DOI: 10.1002/ejic.200800305

N-Heterocyclic Carbenes in Lewis Acid/Base Stabilised Phosphanylboranes

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Dedicated to Professor Heinrich Nöth on the occasion of his 80th birthday

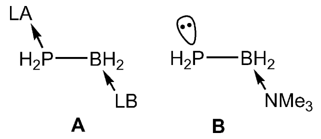
Keywords: Boron / Phosphorus / Gallium / Carbenes / Lewis acids / Lewis bases

The reactions of 2-borane-1,3,4,5-tetramethylimidazoline ($BH_3{\cdot}NHC^{Me}$) with selected phosphane adducts of the Lewis acids $B(C_6F_5)_3$ and $Ga(C_6F_5)_3$ are studied. Among others, adducts $(C_6F_5)_3Ga{\cdot}PH_2Cp^{*}$ (**1a**) and $(C_6F_5)_3B{\cdot}PH_2Cp^{*}$ (**2**) are used as starting materials. When the $(C_6F_5)_3Ga$–phosphane adducts **1a** and $(C_6F_5)_3Ga{\cdot}PPhH_2$ are treated with $BH_3{\cdot}NHC^{Me}$, the Lewis acid/base stabilised phosphanylboranes $(C_6F_5)_3Ga{\cdot}P(Cp^{*})HBH_2{\cdot}NHC^{Me}$ (**3a**) and $(C_6F_5)_3Ga{\cdot}P(Ph)HBH_2{\cdot}NHC^{Me}$ (**3b**) are formed, respectively, by a hydrogen elimination reaction. In contrast, the reaction of $BH_3{\cdot}NHC^{Me}$ with the $(C_6F_5)_3B$–phosphane adducts $(C_6F_5)_3B{\cdot}PH_2R$ [R = H, R = Cp* (**2**) and R = Ph] in CH_2Cl_2 at room temperature leads to the formation of a salt with the general formula $[(C_6F_5)_3BH][RPH_2{\cdot}BH_2{\cdot}NHC^{Me}]$ (**4a**: R = H, **4b**: R = Cp*, **4c**: R = Ph). To synthesise the Lewis acid/base stabilised phosphanylborane with $(C_6F_5)_3B$ as a Lewis acid and 1,3,4,5-tetramethylimidazolylidene (NHC^{Me}) as a Lewis base, a different synthetic pathway was applied: the replacement reaction of the Lewis base. At room temperature, NHC^{Me} displaced the amine in $(C_6F_5)_3B{\cdot}P(Ph)HBH_2{\cdot}NMe_3$ to yield $(C_6F_5)_3B{\cdot}P(Ph)HBH_2{\cdot}NHC^{Me}$ (**5**). All compounds were comprehensively characterised by spectroscopic methods. Compounds **1a**, **1b**, **2**, **3a**, **3b** and **5** were additionally characterised by X-ray crystallographic analysis.

Introduction

In the last years, much attention has been given to hydrogen activation because of its importance for hydrogen storage applications. Next to metal hydrides as storage media, main group compounds such as amine–borane[1,2] were studied, because of their high potential for hydrogen storage capacity (i.e., $H_3N{\cdot}BH_3$ contains 19.6 wt.-% hydrogen[1]). In contrast, the well-known phosphane–borane compounds synthesised in the groups of Nöth and Paine,[3,4] Power[5,6] and others have not been considered in this specific context until Stephan et al. discovered the first reversible, metal-free hydrogen activation with the compound $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$.[7] Furthermore, it has been realised that simple phosphane–borane mixtures can be used for H_2 activation under mild conditions.[8]

The group 13/15 compounds of the general formula $H_3E–E'H_3$ (E = element of the group 15, E′ = element of the group 13) can be activated by thermal or catalytic methods to liberate H_2. Oligophosphanylboranes $[HRP–BH_2]_n$ (n = 3, 4; R = Ph) were synthesised by a dehydrocoupling reaction at elevated temperatures[9,10] or catalysed by Rh^I complexes as Manners et al. have demonstrated.[11,12] Denis et al. described the synthesis of the polymeric phosphanylborane $[H_2P–BH_2]_n$ by a dehydrocoupling reaction catalysed by $B(C_6F_5)_3$.[13] However, so far all attempts to isolate the parent monomeric compound of this class $[H_2P–BH_2]$ were to no avail and only theoretical investigations on the compound have been performed.[14–16] Our approach to the parent compounds of phosphanylboranes was to stabilise them by the coordination of Lewis acids and Lewis bases of type **A** compounds (Scheme 1). In these instances, the lone pair of electrons of the phosphorus atom is occupied by a Lewis acid (LA) and the boron atom is coordinated by a Lewis base (LB).[17–20] Furthermore, we were able to synthesise the first hydrogen-substituted phosphanylborane that is only stabilised by the Lewis base NMe_3 (**B**).[21]



Scheme 1. LA = $W(CO)_5$, $Cr(CO)_5$, $B(C_6F_5)_3$, $Ga(C_6F_5)_3$; LB = NMe_3.

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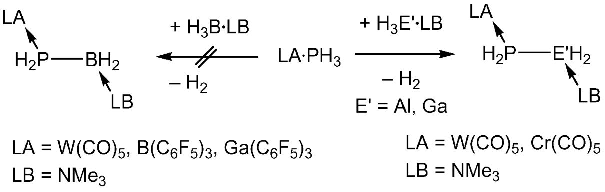
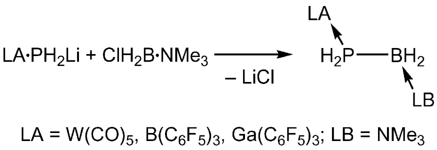
Whereas the LA/LB-stabilised phosphanylalanes and -gallanes are accessible by a hydrogen elimination reaction,[19,20] this synthetic pathway fails when $H_3B{\cdot}NMe_3$ is used as the starting material [Equation (1)].



(1)

The LA/LB-stabilised phosphanylboranes are available by a salt elimination reaction as shown in Equation (2).[17,18]



(2)

Herein we report the synthesis and characterisation of LA/LB-stabilised phosphanylboranes with 1,3,4,5-tetramethylimidazolylidene (NHC^{Me}) as a Lewis base and $Ga(C_6F_5)_3$ as a Lewis acid by a hydrogen elimination reaction. Furthermore, we observed different reaction behaviour depending on the Lewis acid: by using $B(C_6F_5)_3$ as Lewis acid and NHC^{Me} as Lewis base, the salts $[(C_6F_5)_3BH][RPH_2{\cdot}BH_2{\cdot}NHC^{Me}]$ are formed [R = H, Cp*(C_5Me_5), Ph].

Results and Discussion

Synthesis and Characterisation of the Starting Materials

The synthesis of the starting materials is described for those compounds which have not yet been published in the literature. The Lewis acid/base adducts $(C_6F_5)_3Ga{\cdot}PH_2Cp^*$ (**1**) and $(C_6F_5)_3B{\cdot}PH_2Cp^*$ (**2**) (Cp* = C_5Me_5, pentamethylcyclopentadienyl) were prepared by the reaction of the Lewis acid {**1**: $(C_6F_5)_3Ga{\cdot}Et_2O$ [Equation (3)], **2**: $(C_6F_5)_3B$ [Equation (4)]} with PH_2Cp^* at room temperature in toluene.

$$(C_6F_5)_3Ga{\cdot}Et_2O + Cp^*PH_2 \xrightarrow[-\ Et_2O]{\text{toluene, r.t.}} \underset{\mathbf{1a}}{(C_6F_5)_3Ga{\cdot}PH_2Cp^*} \qquad (3)$$

$$(C_6F_5)_3B + Cp^*PH_2 \xrightarrow{\text{toluene, r.t.}} \underset{\mathbf{2}}{(C_6F_5)_3B{\cdot}PH_2Cp^*} \qquad (4)$$

The ^1H NMR spectra of the products show a doublet (**1a**: $\delta = 4.08$ ppm, $^1J_{P,H} = 348$ Hz; **2**: $\delta = 4.71$ ppm, $^1J_{P,H} = 394$ Hz) attributable to the PH_2 protons. The signals for the Cp* protons arise at different chemical shifts with an integration ratio of 3:6:6 indicating no fluxional behaviour of the Cp* moiety. The ^{31}P NMR spectra reveal triplets (**1a**: $\delta = -65.3$ ppm, $^1J_{P,H} = 347$ Hz; **2**: $\delta = -38.3$ ppm, $^1J_{P,H} = 394$ Hz). Whereas in the FD-MS spectrum of **1a** the molecular ion peak was observed, for **2** only the fragments $[B(C_6F_5)_3]^+$ and $[Cp^*PH_2]^+$ are detected.

Figure 1 shows the X-ray structure of **1a** in the crystal. The Ga–P bond length in **1a** [2.442(1) Å] is within the normal range for dative Ga–P single bonds, which may vary from 2.40 to 2.46 Å.[5,22,23] The B–P bond length in compound **2** [2.040(2) Å] (Figure 2) is in good agreement with the B–P bond lengths found for $(C_6F_5)_3B{\cdot}PH_3$ [2.044(8), 2.046(8), 2.048(8) Å], whose unit cell contains three independent molecules.[24]

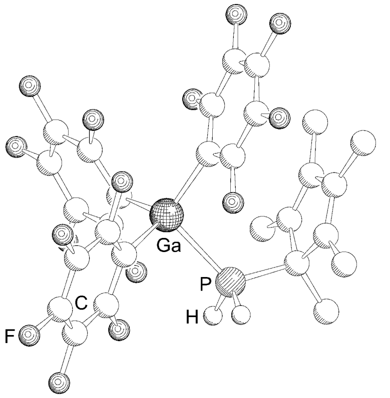


Figure 1. Molecular structure of **1a** in the crystal. Selected bond lengths [Å] and angles [°]: Ga–P 2.442(1), P–C(Cp*) 1.856(3), Ga–P–C(Cp*) 121.0(1); **2**: B–P 2.040(2), P–C(Cp*) 1.871(2), B–P–C(Cp*) 123.9(1).

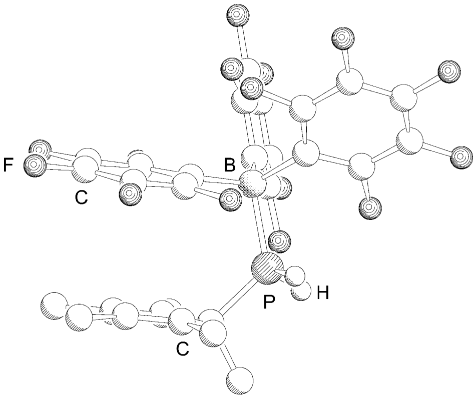


Figure 2. Molecular structure of **2** in the crystal. The hydrogen atoms of the Cp* ring are omitted for clarity. Selected bond lengths [Å] and angles [°]: B–P 2.040(2), P–C(Cp*) 1.871(2), B–P–C(Cp*) 123.9(1).

Initial attempts to synthesise $(C_6F_5)_3Ga{\cdot}PH_2Cp^*$ produced the compound $(C_6F_5)_3Ga{\cdot}OPH_2Cp^*$ (**1b**).[25] We assume that **1b** is a decomposition product of **1a**, most likely formed through the unintended presence of air.

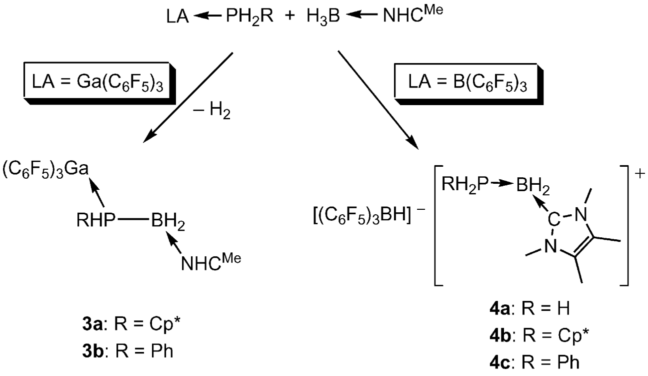
As a second starting material, 2-borane-1,3,4,5-tetramethylimidazoline ($BH_3{\cdot}NHC^{Me}$) was used. This compound was first synthesised and published by Kuhn et al.

in 1993, but was so far not characterised by X-ray structural analysis.[26] We obtained single crystals of $BH_3{\cdot}NHC^{Me}$ from a hexanes solution at –25 °C.[25]

Synthesis of Lewis Acid/Base Stabilised Phosphanylboranes

In general, B–P bonds can be formed by hydrogen elimination when a catalyst and/or elevated temperatures are used. Often, most methods need the combination of both.[11–13] For the first time, we have found now that the synthesis of LA/LB-stabilised phosphanylboranes with $Ga(C_6F_5)_3$ as the Lewis acid and NHC^{Me} as Lewis base is performed by an uncatalysed H_2 elimination reaction at room temperature.

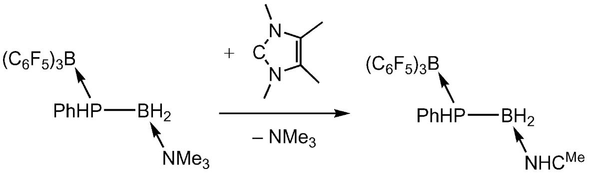
When $(C_6F_5)_3Ga{\cdot}PCp^*H_2$ (**1a**) or $(C_6F_5)_3Ga{\cdot}PPhH_2$[18] is treated with $BH_3{\cdot}NHC^{Me}$ in nonpolar solvents at room temperature, LA/LB-stabilised phosphanylboranes **3a** or **3b**, respectively, are formed (Scheme 2). At room temperature, the formation of **3a** does not occur quantitatively, so the reaction was heated at reflux overnight to improve the yields.



Scheme 2. Reaction of LA–phosphane adducts with $BH_3{\cdot}NHC^{Me}$.

In contrast to Ga compounds **3a** and **3b**, very different results were obtained upon treatment of the $(C_6F_5)_3B$–phosphane adducts $(C_6F_5)_3B{\cdot}PH_3$,[24] $(C_6F_5)_3B{\cdot}PH_2Cp^*$ (**2**) or $(C_6F_5)_3B{\cdot}PH_2Ph$[13] with $BH_3{\cdot}NHC^{Me}$ at room temperature in CH_2Cl_2. In this case, no formation of LA/LB-stabilised phosphanylboranes is observed; rather, the salts $[(C_6F_5)_3BH][RPH_2{\cdot}BH_2{\cdot}NHC^{Me}]$ (**4a**: R = H, **4b**: R = Cp*, **4c**: R = Ph) are obtained as colourless viscous oils (Scheme 2). Similar cations can be found in the salt $[PH_3{\cdot}BH_2{\cdot}NMe_3]^+[(CO)_5W{\cdot}SnCl_3]^-$ synthesised by Schwan in our group and in $[(R_3P)_2BH_2]^+[B(cat)_2]^-$ (R = Me, Et; cat = 1,2-$O_2C_6H_4$) synthesised by Marder and Baker et al.[27]

To synthesise LA/LB-stabilised phosphanylboranes with $(C_6F_5)_3B$ as Lewis acid and NHC^{Me} as Lewis base, another synthetic pathway was used. The reaction of $(C_6F_5)_3B{\cdot}P(Ph)HBH_2{\cdot}NMe_3$[18] with NHC^{Me} in toluene at room temperature leads to a substitution of the Lewis base. NMe_3 is liberated and the compound $(C_6F_5)_3B{\cdot}P(Ph)HBH_2{\cdot}NHC^{Me}$ (**5**) is formed as a colourless crystalline compound [Equation (5)].

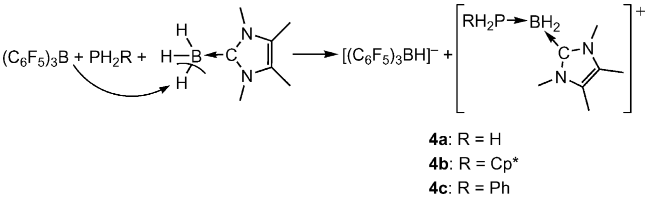


5 (5)

Computational Studies of the Reaction Mechanism

As a reaction mechanism of the formation of ionic compounds **4** one can postulate the dissociation of the $(C_6F_5)_3B$–phosphane adduct in the first step [Equation (6)]. A reversible adduct formation between phosphanes and fluorinated triarylboron compounds such as $(C_6F_5)_3B{\cdot}PH_3$ was also described by Bradley et al.[28] As a second step, the free Lewis acid $(C_6F_5)_3B$ abstracts a hydride from the BH_3 group, which results in the formation of a boronium cation stabilised by a PH_2R moiety (**4a**: R = H, **4b**: R = Cp*, **4c**: R = Ph) [Equation (7)].

$$(C_6F_5)_3B \leftarrow PH_2R \rightleftharpoons (C_6F_5)_3B + PH_2R \qquad (6)$$

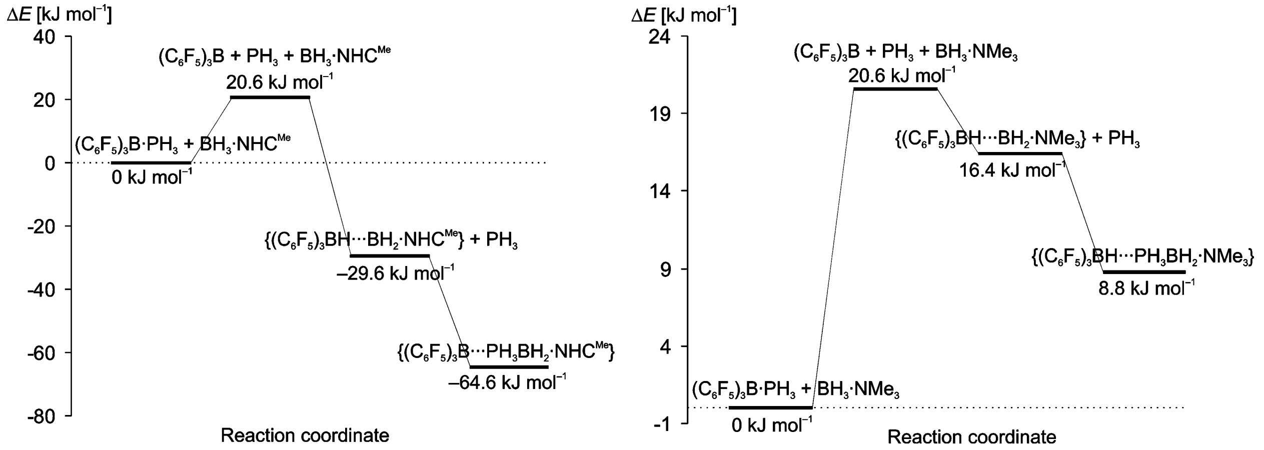


(7)

To support the postulated reaction mechanism, density functional theory (DFT) calculations were applied on the single steps of the model reaction between $(C_6F_5)_3B{\cdot}PH_3$ and $BH_3{\cdot}NHC^{Me}$.[25,29] The results of the calculated reaction energies are listed in Table 1. Scheme 3 illustrates the changes in energy between the single steps.[30] When comparing the energies of reactions (1) and (2), we notice that the formation of a LA/LB-stabilised phosphanylborane by a hydrogen elimination reaction is slightly favoured [reaction (2)] relative to the formation of the ionic species $[(C_6F_5)_3BH][PH_3{\cdot}BH_2{\cdot}NHC^{Me}]$ [reaction (1)], although the H_2 elimination reaction could not be observed experimentally. The dissociation of $(C_6F_5)_3B$ and PH_3 [reaction (3)] possesses an activation barrier of 20.6 kJ mol^{-1} (Scheme 3, left). The following hydride abstraction reaction [reaction (4)] is clearly favoured by 50.2 kJ mol^{-1}. This step compensates the dissociation energy of the adducts. The stabilisation of the boronium cation by PH_3 [reaction (5)] leads to a further gain in energy by 29.6 kJ mol^{-1}. It is not clarified yet if the hydride abstraction reaction and the coordination of PH_3 proceed in two separate steps or if the reaction follows a concerted mechanism. The formation of **4a** from $(C_6F_5)_3B{\cdot}PH_3$ and $BH_3{\cdot}NHC^{Me}$ results in a total energy gain of 64.6 kJ mol^{-1}. Reaction (1) is also thermodynamically allowed by $\Delta G^{\circ}_{298} = -1.4$ kJ mol^{-1}.

Table 1. Calculated energies, standard enthalpies and standard Gibbs energies (kJ mol^{-1}; gas-phase reaction) at 298 K (B3LYP/6-31G*). $BAr^F = B(C_6F_5)_3$, NHC^{Me} = 1,3,4,5-tetramethylimidazolylidene. Compounds in curly brackets identify a contact ion pair.

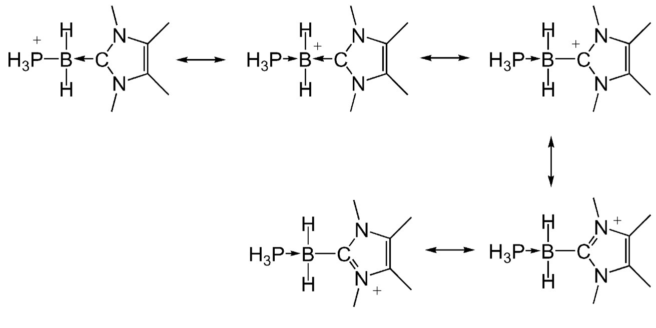
	Reaction	$\Delta E°_0$	$\Delta H°_{298}$	$\Delta G°_{298}$
(1)	$BAr^F{\cdot}PH_3 + BH_3{\cdot}NHC^{Me} = \{BAr^FH{\cdots}PH_3BH_2{\cdot}NHC^{Me}\}$	–64.6	–55.2	–1.4
(2)	$BAr^F{\cdot}PH_3 + BH_3{\cdot}NHC^{Me} = BAr^F{\cdot}PH_2BH_2{\cdot}NHC^{Me} + H_2$	–73.4	–80.1	–53.4
(3)	$BAr^F{\cdot}PH_3 = BAr^F + PH_3$	20.6	11.5	–39.2
(4)	$BAr^F + BH_3{\cdot}NHC^{Me} = \{BAr^FH{\cdots}BH_2{\cdot}NHC^{Me}\}$	–50.2	–43.3	22.1
(5)	$\{BAr^FH{\cdots}BH_2{\cdot}NHC^{Me}\} + PH_3 = \{BAr^FH{\cdots}PH_3BH_2{\cdot}NHC^{Me}\}$	–35.1	–23.4	15.6
(6)	$BAr^F{\cdot}PH_3 + BH_3{\cdot}NMe_3 = \{BAr^FH{\cdots}PH_3BH_2{\cdot}NMe_3\}$	8.8	18.1	60.5
(7)	$BAr^F{\cdot}PH_3 + BH_3{\cdot}NMe_3 = BAr^F{\cdot}PH_2BH_2{\cdot}NMe_3 + H_2$	–26.6	–34.8	–24.3
(8)	$BAr^F + BH_3{\cdot}NMe_3 = \{BAr^FH{\cdots}BH_2{\cdot}NMe_3\}$	–4.2	1.9	54.7
(9)	$\{BAr^FH{\cdots}BH_2{\cdot}NMe_3\} + PH_3 = \{BAr^FH{\cdots}PH_3BH_2{\cdot}NMe_3\}$	–7.6	4.7	45.0



Scheme 3. Change in energies in the systems $(C_6F_5)_3B{\cdot}PH_3 + BH_3{\cdot}NHC^{Me}$ (left) and $(C_6F_5)_3B{\cdot}PH_3 + BH_3{\cdot}NMe_3$ (right). Compounds in curly brackets identify a contact ion pair.

For the system $(C_6F_5)_3B{\cdot}PH_3$ and $BH_3{\cdot}NMe_3$, experimentally neither the hydrogen elimination [reaction (7)] reaction nor the formation of an ionic product [reaction (6)] is observed. In calculations we found that reaction (6) in Table 1 with $\Delta G°_{298}$ = 60.5 kJ mol^{-1} is strongly prohibited. The right part in Scheme 3 shows the changes in energies for the partial steps of the reaction leading to the salt formation [reactions (6) to (9), Table 1]. What attracts attention is that the initial energy for the dissociation of $(C_6F_5)_3B$ and PH_3 cannot be compensated by the following reaction steps, which gives an explanation for the experimental fact that ionic products are not formed in these reactions. An explanation of the different reactivities could be the fact that the positive charge of the boronium cation can be delocalised with the carbene ligand, which thus stabilises the system (Scheme 4).

According to Mulliken population analysis, the partial charge on the NMe_3 moiety in $[PH_3{\cdot}BH_2{\cdot}NMe_3]^+$ is +0.50, whereas on the NHC^{Me} unit in $[PH_3{\cdot}BH_2{\cdot}NHC^{Me}]^+$ it is +0.76. This observation supports larger delocalisation of the positive charge on the carbene ligand like that proposed in Scheme 4.[28,30]



Scheme 4. Possibilities of delocalisation of the positive charge in the $[PH_3{\cdot}BH_2{\cdot}NHC^{Me}]^+$ cation.

Computations predict that the H_2 elimination reactions (10) and (11) (Table 2) between $Ga(C_6F_5)_3$–phosphane adducts and $BH_3{\cdot}NHC^{Me}$ are exothermic by 58 and 68 kJ mol^{-1}, respectively, whereas the ion-pair formation reactions (12) and (13) (Table 2) are only slightly exothermic by 8 and 12 kJ mol^{-1}, respectively. Furthermore the standard Gibbs energies for reactions (10) and (11) are negative at 298 K so these reactions are allowed thermodynamically.

Table 2. Calculated energies, standard enthalpies and standard Gibbs energies (kJ mol^{-1}; gas-phase reaction) at 298 K (B3LYP/6-31G*). GaAr^F = Ga(C_6F_5)$_3$, NHC^{Me} = 1,3,4,5-tetramethylimidazolylidene. Compounds in curly brackets identify a contact ion pair.

Reaction		$\Delta E°_0$	$\Delta H°_{298}$	$\Delta G°_{298}$
(10)	GaAr^F·P(Ph)H$_2$ + BH$_3$·NHC^{Me} = GaAr^F·P(Ph)HBH$_2$·NHC^{Me} + H$_2$	–62.2	–68.4	–41.2
(11)	GaAr^F·P(Cp*)H$_2$ + BH$_3$·NHC^{Me} = GaAr^F·P(Cp*)HBH$_2$·NHC^{Me} + H$_2$	–53.5	–58.7	–32.1
(12)	GaAr^F·P(Ph)H$_2$ + BH$_3$·NHC^{Me} = {GaAr^{F}H···P(Ph)H$_2$BH$_2$·NHC^{Me}}	–15.7	–11.7	55.1
(13)	GaAr^F·P(Cp*)H$_2$ + BH$_3$·NHC^{Me} = {GaAr^{F}H···P(Cp*)H$_2$BH$_2$·NHC^{Me}}	–12.3	–7.8	66.8

In contrast, Gibbs energy values for reactions (12) and (13) are positive; thus, these reactions are thermodynamically forbidden at 298 K.[32]

Spectroscopic Characterisation of Lewis Acid/Base Stabilised Phosphanylboranes

In the ^{1}H NMR spectra of **3a**,**b**, two singlets [**3a**: δ = 1.15 (CCH_3), 2.63 ppm (NCH_3); **3b**: δ = 1.13 (CCH_3), 2.64 ppm (NCH_3)] for the methyl groups of the N-heterocyclic carbenes are detected. Furthermore, three signals of three different methyl groups of the Cp* substituent are observed, which is characteristic for a η^1 bonding mode of each Cp* ring. The PH protons can be detected as corresponding doublets (**3a**: δ = 4.42 ppm, $^1J_{P,H}$ = 313 Hz; **3b**: δ = 4.76 ppm, $^1J_{P,H}$ = 325 Hz). In addition to the $^1J_{P,H}$ coupling for **3b**, a small $^3J_{H,H}$ coupling constant ($^3J_{H,H}$ = 7 Hz) is detected. In the ^{31}P NMR spectra, broad doublets are observed (**3a**: δ = –72.2 ppm, $^1J_{P,H}$ = 314 Hz; **3b**: δ = –71.8 ppm, $^1J_{P,H}$ = 326 Hz).

Both compounds **3a** and **3b** show similar chemical shifts in their ^{11}B NMR spectra (**3a**: δ = –35.3 ppm, **3b**: δ = –32.8 ppm), and the signal of the H$_3$B·NHC^{Me} starting material occurs in the same region (δ = –35.0 ppm).[26] In both cases, no B–H coupling can be observed due to the broadness of the signals. No molecular ion peak is detected in the MS (EI) spectra of either **3a** or **3b** and only the [BH$_2$·NHC^{Me}]$^+$ fragment is found. In the IR spectrum of both compounds the corresponding P–H and B–H stretching modes are detected.

The MS (ESI) spectra of **4a**–**c** show the anion peak [(C_6F_5)$_3$BH]$^-$ with 100% relative abundance as a single signal in the anion subspectrum and the corresponding molecular ion peak of the cations of **4b** and **4c** in the cation subspectrum. The cation subspectrum of **4a** shows a [PH$_2$(BH$_2$·NHC^{Me})$_2$]$^+$ fragment as the most intense signal, but the [PH$_3$BH$_2$·NHC^{Me}]$^+$ cation could not be detected. The IR spectra of compounds **4a**–**c** reveal absorptions in the range from 2030 to 2349 cm^{-1} for the P–H stretching modes and the B–H stretching modes appear between 2445 and 2380 cm^{-1}. The MS (ESI) spectra of **5** show the corresponding molecular ion peak. The IR spectrum of **5** shows B–H stretching modes in a characteristic region (2460, 2419 cm^{-1}) and a signal for the P–H vibration at 2316 cm^{-1}.

The ^{1}H NMR spectra of **4a**–**c** show the signals for the NHC^{Me} moiety at very similar chemical shifts (**4a**: δ = 2.15, 3.63 ppm; **4b**: δ = 2.14, 3.50 ppm; **4c**: δ = 2.16, 3.60 ppm). In addition, the signals for the R substituent (**4b**: R = Cp*, three signals at δ = 1.36, 1.81, 1.82 ppm; **4c**: R = Ph, two multiplets at δ = 7.51–7.57, 7.59–7.69 ppm) are detected. Compound **4a** shows a doublet of triplets at δ = 4.60 ppm ($^1J_{P,H}$ = 401 Hz, $^3J_{H,H}$ = 8 Hz) for the PH$_3$ protons. The signal for the PH$_2$ unit in **4b** arises at δ = 4.69 ppm as a doublet of triplets ($^1J_{P,H}$ = 374 Hz, $^3J_{H,H}$ = 7 Hz), and for **4c** the PH$_2$ group is detected as a doublet of triplets at δ = 5.79 ppm ($^1J_{P,H}$ = 398 Hz, $^3J_{H,H}$ = 7.5 Hz). The known ^{1}H NMR signal of the [(C_6F_5)$_3$BH]$^-$ anion could only be detected in the ^{1}H NMR spectrum of **4b**.[27]

The ^{31}P NMR spectrum of **4a** shows a broad quartet at δ = –119.2 ppm ($^1J_{P,H}$ = 401 Hz). This is in close agreement with the ^{31}P NMR spectroscopic data found for [PH$_3$·BH$_2$·NMe$_3$][(CO)$_5$W·SnCl$_3$].[27] This compound shows a quartet at δ = –117.8 ppm with a similar hydrogen–phosphorus coupling constant of $^1J_{P,H}$ = 418 Hz. In case of **4b** and **4c**, respectively, a broad triplet is detected in the ^{31}P NMR spectra (**4b**: δ = –40.8 ppm, $^1J_{P,H}$ = 374 Hz; **4c**: δ = –57.9 ppm, $^1J_{P,H}$ = 398 Hz). The signals are broadened because of the phosphorus–boron coupling. Comparison of the ^{31}P NMR spectroscopic data of **4c** (δ = –57.9 ppm, $^1J_{P,H}$ = 398 Hz) with that of (C_6F_5)$_3$B·P(Ph)HBH$_2$·NHC^{Me} (**5**; δ = –43.8 ppm, $^1J_{P,H}$ = 351 Hz) shows that the phosphorus signal of the cation is shifted upfield and shows a larger hydrogen–phosphorus coupling constant.

The BH$_2$ units of the cations are always detected as very broad signals in the ^{11}B NMR spectra. Compound **4a** shows a doublet of triplets (δ = –37.6 ppm, $^1J_{B,H}$ = 92 Hz, $^1J_{B,P}$ = 37 Hz), which is the best-resolved signal for the BH$_2$ unit in the row **4a**–**c**. The ^{11}B NMR signal of cation **4b** is detected as a broad doublet at δ = –37.8 ppm, where only the $^1J_{B,P}$ coupling constant (48 Hz) can be observed. The ^{11}B NMR spectra of **4c** shows a very broad signal for the BH$_2$ group at δ = –35.6 ppm. In comparison to the chemical shift of the BH$_3$·NHC^{Me} starting material (δ = –34.9 ppm), compound **3a** (δ = –35.3 ppm) or **3b** (δ = –32.8 ppm), the shift of the signals for the BH$_2$ units in **4a**–**c** support the coordination of the NHC^{Me} Lewis base. The ^{11}B NMR spectroscopic data of [(C_6F_5)$_3$BH]$^-$ were already described by Shore et al.[33] and the ^{19}F NMR spectroscopic data were discussed by Santini et al.[34]

The ^{31}P NMR spectrum of **5** shows a doublet at δ = –43.8 ppm ($^1J_{P,H}$ = 351 Hz). Whereas the ^{11}B NMR spectrum of the starting material shows a broad signal at δ = –10.8 ppm arising for the BH$_2$ unit,[18] the BH$_2$ group in **5** can be detected as a broad singlet at δ = –33.2 ppm. The ^{19}F NMR signals detected for **5** (δ = –128.1, –158.8, –164.6 ppm) are clearly shifted downfield relative to those found for compounds **4a**–**c**. The influence of the different Lewis bases NMe_3 and NHC^{Me} is responsible for the different chemical shifts.

X-ray Structural Characterisation of LA/LB-Stabilised Phosphanylboranes 3a, 3b and 5

The structures of **3a**,**b** and **5** were confirmed by X-ray diffraction studies (Table 4). Selected bond lengths and angles for compounds **3a**,**b** are listed in Table 3 and those for compound **5** in Figure 4. Compound **3a** crystallises in the monoclinic space group $P2_1/c$ with two independent molecules (A and B) in the unit cell. Compound **3b** crystallises in the monoclinic space group $P2_1/n$ and **5** crystallises in the monoclinic space group $C2/c$. Compounds **3a**,**b** (Figure 3) and **5** (Figure 4) show the same $HRP–BH_2$ structural motif (**3a**: R = Cp*, **3b** and **5**: R = Ph) in the solid state. The phosphorus atom of the $HRP–BH_2$ fragment coordinates the Lewis acid [**3a**, **3b**: $Ga(C_6F_5)_3$; **5**: $B(C_6F_5)_3$] and the NHC^{Me} Lewis base coordinates to the boron atom of this fragment so that the boron and the phosphorus atoms are surrounded by four substituents. The substituents around the P–B bond adopt a slightly staggered conformation, whereas the Lewis acid and the Lewis base in **3b** adopt an antiperiplanar geometry [$Ga–P–B–C_{NHC}$ torsion angle: 176.26(1)°]. In **3a** and **5**, a synclinal arrangement of the Lewis acid and the Lewis base for **3b** [67.9(3) and 82.0(3)°] and **5** [80.2(4)°] is found.[35]

Table 3. Selected bond lengths [Å] and angles [°] of **3a** (molecules A and B) and **3b**.

	3a: A	**3a**: B	**3b**
Ga–P	2.392(1)	2.407(1)	2.405(1)
P–B	1.982(4)	1.978(4)	1.982(6)
$B–C_{NHC}$	1.610(5)	1.596(5)	1.588(7)
$C_{NHC}–N(1)$	1.359(4)	1.360(4)	1.344(5)
$C_{NHC}–N(2)$	1.349(4)	1.349(5)	1.344(5)
Ga–P–B	118.37(13)	118.65(13)	122.3(2)
$P–B–C_{NHC}$	111.1(2)	112.1(2)	104.0(4)
$N(1)–C_{NHC}–N(2)$	105.2(3)	105.6(3)	104.3(5)
$Ga–P–B–C_{NHC}$	67.9(3)	82.0(3)	176.26(1)

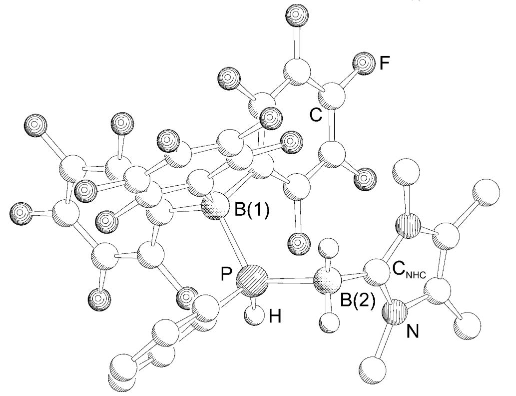


Figure 4. Molecular structure of **5** in the crystal. The hydrogen atoms of the phenyl group are omitted for clarity. Selected bond lengths [Å] and angles [°]: B(1)–P 2.035(2), P–B(2) 1.979(2), B(2)–C_{NHC} 1.607(3), C_{NHC}–N(1) 1.353(2), C_{NHC}–N(2) 1.353(2), B(1)–P–B(2) 119.54(8), P–B(2)–C_{NHC} 110.1(1), N(1)–C_{NHC}–N(2) 105.2(2), B(1)–P–B(2)–C_{NHC} 80.2(4).

The Ga–P bond lengths found in **3a** [A: 2.392(1) Å, B: 2.407(1) Å] and **3b** [2.405(1) Å] are slightly shorter than the corresponding bond found in starting material **1** [2.442(1) Å] and $(C_6F_5)_3Ga·P(Ph)H_2$ [2.477(1) Å], respectively.[18] A good agreement is found when comparing the Ga–P bond lengths with the respective bond length in the LA/LB-stabilised phosphanylboranes $(C_6F_5)_3Ga·PH_2BH_2·NMe_3$ [2.393(1) Å] and $(C_6F_5)_3Ga·P(Ph)HBH_2·NMe_3$ [2.424(1) Å].[18] Compound **5** reveals a dative B(1)–P bond length of 2.035(2) Å, which is close to the B–P bond length found in $(C_6F_5)_3B·PPhH_2$ (2.039 Å)[13] and $(C_6F_5)_3B·PH_3$ [2.046(8) Å].[24] The central P–B bond lengths of **3a** [1.982(4) and 1.978(4) Å], **3b** [1.982(6) Å] and **5** [P–B(2): 1.979(2) Å] agree well with usual P–B single bond lengths, which range from 1.90 to 2.0 Å.[3–5] Especially, the comparison with other LA/LB-stabilised phosphanylboranes show a good agreement in the P–B bond length [$(C_6F_5)_3B·PH_2BH_2·NMe_3$: 1.989(4) Å, $(C_6F_5)_3B·P(Ph)HBH_2·NMe_3$: 1.974(3) Å or $(C_6F_5)_3Ga·PH_2BH_2·NMe_3$: 1.992(2) Å]. Although the $B–C_{NHC}$ bond of **3b** [1.588(7) Å] reveals the same length as the $B–C_{NHC}$ bond in starting material **1a** [1.588(4) Å], the corresponding bonds in **3a** [1.610(5) and 1.596(5) Å] and **5** [1.607(3) Å] are slightly elongated.

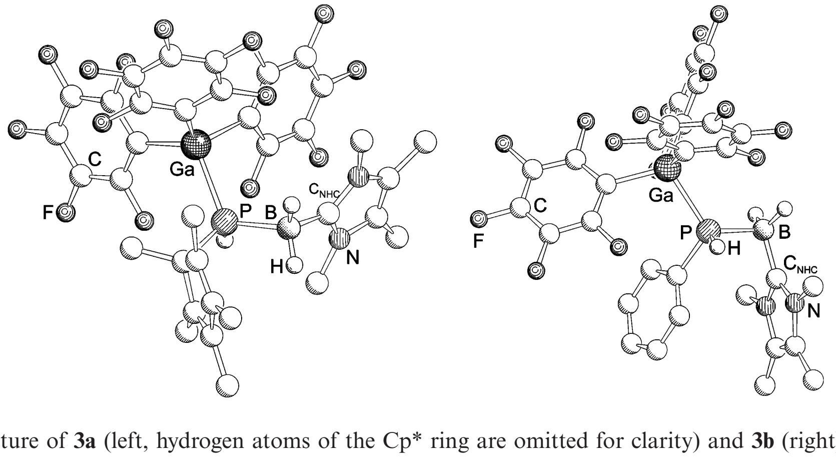


Figure 3. Molecular structure of **3a** (left, hydrogen atoms of the Cp* ring are omitted for clarity) and **3b** (right) in the crystal.

Conclusions

The results reported herein have shown that depending on the chosen Lewis acid $(C_6F_5)_3B$ or $(C_6F_5)_3Ga$ the reaction between $(C_6F_5)_3E{\cdot}PH_2R$ and $BH_3{\cdot}NHC^{Me}$ (E = Ga or B, R = H, Cp*, Ph) leads to different products. The reaction of $(C_6F_5)_3Ga{\cdot}PH_2R$ [R = Cp* (**1a**), Ph] with $BH_3{\cdot}NHC^{Me}$ proceeds at room temperature by a hydrogen elimination reaction to form the LA/LB-stabilised phosphanylboranes **3a** and **3b**. Thus, for the first time, a P–B bond can be formed by a hydrogen elimination reaction under the applied mild conditions. By using $(C_6F_5)_3B{\cdot}PH_2R$ [R = H, Cp* (**2**), Ph], the reaction with $BH_3{\cdot}NHC^{Me}$ leads to viscous oils of ionic products of the formula $[(C_6F_5)_3BH][RPH_2{\cdot}BH_2{\cdot}NHC^{Me}]$ (**4a**: R = H, **4b**: R = Cp*, **4c**: R = Ph). DFT calculations give some insight into the preferred type of the corresponding experimentally observed reaction. However, the synthesis of the LA/LB-stabilised phosphanylborane (**5**) with $(C_6F_5)_3B$ as the LA and NHC^{Me} as the LB was achieved by a Lewis base substitution reaction. In the solid state, the substituents around the P–B core of the phosphanylboranes **3a**,**b** and **5** show a staggered conformation. The LA and the LB in **3b** adopt an antiperiplanar geometry, whereas the LA and the LB in **3a** and **5** show a synclinal arrangement.

Experimental Section

General Techniques: All manipulations were performed under an atmosphere of dry nitrogen by using standard glove box and Schlenk techniques. Solvents were degassed and purified by standard procedures. The compounds $(C_6F_5)_3B$,[36] $(C_6F_5)_3Ga{\cdot}Et_2O$,[36] Cp^*PH_2 ($Cp^* = C_{10}H_{15}$),[37] $(C_6F_5)_3B{\cdot}PH_3$,[24] $(C_6F_5)_3B{\cdot}PH_2Ph$,[13] $(C_6F_5)_3Ga{\cdot}PH_2Ph$,[18] 1,3,4,5-tetramethylimodazol-2-ylidene (NHC^{Me}),[38] 2-boran-1,3,4,5-tetramethylimodazoline $H_3B{\cdot}NHC^{Me}$[26] and $(C_6F_5)_3B{\cdot}PHPh–BH_2{\cdot}NMe_3$[18] were prepared according to the literature procedures or former published methods of our research group. The NMR spectra were recorded with either an Avance 300 (^1H: 300.132 MHz, ^{31}P: 121.468 MHz, ^{19}F: 282.404 MHz) or Avance 400 spectrometer [^1H: 400.13 MHz, ^{31}P: 161.976 MHz, ^{11}B: 128.378 MHz, $^{13}C(^1H)$: 100.623 MHz] with δ [ppm] referenced to external $SiMe_4$ (^1H, ^{13}C), H_3PO_4 (^{31}P), $BF_3{\cdot}Et_2O$ (^{11}B) or $CFCl_3$ (^{19}F). IR spectra were measured with a DIGILAB (FTS 800) FTIR spectrometer. All mass spectra were recorded with a ThermoQuest Finnigan TSQ 7000 (ESI MS) or a Finnigan MAT 95 (FD MS and EI MS). The C, H, N analyses were measured with an Elementar Vario EL III apparatus.

$(C_6F_5)_3Ga{\cdot}PH_2Cp^*$ (1a): A mixture of $(C_6F_5)_3Ga{\cdot}Et_2O$ (3.55 g, 5.5 mmol) and Cp^*PH_2 (0.926 g, 5.5 mmol) in toluene (50 mL) was stirred for 18 h at room temperature. After removal of the solvent in vacuo, the residue was dried at 10^{-3} bar until a fine, white powder of **1a** was obtained. Recrystallisation of the residue from *n*-hexane at –25 °C yielded colourless crystals of **1a**. Yield: 3.6 g (88.7%). On one occasion we obtained colourless crystals of **1b**, presumably by decomposition of **1a**. The crystals grew in a Schlenk tube that was stored for several weeks at 4 °C. Data for **1a**: ^1H NMR (C_6D_6, 25 °C): δ = 0.6 (d, $^3J_{P,H}$ = 15 Hz, 3 H, Cp*), 1.25 (s, 6 H, Cp*), 1.28 (s, 6 H, Cp*), 4.08 (d, $^1J_{P,H}$ = 348 Hz, 2 H, PH_2) ppm. ^{31}P NMR (C_6D_6, 25 °C): δ = –65.3 (t, $^1J_{P,H}$ = 348 Hz, PH_2) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = –65.3 (s, PH) ppm. ^{19}F NMR (C_6D_6, 25 °C): δ = –121.8 (m, 6 F, *o*-F), –152.5 (t, $^3J_{F,F}$ = 19.1 Hz, 3 F, *p*-F), –160.9 (m, 6 F, *m*-F) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 9.5 (s, $C\mathbf{C}H_3$, Cp*), 10.6 (s, $C\mathbf{C}H_3$, Cp*), 20.9 (d, $^2J_{C,P}$ = 5.9 Hz, $PC\mathbf{C}H_3$, Cp*), 50.9 (d, $^1J_{C,P}$ = 14.5 Hz, P**C**, Cp*), 113.6 [t, $^2J_{C,F}$ = 45.5 Hz, Ga**C**, $Ga(C_6F_5)_3$], 134.9 (s, PC**C**, Cp*), 137.3 [dm, $^1J_{C,F}$ = 254.3 Hz, *m*-C, $Ga(C_6F_5)_3$], 140.3 (s, PCC**C**, Cp*), 141.8 [dm, $^1J_{C,F}$ = 252.4 Hz, *p*-C, $Ga(C_6F_5)_3$], 149.0 [dm, $^1J_{C,F}$ = 233.8 Hz, *o*-C, $Ga(C_6F_5)_3$] ppm. MS (FD, toluene): *m/z* (%) = 739 (15) $[M]^+$, 570 (33), 335 (34) $[(C_6F_5)_2H]^+$, 168 (100) $[M - Ga(C_6F_5)_3]^+$. IR (KBr): $\tilde{\nu}$ = 2971 (vs, CH), 2918 (vs, CH), 2862 (s, CH), 2747 (m), 2635 (m), 2577 (m), 2541 (m), 2400 (w, PH), 2372 (s, PH), 2329 (m, br.), 2223 (w), 2091 (w), 2049 (w), 1918 (w, br.), 1860 (w, br.), 1640 (vs), 1513(vs), 1469 (vs, br.), 1377 (m), 1367 (m), 1268 (vs), 1235 (m), 1132 (m), 1115 (w, sh.), 1080 (vs), 1055 (s, sh.), 1010 (m), 961 (vs), 855 (m), 837 (s), 795 (s), 744 (m), 721 (s), 616 (s), 610 (m, sh.), 591 (s), 518 (w), 491 (m) cm^{-1}. $C_{28}H_{17}F_{15}GaP$ (739.1): calcd. C 45.50, H 2.32; found C 45.41, H 2.30. Data for **1b**: ^1H NMR (C_6D_6, 25 °C): δ = 0.89 (d, $^3J_{P,H}$ = 21 Hz, $PCCH_3$, 3 H, Cp*), 2.35 (s, 12 H, Cp*), 5.57 (d, $^1J_{P,H}$ = 512 Hz, 2 H, PH_2) ppm. ^{31}P NMR (C_6D_6, 25 °C): δ = 34.5 (t, $^1J_{P,H}$ = 512 Hz, PH_2) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 34.5 (s, PH_2) ppm. ^{19}F NMR (C_6D_6, 25 °C): δ = –124.9 (m, 6 F, *o*-F), –153.0 (t, $^3J_{F,F}$ = 20 Hz, 3F *p*-F), –161.2 (m, 6 F, *m*-F) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 9.0 (s, $C\mathbf{C}H_3$, Cp*), 9.7 (s, $C\mathbf{C}H_3$, Cp*), 55.1 (d, $^1J_{P,C}$ = 54 Hz, P**C**, Cp*), 113.7 [t, $^2J_{C,F}$ = 46 Hz, Ga**C**, $Ga(C_6F_5)_3$], 130.7 (s, PC**C**, Cp*), 136.1 [dm, $^1J_{C,F}$ = 256 Hz, *m*-C, $Ga(C_6F_5)_3$], 140.5 [dm, $^1J_{C,F}$ = 254 Hz, *p*-C, $Ga(C_6F_5)_3$], 142.7 (s, PCCC, Cp*), 147.9 [dm, $^1J_{C,F}$ = 234 Hz, *o*-C, $Ga(C_6F_5)_3$] ppm. MS (FD, toluene): *m/z* (%) = 754 (100) $[M]^+$, 1508.5 (5) $[2M]^+$. IR (KBr): $\tilde{\nu}$ = 2975 (s, CH), 2924 (s, CH), 2872 (s, CH), 2750 (w), 2635 (w), 2575 (w), 2539 (w), 2471 (w), 2420 (m, sh., PH), 2399 (s, PH), 2324 (m), 2223 (w), 2082 (w), 2041 (w), 1917 (w), 1860 (w), 1712 (m), 1640 (vs), 1578 (m), 1510 (vs), 1461 (vs, br.), 1379 (s), 1365 (vs), 1271 (vs), 1221 (w), 1149 (vs, POGa), 1068 (vs, br.), 1011 (vs), 962 (vs), 888 (w), 799 (s), 743 (m), 721 (m), 696 (m), 611 (s), 569 (m), 538 (w), 522 (w), 491 (m), 435 (m) cm^{-1}. $C_{28}H_{17}F_{15}GaOP$ (755): calcd. C 44.54, H 2.27; found C 44.35, H 1.94.

$(C_6F_5)_3B{\cdot}PH_2Cp^*$ (2): A mixture of $B(C_6F_5)_3$ (2.9 g, 5.66 mmol) and Cp^*PH_2 (0.954 g, 5.67 mmol) in toluene (40 mL) was stirred for 18 h at room temperature. After removal of the solvent in vacuo, the residue was washed with *n*-hexane (3 × 10 mL). Single crystals of **2** were obtained by recrystallisation from *n*-hexane at –25 °C as colourless plates. Yield: 3.52 g (91.4%). ^1H NMR (C_6D_6, 25 °C): δ = 0.51 (d, $^3J_{P,H}$ = 17 Hz, 3 H, Cp*), 1.33 (d, $^5J_{P,H}$ = 3 Hz, 6 H, Cp*), 1.37 (s, 6 H, Cp*), 4.71 (d, $^1J_{P,H}$ = 394 Hz, 2 H, PH_2) ppm. ^{31}P NMR (C_6D_6, 25 °C): δ = –38.3 (t, $^1J_{P,H}$ = 394 Hz, PH_2) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = –38.3 (s, PH_2) ppm. ^{19}F NMR (C_6D_6, 25 °C): δ = –129.5 (m, 6 F, *o*-F), –155.6 (br. s, 3 F, *p*-F), –163.1 (m, $^3J_{F,F}$ = 19 Hz, 6 F, *m*-F) ppm. ^{11}B NMR (C_6D_6, 25 °C): δ = –15.5 [br. s, $B(C_6F_5)_3$] ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 9.7 (s, CCH_3, Cp*), 10.8 (s, CCH_3, Cp*), 21.6 (s, $PCCH_3$, Cp*), 51.6 (d, $^1J_{C,P}$ = 23.5 Hz, PC), 155.5 [br. m, BC, $B(C_6F_5)_3$], 135.4 (s, PCC, Cp*), 137.5 [dm, $^1J_{C,F}$ = 253 Hz, *m*-C, $B(C_6F_5)_3$], 139.8 (d, $^3J_{C,P}$ = 7 Hz, PCCC, Cp*), 140.6 [dm, $^1J_{C,F}$ = 250 Hz, *p*-C, $B(C_6F_5)_3$], 148.5 [dm, $^1J_{C,F}$ = 242 Hz, *o*-C, $B(C_6F_5)_3$] ppm. MS (FD, toluene): *m/z* (%) = 512 (100) $[M - PH_2Cp^*]^+$, 335 (5) $[(C_6F_5)_2H]^+$, 168 (50) $[M - B(C_6F_5)_3]^+$. IR (KBr): $\tilde{\nu}$ = 2965 (s, CH), 2942 (s, CH), 2922 (s, CH), 2863 (s, CH), 2745 (m, br.), 2567, (w, br.), 2454 (m), 2409 (m, PH), 2349 (w, PH), 2227 (w), 2096 (w, br.), 2045 (w, br.), 1869 (w, br.), 1647 (vs), 1596 (m), 1522 (vs), 1471 (vs, br.), 1453 (s, sh.), 1386 (s), 1377 (s), 1285 (s), 1234 (m), 1093 (vs, br.), 1022 (w, sh.), 980 (vs), 931 (w), 899 (m), 859 (m), 800 (m, sh.), 786 (s), 773 (s), 761 (s), 741 (s), 683 (s), 670 (s), 657 (m), 632 (m), 611 (w), 593 (m), 570 (m), 512 (w) cm^{-1}. $C_{28}H_{17}BF_{15}P$ (680.2): calcd. C 49.44, H 2.52; found C 49.29, H 2.56.

$(C_6F_5)_3Ga\cdot P(Cp^*)HBH_2\cdot NHC^{Me}$ (3a): A mixture of **1** (250 mg, 0.34 mmol) and $H_3B\cdot NHC^{Me}$ (47 mg, 0.34 mmol) in toluene (30 mL) was heated at reflux for 18 h. The slightly yellow solution was cooled to room temperature, concentrated to 1–2 mL in vacuo and layered with *n*-hexane (2–3 mL). From this mixture, colourless plates of **3a** were obtained, which were separated and washed with *n*-hexane (3 × 5 mL). Yield: 213 mg (72%). ^{1}H NMR (C_6D_6, 25 °C): δ = 1.15 (s, 6 H, NHC^{Me}, CCH_3), 1.37 (d, $^{3}J_{P,H}$ = 16 Hz, $PCCH_3$, 3.5 H, Cp*), 1.47 (s, CCH_3, 3 H, Cp*), 1.60 (s, CCH_3, 6 H, Cp*), 1.90 (s, CCH_3, 3 H, Cp*), 2.63 (s, NCH_3, 6 H, NHC^{Me}), 4.42 (dd, $^{1}J_{P,H}$ = 313 Hz, $^{3}J_{H,H}$ = 16 Hz, 1 H, PH) ppm. ^{31}P NMR (C_6D_6, 25 °C): δ = –72.2 (d, $^{1}J_{P,H}$ = 314 Hz, PH) ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 25 °C): δ = –72.2 (s, PH) ppm. ^{11}B NMR (C_6D_6, 25 °C): δ = –35.3 (br. s, BH_2) ppm. $^{11}B\{^{1}H\}$ NMR (C_6D_6, 25 °C): δ = –35.3 (br. s, BH_2) ppm. ^{19}F NMR (C_6D_6, 25 °C): δ = –121.0 [m, *o*-F, 6 F, $Ga(C_6F_5)_3$], –155.5 [t, $^{3}J_{F,F}$ = 20 Hz, *p*-F, 3 F, $Ga(C_6F_5)_3$], –162.0 [m, *m*-F, 6 F, $Ga(C_6F_5)_3$] ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 25 °C): δ = 7.5 (s, CCH_3, NHC^{Me}), 10.9 (d, $^{3}J_{C,P}$ = 24 Hz, $PCCCH_3$, Cp*), 10.4 (d, $^{4}J_{C,P}$ = 14 Hz, $PCCCCH_3$), 20.4 (s, $PCCH_3$, Cp*), 31.6 (s, NCH_3, NHC^{Me}), 52.7 (d, $^{1}J_{C,P}$ = 14 Hz, P*C*, Cp*), 117.9 [t, $^{2}J_{C,F}$ = 50 Hz, GaC, $Ga(C_6F_5)_3$], 124.7 (s, C=C, NHC^{Me}), 137.05 (d, $^{2}J_{C,P}$ = 7 Hz, PCC, Cp*), 137.1 [dm, $^{1}J_{C,F}$ = 259 Hz, *m*-C, $Ga(C_6F_5)_3$], 138.4 (s, PCCC, Cp*), 140.9 [dm, $^{1}J_{C,F}$ = 249 Hz, *p*-C, $Ga(C_6F_5)_3$], 149.2 [dm, $^{1}J_{C,F}$ = 234 Hz, *o*-C, $Ga(C_6F_5)_3$], 159.3 (br. m, BC, NHC^{Me}) ppm. MS (EI, 70 eV, toluene): *m*/*z* (%) = 570 (6) $[(C_6F_5)_3Ga]^+$, 403 (13) $[(C_6F_5)_2Ga]^+$, 304 (14) $[(C_6F_5)BH_2\cdot NHC^{Me}]^+$, 137 (100) $[BH_2\cdot NHC^{Me}]^+$. IR (KBr): ṽ = 2959 (m, CH), 2924 (s, br., CH), 2861 (m, br., CH), 2426 (m, BH), 2399 (m, BH), 2349 (w, PH), 1639 (s), 1609 (w), 1509 (vs), 1378 (m), 1268 (s), 1232 (m), 1159 (w), 1128 (m), 1076 (s, br.), 1024 (m), 960 (vs), 898 (m, br.), 856 (w), 790 (s), 721 (m), 665 (w), 610 (m), 489 (m) cm^{-1}.

$(C_6F_5)_3Ga\cdot P(Ph)HBH_2\cdot NHC^{Me}$ (3b): $H_3B\cdot NHC^{Me}$ (61 mg, 0.44 mmol) was added to a solution of $(C_6F_5)_3Ga\cdot PPhH_2$ (300 mg, 0.44 mmol) in C_6D_6 (5 mL) and stirred for 18 h at room temperature. The formation of H_2 was observed, and the colour of the solution turned to light yellow. After concentration of the the solution to a volume of 1–2 mL, it was layered with *n*-hexane (2–3 mL). Colourless, cubic crystals were formed that were separated and washed with *n*-hexane (3 × 3 mL). Yield: 194 mg (54%). ^{1}H NMR (C_6D_6, 25 °C): δ = 1.13 (s, CCH_3, 6 H, NHC^{Me}), 2.64 (s, NCH_3, 6 H, NHC^{Me}), 4.76 (dt, $^{1}J_{P,H}$ = 325 Hz, $^{3}J_{H,H}$ = 7 Hz, 1 H, PH), 6.9 (m, 3 H, Ph), 7.4 (m, 2 H, Ph) ppm. ^{31}P NMR (C_6D_6, 25 °C): δ = –71.8 (d, $^{1}J_{P,H}$ = 326 Hz, PH) ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 25 °C): δ = –71.8 (s, PH) ppm. ^{11}B NMR (C_6D_6, 25 °C): δ = –32.8 (br. s, BH_2) ppm. $^{11}B\{^{1}H\}$ NMR (C_6D_6, 25 °C): δ = –32.8 (br. s, BH_2) ppm. ^{19}F NMR (C_6D_6, 25 °C): δ = –121.8 [m, 6 F, *o*-F, $Ga(C_6F_5)_3$], –155.0 [t, $^{3}J_{F,F}$ = 20 Hz, 3 F, *p*-F, $Ga(C_6F_5)_3$], –162.1 [m, 6 F, *m*-F, $Ga(C_6F_5)_3$] ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 25 °C): δ = 7.5 (s, CCH_3, NHC^{Me}), 31.9 (s, NCH_3, NHC^{Me}), 116.3 [m, GaC, $Ga(C_6F_5)_3$], 125.0 (s, C=C, NHC^{Me}), 128.7 (d, $^{2}J_{C,P}$ = 9 Hz, *m*-C, Ph), 129.7 (d, $^{4}J_{C,P}$ = 3 Hz, *p*-C, Ph), 132.8 (d, $^{3}J_{C,P}$ = 8 Hz, *o*-C, Ph), 137.1 [dm, $^{1}J_{C,F}$ = 257 Hz, *m*-C, $Ga(C_6F_5)_3$], 141.1 [dm, $^{1}J_{C,F}$ = 249 Hz, *p*-C, $Ga(C_6F_5)_3$], 149.2 [dm, $^{1}J_{C,F}$ = 236 Hz, *o*-C, $Ga(C_6F_5)_3$] ppm. MS (EI, 70 eV, CH_2Cl_2): *m*/*z* (%) = 570 (14) $[(C_6F_5)_3Ga]^+$, 403 (34) $[(C_6F_5)BH\cdot NHC^{Me}]^+$, 168 (35) $[C_6F_5H]^+$, 137 (100) $[BH_2\cdot NHC^{Me}]^+$. IR (C_6D_6): ṽ = 2958 (s, br., CH), 2928 (m, CH), 2867 (m, CH), 2630 (w), 2572 (w), 2536 (w), 2428 (s, BH), 2398 (s, BH), 2349 (w, sh., PH), 2220 (w), 1638 (s), 1580 (w), 1555 (m), 1509 (vs), 1463 (vs, br.), 1360 (m), 1330 (s), 1268 (m), 1158 (w), 1074 (vs, br.), 1023 (m, br.), 960 (vs), 886 (m), 811 (s), 793 (m), 443 (m), 694 (m), 608 (m), 504 (vs), 491 (vs) cm^{-1}. $C_{31}H_{20}BF_{15}GaN_2P$ (817): calcd. C 45.57, H 2.47, N 3.43; found C 44.98, H 2.18, N 3.49.

$[(C_6F_5)_3BH]^-[PH_3\cdot BH_2\cdot NHC^{Me}]^+$ (4a): $H_3B\cdot NHC^{Me}$ (121 mg, 0.88 mmol) was added to a solution of $(C_6F_5)_3B\cdot PH_3$ (480 mg, 0.88 mmol) in CH_2Cl_2 (10 mL). After stirring the solution for 5 h at room temperature the solvent was removed in vacuo and **4a** was obtained as a colourless, viscous oil. Yield: 427 mg (71%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 2.15 (s, CCH_3, 6 H, NHC^{Me}), 3.63 (s, NCH_3, 6 H, NHC^{Me}), 4.6 (dt, $^{1}J_{P,H}$ = 401 Hz, $^{3}J_{H,H}$ = 8 Hz, PH_3, 3 H) ppm. ^{31}P NMR (CD_2Cl_2, 25 °C): δ = –119.2 (q, $^{1}J_{P,H}$ = 401 Hz, PH_3) ppm. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ = –119.2 (s, PH_3) ppm. ^{11}B NMR (CD_2Cl_2, 25 °C): δ = –25.6 {d, $^{1}J_{B,H}$ = 93 Hz, BH, $[(C_6F_5)_3BH]^-$}, –37.6 (br. dt, $^{1}J_{B,H}$ = 92 Hz, $^{1}J_{B,P}$ = 37 Hz, BH_2) ppm. $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ = –25.6 {s, BH, $[(C_6F_5)_3BH]^-$}, –37.7 (br. d, $^{1}J_{B,P}$ = 45 Hz, BH_2) ppm. ^{19}F NMR (CD_2Cl_2, 25 °C): δ = –133.9 {m, *o*-F, 6 F, $[(C_6F_5)_3BH]^-$}, –164.3 {t, $^{3}J_{F,F}$ = 20 Hz, *p*-F, 3 F, $[(C_6F_5)_3BH]^-$}, –167.3 {m, *m*-F, 6 F, $[(C_6F_5)_3BH]^-$} ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ = 8.7 (s, CCH_3, NHC^{Me}), 33.3 (s, NCH_3, NHC^{Me}), 125.5 {br. m, BC, $[(C_6F_5)_3BH]^-$}, 127.8 (s, C=C, NHC^{Me}), 136.8 {dm, $^{1}J_{C,F}$ = 243 Hz, *m*-C, $[(C_6F_5)_3BH]^-$}, 138.2 {dm, $^{1}J_{C,F}$ = 244 Hz, *p*-C, $[(C_6F_5)_3BH]^-$}, 148.5 {dm, $^{1}J_{C,F}$ = 241 Hz, *o*-C, $[(C_6F_5)_3BH]^-$} ppm. MS (ESI–, CHCN): *m*/*z* (%) = 513 (100) $[(C_6F_5)_3BH]^-$. MS (ESI+, CHCN): *m*/*z* (%) = 307 (100) $[PH_2(BH_2\cdot NHC^{Me})_2]^+$, 261 (4) $[BH_2\cdot(NHC^{Me})_2]^+$, 139 (5) $[BH_3\cdot NHC^{Me} + H]^+$, 125 (67) $[NHC^{Me} + H]^+$. IR (THF): ṽ = 2612 (w, br.), 2576 (w, br.), 2436 (m, vbr., BH), 2398 (m, vbr., BH), 2349 (w, PH), 2285 (w, PH), 2029 (w), 1640 (s), 1548 (w), 1508 (vs), 1465 (vs), 1376 (m), 1273 (s), 1224 (m), 1103 (s, br.), 1016 (m, br.), 970 (vs), 807 (m), 765 (m), 735 (m), 661 (w), 646 (w), 601 (w), 567 (m) cm^{-1}.

$[(C_6F_5)_3BH]^-[PH_2Cp^*\cdot BH_2\cdot NHC^{Me}]^+$ (4b): $H_3B\cdot NHC^{Me}$ (61 mg, 0.44 mmol) was added to a solution of **2** (300 mg, 0.44 mmol) in CH_2Cl_2 (5 mL). After stirring the solution for 4 h at room temperature the solvent was removed in vacuo and **4b** was obtained as a colourless, viscous oil. Yield: 284 mg (79%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 1.36 (d, $^{3}J_{P,H}$ = 17 Hz, $PCCH_3$, 3 H, Cp*), 1.81 (d, $^{5}J_{P,H}$ = 4 Hz, CCH_3, 6 H, Cp*), 1.82 (s, CCH_3, 6 H, Cp*), 2.14 (s, CCH_3, 6 H, NHC^{Me}), 3.50 (s, NCH_3, 6 H, NHC^{Me}), 3.58 {br. q, $^{1}J_{H,B}$ = 91 Hz, 1 H, $[(C_6F_5)_3BH]^-$}, 4.69 (dt, $^{1}J_{P,H}$ = 374 Hz, $^{3}J_{H,H}$ = 7 Hz, 2 H, PH_2) ppm. ^{31}P NMR (CD_2Cl_2, 25 °C): δ = –40.8 (t, $^{1}J_{P,H}$ = 374 Hz, PH_2) ppm. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ = –40.8 (s, PH_2) ppm. ^{11}B NMR (CD_2Cl_2, 25 °C): δ = –25.6 {d, $^{1}J_{B,H}$ = 90 Hz, BH, $[(C_6F_5)_3BH]^-$}, –37.8 (br. td, $^{1}J_{B,P}$ = 48 Hz, BH_2) ppm. $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ = –25.6 {s, $[(C_6F_5)_3BH]^-$}, –37.8 (br. d, $^{1}J_{B,P}$ = 41.5 Hz, BH_2) ppm. ^{19}F NMR (CD_2Cl_2, 25 °C): δ = –133.8 {m, *o*-F, 6 F, $[(C_6F_5)_3BH]^-$}, –164.4 {t, $^{3}J_{F,F}$ = 20 Hz, *p*-F, 3 F, $[(C_6F_5)_3BH]^-$}, –167.4 {m, *m*-F, 6 F, $[(C_6F_5)_3BH]^-$} ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ = 8.8 (s, CCH_3, NHC^{Me}), 10.1 (s, CCH_3, Cp*), 11.4 (s, C*C*H$_3$, Cp*), 19.0 (d, $^{2}J_{C,P}$ = 5 Hz, $PCCH_3$, Cp*), 33.3 (s, NCH_3, NHC^{Me}), 50.6 (d, $^{1}J_{C,P}$ = 25 Hz, PC, Cp*), 125.0 {br. m, BC, $[(C_6F_5)_3BH]^-$}, 127.1 (s, C=C, NHC^{Me}), 134.4 (s, PCC, Cp*), 136.8 {dm, $^{1}J_{C,P}$ = 250 Hz, *m*-C, $[(C_6F_5)_3BH]^-$}, 138.1 {dm, $^{1}J_{C,P}$ = 239 Hz, *p*-C, $[(C_6F_5)_3BH]^-$}, 141.3 (d, $^{3}J_{C,P}$ = 7 Hz, PCCC, Cp*), 148.5 {dm, $^{1}J_{C,P}$ = 233 Hz, *o*-C, $[(C_6F_5)_3BH]^-$} ppm. MS (ESI–, CHCN): *m*/*z* (%) = 513 (100) $[(C_6F_5)_3BH]^-$. MS (ESI+, CHCN): *m*/*z* (%) = 441 (10.5) $[Cp^*PH(BH_2\cdot NHC^{Me})_2]^+$, 305 (100) $[PH_2Cp^*\cdot BH_2\cdot NHC^{Me}]^+$, 125 (15) $[NHC^{Me} + H]^+$. IR (THF): ṽ = 2741 (m, br.), 2661 (w), 2612 (w), 2574 (m), 2445 (s, vbr., BH, K$^+$), 2380 (s, vbr., BH, K$^+$), 2346 (sh., BH, A$^-$), 2279 (m, PH), 2171 (w, PH), 2030 (w), 1640 (s), 1603 (w), 1580 (w), 1547 (w), 1509 (vs), 1467 (vs), 1456 (vs), 1376 (m), 1273 (s), 1104 (vs, br.), 1030 (m), 969 (vs), 922 (vs, br.), 805 (w), 765 (m), 735 (s), 660 (m), 601 (w), 567 (m), 468 (w) cm^{-1}.

$[(C_6F_5)_3BH]^-[PH_2Ph\cdot BH_2\cdot NHC^{Me}]^+$ (4c): $H_3B\cdot NHC^{Me}$ (136 mg, 0.987 mmol) was added to a solution of $(C_6F_5)_3B\cdot PH_2Ph$ (614 mg, 0.987 mmol) in CH_2Cl_2 (20 mL). After stirring the solution for 5 h at room temperature the solvent was removed in vacuo and **4c** was obtained as a colourless, viscous oil. Yield: 601 mg (80%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 2.16 (s, CCH_3, 6 H, NHC^{Me}), 3.60 (s, NCH_3, 6 H, NHC^{Me}), 5.79 (dt, $^1J_{P,H}$ = 398 Hz, $^3J_{H,H}$ = 7.5 Hz, 2 H, PH), 7.51–7.57 (m, 2 H, Ph), 7.59–7.69 (m, 3 H, Ph) ppm. ^{31}P NMR (CD_2Cl_2, 25 °C): δ = –57.9 (t, $^1J_{P,H}$ = 398 Hz, PH_2) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = –57.9 (s, PH_2) ppm. ^{11}B NMR (CD_2Cl_2, 25 °C): δ = –25.5 {d, $^1J_{B,H}$ = 92 Hz, BH, $[(C_6F_5)_3BH]^-$}, –35.6 (br. s, BH_2) ppm. ^{11}B{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = –25.5 {s, BH, $[(C_6F_5)_3BH]^-$}, –35.5 (s, BH_2) ppm. ^{19}F NMR (CD_2Cl_2, 25 °C): δ = –133.7 {m, *o*-F, 6 F, $[(C_6F_5)_3BH]^-$}, –164.3 {t, $^3J_{F,F}$ = 20 Hz, *p*-F, 3 F, $[(C_6F_5)_3BH]^-$}, –167.3 {m, *m*-F, 6 F, $[(C_6F_5)_3BH]^-$} ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 8.6 (s, CCH_3, NHC^{Me}), 33.3 (s, NCH_3, NHC^{Me}), 115.8 (d, $^1J_{C,P}$ = 64 Hz, PC, Ph), 125.6 {br. s, BC, $[(C_6F_5)_3BH]^-$}, 126.1 (s, C=C, NHC^{Me}), 127.7 (s, *m*-C, Ph), 130.3 (d, $^3J_{C,P}$ = 11 Hz, *p*-C, Ph), 133.7 (d, $^2J_{C,P}$ = 10 Hz, *o*-C, Ph), 136.9 {dm, $^1J_{C,F}$ = 250 Hz, *m*-C, $[(C_6F_5)_3BH]^-$}, 138.3 {dm, $^1J_{C,F}$ = 244 Hz, *p*-C, $[(C_6F_5)_3BH]^-$}, 148.7 {dm, $^1J_{C,F}$ = 236 Hz, *o*-C, $[(C_6F_5)_3BH]^-$}, 153.3 (br. s, BC, NHC^{Me}) ppm. MS (ESI–, CHOH, $CH_3COO^-NH_4^+$): *m*/*z* (%) = 513 (100) $[(C_6F_5)_3BH]^-$. MS (ESI+, CH_3OH, $CH_3COO^-NH_4^+$): *m*/*z* (%) = 383 (100) $[PPhH(BH_2\cdot NHC^{Me})_2 + 2H]^+$, 247 (12) $[PH_2Ph\cdot BH_2\cdot NHC^{Me}]^+$, 137 (51) $[BH_2\cdot NHC^{Me}]^+$, 125 (13) $[NHC^{Me} + H]^+$. IR (THF): $\tilde{\nu}$ = 2446 (w, vbr., BH, K^+), 2401 (m, vbr., BH, K^+), 2356 (sh., BH, A^-), 2302 (m, PH), 2189 (w, PH), 1639 (m), 1508 (vs), 1470 (s), 1438 (w), 1376 (m), 1261 (s), 1114 (s, br.), 1012 (m), 970 (vs), 807 (s, br.), 711 (s), 678 (m), 567 (m), 467 (w) cm^{-1}.

$(C_6F_5)_3B\cdot P(Ph)HBH_2\cdot NHC^{Me}$ (5): $H_3B\cdot NHC^{Me}$ (55 mg, 0.44 mmol) was added to a solution of $(C_6F_5)_3B\cdot PPhHBH_2\cdot NMe_3$ (0.304 g, 0.44 mmol) in toluene (10 mL). Incipiently showing a red colour, the solution turned light yellow after stirring for 18 h at room temperature. After concentration of the solution to a volume of 0.5–1 mL, it was layered with *n*-hexane (2–3 mL). After 3 weeks at 8 °C colourless prisms were formed, which were separated and washed with *n*-hexane (2 × 5 mL). Yield: 123 mg (37%) ^{1}H NMR (C_6D_6, 25 °C): δ = 1.08 (s, CCH_3, 6 H, NHC^{Me}), 2.62 (s, NCH_3, 6 H, NHC^{Me}), 5.66 (d, $^1J_{P,H}$ = 351 Hz, 1 H, PH), 6.8–7.4 (m, Ph) ppm. ^{31}P NMR (C_6D_6, 25 °C): δ = –43.8 (d, $^1J_{P,H}$ = 351 Hz, PH) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ = –43.8 (s, PH) ppm. ^{11}B NMR (C_6D_6, 25 °C): δ = –14.4 [br. s, $B(C_6F_5)_3$], –33.2 (br. s, BH_2) ppm. ^{11}B{^{1}H} NMR (C_6D_6, 25 °C): δ = –14.4 [br. s, $B(C_6F_5)_3$], –33.2 (br. s, BH_2) ppm. ^{19}F NMR (C_6D_6, 25 °C): δ = –128.1 [s, *o*-F, 6 F, $B(C_6F_5)_3$], –158.8 [t, $^3J_{F,F}$ = 21 Hz, *p*-F, 3 F, $B(C_6F_5)_3$], –164.6 [m, *m*-F, 6 F, $B(C_6F_5)_3$] ppm. ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ = 7.6 (s, CCH_3, NHC^{Me}), 31.9 (s, NCH_3, NHC^{Me}), 119.4 [m, BC, $B(C_6F_5)_3$], 124.9 (s, C=C, NHC^{Me}), 128.5 (s, *m*-C, Ph), 130.2 (s, *p*-C, Ph), 133.3 (d, $^2J_{C,P}$ = 6 Hz, *o*-C, Ph), 137.4 [dm, $^1J_{C,F}$ = 244 Hz, *m*-C, $B(C_6F_5)_3$], 139.8 [dm, $^1J_{C,F}$ = 231 Hz, *p*-C, $B(C_6F_5)_3$], 148.7 [dm, $^1J_{C,F}$ = 232 Hz, *o*-C, $B(C_6F_5)_3$] ppm. MS (ESI–, $CHCOOC_2H_5$, CH_3OH, $CH_3COO^-NH_4^+$): *m*/*z* (%) = 757 (100) $[M - H]^-$, 529 (31) $[B(C_6F_5)_3\cdot NH_3]^-$. MS (ESI+, $CHCOOC_2H_5$, CH_3OH, $CH_3COO^-NH_4^+$): *m*/*z* (%) = 776 (100) $[M + NH_4]^+$, 383 (17) $[PPhH(BH_2\cdot NHC^{Me})_2 + 2H]^+$, 247 (28) $[PPhH_2\cdot BH_2\cdot NHC^{Me}]^+$. IR (KBr): $\tilde{\nu}$ = 2957 (m, CH), 2925 (s CH), 2859 (m, br., CH), 2460 (m, br., BH), 2419 (m, br., BH), 2316 (w, br., PH), 1644

Table 4. Crystallographic data for $BH_3\cdot NHC^{Me}$ and compounds **1a**, **1b**, **2**, **3a**,**b** and **5**.

	$BH_3\cdot NHC^{Me}$	**1a**	**1b**	**2**	**3a**	**3b**	**5**
Empirical formula	$C_7H_{15}N_2B$	$C_{28}H_{17}F_{15}GaP$	$C_{28}H_{17}F_{15}GaPO$	$C_{28}H_{17}F_{15}BP$	$C_{35}F_{15}H_{30}N_2GaPB\cdot 0.25C_7H_7\cdot 0.25C_6H_{14}$	$C_{31}H_{20}F_{15}N_2GaPB$	$C_{31}H_{20}F_{15}N_2B_2P\cdot 0.5C_7H_8$
Formula mass	138.02	739.11	755.1	680.2	875.11	816.99	800.11
λ [Å]	1.54178	0.71073	0.71073	0.71073	0.71073	1.54178	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
T [K]	123(1)	173(1)	203(2)	123(1)	123(1)	123(2)	123(1)
Space group	$P\,2_1/c$	$P\,2_1/n$	$P\bar{1}$	$P\,2_1/n$	$P\,2_1/c$	$P\,2_1/n$	$C\,2/c$
a [Å]		10.127(2)	10.392(2)	8.8220(18)	23.493(2)	13.5347(3)	30.027(3)
b [Å]	16.912(5)	15.930(3)	10.463(2)	19.650(4)	16.7946(12)	10.0972(2)	14.3337(12)
c [Å]	10.313(5)	18.515(4)	14.033(3)	16.408(3)	25.162(2)	23.9708(5)	16.9845(14)
α [°]	90	90	97.94(3)	90	90	90	90
β [°]	90.411(5)	105.15(3)	102.25(3)	105.31(3)	114.338(10)	92.223(2)	109.829(10)
γ [°]	90	90	97.23(3)	90	90	90	90
V [Å^3]	1714.8(13)	2883.0(10)	1457(5)	2743.4(10)	9045.5(14)	3273.45(12)	6876.7(11)
Z	8	4	2	4	8	4	8
D_{calcd} [mg m^{-3}]	1.069	1.703	1.720	1.647	1.285	1.658	1.546
μ [mm]$^{-1}$	0.479	1.126	0.118	0.222	0.730	2.655	0.191
F (000)	608	1464	748	1360	3520	1624	3240
2θ range	8.58–102.65	3.42–51.9	3.98–48.04	5.22–51.74	3.8–51.76	4.99–124.21	4.38–51.82
Index ranges	$-9 \le h \le 9$	$-11 \le h \le 12$	$-11 \le h \le 11$	$-10 \le h \le 10$	$-28 \le h \le 28$	$-13 \le h \le 13$	$-36 \le h \le 36$
	$-17 \le k \le 16$	$-19 \le k \le 19$	$-11 \le k \le 11$	$-23 \le k \le 23$	$-20 \le k \le 20$	$-10 \le k \le 6$	$-17 \le k \le 17$
	$-10 \le l \le 10$	$-22 \le l \le 22$	$-16 \le l \le 15$	$-20 \le l \le 19$	$-30 \le l \le 30$	$-24 \le l \le 24$	$-20 \le l \le 20$
Reflections collected	9110	19826	9314	14639	83936	8813	35140
Independent reflections	1823	5477	4272	4976	17250	3543	6654
Goodness-of-fit on F^2	0.921	1.025	1.141	1.041	0.824	0.784	1.081
R_{int}	0.087	0.0855	0.1297	0.0558	0.1040	0.0416	0.0359
Parameters	213	419	428	419	999	473	523
R_1[a] [$I > 2s(I)$]	0.0460	0.0418	0.0718	0.0375	0.0437	0.0352	0.0422
wR_2[b] (all data)	0.1215	0.1177	0.1977	0.1075	0.1026	0.0582	0.1246
Max/min $\Delta\rho$ [e Å^{-3}]	0.22/–0.27	0.908/–0.989	0.379/–0.549	0.366/–0.281	0.823/–0.306	0.334/–0.252	0.569/–0.324

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \sqrt{\Sigma[w(F_o^2 - F_c^2)^2]}/\sqrt{\Sigma[w(F_o^2)^2]}$.

(m), 1558 (w), 1516 (vs), 1464 (vs, br.), 1375 (w), 1279 (m), 1090 (s, br.), 1028 (w), 980 (s, br.), 857 (w), 804 (w, br.), 788 (m), 771 (w), 745 (w), 696 (w), 670 (m), 574 (m) cm^{-1}.

Crystal-Structure Analysis: The crystal structure analysis of **1**, **2**, **3a** and **5** was performed with a STOE IPDS diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The crystal structure analysis of **3b** was performed with an Oxford Gemini Ultra diffractometer with Cu-K_α (λ = 1.54178 Å). The structures were solved by direct methods with the SHELXS-97 program, and full-matrix least-squares refinement on F^2 in SHELXL-97 was performed with anisotropic displacements for non-H atoms.[39] Hydrogen atoms at the carbon atoms were located in idealised positions and refined isotropically according to the riding model. The hydrogen atoms at the phosphorus and boron atoms were localised by residual electron density and freely refined. These results are summarised in Table 4. Compound **5** crystallises with 0.5 molecules of toluene per molecular unit, which was considered by solving the structure. When solving structure **3a**, it was not possible to adjust the other disordered solvent molecules in the unit cell into the structural model. Because of the volume expansion of the found electron density, we assume that **3a** crystallises with two molecules of *n*-hexane and two molecules of toluene in the unit cell. Subsequently, for solving the structure **3a** the program SQUEZZE[40] was used.

CCDC-679314 (for BH$_3$·NHC^{Me}), -679315 (for **1a**), -679316 (for **1b**), -679317 (for **2**), -679318 (for **3a**), -679319 (for **3b**) and -679320 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental, analytical and crystallographic details of compound **1b**; crystallographic data of BH$_3$·NHC^{Me}; optimised geometries of {BAr^{F}H···BH$_2$·NHC^{Me}}, PH$_3$BH$_2$·NHC^{Me}, {BAr^{F}H···PH$_3$BH$_2$·NHC^{Me}} and {BAr^{F}H···PH$_3$BH$_2$·NMe$_3$}.

Acknowledgments

This work was comprehensively supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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[30] We discuss $\Delta E°_0$ values because we are primarily concerned about energy changes. It is expected that reaction energies will be similar in the gas phase and in the inert solvent, whereas entropy values are much more different for the gas phase and solution reactions.
[31] Mulliken partial charges: [PH$_3$·BH$_2$·NMe$_3$]$^+$: PH$_3$ (0.476) BH$_2$ (0.025) NMe$_3$ (0.499); [PH$_3$·BH$_2$·NHC^{Me}]$^+$: PH$_3$ (0.4556) BH$_2$ (–0.2166) NHC^{Me} (0.761).
[32] We believe that the difference between B(C$_6$F$_5$)$_3$ and Ga(C$_6$F$_5$)$_3$ systems comes from the fact that for B(C$_6$F$_5$)$_3$ both ion-pair formation and H$_2$ elimination are allowed thermodynamically, whereas for Ga(C$_6$F$_5$)$_3$ only H$_2$ elimination is allowed and ion-pair formation is forbidden. If H$_2$ elimination

has a bigger activation barrier than ion-pair formation, the ion pair will be formed with $B(C_6F_5)_3$ owing to kinetics reasons.

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Received: March 25, 2008