted much recent attention due to their potential applications in hydrogen-storage [1–4] and as precursors for BN-oligomers, polymers [5,6] and materials such as BN-nanotubes [7–9] and graphene analogues [9–11].

Since the comprehensive 1995 review by Paine and Noeth [12] there have been no reviews of $R_2PBR'_2$ compounds per se but they have featured in the reviews by Power et al. on π-bonding between p-block elements [13,14] and the reviews by Manners et al. [6,15,16] and Weller et al. [17] which deal with phosphine–borane dehydrocoupling. This review will primarily concern the literature in the period 1995–2014, highlighting the recent developments in monomeric $R_2PBR'_2$ compounds; oligomeric and polyphosphinoboranes are outside of the scope of this review.

2. Structures of phosphinoboranes and borylphosphines

It is of interest to compare the P—B bonding in $R_2PBR'_2$ with the N—B bonding in $R_2NBR'_2$. The greater covalent radius of P than N naturally leads to P—B bonds being longer than their N—B counterparts. Thus, the P—B bond length of 1.762(4) Å in Cy_2P—$B(C_6F_5)_2$ [18], which is the shortest recorded P—B bond in a phosphinoborane, is much longer than the 1.372(2) Å in Me_2N—$B(C_6F_5)_2$ [19]. A defining characteristic of aminoboranes is the strong N═B double bond. Calculations carried out in the early 1990s [20,21] suggested that the π-component of the P═B in structures with planar phosphorus centres are similar in strengths to N═B bonds. It was suggested that the reason the P═B is less important is because of the strong preference for a pyramidalised phosphorus environment, as evidenced by the high barrier to inversion at P in tertiary phosphines [22]; calculations showed that the boryl group reduces this inversion barrier from 34.2 kcal/mol for PH_3 to 5.9 kcal/mol for H_2BPH_2 [20]. The conclusions from more recent calculations suggest that the π- and σ-bonding in the optimised H_2BPH_2 structure are significantly weaker than in H_2BNH_2 (see below, Section 3.1).

Fu et al. [23] made a direct comparison of N—B with P—B π-bonding in the structures of the boratobenzenes $[C_5H_5B$—$EPh_2]^-$ (E = P, N). In the diphenylamido compound, the N is planar (Σ(angles at N) = 360°) and the N—B bond length is short (1.510(10) Å) whereas in the diphenylphosphido compound the P is pyramidal (Σ(angles at P) = 310°) and the P—B bond length is long (1.968(7) Å). By tuning of the substituents at P and B, $R_2PBR'_2$ compounds with varying degrees of P—B π-bond character have been obtained. Similar considerations have been expressed in discussing the bonding in silenes (R_2Si═CR'_2) which are isoelectronic with phosphinoboranes (R_2P═BR'_2) [24–26].

The P—B π-bonding will be maximised by planar geometry at P and therefore the closer the sum of the angles at P is to 360°, the greater the potential P—B bond order. As a result, it might be expected that the P—B bond length and the sum of angles at P would be negatively correlated. The X-ray crystal structures of over 35 $R_2PBR'_2$ compounds have been determined and Table 1 contains structures reported post-1995; Noeth reviewed earlier crystal structures [12]. A plot of all of the $R_2PBR'_2$ structures is given in Fig. 2

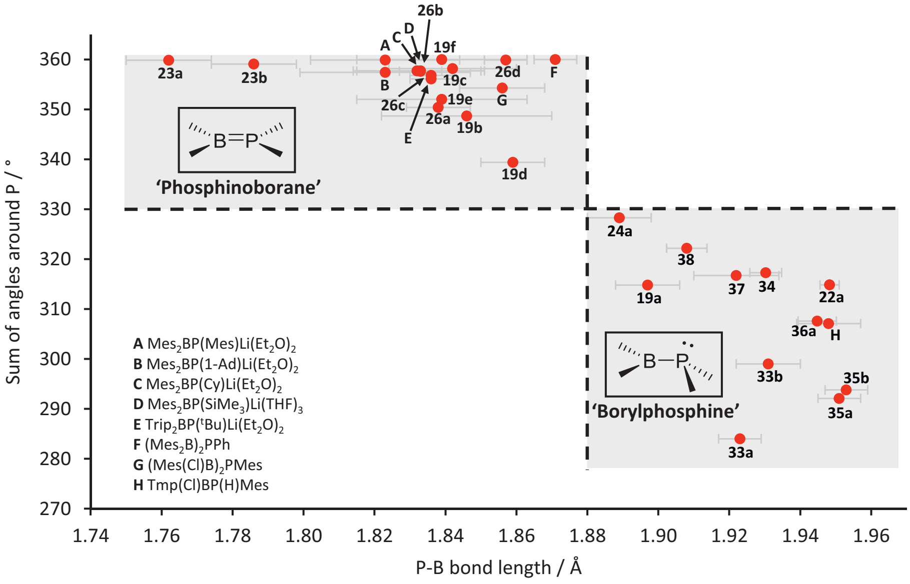

Fig. 2. Plot of the sum of the angles around phosphorus (°) against the P—B bond length (Å). Grey horizontal bars represent ± (3× esd). The geometrical data for structures **A–H** and **19a–f** were taken from reference [12]. The data for all other complexes can be found in Table 1. Mes = 2,4,6-$Me_3C_6H_2$, 1-Ad = 1-adamantyl, Trip = 2,4,6-$[(CH_3)_2CH]_3C_6H_2$, Tmp = 2,2,6,6-tetramethylpiperidino.