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Syntheses and structures of dimeric sodium and potassium complexes of 2,6-diisopropyl-anilidophosphine borane ligand

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Abstract. We report here the syntheses and structural studies of dimeric sodium and potassium complexes of composition $[Na(THF)_2\{Ph_2P(BH_3)N(2,6\text{-}^iPr_2C_6H_6)\}]_2$ (**2**) and $[K(THF)_2\{Ph_2P(BH_3)N(2,6\text{-}^iPr_2C_6H_6)\}]_2$ (**3**). The sodium complex **2** was readily prepared by the reaction of sodium bis(trimethylsilyl)amide with 2,6-diisopropylanilidophosphine-borane ligand $[2,6\text{-}^iPr_2C_6H_3NHP(BH_3)Ph_2]$ (**1-H**) at ambient temperature. The potassium complex **3** was prepared by two synthetic routes: in the first method, the ligand **1-H** was made to react with potassium hydride at room temperature to afford the corresponding potassium complex. The potassium bis(trimethylsilyl)amides were made to react with protic ligand **1-H** in the second method to eliminate the volatile bis(trimethyl)silyl amine. Solid-state structures of both the new complexes were established by single crystal X-ray diffraction analysis. In the molecular structures of complexes **2**, the sodium metal is coordinated by the anilido nitrogen (η^1) and borane group (η^1) attached to the phosphorus atom of ligand **1**. In contrast, for compound **2**, ligand **1** displays $\eta^6\pi$-arene interaction from 2,6-diisopopylphenyl ring with potassium atom along with η^3 interaction of BH_3 group due to larger ionic radius of potassium ion.

Keywords. Sodium; potassium; π-arene interaction; borane; phosphorus.

1. Introduction

Various P–N ligands are one of the alternatives of well-known cyclopentadienyl and its derivative ligands, which are successfully used today in the design of new transition-metal compounds having well-defined reaction centres.[1,2] Recently, there has been significant research effort in employing inorganic amines and imines to study coordination chemistry. The P–N ligand systems such as monophosphanylamides (R_2PNR')[3–7] diphosphanylamides ($(Ph_2P)_2N$),[4,8–11] phosphoraneiminato (R_3PN),[12,13] phosphiniminomethanides ($(RNPR'_2)_2CH$),[15–22] phosphinimin-methandiides ($(RNPR'_2)_2C$),[23–27] and diimino-phosphinates ($R_2P(NR')$)[28–31] are well-known as ligands and have proved their importance in transition and rare earth metal chemistry. We have recently introduced a series of phosphineamines $[Ph_2PNHR]$ (**A**) (R = 2,6-$Me_2C_6H_3CHPh_2$, CPh_3) and their chalcogen derivatives $[Ph_2P(O)NHR]$ (**NPO**), $[Ph_2P(S)NHR]$ (**NPS**) and $[Ph_2P(Se)NHR]$ (**NPSe**) (chart 1) to the chemistry of alkali metals and the heavier alkaline earth metals.[32–39] Phosphineamine **A** can coordinate with metals through the nitrogen and phosphorus atoms resulting in a highly strained three-membered metallacycle as reported by Roesky and others.[40–44] Thus, due to the presence of three adjacent potential donor atoms, the polymetallacyclic structural motif of the metal complexes was explored. The basicity of the nitrogen atom adjacent to the phosphorus atom in the amidophosphines (**A**) has remained the driving factor in the ability of the nitrogen and the phosphorus to effectively coordinate with an electron-deficient group. It is well-accepted that in acyclic phosphineamines the tricoordinate nitrogen atom assumes a planar configuration with respect to its substituents and thus demonstrates diminished basicity due to enhanced N(pπ)-P(dπ) bonding.[45–53] Very recently, the Verdaguer and Kolodiazhnyi groups reported a series of chiral aminophosphine borane compounds and their applications in asymmetric catalysis and hydrogenolysis.[54,55] However, reports of their use as coordinating ligands towards alkali metals and alkaline earth metals are not available to date. In the continuation of our study to develop **NPB** ligand (chart 1), we have recently prepared $\{(Ph_2CHNHP(BH_3)Ph_2)\}$ and introduced it into alkali and alkaline earth metal chemistry.[56,57] We have observed that depending on the steric bulk present in the nitrogen and ionic radius of the metal ion, BH_3 group coordinates either as η^1 or η^3

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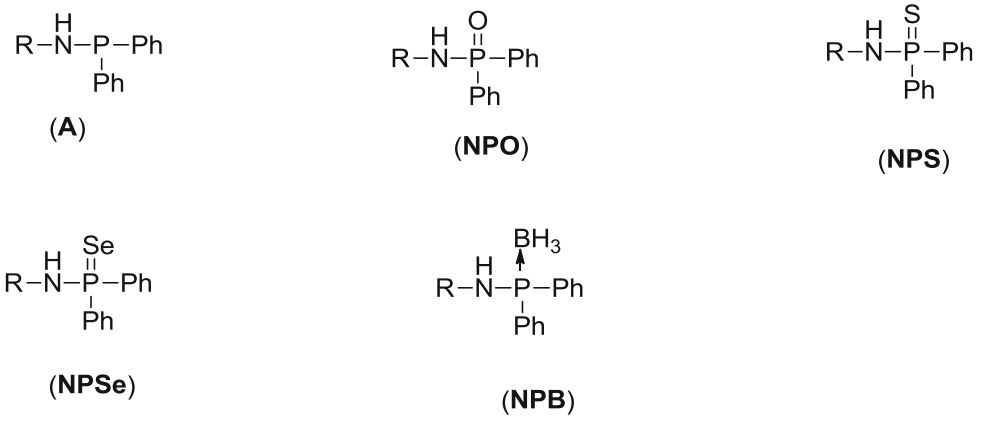


Chart 1. Various phosphinamines and its chalcogen and borane derivatives.

modes. To gain more insight, we planned to introduce more bulky 2,6-diisopropyl anilidophosphine borane into the alkali metal chemistry as the precursor compound. The bonding in alkali metal complexes can help us understand the coordination behaviour of alkaline earth metal complexes as group 1 and 2 metals have a number of similarity in corresponding organometallic complexes.

In this context, detailed synthetic and structural features of the sodium and potassium anilidophosphine-borane complexes with the composition $[Na(THF)_2\{Ph_2P(BH_3)N(2,6\text{-}^{i}Pr_2\text{-}C_6H_3)\}]_2$ (**2**) and $[K(THF)_2\{Ph_2P(BH_3)N(2,6\text{-}^{i}Pr_2\text{-}C_6H_3)\}]_2$ (**3**) are presented.

2. Experimental

2.1 *General information*

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. THF was pre-dried over a sodium wire and distilled under nitrogen from sodium and benzophenoneketyl prior to use. *n*-Pentane was distilled under nitrogen from $LiAlH_4$ and stored in the glove box. ^1H NMR (400 MHz), $^{11}B\{^1H\}$ (128.3 MHz) and $^{31}P\{^1H\}$ NMR (161.9 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. $[KN(SiMe_3)_2]$,[58] and [CR2,CR6-$^{i}Pr_2C_6H_3NHP(BH_3)Ph_2$] (**1-H**)[56] were prepared according to published procedures. $[NaN(SiMe_3)_2]$ and KH were purchased from Sigma Aldrich and used without further purification.

2.2 *Synthesis of* $[Na(THF)_2\{Ph_2P(BH_3)N(2,6\text{-}^{i}Pr_2C_6H_3)\}]_2$ (*2*)

In a dry 50 mL Schlenk flask, *N*-(2,6-diisopropylphenyl)-diphenylphosphinamine (200 mg, 0.533 mmol) was placed and 5 mL of THF was added to it. To this resulting solution, a THF solution of $[NaN(SiMe_3)_2]$ (97.73 mg, 0.533 mmol and 5 mL THF) was added dropwise at room temperature. The reaction mixture was kept under stirring for 6 h. Then, the solvent was evaporated under *vacuo*, to result a white residue. The title compound was re-crystallized from a solution of THF and *n*-pentane (3:1) at −40°C.

Yield: 242 mg (84%).

^1H NMR (400 MHz, C_6D_6): δ 7.86−7.78 (m, 4H, ArH), 7.10−7.05 (m, 8H, ArH), 7.00−6.96 (m, 1H, ArH), 3.68 (sept, $^1J_3 = 6.3$ Hz. 2H, $CH(CH_3)_2$), 3.44 (br, THF), 1.32 (br, THF), 0.95 (d, $^1J_3 = 5.32$ Hz. 12H, CH_3), 0.21 (br, 3H, BH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 152.2 (ipso-ArC), 145.8 (*o*-ArC), 143.7 (*ipso*-Ph), 130.4 (o-Ph), 129.8 (m-Ph), 127.5 (o-Ph), 124.3 (m-ArC), 117.9 (p-ArC), 65.4 (THF), 28.7 ($CH(CH_3)_2$), 25.4 (THF), 24.4 ($CH(CH_3)_2$) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 36.4 (d, $J_{P-B} = 165.5$ Hz) ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6): δ−34.6 (d) ppm. FT-IR (selected frequencies): ν 2384 (B−H), 1435 (P−C), 932 (P−N), 608 (P−B) cm^{-1}. Elemental analysis: $C_{64}H_{92}B_2N_2Na_2O_4P_2$ (1082.98); Calculated: C 70.98 H 8.56 N 2.59, Found: C 70.28 H 7.99 N 2.15.

2.3 *Synthesis of* $[K(THF)_2\{Ph_2P(BH_3)N(2,6\text{-}^{i}Pr_2\text{-}C_6H_3)\}]_2$ (*3*)

Route 1: In a dry 50 mL Schlenk flask, potassium hydride (25.65 mg, 0.64 mmol) was measured; and to this 10 mL of THF was added. To this solution, *N*-(2,6-diisopropylphenyl)-diphenylphosphinamine (200 mg,

0.533 mmol) in 10 mL THF was slowly added. Resulting reaction mixture was kept under stirring for 6 h at room temperature. Reaction mixture was filtered and evaporated under *vacuo*; the white residue obtained was re-crystallized from THF/*n*-pentane (3:1) solution at −40°C. Yield: 460 mg (73%).

Route 2: In dry 50 mL Schlenk flask, *N*-(2,6-diisopropylphenyl)-diphenylphosphinamine (200 mg, 0.533 mmol) was measured; to this 15 mL of THF was added. Further [$KN(SiMe_3)_2$] (106.32 mg, 0.533 mmol and 10 mL THF) was added drop-wise. Resulting reaction mixture was placed under stirring at room temperature. After 6 h, reaction mixture was evaporated under *vacuo* and white residue was obtained. The title compound was re-crystallized from THF-/*n*-pentane (3:1) mixture at −40°C. Yield: 442 mg (70%).

^{1}H NMR (400 MHz, C_6D_6): δ 8.00−7.95 (m, 4H, ArH), 7.18−7.15 (m, 4H, ArH), 7.09−7.05 (m, 2H, ArH), 7.00−6.98 (m, 1H, ArH), 3.68 (m, 2H, C*H*$(CH_3)_2$), 3.40 (br, THF), 1.35 (br, THF), 1.06 (d, J = 6.80 Hz. 12H, CH(C*H*$_3)_2$), 0.65 (br, 3H, BH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, C6D6): δ 152.8 (*ipso*-ArC), 145.1 (*o*-ArC), 142.7 (*ipso*-Ph), 131.5 (*o*-Ph), 129.1 (*m*-Ph), 128.0 (*o*-Ph), 123.1 (*m*-ArC), 118.2 (*p*-ArC), 67.8 (THF), 28.4 (*C*H$(CH_3)_2$), 25.6 (THF), 24.0 (CH(*C*H$_3)_2$) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 36.9 (d, J_{P-B} = 145.7 Hz) ppm. ^{11}B{^{1}H} NMR (128.3 MHz, C_6D_6): δ−34.5 (br) ppm. FT-IR (selected frequencies): ν 2382 (B−H), 1435 (P−C), 933 (P−N), 608 (P−B) cm^{-1}. Elemental analysis: $C_{136}H_{200}B_4K_4N_4O_{10}P_4$ (2374.32); Calculated: C 68.79 H 8.49 N 2.36, Found: C 68.22 H 8.09 N 2.12.

2.4 *Single-crystal X-ray structure determinations*

Single crystals of compounds **2** and **3** were grown from a solution of THF/pentane mixture (3:1) under inert atmosphere at a temperature of −40°C. In each case, a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were made on an Agilent Supernova X-calibur Eos CCD detector with graphite-monochromatic CuKα (1.54184 Å) radiation. Crystal data and structure refinement parameters are summarised in table 1. The structures were solved by direct methods (SIR92)[59] and refined on F^2 by full-matrix least-squares methods; using SHELXL-97.[60] Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement at calculated positions riding on their carrier atoms. The function minimised was $[\Sigma w(Fo^2 - Fc^2)^2]$ (w = $1/[\sigma^2 (F_o^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(F_o^2,0) + 2Fc^2) / 3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions of R_1 and wR_2 were $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this study have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication, Nos. CCDC 1025326 (**2**), 1025326 (**3**), Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + (44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

3. Results and Discussion

3.1 *Alkali metal complexes*

The sodium complex [$Na(THF)_2\{Ph_2P(BH_3)N(2,6\text{-}^iPr_2C_6H_6)\}]_2$ (**2**) was readily prepared in good yield by the reaction of sodium bis(trimethylsilyl)amide with 2,6-diisopropylanilidophosphine borane (**1-H**) in 1:1 molar ratio in THF at room temperature via the elimination of volatile hexamethyldisilazane (scheme 1). The potassium complex [$K(THF)_2\{Ph_2P(BH_3)N(2,6\text{-}^iPr_2C_6H_6)\}]_2$ (**3**) was obtained by two routes. In the first method, potassium hydride was used to react with ligand **1-H** to give complex **3** in good yield (scheme 1). In the second route, similar to complex **2**, the protic ligand **1-H** was reacted with potassium bis(trimethylsilyl)amide in THF in 1:1 molar ratio to afford complex **3** in good yield. The sodium complex **2** and the potassium complex **3** were re-crystallized from a mixture of THF/*n*-pentane (3:1). Both the complexes were characterized by spectroscopic/analytical techniques and the molecular structures of complexes **2** and **3** were established by single crystal X-ray diffraction analysis.

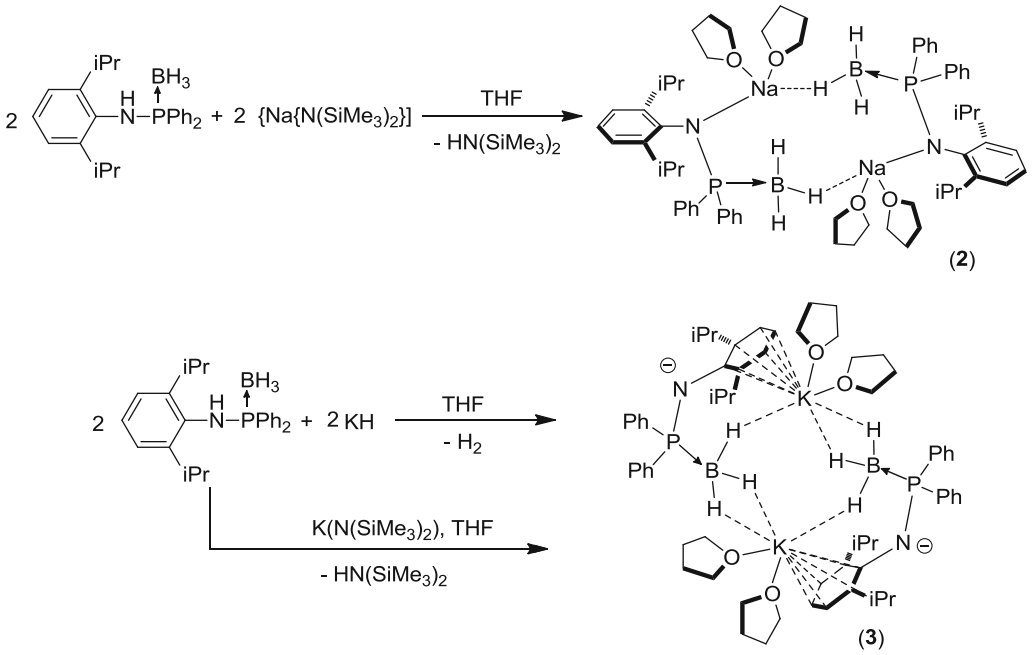
In the FT-IR spectra, the characteristic signal for the P−B bond stretching at 608 cm^{-1} for complexes **2** and **3** were observed along with another characteristic signal at 2382 cm^{-1} for **2**, (2384 cm^{-1} for **3**) assigned to the B−H stretching frequency. These values correspond well with the values (600 and 2381 cm^{-1}) of the neutral ligand **1** as reported by us.[56] Both the reactions for synthesis of sodium and potassium complexes (route 1 for **3**) can be monitored by ^{1}H NMR spectroscopy as one can observe the rapid disappearance of amine proton NH signal (3.71 ppm) of **1-H** due to deprotonation. In ^{1}H NMR spectra measured in C_6D_6, the characteristic septet signals due to isopropyl CH protons for both the compounds **2** and **3** were observed at δ 3.68 ppm

Table 1. Structural and refinement parameters for complexes **2** and **3**.

Crystal	**2**	**3**
CCDC No.	1025326	1025327
Empirical formula	$C_{64}H_{92}B_2N_2Na_2O_4P_2$	$C_{136}H_{200}B_4K_4N_4O_{10}P_4$
Formula weight	1082.94	2374
T(K)	150(2)	150(2) K
λ (Å)	1.54184	1.54184
Crystal system	Monoclinic	Triclinic
Space group	$P\,2_1/c$	*P-1*
a (Å)	12.5432(3)	10.6594(7)
b (Å)	18.7979(5)	13.5838(10)
c (Å)	29.4544(6)	23.9072(13)
α (°)	90	93.998(5)
β (°)	111.617(2)	96.214(5)
γ (°)	90	96.133(6)
V (Å^3)	6456.5(3)	3410.0(4)
Z	4	1
D_{calc} Mg cm^{-3}	1.114	1.156
μ (mm^{-1})	1.084	2.034
F (000)	2336	1599
Theta range for data collection	3.23 to 70.61 deg.	3.28 to 70.76 deg.
Limiting indices	$-15 <= h <= 13$ $-18 <= k <= 22$ $-34 <= l <= 35$	$-12 <= h <= 13$ $-16 <= k <= 16$ $-29 <= l <= 19$
Reflections collected/unique	28296/12168 [R(int) = 0.0298]	26057/12819 [R(int) = 0.0311]
Completeness to theta	98.2%	97.7%
Absorption correction	Semi-empirical	Semi-empirical
Maximum and minimum transmission	1.0000 and 0.78285	1.00000 and 0.63162
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	12168/0/717	12819/0/737
Goodness-of-fit on F^2	1.041	1.054
Final R indices [I > 2sigma(I)]	R1 = 0.0493 wR2 = 0.1299	R1 = 0.0693 wR2 = 0.1958
R indices (all data)	R1 = 0.0580 wR2 = 0.1386	R1 = 0.0784 wR2 = 0.2066
Largest difference peak and hole	0.695 and −0.801 e.A^{-3}	1.515 and −0.830 e.A^{-3}

along with coupling constant $^3J_{H-H}$ of 6.3 Hz and those are high field shifted with respect to **1-H** (δ 2.91 ppm. Multiplet resonance signals in the region of δ 8.00−7.95 ppm and δ 7.18−7.15 ppm represent the aromatic phenyl ring protons and are almost unaffected in comparison to neutral ligand **1-H** after complex formation. In $^{31}P\{^1H\}$ NMR spectra, each complex exhibits a doublet signal at δ 36.4 (**2**) and 36.9 ppm (**3**), respectively. Thus, for both the complexes **2** and **3**, the resonance for the phosphorus atom is shifted to high field with respect to that of neutral ligand **1-H** (54.6 ppm). This result can be attributed to the fact that the phosphorus atom is highly influenced by the electron-deficient borane (BH_3) group attached to it. The doublet signal is caused by the coupling between ^{31}P and ^{11}B atoms adjacent to each other, and a coupling constant (165.5 Hz for **2**) is observed (see supplementary information). However, the doublet is not well-resolved due to the presence of ^{10}B nuclei, which is NMR active as well. Similar observation is reported in literature.[57] In the $^{11}B\{^1H\}$ NMR spectra, we observed broad doublets at δ − 34.6 and −34.5 ppm for **2** and **3**, respectively, and the broadening is presumably caused by coupling to the adjacent phosphorus atom (figure 1).

The diamagnetic sodium complex **2** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. In contrast, the analogous potassium complex **3** crystallizes in triclinic space group $P-1$ with two independent molecules in the asymmetric unit. Details of the structural and refinement parameters for **2** and **3** are provided in table 1. Molecular structures of complexes **2** and **3** are shown in figures 2 and 3,



Scheme 1. Synthesis of complexes **2** and **3** from 2,6-diisopropyl-anilidiphosphine borane ligand **1-H**.

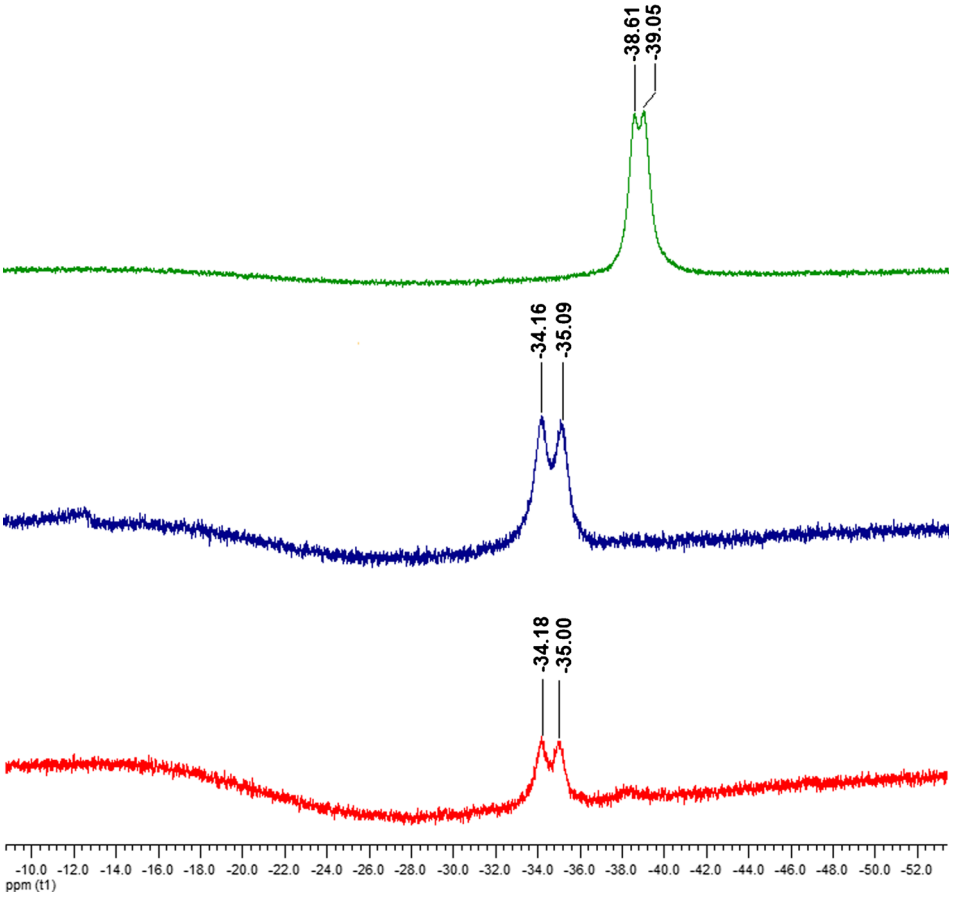


Figure 1. $^{11}B\{^{1}H\}$ NMR spectra for compounds **1, 2** and **3**.

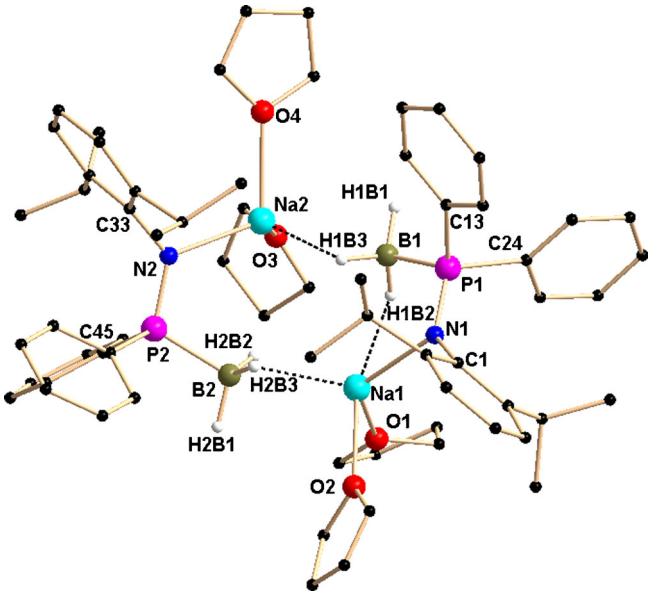


Figure 2. Molecular structure of complex **2**. Hydrogen atoms (except H1B1, H1B2, H1B3, H2B1, H2B2, and H2B3) are omitted for clarity. Selected bond distances (Å) and angles (°). Na1-N1 2.3828(16), Na1-B2 2.839(2), Na1-P1 3.3056(8), Na1-B1 3.028(2), Na1-H2B3 2.29(2), P1-N1 6015(15), P1-B1 1.920(2), P2-N2 1.6051(15), P2-B2 1.914(2), Na2-B1 2.877(2), Na2-H1B3 2.24(2), Na2-N2 2.3363(16), Na2-P2 3.4184(8), Na2-O4 2.3794(16), Na2-O3 2.3319(15), Na1-O1 2.3112(17), Na1-O2 2.3631(18), P1-N1-Na1 110.59(7), N1-P1-B1 106.72(9), P1-B1-Na2 147.18(12), P2-N2-Na2 119.13(8), N2-P2-B2 110.20(9), P2-B2-Na1 148.54(12).

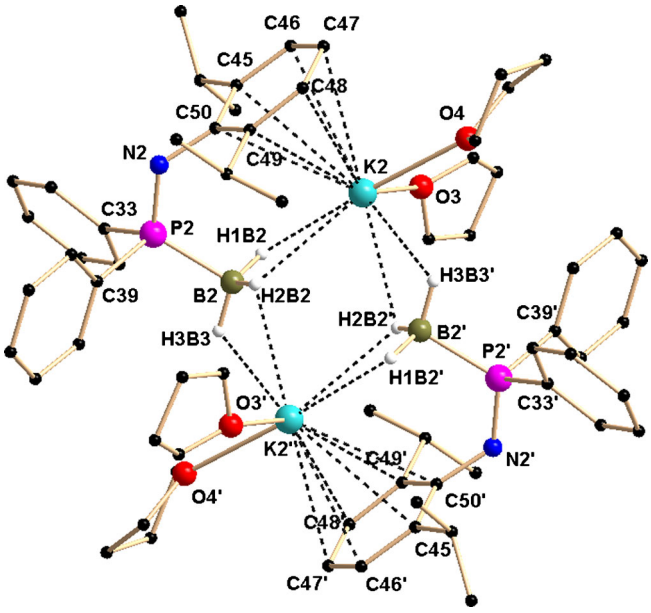


Figure 3. Molecular structure of complex **3**. Hydrogen atoms (except H1B2, H2B2, H3B3, H2B2′, H1B2′ and H1B3′) are omitted for clarity. Selected bond distances (Å) and angles (°). K1-B1 3.294(4), K1-H1B1 2.77(3), K1-H2B1 2.88(4), K1-O2 2.678(3), K1-C13 3.202(3), K1-C15 3.303(3), K1-C17 3.303(3), K1-O2 2.678(3), K1-O1 2.655(3), K1-B1′ 3.275(3), B1-H1B1 1.18(4), B1-H2B1 1.12(4), P1-B1 1.930(3), P1-N1 1.596(2), N1-C13 1.391(3), N1-P1-B1 118.30(14), P1-B1-K1 106.16(14), C13-K1-B1 64.34(8), C13-N1-P1 127.5(2), K1′-B1-K1 98.46(9), B1′-K1-B1 81.54(9).

respectively. In the solid state, the sodium complex **2** is non-centrosymmetric and dimeric in nature. The coordination polyhedron is formed by the ligation of two anilidophosphine−borane ligands **1** and two THF molecules. Each of the sodium ions is chelated by one anilido nitrogen atom from ligand **1** and borane group through η^1 coordination of one hydrogen atom with Na1–B2 bond distance of 2.839(2) Å and a Na2–B1 bond distance of 2.877(2) Å along with two additional THF molecules. Thus, the geometry around each sodium ion can be best described as distorted tetrahedral. Similar η^1 connectivity of boranes has been reported by us and other research groups.[57,61] Chelation from ligand **1** to two sodium atoms via two amido nitrogen atoms and hydrogen atoms of the two BH_3 groups exhibits a tub-shaped $Na_2P_2N_2(BH_3)_2$ core with mean bond angles N1–P1–B1 106.72(9)° and N2–P2–B2 110.20(9)°. The Na1–P1 3.3056(8) distance of 3.3056(8) Å is slightly longer than the bond distances of 2.9661(17) and 2.9474(16) Å reported for [[{$(Me_3Si)_2CH$} $P(BH_3)(C_6H_4$-2-SMe)}] $[Na(tmeda)]_\infty$ by Izod and co-workers,[62] and it is larger than the sum of the covalent radii (3.00 Å) of sodium and phosphorus. Thus, it can be concluded that no interaction between phosphorus and sodium atoms is observed. The bond distances Na1–N1 2.3828(16), Na1–O1 2.3112(17), and Na1–O2 2.3631(18) Å are in the range of previously reported values.[63] The P1–B1 bond distance (1.920(2) Å) remains almost unchanged compared to that of the free ligand **1-H** (1.908(3) Å). In multinuclear NMR, only one set of signals are observed due to the fluxional behaviour of the sodium complex **2** (vide supra).

Unlike the sodium complex **2**, the potassium complex **3** is centrosymmetric and dimeric in nature. The coordination polyhedron is formed by the borane groups and the phenyl ring carbon atoms are present in the anilidophosphine borane ligand **1**. It is noteworthy that the anionic amido nitrogen is not bonded to the positively charged potassium ion due to high steric congestion of ligand. As a result, each potassium ion is coordinated by the hydrogen atoms of two BH_3 groups via η^3 mode and adjacent anilido-phenyl ring π-electron density through η^6 coordination mode. This moiety demonstrates a preference for π-arene interactions over conventional amido donation. This

manifests itself as two η^6:η^3-bound NPB ligand, which is observed for the first time to the best of our knowledge for a ligand having nitrogen, phosphorus and boron atoms. Recent studies by Junk *et al.* reported that similar phenomena in potassium chemistry are observed for sterically hindered amido and formamidinate ligands, respectively.[64,65] Thus, complex **3** exhibits a diamond-shaped $K_2(BH_3)_2$ core with a mean B1−K1−B1′ bond angle of 81.54(9)° and a mean K1−B1−K1′ bond angle of 98.46(9)°. Each BH_3 group of the two ligands coordinates with two potassium atoms in a η^3 fashion through the hydrogen atoms of BH_3 group with a K1−B1 bond length of 3.294(4) Å and a K1−B1′ bond length of 3.275(3) Å, which are in the range of the previously reported $[\{(\eta^2\text{-}Ph_2CHNP(BH_3)Ph_2)K(THF)_2\}_2]$ complex.[57] The P1–N1 bond distance of 1.596(2) Å is similar to ligand **1-H** (1.6561(19) Å). Intuitively, orientation of the anilidophosphine units in **3** generates the least steric buttressing (see figure 3). However, the preference for arene π-electron density and the absence of amido donors, and therefore the existence of two metal environments, is highly unorthodox. Each of the potassium ions in complex **3** resides in distorted trigonal bipyramidal environment, considering the anilidophosphine borane ligand as pseudo bidentate ligand, where two THF and one BH_3 molecules occupy equatorial positions.

4. Conclusion

We have demonstrated the syntheses and structural features of two dimeric complexes of sodium and potassium from sterically bulky anilidophosphine borane ligand. From the molecular structure, it was observed that ligand **1** coordinated with each sodium atom through anilido nitrogen and BH_3 group. In contrast, each potassium ion in complex **3** prefers η^6 arene interaction with the anilido aromatic π electrons and η^3 coordination with BH_3 group present in ligand **1** due to steric crowding of coordinating ligand. The unique feature of ligand **1**, with three potential donor atoms/group, nitrogen, phosphorus and BH_3, makes a clear distinction in molecular structure between the sodium and potassium complexes. Further reactivity studies on these complexes are underway in our laboratory.

Supplementary Information

The ^1H, $^{31}P\{^1H\}$ NMR spectra of compounds **2** and **3** (figures S1–S4) are given in supplementary information (see www.ias.ac.in/chemsci).

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References

1. Britovsek G J P, Gibson V C and Wass D F 1999 *Angew. Chem. Int. Ed.* **38** 428
2. Kempe R 2000 *Angew. Chem. Int. Ed.* **39** 468
3. Fenske D, Maczek B and Maczek K 1997 *Z. Anorg. Allg. Chem.* **623** 1113
4. Kuehl O, Koch T, Somoza F B, Junk P C, Hey-Hawkins E, Plat D, and Eisen M S 2000 *J. Organomet. Chem.* **604** 116
5. Kuehl O, Junk P C and Hey-Hawkins E 2000 *Z. Anorg. Allg. Chem.* **626** 1591
6. Wetzel T G, Dehnen S and Roesky P W **1999** *Angew. Chem. Int. Ed.* **38** 1086
7. Wingerter S, Pfeiffer M, Baier F, Stey T and Stalke D 2000 *Z. Anorg. Allg. Chem.* **626** 1121
8. Roesky P W, Gamer M T, Puchner M and Greiner A 2002 *Chem. Eur. J.* **8** 5265
9. Braunstein P, Durand J, Kickelbick G, Knorr M, Morise X, Pugin R, Tiripicchio A and Ugozzoli F 1999 *Dalton Trans.* 4175
10. Knoerr M and Strohmann C 1999 *Organometallics* **18** 248
11. Braunstein P, Cossy J, Knorr M, Strohmann C and Vogel P 1999 *New J. Chem.* **23** 1215
12. Dehnicke K and Weller F 1997 *Coord. Chem. Rev.* **158** 103
13. Dehnicke K, Krieger M and Massa W 1999 *Coord. Chem. Rev.* **182** 19
14. Panda T K and Roesky P W 2009 *Chem. Soc. Rev.* **38** 2782
15. Imhoff P, Guelpen J H,Vrieze K, Smeets W J J, Spek A L and Elsevier C J 1995 *Inorg. Chim. Acta* **235** 77
16. Avis M W, van der Boom M E, Elsevier C J, Smeets W J J and Spek A L 1997 *J. Organomet. Chem.* **527** 263
17. Avis M W, Elsevier C J, Ernsting J M, Vrieze K, Veldman N, Spek A L, Katti K V and Barnes C L 1996 *Organometallics* **15** 2376
18. Avis M W, Vrieze K, Kooijman H, Veldman N, Spek A L and Elsevier C J 1995 *Inorg. Chem.* **34** 4092
19. Imhoff P, Asselt R V, Ernsting J M, Vrieze K, Elsevier C J, Smeets W J J, Spek A L and Kentgens A P M 1993 *Organometallics* **12**, 1523
20. Ong C M, McKarns P and Stephan D W 1999 *Organometallics* **18** 4197
21. Gamer M T, Dehnen S and Roesky P. W 2001 *Organometallics* **20** 4230
22. Aharonian G, Feghali K, Gambarotta S and Yap G P A 2001 *Organometallics* **20** 2616

23. Cavell R G, Kamalesh Babu R P and Aparna K 2001 *J. Organomet. Chem.* **617–618** 158
24. Kamalesh Babu R P, McDonald R and Cavell R G 2000 *Chem. Commun.* 481
25. Aparna K, Kamalesh Babu R P, McDonald R and Cavell R G 2001 *Angew. Chem. Int. Ed.* **40** 4400
26. Kasani A, Kamalesh Babu R P, McDonald R and Cavell R G 1999 *Organometallics* **18** 3775
27. Aparna K, McDonald R, Fuerguson M and Cavell R G 1999 *Organometallics* **18** 4241
28. Edelmann F T 1996 *Top. Curr. Chem.* **179** 113
29. Reissmann U, Poremba P, Noltemeyer M, Schmidt H G and Edelmann F T 2000 *Inorg. Chim. Acta* **303** 156
30. Recknagel A, Steiner A, Noltemeyer M, Brooker S, Stalke D and Edelmann F T 1991 *J. Organomet. Chem.* **414** 327
31. Recknagel A, Witt M and Edelmann F T 1989 *J. Organomet. Chem.* **371** C40
32. Naktode K, Kottalanka R K and Panda T K 2012 *New J. Chem.* **36** 2280
33. Kottalanka R K, Naktode K and Panda T K 2013 *J. Mol. Str.* **1036** 188
34. Kottalanka R K, Naktode K, Anga S, Nayek H P and Panda T K 2013 *Dalton Trans.* **42** 4947
35. Naktode K, Kottalanka R K, Jana S K and Panda T K 2013 *Z. Anorg. Allg. Chem.* **639** 999
36. Kottalanka R K, Anga S, Jana S K and Panda T K 2013 *J. Organomet. Chem.* **740** 104
37. Kottalanka R K, Adimulam H, Bhattacharjee J, Vignesh Babu H and Panda T K 2014 *Dalton Trans.* **43** 8757
38. Naktode K, Das Gupta S, Kundu A, Jana S K, Nayek H P, Mallik B S and Panda T K 2014 *Aust. J. Chem.* 10.1071/CH14078
39. Bhattacharjee J, R K Kottalanka, Adimulam H and Panda T K 2014 *J. Chem. Sci.* doi: 10.1007/s12039-014-0711-z
40. Wiecko M, Gimt D, Rastatter M, Panda T K and Roesky P W 2005 *Dalton Trans.* **36** 2147
41. Panda T K, Gamer M T and Roesky P W 2006 *Inorg. Chem.* **45** 910
42. Agarwal S, Mast C, Dehnicke K and Greiner A 2000 *Macromol. Rapid Commun.* **21** 195
43. Ravi P, Groeb T, Dehnicke K and Greiner A 2001 *Macromolecules* **34** 8649
44. Halcovitch N R and Fryzuk M D 2012 *Dalton Trans.* **41** 1524
45. Cowley A H, Lattman M, Stricklen P M and Verkade J G 1982 *Inorg. Chem.* **21** 543
46. Gonbeau D, Sanchez M and Pfister- Guillouzo G 1981 *Ibid.* **20** 1966
47. Worley S D, Hargis J H, Chang L, Mattson G A and Jennings W B 1979 *Inorg. Chem.* **18** 3581
48. Kroshefsky R D, Weiss R and Verkade J G 1979 *Inorg. Chem.* **18** 469
49. Kroshefsky R D, Verkade J G and Pipal J R 1979 *Phosphorus Sulfur* **6** 377
50. Kroshefsky R D and Verkade J G 1979 *Phosphorus Sulfur* **6** 391
51. Vande Griend L J, Verkade J G, Pennings J F M and Buck H M 1977 *J. Am. Chem. Soc.* **99** 2459
52. Hodaes R V, Houle F A, Beauchamp J L, Montag R A and Verkade J G 1980 *J. Am. Chem. Soc.* **102** 932
53. Lee T H, Jolly W L, Bakke A A, Weiss R and Verkade J G 1980 *J. Am. Chem. Soc.* **102** 2631
54. Reves M, Ferrer C, Leon T, Doran S, Etayo P, Ferran A V, Riera A and Verdaguer X 2010 *Angew. Chem. Int. Ed.* **49** 9452
55. Kolodiazhnyi O I, Gryshkun E V, Andrushko N V, Freytag M P, Jones G and Schmutzler R 2003 *Tetrahedron: Asymmetry* **14** 181
56. Kottalanka R K, Laskar P, Naktode K, Mallik B S and Panda T K 2013 *J. Mol. Str.* **1047** 302
57. Kottalanka R K, Anga S, Naktode K, Laskar P, Nayek H P and Panda T K 2013 *Organometallics* **32** 4473
58. Ahman J and Somfai P 1995 *Synth. Commun.* **25** 2301
59. Altomare A, Burla M C, Camalli G, Cascarano G, Giacovazzo C, Gualiardi A and Polidori G 1994 *J. Appl. Crystallagr.* **27** 435
60. Sheldrick G M 2008 *Acta Crystallagr.* **A64** 112
61. Marks T J and Kolb J R 1977 *Chem. Rev.* **77** 263
62. Izod K, Watson J M, Clegg W and Harrington R W 2012 *Eur. J. Inorg. Chem.* **2012** 1696
63. Vande Griend L J, Verkade J G, Pennings J F M and Buck H M 1977 *J. Am. Chem. Soc.* **99** 459
64. Cole M L, Davies A J, Jones C and Junk P C 2007 *J. Organomet. Chem.* **692** 2508
65. Cole M L and Junk P C 2003 *J. Organomet. Chem.* **666** 55