CHEMCOMM
Communication
www.rsc.org/chemcomm

Formation of the monoanion $[Ar^*P(BH_3)(\mu\text{-}BH_2)_2H]^-$ with a symmetrically bridging hydride from the attempted synthesis of the dianion $[Ar^*P(BH_3)_3]^{2-}$†

Valentyn L. Rudzevich, Heinz Gornitzka, Vadim D. Romanenko* and Guy Bertrand

Laboratoire d'Hétérochimie Fondamentale et Appliquée, UMR CNRS 5069, Université Paul Sabatier, 118, route de Narbonne, F-31062 Toulouse Cédex 04, France. E-mail: gbertran@chimie.ups-tlse.fr

Received (in Cambridge, UK) 7th June 2001, Accepted 23rd July 2001
First published as an Advance Article on the web 14th August 2001

Addition of an excess of Bu^{n}Li to the bis(borano)phosphide complex $[Ar^*PH(BH_3)_2]^-Li^+$ 1 (Ar* = 2,4,6-tri-*tert*-butylphenyl) and subsequent treatment with BH_3, gives the anionic complex $[Ar^*P(BH_3)(\mu\text{-}BH_2)_2H]^-Li^+$ 2 instead of the expected tris(borano)phosphide dilithium, $[Ar^*P(BH_3)_3]^{2-}2Li^+$ 3.

Borane complexes of trivalent organophosphorus derivatives have been extensively used in organic synthesis.[1] In particular, borane-stabilized phosphide anions of the type $[R^1R^2PBH_3]^-$, which are readily available by deprotonation of the corresponding secondary phosphine– or phosphinite–borane adducts, have been found to be valuable intermediates for the preparation of enantiomerically pure phosphines with chiral carbon skeletons or stereogenic phosphorus centres.[2] It may be assumed that application of a conceptually similar approach (P–H deprotonation/P–B complexation) to primary phosphines and PH_3 would lead to a series of reactive anions $[R_nH_{3-n-m}P(BH_3)_{m+1}]^{m-}$ (n = 1, m = 1, 2 or n = 0, m = 1–3). However, surprisingly, few investigations of borane-stabilized RP^{2-} and P^{3-} anions have been reported to date. An early ^1H NMR spectroscopic study claimed that stepwise removal of protons from $[H_2P(BH_3)_2]^-$ followed by complexation of intermediates with BH_3 afforded $[HP(BH_3)_3]^{2-}$ and $[P(BH_3)_4]^{3-}$ anions. Yet, the observed formation of $LiBH_4$ leaves some doubts as to the true structure of the anionic products.[3]

The Cambridge Structural Database reveals that trivalent phosphorus derivatives in which the phosphorus is bonded to two or three boron atoms have rarely been characterized in the solid state, and those identified are limited to polyhedral compounds,[4] neutral diborylphosphines[5] and various heterocyclic systems.[6] No poly(borane)phosphide anions have so far been characterized by X-ray crystallography. Here we report the synthesis of the $[Ar^*PH(BH_3)_2]^-$ anion (Ar* = 2,4,6-tri-*tert*-butylphenyl) and its subsequent deprotonation and complexation with BH_3.

The $[Ar^*HP(BH_3)_2Li]$ complex **1** was prepared in 95% yield by metallation of Ar^*PH_2 with an equimolar amount of Bu^{n}Li in thf solution and subsequent addition of BH_3 (2 equiv.).‡ An alternative route to **1**, based on the preparation of the $Ar^*PH_2{\cdot}BH_3$ adduct and its subsequent deprotonation, led to the formation of a complex mixture of products. The ^{31}P NMR spectrum of **1** in C_6D_6 displays a broad doublet at δ −53 [^1J(PH) 340 Hz]. The resonance is considerably shifted toward low field compared to that of Ar*P(H)Li [δ −108, ^1J(PH) 172 Hz]. The signal observed by ^{11}B NMR spectroscopy (δ −30.6) was very broad ($W_{1/2}$ ~ 350 Hz) in both the ^{11}B proton-coupled and decoupled spectra, with no observable ^{11}B–^{31}P coupling. Furthermore, the signal attributable to BH_3 units in ^1H-{^{11}B} and ^1H-{^{31}P} spectra is not resolved and appeared as a broad singlet at δ 1.54.

The molecular structure of **1** is depicted in Fig. 1.§ The compound crystallizes with three molecules of thf and can be described by the formula $[Ar^*HP(BH_3)_2Li(thf)_3]$. Two different BH_3 units are found in the crystal: one shows contacts of two hydridic hydrogen atoms with Li through a μ_2-type interaction, while the hydridic hydrogen atoms of the other are not involved in the Li–H bonding. The bond distance between phosphorus and boron engaged in B–H···Li coordination [P(1)–B(1), 1.955 Å] is shorter than that found for the 'free' BH_3 group [P(1)–B(2) 1.984 Å]. It is apparent that the sterically demanding Ar* group has no significant influence on the molecular geometry of **1** since the Li(1)–B(1) distance (2.430 Å) is quite similar to those found in $Li{\cdots}(H)_2BH_2$ complexes in which the BH_4^- group acts as a μ_2 donor.[7]

In marked contrast to the PH-acid type behaviour generally shown by secondary phosphine–borane complexes, $R^1R^2(H)PBH_3$, compound **1** does not react with KH at room temperature in thf. The reaction with Bu^{n}Li in a 1:1 molar ratio only proceeds partially; complete deprotonation of **1** requires an excess of Bu^{n}Li (*ca.* 2.0 equiv., toluene, −50 °C), according to ^{31}P NMR spectroscopy. Removal of the solvent and extraction of the residue with pentane gave a pale yellow moisture-sensitive oil that exhibits strong, basic properties (on addition of $CHCl_3$ the complex **1** is regenerated immediately). Both ^{11}B– and ^{31}P–^1H coupled NMR spectra show a single broad resonance (δ_P −143.9 , δ_B −27.8), indicating the absence of a PH bond. Addition of excess borane to a toluene solution of the deprotonated product at −50 °C results in the formation of a mixture of the complex **2**‡ (δ_P −161.8 , δ_B −28.4) and $LiBH_4$ (δ_B −42.1) (Scheme 1). After crystallization from toluene–pentane solution, single colourless crystals of the phosphorus-containing complex were obtained, suitable for the determination of its molecular structure in the solid state.§ Compound **2** crystallizes as a dimer and can be described by the formula $[Ar^*P(BH_3)(\mu\text{-}BH_2)_2HLi(thf)_2]_2$ (Fig. 2). The most prominent feature of **2** is the presence of both a four-membered heterocyclic ring with a symmetrically bridging hydride P(μ-

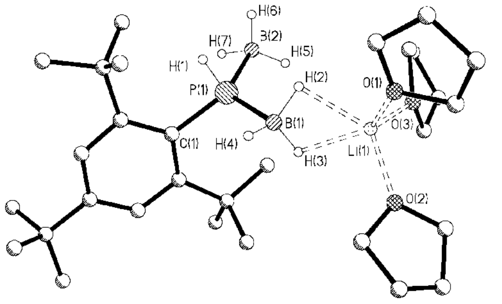


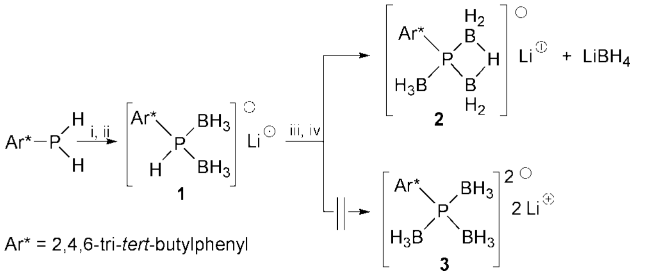
Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): B(1)–P(1) 1.955(3), B(2)–P(1) 1.984(3), P(1)–C(1) 1.860(2), B(1)–Li(1) 2.430(5), B(1)–H(2) 1.12(3), B(1)–H(3) 1.06(3), B(1)–H(4) 1.08(3), B(2)–H(5) 1.02(3), B(2)–H(6) 1.02(4), B(2)–H(7) 1.18(4); B(1)–P(1)–B(2) 121.52(14), P(1)–B(1)–Li(1) 139.2(2), C(1)–P(1)–B(1) 113.05(11), C(1)–P(1)–B(2) 117.88(12).

---

† Electronic supplementary information (ESI) available: crystallographic details and colour ORTEP views of **1** and **2**. See http://www.rsc.org/suppdata/cc/b1/b105030n/

DOI: 10.1039/b105030n

This journal is © The Royal Society of Chemistry 2001



Scheme 1 Synthesis of the borane–phosphide complexes **1** and **2**. *Reagents and conditions*: i, Bu^{n}Li (1 equiv.), thf, −50 °C; ii, BH$_3$·thf (2 equiv.), thf, −40 °C, 2 h; iii, Bu^{n}Li (2 equiv.), toluene, −50 °C, 2 h; iv, BH$_3$·thf (2 equiv.), toluene, −30 °C, 1 h.

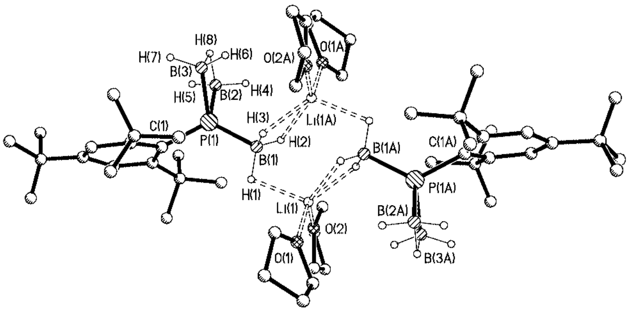


Fig. 2 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): B(1)–P(1) 1.961(2), B(2)–P(1) 1.924(2), B(3)–P(1) 1.913(2), B(1)–H(1) 1.12(2), B(1)–H(2) 1.13(2), B(1)–H(3) 1.09(2), B(2)–H(4) 1.12(2), B(2)–H(5) 1.12(2), B(3)–H(6) 1.11(2), B(3)–H(7) 1.11(2), P(1)–C(1) 1.845(1), B(1)–Li(1) 2.563(3), B(1)–Li(1A) 2.548(3); B(2)–P(1)–B(3) 62.91(10), B(1)–P(1)–B(2) 118.27(9), B(1)–P(1)–B(3) 115.26(9), P(1)–B(1)–Li(1) 154.39(11), P(1)–B(1)–Li(1A) 114.66(11), C(1)–P(1)–B(1) 123.45(7), C(1)–P(1)–B(3) 110.68(8), C(1)–P(1)–B(2) 110.94(8). The molecule of toluene has been omitted for clarity.

BH$_2$)$_2$H, and a BH$_3$ unit. The P(1)–B(2) and P(1)–B(3) bonds in the four-membered ring are slightly shorter than the exocyclic P(1)–B(1) bond distances, indicating that, as expected, B(2) and B(3) are stronger electron acceptors than B(1). The B(2)–B(3) distance in **2** is 2.00 Å, approximately 0.1 Å larger than in neutral μ-aminodiboranes [R$_2$N(μ-BH$_2$)$_2$H].[8] Two H atoms of the BH$_3$ group coordinate through a μ$_1$-interaction to two different Li cations forming an eight-membered ring. The Li···B(1) distances (2.548–2.563 Å) compare well with those found in other H$_3$B–H···Li interactions.[7] The coordination sphere of each Li atom is completed by two molecules of thf. In solution, no evidence for or against the dimeric structure can be found, but the presence of the hydride bridging two boron atoms is strongly suggested by the presence of an upfield broad doublet at δ −0.65 [^2J(PH) 36 Hz] in the ^{1}H NMR spectrum.

In conclusion, we have demonstrated that accumulation of negative charge on phosphorus by H$^+$/Li$^+$ replacement in complex **1** resulted in a considerable increase in the reduction properties of BH$_3$ groups. This results in the formation of the monoanionic bridging complex **2** observed along with LiBH$_4$, instead of the expected dianionic tris(borano)phosphide complex **3**. Compound **2** does not react with KH in the presence of 18-crown-6 (thf, 20 °C, 24 h), despite the presence of the electron deficient 3c–2e B–H–B bond. Thus, it appears that the anionic μ-(boratophosphino)diboranes are considerably more stable than previously described neutral μ-phosphinodiboranes, [R$_2$P(μ-BH$_2$)$_2$H].[9]

Thanks are due to the CNRS for financial support of this work, to the University Paul Sabatier for a grant to V. L. R.

Notes and references

‡ *Selected NMR data* for Ar*(H)$_2$PBH$_3$: ^{31}P(CDCl$_3$): δ −61.5 (t, $^1J_{PH}$ 371 Hz); ^{11}B(CDCl$_3$): δ −33.6 (br s). For **1**, ^{31}P(C$_6$D$_6$): δ −53.3 (d, $^1J_{PH}$ 340 Hz); ^{11}B(C$_6$D$_6$): δ −30.6 (br s); ^{1}H (C$_6$D$_6$): δ 1.41 (s, 9H, *p*-Bu^t), 1.48 (br s, thf), 1.54 (br s, 6H, BH$_3$), 1.99 (s, 18H, *o*-Bu^t), 3.72 (br s, thf), 5.96 (d, $^2J_{PH}$ 371 Hz, 1H, PH), 7.72 (s, 2H, H$_{arom}$). ^{13}C (CDCl$_3$): δ 25.5 (s, thf), 31.4 [s, *p*-C(CH$_3$)$_3$], 34.2 [s, *o*-C(CH$_3$)$_3$], 34.7 [s, *p*-C(CH$_3$)$_3$], 38.8 [s, *o*-C(CH$_3$)$_3$], 68.6 (s, thf), 122.8 (d, $^3J_{PC}$ 8.3 Hz, *m*-C$_{arom}$), 129.7 (d, $^1J_{PC}$ 28.7 Hz, *ipso*-C$_{arom}$), 148.3 (d, $^4J_{PC}$ 2.8 Hz, *p*-C$_{arom}$), 154.9 (d, $^2J_{PC}$ 3.7 Hz, *o*-C$_{arom}$). For **2**, ^{31}P (C$_6$D$_6$): δ −161.8 (br s); ^{11}B(C$_6$D$_6$): δ −28.4 (br s); ^{1}H{^{11}B} (C$_6$D$_6$): δ −0.65 (d, $^2J_{PH}$ 36 Hz, 1H, BHB), 1.39 (s, 9H, *p*-Bu^t), 1.49 (thf), 1.61 (br s, 7H, BH$_3$ and BH$_2$), 2.12 (s, 18H, *o*-Bu^t), 3.68 (thf), 7.67 (d, 2H, $^4J_{PH}$ 2.8 Hz, H$_{arom}$). ^{13}C (CDCl$_3$): δ 25.45 (s, (thf), 31.26 [s, *p*-C(CH$_3$)$_3$], 34.45 [s, *p*-C(CH$_3$)$_3$], 38.82 [s, *o*-C(CH$_3$)$_3$], 39.88 [d, $^3J_{CP}$ 2.8 Hz, *o*-*C*(CH$_3$)$_3$], 68.75 (s, thf), 122.92 (d, $^3J_{CP}$ 9.2 Hz, *m*-C$_{arom}$), 127.13 (d, $^1J_{CP}$ 49 Hz, *ipso*-C$_{arom}$), 148.03 (d, $^4J_{CP}$ 2.8 Hz, *p*-C$_{arom}$), 157.73 (d, $^2J_{CP}$ 4.6 Hz, *o*-C$_{arom}$).

§ *X-Ray structure analysis*: *Crystal data for*: **1**: C$_{30}$H$_{60}$B$_2$LiO$_3$P, M = 528.31, orthorhombic, space group $P2_12_12_1$, a = 9.4853(5), b = 11.0044(5), c = 32.8968(16) Å, V = 3433.8(3) Å^3, Z = 4, μ(Mo-Kα) = 0.105 mm^{-1}, T = 193(2) K, final $R1$ = 0.0505, $wR2$ = 0.1299, GOF (on F^2) = 1.078.

For **2**: C$_{33}$H$_{61}$B$_3$LiO$_2$P, M = 560.16, triclinic, space group $P\bar{1}$, a = 9.8395(8), b = 11.2345(9), c = 16.5435(13) Å, α = 96.708(2), β = 98.842(2), γ = 91.449(2)°, V = 1792.9(2) Å^3, Z = 2, μ(Mo-Kα) = 0.102 mm^{-1}, T = 193(2) K, final $R1$ = 0.0499, $wR2$ = 0.1379, GOF (on F^2) = 1.036.

Both structures were solved using the direct methods option on SHELXS.[10] Full matrix least-squares refinements based on F^2 were subsequently performed using SHELXL-97.[11]

CCDC reference numbers 167806 and 167807. See http://www.rsc.org/suppdata/cc/b1/b105030n/ for crystallographic data in CIF or other electronic format.

1 A. Pelter, K. Smith and H. C. Brown, *Borane Reagents*, Academic Press, London, 1988.

2 For reviews, see: J. Holz, M. Quirmbach and A. Börner, *Synthesis*, 1997, 983; M. Ohff, J. Holz, M. Quirmbach and A. Börner, *Synthesis*, 1998, 1391; see also: B. Wolfe and T. Livinghouse, *J. Am. Chem. Soc.*, 1998, **120**, 5116; M. Al-Masum and T. Livinghouse, *Tetrahedron Lett.*, 1999, **40**, 7731; K. Nagata, S. Matsukawa and T. Imamoto, *J. Org. Chem.*, 2000, **65**, 4185.

3 E. Mayer, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 416; see also: N. R. Thompson, *J. Chem. Soc.*, 1965, 6290; R. W. Rudolph, R. W. Parry and C. F. Farran, *Inorg. Chem.*, 1966, **5**, 723; J. W. Gilje, K. W. Morse and R. W. Parry, *Inorg. Chem.*, 1967, **6**, 1761; E. Mayer and A. W. Laubengayer, *Monatsh. Chem.*, 1970, **101**, 1138.

4 L. J. Todd, I. C. Paul, J. L. Little, P. S. Welcker and C. R. Peterson, *J. Am. Chem. Soc.*, 1968, **90**, 4490; T. D. Getman, H.-B. Deng, L.-Y. Hsu and S. G. Shore, *Inorg. Chem.*, 1989, **28**, 3612; S. R. Bunkhall, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1990, 73; F. Meyer, P. Paetzold and U. Englert, *Chem. Ber.*, 1994, **127**, 93.

5 See, for example: R. A. Barlett, H. V. Rasika Dias and P. P. Power, *Inorg. Chem.*, 1988, **27**, 3913; D. Dou, G. L. Wood, E. N. Duesler, R. T. Paine and H. Nöth, *Inorg. Chem.*, 1992, **31**, 1695.

6 G. J. Bullen and P. R. Mallinson, *J. Chem. Soc., Dalton Trans.*, 1973, 1295; G. R. Clark and G. J. Palenik, *Aust. J. Chem.*, 1975, **28**, 1187; B. Kaufmann, R. Jetzfellner, E. Leissring, K. Issleib, H. Nöth and M. Schmidt, *Chem. Ber.*, 1997, **130**, 1677.

7 N. Edelstein, *Inorg. Chem.*, 1981, **20**, 197; W. Lippert, H. Nöth, W. Ponikwar and T. Seifert, *Eur. J. Inorg. Chem.*, 1999, 817.

8 A. F. Wells, *Structural Inorganic Chemistry*, University Press, Oxford, 1986.

9 H. Hofstötter and E. Mayer, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 413; H. Hofstötter and E. Mayer, *Monatsh. Chem.*, 1974, **105**, 712.

10 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

11 SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen, 1997.