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Synthesis, spectroscopic characterisation and transmetalation of lithium and potassium diaminophosphanide-boranes†‡

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A secondary diaminophosphane-borane $(Et_2N)_2PH(BH_3)$ was prepared from a chlorophosphane precursor and $LiBH_4$ and metalated by reaction with anion bases (*n*-BuLi, $KN(SiMe_3)_2$) to yield the corresponding metal diaminophosphanide-boranes $[(Et_2N)_2P(BH_3)]M$ (M = Li, K). Multinuclear NMR studies permitted the first spectroscopic characterisation of the metalation products and revealed the presence of monomeric (for M = Li) contact ion pairs in solution. NMR spectroscopic evidence that the ions in each pair interact *via* Li⋯P- rather than $Li\cdots H_3B$-interactions as had been inferred for a Ph-substituted analogue was confirmed by DFT studies, which revealed also that the borane coordination plays a decisive role in boosting the PH-acidity of the original secondary diaminophosphane precursor. Transmetalation of the potassium and lithium diaminophosphanide-boranes with Cu(I) and Zn(II) chlorides afforded the first functional transition metal complexes of a P-heteroatom-functionalised phosphanide-borane ligand. Both products were fully characterised. Thermolysis of the Cu-complex induced a reaction which involved transfer of an NHC ligand from the metal to the phosphorus atom and yielded a phosphaalkene NHC=PH (NHC = N-heterocyclic carbene) as the major phosphorus-containing product.

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Introduction

Alkaline metal phosphanides of general composition R_2PM (M being mostly one of Li, Na, K) have since their discovery in the late 1950s[1–3] become indispensable as synthetic tool for the formation of new phosphorus-element bonds *via* coupling of the nucleophilic R_2P-fragment with suitable electrophiles in metathesis reactions. The substituents R in the phosphanide unit are generally alkyls or aryls, but the phosphorus atom may also carry hydride[4] or trialkylsilyl-moieties (mostly Me_3Si),[5,6] respectively. The resulting primary or secondary phosphanides (H_2PM or R(H)PM) as well as silyl phosphanides (especially $(Me_3Si)_2PM$) are useful synthons for the assembly of complex molecular architectures since the ancillary substituents permit further post-functionalization after the initial metathesis step.

In contrast to these well-established species, phosphanides with electronegative substituents, in particular amino groups, are very scarce. The only reference to the preparation of such compounds is a patent which claims the synthesis of mixtures of R_2NPLi_2 and $(R_2N)_2PLi$ (R = Me, Et) from the reaction of the appropriate amides with P_4. However, no characterisation data are reported, and pure products do not seem to have been isolated.[7] Transition metal complexes $[\{(R_2N)_2P\}Fe(CO)_4]K$[8] (**I**, R = Et, Ph) and $[\{Me_2N(Ph_3C)P\}W(CO)_5]K$[9] (**II**), which can formally be described as species containing anionic mono- or diaminophosphanide ligands, were produced by deprotonation of appropriate PH-substituted precursor complexes and spectroscopically characterised. Even if it cannot be ruled out that the metal atom in **I**, **II** participates to some extent in the stabilisation of the negative charge, both species were shown to react as P-centred nucleophiles.[8,9] Last, but not least, the group of Knochel reported[10] that reduction of a chlorophosphane-borane **1** with lithium at −78 °C and subsequent addition of electrophiles afforded phosphane-boranes **3** (Scheme 1). The reaction was claimed to proceed *via* a phosphanide-borane intermediate **2** which was, however, neither positively identified nor further characterised. The process provides nonetheless an attractive entry to a new synthesis of substituted diaminophosphanes $(R_2N)_2PR'$ which augments the known

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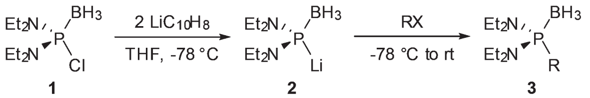
† Dedicated to Prof. Dr P. P. Power on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Representation of ^1H, ^{31}P, ^{11}B NMR spectra of **2**, **5**, **6**, **8**, **9**, ^1H, ^7Li HOESY and ^1H DOSY NMR spectra for **2**, ^1H NOESY NMR spectrum for **6**; computed energies and atomic coordinates for $(Et_2N)_2P(BH_3)Li(OEt_2)_n$ (n = 0–3). CCDC 1582551 and 1582554. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt04110a



Scheme 1 Reported synthesis[10] of diaminophosphane-boranes **3** *via* an intermediate lithium phosphanide-borane **2** (R = alkyl, allyl, benzyl, aryl; X = halide or mesylate).

route involving substitution of an electrophilic phosphorus-containing precursor by suitable organometallic nucleophiles. The target diaminophosphanes are amenable to further post-functionalisation by *nucleophiles* rather than electrophiles. This makes them valuable synthetic building blocks whose reactivity complements that of secondary phosphanes or silyl phosphanes, respectively.

Our interest in the chemistry and applications of neutral metal complexes containing $(R_2N)_2P$-moieties[11,12] prompted us to explore the use of diaminophosphanide-boranes like **2** as reagents for the introduction of nucleophilic aminophosphanyl fragments into transition metal complexes in greater detail. Here, we report on a new access route to **2**, its first spectroscopic characterisation, and on transmetalation reactions which give rise to isolable transition metal diaminophosphanide-borane complexes.

Experimental

Materials and methods

All reactions were carried out under an atmosphere of inert Argon and in flame-dried glassware. Solvents were dried by standard procedures. NMR spectra were recorded on Bruker Avance 250 (^{1}H/^{13}C/^{31}P/^{11}B 250.0/62.9/101.2/80.2 MHz) or Avance 400 (^{1}H/^{13}C/^{31}P/^{11}B 400.1/100.5/161.9/128.3 MHz) instruments. Chemical shifts were referenced to ext. TMS (^{1}H, ^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P), $BF_3\cdot Et_2O$ (Ξ = 32.083974 MHz, ^{11}B). Elemental analyses were done with an Elementar Micro Cube elemental analyzer. Mass spectra were obtained with a Bruker Daltonics Mikrotof-Q-Mass spectrometer. $(Et_2N)_2PCl$[13] and (IDipp)CuCl[14] (IDipp = 1,3-bis-(2,6-diisopropylphenyl)-imidazolylidene) were prepared as reported. $ZnCl_2$(tmeda) was obtained from Sigma Aldrich and used as received.

Synthetic procedures

Bisdiethylaminophosphane-borane (5). $(Et_2N)_2PCl$ (1.60 g, 7.60 mmol) was dissolved in anhydrous Et_2O (85 ml). $LiBH_4$ (2.3 ml of a 4 M solution in THF, 9.2 mmol) was added dropwise and the reaction mixture stirred for 2 h at room temperature. To complete the reduction, $LiALH_4$ (0.25 ml of a 1 M solution in THF, 0.25 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. The further work-up was carried out in air. The reaction mixture was washed carefully with demineralized water (4 × 100 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue containing the crude product and some solvent was purified *via* flash chromatography over silica (deactivated with 1% NEt_3) using PE/EtOAc (3 : 2) as eluent. After removing the volatiles, the product was obtained as light yellow, highly viscous oil (1.17 g, 6.20 mmol, yield 82%).

^{1}H NMR (C_6D_6): δ = 6.26 (dq, $^1J_{PH}$ = 433 Hz, $^3J_{HH}$ = 4.3 Hz, 1 H, PH), 3.0–2.6 (m, NCH_2, 8 H), 1.50 (broad q, $^1J_{BH}$ = 93 Hz, 3 H, BH_3), 0.80 (t, $^3J_{HH}$ = 7.1 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ = 41.4 (d, $^2J_{PC}$ = 3 Hz, NCH_2), 13.9 (d, $^3J_{PC}$ = 2 Hz, CH_3). ^{31}P NMR (C_6D_6): δ = 80.3 (q, $^1J_{PB}$ = 72 Hz). ^{11}B NMR (C_6D_6): δ = −39.1 (dq, $^1J_{PB}$ = 73 Hz, $^1J_{BH}$ = 93 Hz). $C_8H_{24}BN_2P$ (190.08): calcd C 50.55 H 12.73 N 14.74, found C 50.75 H 12.95 N 14.51. MS: m/z = 190.1771 ($C_8H_{24}BN_2P^+$).

Metalation of bisdiethylaminophosphane-borane

(a) With n-butyl lithium. Phosphane-borane **5** (40 mg, 0.21 mmol) was dissolved in Et_2O (10 ml) and a solution of *n*-BuLi (0.10 ml of a 2.5 M solution in hexane, 0.25 mmol) was added dropwise. The mixture was stirred for 1 h. For NMR spectroscopic characterisation, volatiles were removed under reduced pressure and the residue dissolved in 0.5 mL THF-d_8.

^{1}H NMR (THF-d_8): δ = 3.20 (ddq, $^2J_{HH}$ = 13.4 Hz, $^3J_{PH}$ = 5.7 Hz, $^3J_{HH}$ = 7.0 Hz, 4 H, NCH_2), 3.06 (ddq, $^2J_{HH}$ = 13.4 Hz, $^3J_{PH}$ = 6.8 Hz, $^3J_{HH}$ = 7.1 Hz, 4 H, NCH_2), 0.97 (t, $^3J_{HH}$ = 7 Hz, 12 H, CH_3), 0.34 (qd, $^1J_{BH}$ = 85 Hz, $^2J_{PH}$ = 10 Hz, 3 H, BH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ = 45.3 (broad, NCH_2), 14.0 (d, $^3J_{PC}$ = 4.0 Hz, CH_3). ^{31}P NMR (THF-d_8): δ = 128.0 (q, $^1J_{PB}$ = 56 Hz); ^{11}B NMR (THF-d_8): δ = −34.6 (dq, $^1J_{PB}$ = 56 Hz, $^1J_{BH}$ = 85 Hz), ^{7}Li NMR (THF-d_8): δ = −0.27 (s).

(b) With $KN(SiMe_3)_2$. Bis(diethylamino)phosphane-borane (**5**, 23 mg, 0.12 mmol) was added to a solution of $KN(SiMe_3)_2$ (960 mg, 0.48 mmol) in Et_2O (5 ml). The mixture was stirred for 1 h. Volatiles were evaporated under reduced pressure and the residue taken up in THF-d_8. NMR studies revealed the presence of **6** beside unreacted $KN(SiMe_3)_2$. Alternatively, dibenzo-18-crown-6 (51 mg, 0.14 mmol) was added to the original reaction mixture and the mixture subjected to the same work-up procedure as described above.

6: ^{1}H NMR (THF-d_8): δ = 3.21 (ddt, $^2J_{HH}$ = −13.4 Hz, $^2J_{PH}$ = 5.7 Hz, $^3J_{HH}$ = 7.1 Hz, 4 H, NCH_2), 3.06 (ddt, $^2J_{HH}$ = −13.4 Hz, $^2J_{PH}$ = 6.4 Hz, $^3J_{HH}$ = 7.0 Hz, 4 H, NCH_2), 0.98 (t, $^3J_{HH}$ = 7.1 Hz, 12 H, CH_3), 0.48 (dq, $^2J_{PH}$ = 10 Hz, $^1J_{BH}$ = 86 Hz, 3 H, BH_3). ^{31}P NMR (THF-d_8): δ = 130.7 (broad q, $^1J_{PB}$ = 52 Hz); ^{11}B NMR (THF-d_8): δ = −32.3 (dq, $^1J_{PB}$ = 53 Hz, $^1J_{BH}$ = 85 Hz).

6(Dibenzo-18-crown-6): ^{1}H NMR (THF-d_8): δ = 6.95 (m, 4 H, C_6H_4), 6.88 (m, 4 H, C_6H_4), 4.24–4.14 (m, 16 H, OCH_2), 3.26 (ddt, $^2J_{HH}$ = −13.3 Hz, $^2J_{PH}$ = 5.7 Hz, $^3J_{HH}$ = 7.0 Hz, 4 H, NCH_2), 3.11 (ddt, $^2J_{HH}$ = −13.3 Hz, $^2J_{PH}$ = 6.6 Hz, $^3J_{HH}$ = 7.0 Hz, 4 H, NCH_2), 0.98 (t, $^3J_{HH}$ = 7.0 Hz, 12 H, CH_3), 0.76 (dq, $^2J_{PH}$ = 10 Hz, $^1J_{BH}$ = 86 Hz, 3 H, BH_3). ^{31}P NMR (THF-d_8): δ = 135.1 (q, $^1J_{PB}$ = 52 Hz).

{Bis(diethylamino)phosphane-borane}-{1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene}-copper(I) (8). *n*-BuLi (0.31 ml of a 2.5 M solution in hexane, 0.79 mmol) was added dropwise to a solution of **5** (0.15 g, 0.79 mmol) in Et_2O (10 ml). The solution was stirred overnight. (IDipp)CuCl (384 mg, 0.79 mmol) was added and stirring continued for 4 h. Volatiles were then removed in vacuum. The residue was treated with hexane. The resulting suspension was filtered over dried silica and the remaining colourless solid extracted with Et_2O (10 ml). Storing the solution at 8 °C afforded **8** as colourless crystals (yield 100 mg, 20%).

^1H NMR (C_6D_6): δ = 7.18 (m, 2 H, C_6H_3), 7.05 (m, 4 H, C_6H_3), 6.25 (s, 2 H, NCH), 3.23–3.00 (m, $N(CH_2)_2$, 8H), 2.54 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, CH), 1.43 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CCH_3), 1.4 (br q, $^1J_{BH} \approx 95$ Hz, 3 H, BH_3), 1.05 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CCH_3), 0.95 (t, $^3J_{HH}$ = 7.0 Hz, 12 H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 130.7 (*p*-C_6H_3), 123.7 (*m*-C_6H_3), 122.4 (NCH), 44.8 (NCH_2), 28.7 ($CHMe_2$), 24.8 (CH_3), 23.7 (CH_3), 15.1 (CH_3). ^{31}P NMR (C_6D_6): δ = 123.8 (broad). $^{11}B\{^1H\}$ NMR (C_6D_6): δ = −33.6 (broad d, $^1J_{PB}$ = 68 Hz). ^{11}B NMR (C_6D_6): δ = −33.6 (broad dq, $^1J_{PB}$ = 68 Hz, $^1J_{BH} \approx 95$ Hz). $C_{35}H_{59}BCuN_4P$ (641.21): calcd C 65.56 H 9.27 N 8.74, found C 65.57 H 9.35 N 8.56.

(Bis(diethylamino)phosphanido-borane)-chlorido-(*N*,*N*′-tetramethylethylenediamine)-zinc(II) (9). A solution of **5** (389 mg, 2.00 mmol) in Et_2O (10 ml) was added drop wise to a stirred solution of $KN(SiMe_3)_2$ (398 mg, 2.00 mmol) in Et_2O (10 ml). After 15 min, $Zn(TMEDA)Cl_2$ (504 mg, 2.00 mmol) was added, and the stirring was continued overnight. The volatiles were then removed under reduced pressure. The residue was treated with hexane (10 ml) and the resulting suspension filtered over dried silica. The remaining colourless solid was then extracted with Et_2O (10 ml). Storing the ether solution at 8 °C afforded **9** as colourless crystals (yield 39%, 320 mg).

^1H NMR (C_6D_6): δ = 3.49 (m, $^2J_{HH}$ = −15.1 Hz, $^2J_{PH}$ = 1.5 Hz, $^3J_{HH}$ = 7.2 Hz, 4 H, NCH_2), 3.44 (m, $^2J_{HH}$ = −15.1 Hz, $^2J_{PH}$ = 2.3 Hz, $^3J_{HH}$ = 7.0 Hz, 4 H, NCH_2), 2.34 (s, 6 H, tmeda-CH_3), 2.04 (s, 6 H, tmeda-CH_3), 1.84 (m, 2 H, tmeda-CH_2), 1.63 (m, 2 H, tmeda-CH_2), 1.47 (broad q, $^1J_{BH}$ = 93 Hz, 3 H, BH_3), 1.13 (t, $^3J_{HH}$ = 7.1 Hz, 12 H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 56.4 (s, tmeda-CH_2), 47.9 (s, tmeda-CH_3), 47.5 (s, tmeda-CH_3), 43.8 (s, NCH_2), 14.8 (d, $^3J_{PC}$ = 3.6 Hz, CH_3). ^{31}P NMR (C_6D_6): δ = 94.2 (q, $^1J_{PB}$ = 74 Hz); ^{11}B NMR (C_6D_6): δ = −33.7 (d, $^1J_{PB}$ = 70 Hz).

Thermolysis of 8. A solution of **8** (12 mg, 18 μmol) in toluene-d_8 (2 mL) was heated to 95 °C for 3 h. After cooling to room temperature, ^{31}P, $^{31}P\{^1H\}$, and ^1H,^{31}P HMQC NMR spectra were recorded. The identification of **10** as the main product (80% by spectral integration) was derived from a comparison of the observed spectral data with those of an authentic sample. No work-up was attempted.

$^{31}P\{^1H\}$ NMR (toluene-d_8): δ = −5.7 (s), −133.6 (s); ^{31}P NMR (toluene-d_8): δ = −5.7 (d, $^1J_{PH}$ = 643 Hz), −133.6 (d, $^1J_{PH}$ = 165 Hz; **10**).

Crystallography

X-ray diffraction studies were carried out using a Bruker Kappa Apex II diffractometer equipped with a Duo CCD-detector and a KRYO-FLEX cooling device with Mo-K_α radiation (λ = 0.71073 Å) at T = 130(2) K. The structures were solved by direct methods (SHELXS-97[15]) and refined with a full-matrix least-squares scheme on F^2 (SHELXL-2014 and SHELXL-97[15]). Semi-empirical absorption corrections were applied. Non-hydrogen atoms were refined anisotropically, hydrogen atoms at boron isotropically, and all other hydrogen atoms with a riding model. Complex **8** co-crystallizes with a solvent molecule (Et_2O) part of which is disordered. The disordered atoms were refined isotropically and with restraints. CCDC 1582554 (**8**) and 1582551 (**9**)‡ contain the supplementary crystallographic data for this paper.

8: colourless prisms, $C_{35}H_{59}BCuN_4P{\cdot}C_4H_{10}O$, M = 715.30 g mol^{-1}, crystal size 0.63 × 0.40 × 0.38 mm, monoclinic, space group $P2_1/c$ (no. 14), a = 12.4854(9) Å, b = 16.7096(12) Å, c = 20.7813(17) Å, β = 90.058(7)°, V = 4335.5(6) $Å^3$, Z = 4, ρ(calcd) = 1.096 Mg m^3, $F(000)$ = 1552, θ_{max} = 30.5°, μ = 0.572 mm^{-1}, max./min. transmission 0.715/0.811, 53 570 reflections measured, 13 161 unique reflections [R_{int} = 0.048] for structure solution and refinement with 430 parameters and 30 restraints, R_1 ($I > 2\sigma(I)$) = 0.042, wR_2 = 0.101, GoF = 1.008, largest diff. peak and hole: 0.679 and −0.504 e $Å^{-3}$.

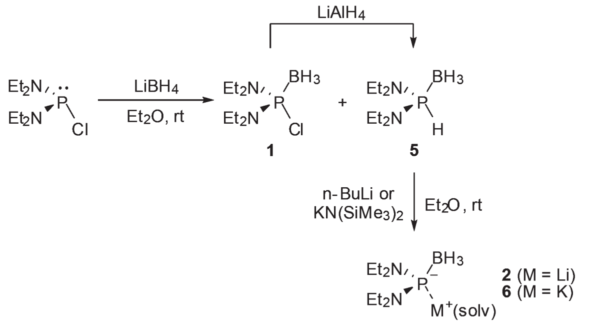
9: colourless blocks, $C_{14}H_{39}BClN_4PZn$, M = 406.09 g mol^{-1}, crystal size 0.18 × 0.08 × 0.06 mm, monoclinic, space group $P2_1/c$ (no. 14), a = 7.7586(8) Å, b = 29.766(3) Å, c = 9.2778(8) Å, β = 96.393(4)°, V = 2129.3(4) $Å^3$, Z = 4, ρ(calcd) = 1.267 Mg m^3, $F(000)$ = 872, θ_{max} = 26.5°, μ = 1.356 mm^{-1}, max./min. transmission 0.927/0.796, 16 133 reflections measured, 4361 unique reflections [R_{int} = 0.054] for structure solution and refinement with 208 parameters and 9 restraints, R_1 ($I > 2\sigma(I)$) = 0.042, wR_2 = 0.091, GoF = 1.002, largest diff. peak and hole: 0.924 and −0.398 e $Å^{-3}$.

Computational studies

RI-DFT[16] calculations were carried with the TURBOMOLE[17] program suite. Energy optimisation of the molecular structures of $(Et_2N)_2P(BH_3)Li(OEt_2)_n$ (Li⋯P-bound isomer, n = 0–3) and $(Et_2N)_2P{-}BH_3{\cdots}Li(OEt_2)_n$ (Li⋯H_3B-bound isomer, n = 0, 2) was carried out using the BP86 functional[18] with a def2-tzvp basis set,[19] Grimme's D3BJ formalism[20] to include dispersion effects, and the conductor-like screening model[21] (COSMO) with the solvent parameters for Et_2O to simulate solvation effects. The final molecular structures were identified as local minima on the energy hypersurface by harmonic vibrational frequency calculations. Natural population analysis[22] was performed with the NBO module implemented in the software.

Results and discussion

Metal alkyl and aryl phosphanides are usually accessed *via* one of two generally applicable routes, *i.e.* reductive bond cleavage in a suitable precursor (frequently a halogeno-phosphane), or metalation of an appropriate secondary phosphane with a strong base, respectively. Both strategies fail for diamino-phosphanides $(R_2N)_2PM$. Reduction of diamino-halogeno-phosphane precursors affords diphosphanes which withstand attempts toward further reductive bond cleavage,[23] and Cowley *et al.* established that sterically protected secondary amino-phosphanes resist all attempts to deprotonation at phosphorus.[24] We found that the same is also true for the sterically less shielded phosphane $(Et_2N)_2PH$ (**4**). Realising that the work



Scheme 2 Preparation and metalation of diaminophosphane-borane **5**.

by Knochel *et al.*[10] implies that borane coordination to a diaminochlorophosphane boosts its liability to undergo reductive PCl-bond cleavage under formation of phosphanide-borane **2** rather than a diphosphane, we wondered if borane coordination can also enhance the acidity of a secondary aminophosphane towards strong bases.

As a starting material for this study we prepared phosphane-borane **5**, which had previously only been obtained in a mixture with other compounds,[25] by borohydride reaction of $(Et_2N)_2PCl$ (Scheme 2). Reaction monitoring by ^{31}P NMR spectroscopy revealed that the starting material is initially converted into a mixture of the target compound **5** and the chlorophosphane-borane **1**. The further reaction of **1** and $LiBH_4$ under Cl/H-exchange is very slow and sluggish, but rapid and quantitative (by ^{31}P NMR) conversion into **5** was accomplished after addition of an appropriate amount of $LiAlH_4$ to the reaction mixture. The product was finally isolated after aqueous work-up as analytically pure, colourless oil and its identity established by multinuclear NMR data (see Experimental). The presence of the P-bound hydrogen atom was readily established by the observation of appropriate ^1H and ^{31}P NMR signals which showed highly characteristic doublet splittings arising from $^1H,^{31}P$ spin coupling ($^1J_{PH}$ = 433 Hz). The product can be handled for short times under air and is thermally stable in refluxing benzene but decomposes to an intractable yellow solid in refluxing toluene.

Reaction of **5** with an equimolar amount of *n*-butyl lithium in ether solution afforded a new product which gave rise to a ^{31}P NMR signal that had been shifted to higher frequency and showed no splitting by $^1J_{PH}$. The newly formed species proved thermally stable but extremely sensitive to traces of moisture which induced hydrolysis under re-formation of **5**. As this sensitivity thwarted as yet all attempts to purify the product by crystallisation, we decided to establish its identity by spectroscopic analysis of samples obtained after evaporation of volatiles and dissolution of the residue in a suitable solvent.

The observation that NMR spectra of samples containing a mixture of the newly formed species and **5** (arising from partial hydrolysis or incomplete conversion of the starting material) displayed signal broadenings attributable to dynamic exchange between both components was interpreted as a first proof for the presence of litthiated phosphanide-borane **2** but impeded concise interpretation of the spectral data. We found, however, that well resolved spectra without interference from the effects of chemical exchange could be obtained when the metalation of **5** was carried out with a large excess of *n*-BuLi (the excess reagent acting in this case as efficient scavenger for adventitious H_2O). Careful analysis of multinuclear (^1H, ^{11}B, ^{13}C, ^{31}P) NMR spectra recorded from such solutions allowed to establish unambiguously that the P-bound hydrogen was absent but the remaining $(Et_2N)_2P(BH_3)$ fragment was still intact. A $^1H,^7Li$-HOESY NMR spectrum§ showed correlations between a strong ^7Li NMR signal ($\delta = -0.27$) and the resonances of NCH_2CH_3- and BH_3-protons of the $(Et_2N)_2P(BH_3)$-unit as well as residual protons in the OCD_2-moiety of the deuterated solvent (THF-d_8). Based on these findings, we assign the metalation product **2** the structure of a tight contact ion pair of composition $[\{(Et_2N)_2P(BH_3)\}\{Li(THF)_n\}]$. A ^1H DOSY spectrum of a mixture of **2** and **5** recorded at −50 °C where the chemical exchange was found to be negligible disclosed a ratio of diffusion coefficients of D(**2**)/D(**5**) = 0.91. This value implies that both species possess very similar hydrodynamic radii and exhibit thus the same degree of aggregation. Since we have no evidence for the formation of any higher aggregates in case of **5**, we therefore assign also to **2** a monomeric structure.

A similar reaction as with *n*-BuLi was observed when **5** was treated with $KN(SiMe_3)_2$. A ^{31}P NMR spectroscopic survey revealed clean formation of a single product which showed a comparable sensitivity towards hydrolysis as **2** but was also readily spectroscopically characterised in solution in the presence of excess amide. The NMR data revealed as in **2** the presence of an intact $(Et_2N)_2P(BH_3)$ fragment and the absence of a P-bound hydrogen atom, and we assign the product thus as potassium phosphanide-borane **6** (Scheme 2). The fact that the observed NMR chemical shifts are similar but not identical to those of **2** (*e.g.* $\delta^{31}P$ 130.7 (**6**) *vs.* 128.0 (**2**) and $\delta^{11}B$ −34.6 (**6**) *vs.* −32.2 (**2**) in THF at 30 °C) is attributable to the influence of the different cations and suggests that **6** should likewise be formulated as a contact ion pair. In line with this hypothesis is the observation of a further change in the ^{31}P NMR chemical shift ($\Delta\delta^{31}P$ +4.4 ppm) upon addition of an equimolar amount (with respect to K^+) of crown ether (dibenzo-18-crown-6). Interestingly, the ^1H NOESY spectrum of this solution revealed cross peaks which connect the signals of the OCH_2-units in the crown ether with those of the NCH_2- and BH_3-moieties. This finding indicates that binding of the cation to the crown ether did not totally disrupt the interaction with the phosphanide fragment so that the resulting complex exhibits still some ion pair character. A similar contact between a crown ether decorated lithium cation and a phosphanide anion had previously been observed in a solid phosphinidenoid metal-pentacarbonyl complex.[26] Apart from the sensitivity towards hydrolysis, solutions of **6** containing dibenzo-18-crown-6 were ther-

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§ The spectrum was recorded at −90 °C. At room temperature, no correlation signals at all were observable, presumably due to unfavourable correlation times.

mally instable and decayed within hours under formation of appreciable amounts of **5** along with products arising from degradation of the crown ether.

The reported ^{1}H NOESY results are best rationalised by assuming that the ion pairing creates both Li···P and Li···H_3B-contacts between the metal cation and the phosphorus atom of the anion fragment. A somewhat different situation had been inferred for lithium diphenylphosphanide-borane. Here, NMR data indicated a structure $Ph_2P–BH_3\cdots Li(THF)_2$ (7) in which the cation is exclusively connected with the hydrides on boron.[27] Since the higher stability of the Li···H_3B- over a Li···P-bound isomer had in that case been confirmed by DFT model studies, we initiated a computational study in order to analyse also the relative stabilities of the two different isomers of **2**. To this end, calculations at the COSMO-RI-BP86-D3BJ/def2-tzvp level were carried out on a "naked" ion pair $[(Et_2N)_2P(BH_3)]Li$ where solvation was only simulated by a continuum model, and on a species $[(Et_2N)_2P(BH_3)][Li(OEt_2)_2]$ under explicit modelling of the cation solvation by two ether molecules. The results of harmonic frequency analyses on energy optimised molecular structures suggest that both the Li···P- and Li···H_3B-bound isomers (see Fig. 1) constitute local minima on the energy hypersurface. The former is favoured by 30.5 kJ mol^{-1} if explicit solvation is neglected, and still by 4.9 kJ mol^{-1} when lithium solvation by two ether molecules is explicitly considered. Comparison of the energy optimised structures for a series of Li···P-bound solvates $[(Et_2N)_2P(BH_3)][Li(OEt_2)_n]$ (n = 0–3, see ESI‡) reveals that an increasing number of solvent molecules induces an overall increase in the P···Li distance from 2.400 Å (n = 0) to 2.509 Å (n = 3). At the same time, the lithium cation is shifted from a P,BH_2-bridging position with agnostic Li···H contacts (1.960 Å) into a "terminal" position where it now completes a regular tetrahedral coordination sphere at the phosphorus atom. The closest Li···H contact (3.791 Å) is in the order of the sum of van der Waals radii. Similar changes had been noticed in an earlier DFT study on lithium phosphanide-borane solvates[27] and reflect in the present case presumably deficits of the continuum models in a realistic description of cation solvation rather than an observable structural trend. Even if in this context comparison of the energies of "naked" Li···P- and Li···H_3B-bound contact ion pairs cannot be assumed to give meaningful results, the persisting energetic preference for the Li···P-bound isomer even after the inclusion of explicit solvent molecules strongly suggests that the Li···H_3B-binding mode that had been inferred for **7** [27] is in case of **2** disfavoured.[28] Even if the DFT results allow no explicit explanation, this finding is in accord with the commonly acknowledged higher nucleophilicity of aminophosphanes as compared to *P*Ph- or *P*H-substituted derivatives.

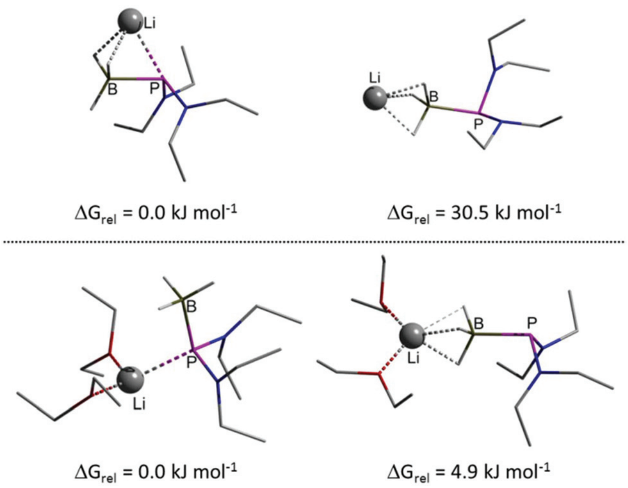
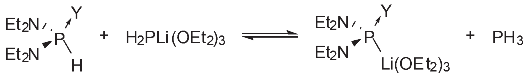


Fig. 1 Molecular structures and relative Gibbs free energies ΔG_{rel} for Li···P- (left) and Li···H_3B-bound isomers (right) of $(Et_2N)_2P(BH_3)Li(OEt_2)_n$ (n = 0, 2) calculated at the COSMO-RI-BP86-D3BJ/def2-tzvp level of theory.

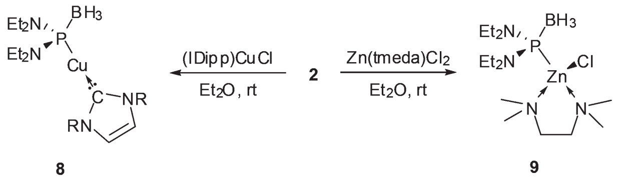
It should be noted that computing the energetics of the isodesmic Li/H exchange reactions shown in Scheme 3, which indicated that metalation of secondary phosphane-borane **5** is by 69 kJ mol^{-1} more exergonic than the analogous reaction of the appropriate free secondary phosphane, confirmed also our initial hypothesis of borane coordination boosting the acidity of the PH-bond in secondary aminophosphanes.

The synthetic potential of diaminophosphanide-boranes had first been demonstrated by Knochel *et al.* in the preparation of organic diethylaminophosphanes $R–P(NEt_2)_2$ and $(Et_2N)_2P–R–P(NEt_2)_2$ *via* nucleophilic substitution of mono- and difunctional organic halides or mesylates with **2**.[10] Having up to now been unable to isolate crystalline samples of lithium and potassium phosphanide-boranes **2** or **6**, we anticipated that analogous reactions of these substrates with suitable metal-based electrophiles might give way to isolable phosphanide-borane derivatives by transmetalation. To this end, we studied reactions of **2** and **6** with the carbene complex (IDipp)CuCl and Zn(tmeda)Cl_2 (IDipp = 1,3-bis-(2,6-diisopropylphenyl)-imidazolylidene; tmeda = tetramethylethylenediamine), respectively. Reaction monitoring by ^{31}P NMR spectroscopy disclosed in each case the formation of a single main product beside **5** (possibly through partial hydrolysis) and minor amounts of as yet unidentified by-products. The major products were isolated in moderate yields after work-up and fully characterised.



Y =	l.p.	BH_3
ΔE+zpe	44.1 kJ mol^{-1}	-35.9 kJ mol^{-1}
ΔG^0	60.2 kJ mol^{-1}	-9.1 kJ mol^{-1}

Scheme 3 Electronic energies including zero-point vibrational correction (Δ*E* + zpe) and Standard Gibbs free energy (Δ*G*) for isodesmic lithium transfer reactions for **4** (Y = l.p.) and **5** (Y = BH_3) calculated at the COSMO-RI-BP86-D3BJ/def2-tzvp level of theory.



Scheme 4 Metathesis reactions of **2** with (IDipp)CuCl and Zn(tmeda)Cl_2 (R = 2,6-diisopropylphenyl, tmeda = tetramethylethylenediamine).

Identification of the products as the expected complexes **8** and **9** (Scheme 4) was most easily feasible from the single-crystal X-ray diffraction data. Crystals of both compounds contain mononuclear complexes that are assembled around metal atoms with quasi-linear (**8**, Fig. 2) or tetrahedral (**9**, Fig. 3) coordination geometry, respectively. The metal-phosphorus distances (**8:** Cu1–P1 2.2112(5) Å; **9:** Zn1–P1 2.3589(8) Å) are close to standard bond lengths in phosphane complexes (Cu–P 2.207 Å, Zn–P 2.413 Å[29]) and, in case of **8**, slightly shorter than the Cu–P distances in diphenylphosphanide-borane complexes containing four-coordinate Cu(I) centres[30] (Cu–P 2.2609(6)–2.2640(5) Å). The various distances in the phosphanide unit and the tetrahedral coordination geometry of the phosphorus atom are normal and differ not significantly between both complexes.

First reactivity studies revealed that the copper complex **8** resisted all attempts to cleave the coordinated borane unit by action of tertiary amines such as Et_3N or DABCO, respectively. Quite interestingly, however, we noticed that heating solutions of **8** in toluene to 95 °C, both in the presence or absence of a tertiary amine, resulted in transformation into a major phosphorus-containing compound (>75%) which was identified by comparison of the observed spectral data with an authentic sample as the phosphaalkene **10**[31] (Scheme 5). The identity of the by-products formed is still unknown, and the elucidation of the reaction mechanism and the origin of the P-bound hydrogen atom in **10** are currently being investigated.

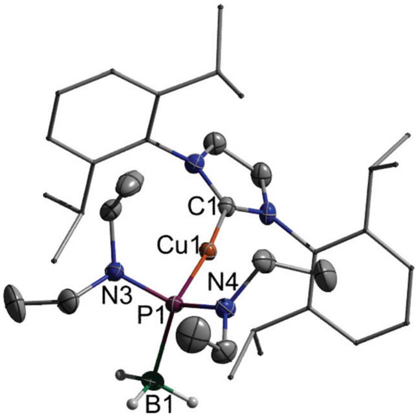


Fig. 2 Representation of the molecular structure of **8** in the crystal. For clarity, hydrogen atoms of CH-bonds were omitted and the Dipp-substituents represented using a wire model. Selected distances [Å] and angles [°]: Cu1–C1 1.9123(16), Cu1–P1 2.2112(5), P1–N3 1.6956(14), P1–N4 1.6975(15), P1–B1 1.944(2), C1–Cu1–P1 172.00(5).

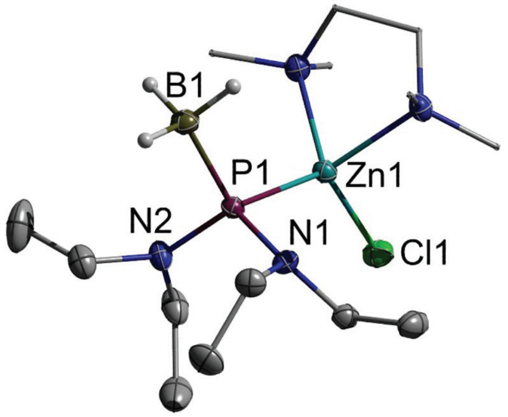
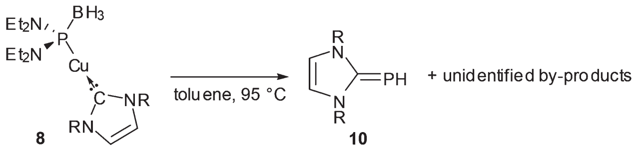


Fig. 3 Representation of the molecular structure of **9** in the crystal. For clarity, hydrogen atoms of CH-bonds were omitted and the carbon atoms in the tmeda-ligand represented using a wire model. Selected distances [Å]: Zn1–Cl1 2.2445(8), Zn1–P1 2.3589(8), P1–N2 1.682(3), P1–N1 1.701(3), P1–B1 1.949(4).



Scheme 5 Thermolysis of complex **8** (R = 2,6-diisopropylphenyl).

Conclusions

The metalation of a secondary diaminophosphane-borane with strong anion bases provides an alternative to the synthesis of thermally stable diaminophosphanide-boranes by metal reduction of diamino-chlorophosphane-borane precursors with appealing prospects to be developed into a widely applicable synthetic protocol. NMR studies suggest that the metalated products exist in solution as contact ion pairs the constituents of which interact through M⋯P interactions and undergo, at least for M = Li, no aggregation to form higher oligomers. DFT studies indicate that ion pairing *via* close Li⋯P contacts is energetically slightly preferable over formation of a hydride-bridged structure $R_2P–BH_3\cdots Li(solv)$ which had previously been reported for lithium diphenylphosphanide-borane. This finding confirms once more that the structures of the ion pairs exhibit a subtle dependence on substituent effects.[28] The reactivity of the diaminophosphanide-boranes as P-centred nucleophiles is emphasised by transmetalation reactions with zinc and copper halides which afforded the first fully characterised metal complexes of the functionalised phosphanide-boranes. The thermal decomposition of the copper complex **8** surprisingly yields phosphaalkene **10** under concomitant transfer of a metal-bound carbene to phosphorus. This finding draws attention to the fact that metalated diaminophosphanide-boranes may show similar behaviour as phosphinidenoid complexes[9,26,32] which can undergo reactions under cleavage of electrofugic (M^+) and nucleofugic (Et_2N^-) substituents and formal transfer of a P(I) fragment ("phosphinidene") to a different substrate. The investigation of the scope of such reactions, as well as the elucidation of the mechanism of the formation of **10**, is the objective of ongoing research in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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