

N- versus P-co-ordination for N–B and P–B bonded BH₃ adducts for various phosphinamine ligands – An experimental and computational study



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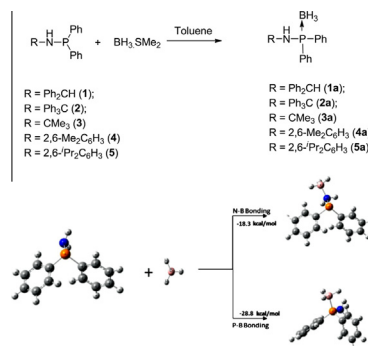
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HIGHLIGHTS

- Various phosphine–borane adducts were synthesized and structurally characterized.
- DFT calculation was carried out.
- Borane prefers to bind phosphorus atom rather than nitrogen atom.

GRAPHICAL ABSTRACT

Experimental and theoretical studies have been made to understand the P-coordination and N-coordination of various phosphinamines towards the borane group.



ARTICLE INFO

Article history:

Received 22 March 2013

Received in revised form 5 May 2013

Accepted 6 May 2013

Available online 17 May 2013

Keywords:

Phosphinamine

Borane

DFT calculation

X-ray analysis

P–B bond/N–B bond

ABSTRACT

The reaction between phosphinamines [Ph₂PNH(CHPh₂)] (1), [Ph₂PNH(CPh₃)] (2) [Ph₂PNH(CMe₃)] (3), [Ph₂PNH(2,6-Me₂C₆H₃)] (4), and [Ph₂PNH(2,6-ⁱPr₂C₆H₃)] (5) with BH₃.SMe₂ yields corresponding adduct [Ph₂P(BH₃)NH(CHPh₂)] (1a), [Ph₂P(BH₃)NH(CPh₃)] (2a), [Ph₂P(BH₃)NH(CMe₃)] (3a), [Ph₂P(BH₃)NH(2,6-Me₂C₆H₃)] (4a), and [Ph₂P(BH₃)NH(2,6-ⁱPr₂C₆H₃)] (5a) respectively. The solid state structures of all the compounds were established by single crystal X-ray diffraction analysis and in the solid state, all the compounds reveal that the phosphorus atom is preferably coordinated to the boron atom. Density functional theory (DFT) based electronic structure calculations were carried out taking various model phosphinamines to react with borane to establish the fact that the basicity of nitrogen atom adjacent to phosphorus in phosphinamines is reduced and thereby least preferred for coordination with borane.

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1. Introduction

Use of various P–N ligands is one of the alternatives of cyclopentadienyl ligands and using this approach, amide ligands are successfully used today for the design of new transition-metal compounds having well defined reaction centres [1,2]. Recently,

there has been a significant research effort in employing inorganic amines and imines. Various P–N systems like monophosphanyl-amides (R₂PNR') [3,4] diphosphanyl-amides ((Ph₂P)₂N) [4,5], phosphoraneiminato (R₃PN) [6], phosphiniminomethanides ((RNP₂)₂-CH), [7–9] phosphiniminomethandiides ((RNP₂)₂C), [10,11] and diiminophosphinates (R₂P(NR')) [12] are well known today as ligands and proved their potency into the transition and f-block metals. Roesky and co-workers introduced one chiral phosphinamine HN(CHMePh)(PPh₂) into the early transition-metal chemistry as well as in lanthanide chemistry [13]. The basicity of

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the nitrogen atom adjacent to phosphorus in aminophosphines has been the subject of much discussion [14]. It is accepted that in acyclic phosphinamines the tricoordinate nitrogen atom assumes a planar configuration with respect to its substituents and thus demonstrates diminished basicity due to enhanced N($p\pi$)–P($d\pi$) bonding [14,15]. Due to a lack of crystallinity, solid-state structural information on phosphinamine compounds in which phosphorus is trivalent is currently small compared to that for four-coordinate phosphorus compounds which is inadequate for comparison. Previous studies have indicated that acyclic phosphinamines behave as “P-donors only” in their reactions with Lewis acid diborane [16]. On the other hand, bis-(borane) adducts are known to form with phosphinamines of the type P(OCR₂CH₂)₂N (R = H, Me). Here the nitrogen atom in the constrained bicyclic structure possesses a pyramidal geometry, which presumably weakens the $p\pi$ – $d\pi$ interaction and enables nitrogen to exhibit a more basic character. [17] So far any computational studies are also not available to know more about $p\pi$ – $d\pi$ interaction between nitrogen and phosphorus atom. Krannich et al. reported by NMR studies, that even P–B bonded mono-adduct is thermodynamically preferable but B–P–N–B bonded bis-adduct and N–B bonded adduct could also be realized by varying the mole ratio of boranes [18]. However structural evidences were not provided. Very recently we have reported various phosphinamines [Ph₂PNH(CHPh₂)] (**1**), [Ph₂PNH(CPh₃)] (**2**) and [Ph₂PNH(CMe₃)] (**3**), [Ph₂PNH(2,6-Me₂C₆H₃)] (**4**), and [Ph₂PNH(2,6-ⁱPr₂C₆H₃)] (**5**) which were introduced in alkalimetal, alkaline earth metal and transition metal chemistry. [19–21] We were interested to address the basicity of the nitrogen as well as phosphorus atom in a phosphinamine ligand when it is reacted with borane to form an adduct. Herein we report the synthetic and structural details of five phosphinamine–borane adducts [Ph₂P(BH₃)NH(CHPh₂)] (**1a**), [Ph₂P(BH₃)NH(CPh₃)] (**2a**), [Ph₂P(BH₃)NH(CMe₃)] (**3a**), [Ph₂P(BH₃)NH(2,6-Me₂C₆H₃)] (**4a**), and [Ph₂P(BH₃)NH(2,6-ⁱPr₂C₆H₃)] (**5a**) along with a DFT study to compare the stability of the P–B bonded mono-adducts and N–B bonded mono-adducts of the various phosphinamines ligands.

2. Experimental

2.1. General

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{−4} torr) line, or in an argon-filled M. Braun glove box. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from LiAlH₄ and stored in the glove box. ¹H NMR (400 MHz), ¹³C{¹H}, ³¹P{¹H} NMR (161.9 MHz) and ¹¹B{¹H} (128.4 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. Starting materials [Ph₂PNH(CHPh₂)] (**1**), [Ph₂PNH(CPh₃)] (**2**) and [Ph₂PNH(CMe₃)] (**3**) [Ph₂PNH(2,6-Me₂C₆H₃)] (**4**), and [Ph₂PNH(2,6-ⁱPr₂C₆H₃)] (**5**) were prepared according to the literature procedure [19].

2.2. Synthesis of [Ph₂P(BH₃)NH(CHPh₂)] (**1a**) [22]

In a pre-dried schlenk flask 1.0 g (2.72 mmol) of N-benzhydryl-1,1diphenylphosphinamine (**1**) in 10 mL toluene was taken and to this borane-dimethylsulfide (0.26 mL, 2.72 mmol) in 5 mL of toluene was added drop wise under the stirring at room temperature. Stirring continued for 12 h. White precipitate was formed, and it

was filtered through G4-frit and dried *in vacuo*. Pure compound was obtained after washing with pentane. (Yield: 1.20 g, (100%). The title compound Ph₂P(BH₃)NHCHPh₂ (**1a**) is soluble in CDCl₃, CH₂Cl₂, THF and hot toluene. The compound **1a** was re-crystallized from hot toluene. ¹H NMR (400 MHz, CDCl₃): δ 7.44–7.49 (m, 4H, ArH), 7.34–7.38 (m, 2H, ArH), 7.24–7.28 (m, 4H, ArH), 7.05–7.19 (m, 10H, ArH), 5.45 (d, 1H, *J* = 9.4 Hz, CH), 2.83 (br, 1H, NH), 1.17 (br, 3H, BH₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.5 (ArC), 143.4 (ArC), 132.1 (P attached ArC), 131.9 (P attached ArC), 131.2 (P attached *o*-ArC), 131.1 (P attached *o*-ArC), 128.5 (P attached *p*-ArC), 128.4 (P attached *m*-ArC), 128.3 (*m*-ArC), 127.3 (*o*-ArC), 127.1 (*p*-ArC), 60.8 (CH) ppm. ³¹P{¹H}NMR (161.9 MHz, CDCl₃): δ 56.8 (d, *J* = 85.8 Hz) ppm. ¹¹B{¹H} NMR (128.4 MHz, CDCl₃): δ = −38.1 (br) ppm. FT-IR (selected frequencies): ν = 3338 (N–H), 1434 (P–C), 999 (P–N), 2383 (B–H), 602 (P–B) cm^{−1}. Elemental analysis calcd (%) for C₂₅H₂₅BNP (381.24): C 78.76, H 6.61, N 3.67; Found C 78.30, H 6.38, N 3.22.

2.3. Synthesis of [Ph₂P(BH₃)NH(CPh₃)] (**2a**)

Same as above for **1a**. Yield is 1.2 gm, (90%). ¹H NMR (400 MHz, CDCl₃): δ 7.43–7.48 (m, 4H, ArH), 7.29–7.33 (m, 2H, ArH), 7.20–7.25 (m, 4H, ArH), 7.16–7.19 (m, 6H, ArH), 7.08–7.11 (m, 9H, ArH), 3.45 (s, 1H, NH), 0.68 (br, 3H, BH₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 145.5 (ArC), 145.4 (ArC), 134.3 (P–ArC), 133.7 (P–ArC), 131.9 (P attached *o*-ArC), 131.8 (P attached *o*-ArC), 130.8 (P attached *p*-ArC), 130.7 (P attached *p*-ArC), 129.5 (*o*-ArC), 128.4 (P attached *m*-ArC), 128.3 (P attached *m*-ArC), 127.8 (*m*-ArC), 127.2 (*p*-ArC), 71.8 (CH) ppm. ³¹P–{¹H}NMR (161.9 MHz, CDCl₃): δ 53.3 (br, s) ppm. ¹¹B–{¹H} NMR (128.4 MHz, CDCl₃): δ −36.0 (br) ppm. FT-IR (selected frequencies): ν = 3212 (N–H), 1436 (P–C), 999 (P–N), 2386 (B–H), 609 (P–B) cm^{−1}. Elemental analysis calcd (%) for C₃₁H₂₉BNP (457.33): C 81.41, H 6.39, N 3.06; Found C 80.97, H 6.13, N 2.82.

2.4. Synthesis of [Ph₂P(BH₃)NH(CMe₃)] (**3a**)

Same as above for **1a**. Yield is 1.00 gm, (100%). ¹H NMR (400 MHz, CDCl₃): δ 7.71–7.76 (m, 4H, ArH), 7.40–7.49 (m, 6H, ArH), 2.05 (bs, 1H, NH), 1.29 (s, 9H, CH₃), 1.17 (br, 3H, BH₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 134.5 (P attached ArC), 133.9 (P attached ArC), 131.8 (P attached *o*-ArC), 131.0 (P attached *p*-ArC), 128.5 (P attached *m*-ArC), 128.4 (P attached *m*-ArC), 53.6 (quaternary C), 32.1 (CH₃) ppm. ³¹P–{¹H}NMR (161.9 MHz, CDCl₃): δ 49.6 (d, *J*_{P–B} = 74 Hz) ppm. ¹¹B–{¹H} NMR (128.4 MHz, CDCl₃): δ 39.9 (br) ppm. FT-IR (selected frequencies): ν = 3374 (N–H), 1435 (P–C), 912 (P–N), 2385 (B–H), 600 (P–B) cm^{−1}. Elemental analysis calcd (%) for C₁₆H₂₃BNP (271.13): C 70.87, H 8.55, N 5.17; Found C 70.48, H 8.29, N 4.93.

2.5. Synthesis of [Ph₂P(BH₃)NH(2,6-Me₂C₆H₃)] (**4a**)

Same as above for **1a**. Yield is 1.07 gm, (97%). ¹H NMR (400 MHz, CDCl₃): δ 7.73–7.78 (m, 4H, P attached ArH), 7.26–7.51 (m, 6H, P attached ArH), 6.95 (s, 3H, ArH), 3.83 (br, 1H, NH), 2.00 (s, 6H, CH₃), 0.88 (br, 3H, BH₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 137.9 (ArC), 136.1 (P–ArC), 131.8 (P attached *o*-ArC), 131.7 (P attached *o*-ArC), 131.3 (P attached *p*-ArC), 128.6 (P attached *m*-ArC), 128.4 (P attached *m*-ArC), 128.4 (*m*-ArC), 125.8 (*o*-ArC) 45.8 (CH₃) ppm. ³¹P–{¹H}NMR (161.9 MHz, CDCl₃): δ 49.6 (d, *J*_{P–B} = 74 Hz) ppm. ¹¹B–{¹H} NMR (128.4 MHz, CDCl₃): δ −39.2 (br) ppm. FT-IR (selected frequencies): ν = 3296 (N–H), 1433 (P–C), 930 (P–N), 2398 (B–H), 604 (P–B) cm^{−1}. Elemental analysis calcd (%) for C₂₀H₂₃BNP (319.17): C 75.26, H 7.26, N 4.39; Found C 74.89, H 6.91, N 4.02.

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