DOI: 10.1002/ejic.200601186

Main Group Lewis Acid/Base-Stabilised Phosphanylboranes

Ariane Adolf,[a] Manfred Zabel,[a] and Manfred Scheer*[a]

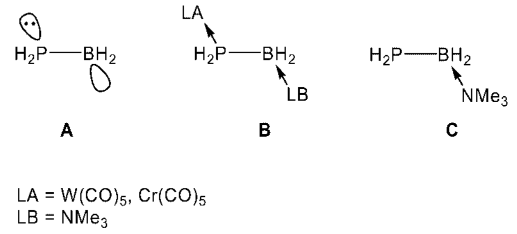
Dedicated to Professor Michael Binnewies on the occasion of his 60th birthday

Keywords: Boron / Phosphorus / Hydrides / Lewis acids / Lewis bases

The parent compounds of phosphanylboranes of the type (LA)H_2P–BH_2(LB) (LA = Lewis acid, LB = Lewis base) stabilised by Lewis acid/Lewis base have been synthesised by using perfluorinated main-group Lewis acids. The Lewis acid–phosphane adducts $(C_6F_5)_3BPH_3$, $(C_6F_5)_3BPPhH_2$ and $(C_6F_5)_3GaPPhH_2$ (**3**) were used as starting materials, which upon lithiation with *n*BuLi react with the chlorinated Lewis base borane adduct $ClBH_2NMe_3$. The LA/LB stabilised phosphanylboranes $(C_6F_5)_3BPH_2BH_2NMe_3$ (**1**), $(C_6F_5)_3BPPhHBH_2NMe_3$ (**4**) and $(C_6F_5)_3GaPPhHBH_2NMe_3$ (**5**), were obtained via salt elimination reactions. $(C_6F_5)_3GaPH_2BH_2NMe_3$ (**2**) was not accessible using this method due to the unavailability of an efficient synthetic route to $(C_6F_5)_3GaPH_3$. The synthesis of **2** could be achieved quantitatively via reaction of $PH_2BH_2NMe_3$ with $(C_6F_5)_3Ga{\cdot}Et_2O$. All products were comprehensively characterised by spectroscopic methods and X-ray crystallography. Additionally, the intermediate products $(C_6F_5)_3BPH_2Li$ and $(C_6F_5)_3GaPPhH_2$ (**3**) were spectroscopically characterised.

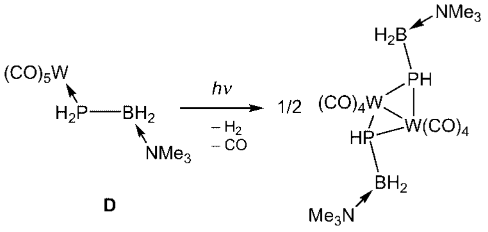
Introduction

Phosphanylboranes $(R_2P–BR'_2)_n$ have attracted much attention since the beginning of the 90's.[1] However, attempts to isolate the parent compound of this class (H_2P–BH_2) (**A**) (Scheme 1) have been futile, and only theoretical investigations on **A** have been performed.[2] Oligophosphanylboranes with the general formula $(HRP–BH_2)_n$ can be synthesised via dehydrocoupling reactions at elevated temperatures[3] or catalysed by either Rh^I complexes (R = Ph)[4] or $B(C_6F_5)_3$ (R = H).[5] Experimentally accessible monomeric phosphanylboranes are mostly stabilised by sterically demanding substituents to avoid intermolecular oligomerisation.[1] Our approach to the parent compounds of phosphanylboranes was to stabilise them by the coordination of Lewis acids and Lewis bases as type **B** compounds. By this way the lone pair of the pnicogen is occupied by a Lewis acid (LA) and the Group 13 element is coordinated by a Lewis base (LB) (**B**).[6] Recently we were able to synthesise the first phosphanylborane **C**, which is stabilised only by a Lewis base.[7]



Scheme 1.

The Lewis acid stabilised phosphanylboranes that we synthesised carry transition metal carbonyls as the Lewis acid.[6] In contrast, less is known about main group Lewis acid stabilised group 13/15 compounds.[5,7,8] A disadvantage of transition metal carbonyls as Lewis acids is their influence on the reactivity of the phosphanylboranes [Equation (1)]. For example, photolysis of compound **D** leads to a dimer with elimination of CO and H_2.[6] Furthermore, the reaction of **D** with iodine leads to oxidation of the tungsten atom with concomitant loss of CO and not, as expected, to halogenation of the phosphorus atom.[9]



(1)

In order to circumvent the problem of CO elimination reactions, we decided to use main group Lewis acids for the synthesis of LA/LB stabilised phosphanylboranes.

---

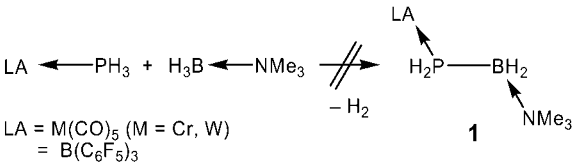
[a] Institut für Anorganische Chemie der Universität Regensburg, 93040 Regensburg, Germany
Fax: +49-941-9434439
E-mail: manfred.scheer@chemie.uni-regensburg.de

Herein we report on the synthesis and characterisation of hydrogen substituted LA/LB stabilised phosphanylboranes with $B(C_6F_5)_3$ and $Ga(C_6F_5)_3$ as main group Lewis acids.[10] Furthermore, the synthesis of the LA/LB stabilised phosphanylboranes is described which are substituted with a phenyl group at the phosphorus atom.

Results and Discussion

Synthesis and Spectroscopic Characterisation of the Lewis Acid/Base-Stabilised Phosphanylboranes

For the synthesis of the type **B** compounds containing transition metal carbonyls as the LA, the salt elimination method was chosen as a general synthetic route since the H_2 elimination had failed. The same behaviour was found for the main group LA containing compounds [Equation (2)].



(2)

Thus, for the synthesis of the LA/LB stabilised phosphanylborane **1** [Equation (3)] $(C_6F_5)_3BPH_3$ was metallated in toluene with *n*BuLi. The ^{31}P NMR spectrum of the in situ generated $[(C_6F_5)_3BPH_2Li]$ in $[D_8]THF$ exhibits a multiplet of triplets at δ = –165.1 ppm (Figure 1). The strongly upfield shifted resonance of the phosphorus nucleus of $[(C_6F_5)_3BPH_2Li]$ can be attributed to the formation of a negatively charged phosphanido complex. The $^1J_{P,H}$ value of 180 Hz of $[(C_6F_5)_3BPH_2Li]$ is comparable with the coupling constant in BH_3PH_2Li ($^1J_{P,H}$ = 175).[11] By treating $[(C_6F_5)_3BPH_2Li]$ with $ClBH_2NMe_3$, $(C_6F_5)_3BPH_2BH_2NMe_3$ (**1**) is formed [Equation (3)].

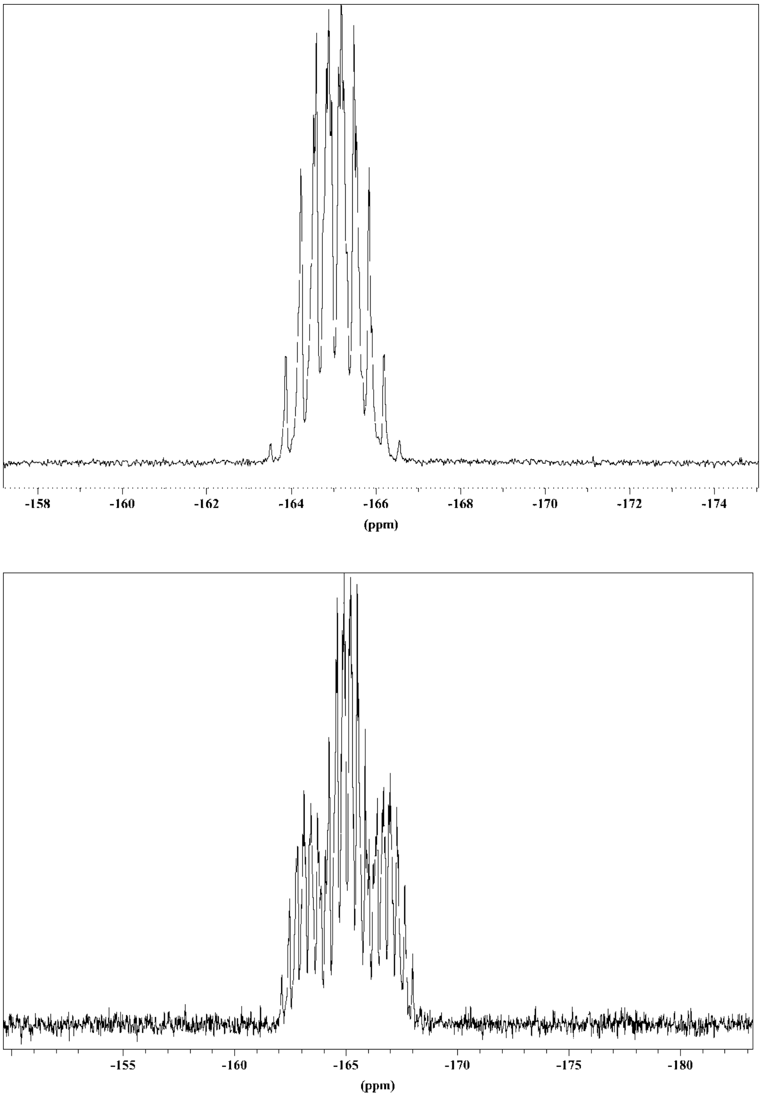
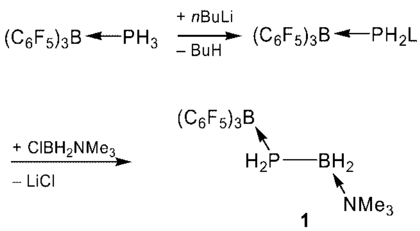
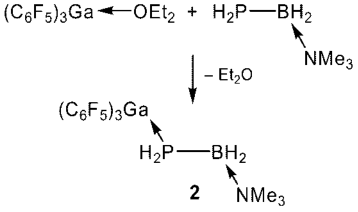


Figure 1. $^{31}P\{^1H\}$ (top) and ^{31}P NMR spectra (bottom) of $[(C_6F_5)_3BPH_2Li]$.



(3)

Since $(C_6F_5)_3GaPH_3$ could not be synthesised in sufficient amounts, the LiCl-elimination route is unsuitable.[12] An elegant way to obtain $(C_6F_5)_3GaPH_2BH_2NMe_3$ (**2**) in quantitative yields is the reaction of $(C_6F_5)_3Ga{\cdot}OEt_2$[13] with $PH_2BH_2NMe_3$ **C** in toluene according to Equation (4).



(4)

Furthermore, the synthesis of the LA/LB stabilised phosphanylboranes bearing a phenyl substituent at the P atom was of interest. This additional stabilisation could be helpful in subsequent investigations concerning the abstraction of the Lewis base.

Since $(C_6F_5)_3BPPhH_2$[5] was already described in the literature, the unknown Ga analogue $(C_6F_5)_3GaPPhH_2$ (**3**) was synthesised in almost quantitative yield by adding $PPhH_2$ to a solution of $(C_6F_5)_3Ga{\cdot}OEt_2$ in toluene [Equation (5)].

$$(C_6F_5)_3Ga{\bullet}OEt_2 + PPhH_2 \xrightarrow[-\,Et_2O]{} \underset{\mathbf{3}}{(C_6F_5)_3Ga \leftarrow PPhH_2} \qquad (5)$$

The ^1H NMR spectrum of **3** shows a doublet at δ = 4.53 ppm ($^1J_{P,H}$ = 369 Hz) attributable to the PH_2 protons. The phenyl protons are detected as multiplets between 6.65 and 6.85 ppm. The $^{31}P\{^1H\}$ NMR spectrum reveals a resonance at δ = –81.4 ppm which is detected as a triplet ($^1J_{P,H}$ = 369 Hz).

$(C_6F_5)_3GaPPhH_2$ (**3**) crystallises as colourless prisms in the triclinic space group $P\bar{1}$. The Ga–P bond length (2.477(1) Å] is within the normal range for Ga–P single bonds, which may vary from 2.256(3) Å to 2.462(3) Å.[1b,14] A π-stacking interaction between the phenyl ring at the P atom and one of the perfluorinated phenyl rings of $(C_6F_5)_3Ga$ is observed (Figure 2) with a distance of 3.851(1) Å between the ring centres, which is longer than the interlayer distance in graphite (3.354 Å). The angle between the planes of these two phenyl rings was determined to be 24.04°. These results are in good agreement with known aryl–perfluoroaryl π-interactions, where the distances and angles between the aromatic rings are in the range of 3.3 to 3.8 Å and 20°, respectively.[15–17]

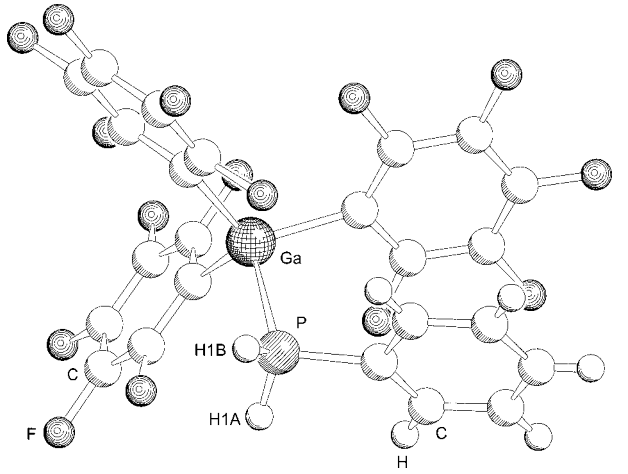
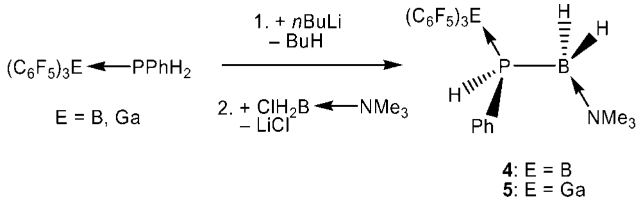


Figure 2. Molecular structure of $(C_6F_5)_3GaPPhH_2$ (**3**) in the crystal.

Metalation of $(C_6F_5)_3GaPPhH_2$ **3** as well as of $(C_6F_5)_3BPPhH_2$ with *n*BuLi leads to $[(C_6F_5)_3EPPhHLi]$ which were then treated with $ClBH_2NMe_3$ to yield colourless crystals of $(C_6F_5)_3BPPhHBH_2NMe_3$ (**4**) and $(C_6F_5)_3GaPPhHBH_2NMe_3$ (**5**), respectively [Equation (6)].



(6)

Only in the mass spectrum of **5** is the molecular ion peak detected. In the case of **1**, **4** and **5** the highest peak is that of the Lewis acid $[E(C_6F_5)_3]^+$. Furthermore, in the mass spectrum of **2** a peak corresponding to $[PH_2BH_2NMe_3]^+$ was found. The IR spectra of the compounds **1**, **2**, **4** and **5** reveal absorptions in the range of 2410 cm^{-1} to 2460 cm^{-1} for the B–H stretching modes and the P–H stretching frequencies appear between 2320 cm^{-1} and 2440 cm^{-1}. The ^{19}F NMR spectra of the products show the three separated resonances for *ortho*-, *meta*- and *para*-fluorine atoms. The *ortho* and the *meta* resonances of **1** are slightly upfield shifted compared to the corresponding resonances of free $(C_6F_5)_3B$.[18] The *para*-fluorine resonance of **1**, in which the boron atom of the Lewis acid is in a tetrahedral environment, is shifted downfield by about 10 ppm relative to that of free $(C_6F_5)_3B$ in which the boron atom possesses a trigonal planar geometry.

In the ^1H NMR spectrum of **1** a singlet is detected at δ = 2.11 ppm for the trimethylamine group, and a doublet at δ = 4.0 ppm ($^1J_{P,H}$ = 345 Hz) arising from the PH_2 protons. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a broadened singlet at δ = –109.8 ppm, while the proton-coupled spectrum reveals a broad triplet ($^1J_{P,H}$ = 345 Hz). Also, the $^{11}B\{^1H\}$ NMR spectrum shows a broad resonance at δ = –0.4 ppm for the BH_2 moiety, which splits into a broad triplet with a boron–hydrogen coupling constant of $^1J_{B,H}$ = 133 Hz when the spectrum is measured with proton coupling. In comparison with the trigonal planar surrounded boron atom of free $B(C_6F_5)_3$, which can be detected in its ^{11}B NMR spectrum at δ = 59.6 ppm, the resonance of the boron atom of the LA in compound **1**, which is in a tetrahedral environment, is shifted strongly upfield and appears at δ = –18.3 ppm as a broad singlet.

The chemical shift for the methyl protons of the Lewis base of **2** is detected at δ = 1.48 ppm in the ^1H NMR spectrum and the PH_2 protons show a broad doublet at δ = 2.85 ppm ($^1J_{P,H}$ = 318 Hz). The ^{31}P NMR spectrum of **2** shows a broad triplet at δ = –161.1 ppm ($^1J_{P,H}$ = 321.8 Hz) and a broad singlet in the case of the $^{31}P\{^1H\}$ NMR spectrum. In the $^{11}B\{^1H\}$ NMR spectrum the resonance for the boron nucleus is detected at δ = –10.81 ppm as a broad singlet, with no discernible fine structure. Acquisition of the proton-coupled spectrum only leads to broadening of this signal.

The ^1H NMR spectrum of **4** shows a singlet at δ = 1.33 ppm which can be assigned to the NMe_3 group, a resonance for the P–H proton, which splits into a doublet at δ = 5.44 ppm ($^1J_{P,H}$ = 353 Hz), and multiplets for the aromatic protons between 6.8 and 7.0 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a resonance at δ = –51.5 ppm, which is detected in the ^{31}P NMR as a doublet ($^1J_{P,H}$ = 352 Hz). The boron atom of the Lewis acid $(C_6F_5)_3B$ can be detected in the ^{11}B NMR and $^{11}B\{^1H\}$ NMR spectra (δ = –14.7 ppm) as can that of the BH_2 group (δ = –10.8 ppm). The latter signal is only revealed as a broad singlet, displaying no splitting into a triplet when a proton-coupled spectrum of **4** is recorded.

The ^1H NMR spectrum of **5** shows a broadened doublet at δ = 4.53 ppm arising from the PH unit ($^1J_{P,H}$ = 328 Hz). The NMe_3 resonance is detected at δ = 1.34 ppm and the protons of the phenyl group are split into a multiplet between 6.8 and 6.9 ppm. The $^{31}P\{^1H\}$NMR spectrum of **5** shows a resonance at δ = –77.9 ppm, which is detected as a triplet ($^1J_{P,H}$ = 328 Hz) in the ^{31}P NMR spectrum. The $^{11}B\{^1H\}$ NMR spectrum shows a broad signal at δ = –9.7 ppm, which reveals slightly broadening in the proton-coupled spectrum.

X-ray Structural Characterisation of the Lewis Acid/Base-Stabilised Phosphanylboranes

The compounds **1**–**5** crystallise as colourless prisms from a mixture of toluene and *n*-hexane. The structures were confirmed by X-ray diffraction studies (Table 2). Selected bond lengths and angles of the compounds **1**, **2**, **4** and **5** are listed in Table 1.

1, **2**, **4** and **5** show the same HRP–BH_2 structural motif [**1**, **2**: R = H (Figure 3); **4**, **5**: R = Ph (Figure 4)] in the solid state. This moiety is coordinated to the Lewis acid (**1**, **4**: $B(C_6F_5)_3$; **2**, **5**: $Ga(C_6F_5)_3$) by the lone pair of the phosphorus atom, so that the phosphorus is surrounded by four substituents. The boron atom is in a tetrahedral environment due to coordination of the Lewis base NMe_3. The Lewis acid (**1**, **4**: $B(C_6F_5)_3$; **2**, **5**: $Ga(C_6F_5)_3$) and the Lewis base NMe_3 adopt a *trans* arrangement and the substituents around the P–B bond are arranged in a slightly staggered geometry. The compounds **1** and **2** are isostructural and crystallise in the centrosymmetric space group $P\bar{1}$ revealing

Table 1. Selected bond lengths [Å] and angles [°] of the phosphanylboranes **1**, **2**, **4** and **5**.

	1	2	4	5
LA_B–P	2.047(3)	–	2.046(3)	–
LA_{Ga}–P	–	2.393(1)	–	2.424(1)
P–B	1.989(4)	1.992(2)	1.974(3)	1.963(2)
B–N	1.601(4)	1.586(3)	1.604(4)	1.606(3)
LA–P–B	122.98(13)	116.55(8)	111.02(10)	114.17(9)
P–B–N	112.2(2)	113.36(14)	116.05(16)	115.06(16)
Torsion angles				
LA–P–B–N	150.781(26)	154.24(14)	170.18(16)	175.61(12)

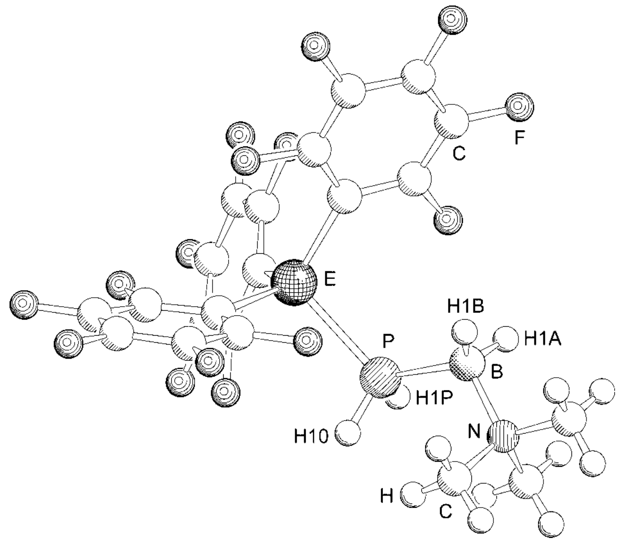


Figure 3. Molecular structures of **1** (E = B) and **2** (E = Ga) in the crystal.

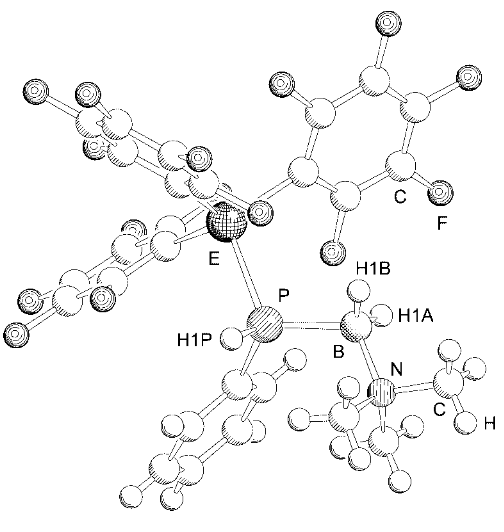


Figure 4. Molecular structure of **4** (E = B) and **5** (E = Ga), respectively in the crystal.

the same staggered geometry around the P–B core as both enantiomers show which are present in the solid state (Figure 5, a).

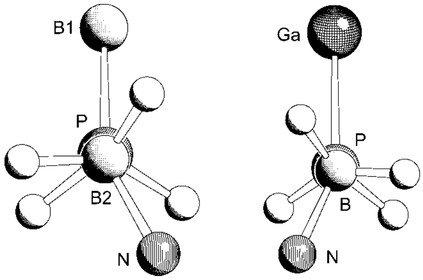


Figure 5. Staggered conformation around the B–P bonds in **1** (left, E = B) and **2** (right, E = Ga).

Besides the LA and LB, **1** and **2** are only substituted by hydrogen atoms. The P–B bond distances of **1** [(1.989(4) Å] and **2** [(1.992(2) Å] agree well with usual P–B single-bond distances, which range from 1.90 Å to 2.0 Å.[1] A comparison with the P–B bond length in $[W(CO)_5PH_2BH_2NMe_3]$ **D** [(1.955(2) Å] shows that compounds **1** and **2** possess slightly longer P–B bond distances. The P–B bond distance in the calculated LA and LB free compound **A** is with 1.90 Å[2b] (1.905 Å[2c]) slightly shortened due to a small P–B π-bond contribution in **A**, which is absent in the LA/LB stabilised molecules **1** and **2**. Whereas the P–B–N angles of **1** [(112.2(2)°] and **2** [(113.36(14)°] are very similar, the LA–P–B angles differ significantly [**1**: 122.98(13)°; **2**: 116.55(8)°], revealing the different valence radii of the boron and gallium atoms in the LA.

Compounds **4** and **5**, which possess a phenyl substituent at the phosphorus atom, show similar structures, although they do not crystallise in the same space group. The values of their P–B bond distances do not differ much. Their P–B–N angles are very similar [**4**: 116.05(16); **5**: 115.06(16)°], as are their LA–P–B angles [**4**: 111.02(10)°; **5**: 114.17(9)°]. The substituents around the P–B core in **4** and **5** adopt a staggered geometry (Figure 6).

Whereas the Ga containing LA substituted compound **5** shows some π-stacking interaction between one of the perfluorinated phenyl rings of the LA and the phenyl substituent at the phosphorus atom (Figure 7), no π-stacking interaction is noticeable in **4**. The center-to-center distance of the phenyl rings in **5** is 4.082 Å, which is longer than the distance between the fluoroaryl and the aryl groups in **3** (3.851 Å). The angle formed by the two planes of the staggered phenyl rings is 29°.

In comparison with the bond distance of the B–P core of the phosphanylboranes the boron containing LA–P bond distances in **1** and **4** are slightly elongated [**1**: 2.076(3) Å; **4**: 2.046(3) Å]. The Ga–P bond distance in compound **5** [2.424(1) Å] shows nearly the same length as that that is found in the starting material **3** [2.477(1) Å], and is in the normal range for a Ga–P single bond, which varies between 2.256(3) Å and 2.462(3) Å.[1b,14] The value of the Ga–P bond length of compound **2** [2.393(1) Å] also lies within this range.

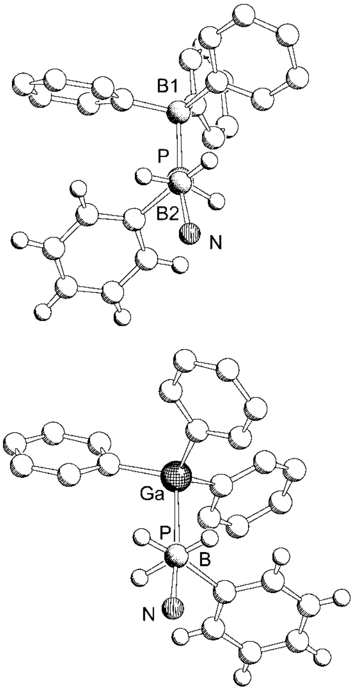


Figure 6. Staggered geometries of **4** (top, E = B) and **5** (bottom, E = Ga). F atoms and Me groups are omitted for clarity.

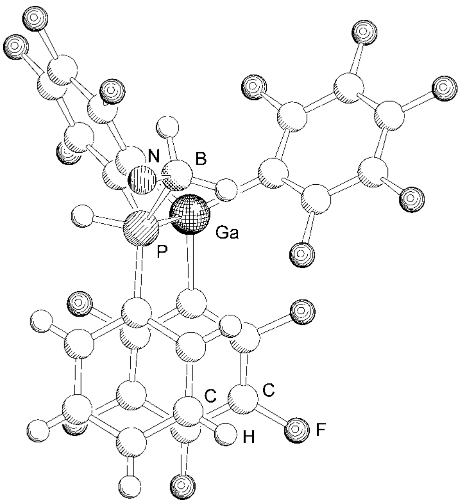


Figure 7. π-stacking interaction in **5**.

In 2003 Denis et al. reported on the dehydrocoupling between $(C_6F_5)_3BPH_2R$ (R = H or Ph) and BH_3/SMe_2 to form $(C_6F_5)_3BPH_2BH_2SMe_2$ and $(C_6F_5)_3BPH(Ph)$-BH_2SMe_2.[5] They described a subsequent polymerization at 20 °C in the case of the phenyl-substituted derivative and at 110 °C for 3 h in the case of the hydrogen substituted derivative, which led to the formation of the polymers $[PHRBH_2]_n$ (R = H or Ph) and $(C_6F_5)_3BSMe_2$, as confirmed by NMR studies. In contrast the NMe_3-substituted LA/LB-stabilised phosphanylboranes **1**, **2**, **4**, and **5**, which we report herein, show a very high thermal stability up to 150 °C, without any signs of decomposition or dehydrocoupling to form polymerisation products.

Conclusions

The results reported herein have shown that we were able to use perfluorinated main group Lewis acids to prepare LA/LB-stabilised phosphanylboranes. The parent compound $H_2P–BH_2$ can be stabilised with NMe_3 as the Lewis base and $B(C_6F_5)_3$ (**1**) or $Ga(C_6F_5)_3$ (**2**) as the main group Lewis acid. Furthermore the synthesis of the phenyl-substituted LA/LB stabilised phosphanylboranes **4** and **5** was achieved. In the solid state, the substituents in all products show a staggered geometry around the central P–B core. In the Ga containing compounds **3** and **5**, π-stacking interactions between one of the perfluorinated phenyl rings of the LA and the phenyl substituent at the phosphorus atom contribute to their stability. These compounds do not show any tendency to polymerise in contrast to previously reported SMe_2-substituted compounds.[5] Furthermore we expect that removal of the Lewis base from the synthesised compounds will yield stable derivatives stabilised only by a Lewis acid. These investigations are in progress.

Experimental Section

General Techniques: All manipulations were performed under an atmosphere of dry nitrogen using standard Glovebox and Schlenk techniques. Solvents were purified and degassed by standard procedures. The compounds $B(C_6F_5)_3$,[13] $(C_6F_5)_3GaOEt_2$,[13] $(C_6F_5)_3BPH_3$,[19] $(C_6F_5)_3BPPhH_2$,[5] $PH_2BH_2NMe_3$,[7] $ClBH_2NMe_3$[20] and $PPhH_2$[21] were prepared according to the literature procedures. *n*BuLi (Fluka, 1.6 molar solution in *n*-hexane) was used as received.

The NMR spectra were recorded on either a Bruker 300 or Avance 400 spectrometer with δ referenced to external $SiMe_4$ (^1H), H_3PO_4 (^{31}P), $BF_3–Et_2O$ (^{11}B) and $CFCl_3$ (^{19}F). IR spectra were measured on a DIGILAB (FTS 800) FT-IR spectrometer. All mass spectra were recorded on a Finnigan MAT 95 (FD) or a Finnigan MAT SSQ 710 A (EI, 70 eV) instrument.

Synthesis of $(C_6F_5)_3BPH_2BH_2NMe_3$ (1): To a solution of $(C_6F_5)_3BPH_3$ (170 mg, 0.31 mmol) in toluene (20 mL), *n*BuLi (0.19 mL, 0.31 mmol) is added dropwise at 0 °C. After stirring the solution at room temperature for 3 h, the formation of $(C_6F_5)_3BPH_2Li$ is confirmed by ^{31}P NMR ($[D_8]$THF, 101.256 MHz, δ = –165.14, mt, $^1J_{P,H}$ = 180 Hz, PH_2). $ClBH_2NMe_3$ (33 mg, 0.31 mmol) is then added and the mixture is stirred at room temperature for 18 h. The LiCl precipitate is filtered through a plug of Celite and the resulting solution is concentrated to 2 mL in vacuo. Colourless crystals of **1** are obtained as prisms by slow diffusion of *n*-hexane into this solution of **1** at room temperature. Yield 163 mg (85%). ^1H NMR (C_6D_6, 25 °C, 250 MHz): δ = 2.11 (s, 9 H, $N(CH_3)_3$), 4.0 (dm, $^1J_{P,H}$ = 345 Hz, 2 H, PH_2) ppm. ^{31}P NMR (C_6D_6, 25 °C, 101.3 MHz): δ = –109.66 (br. t, $^1J_{P,H}$ = 345 Hz, PH_2) ppm. $^{31}P\{^1H\}$ NMR: δ = –109.81 (br. s, PH_2) ppm. ^{11}B NMR (C_6D_6, 25 °C, 96.3 MHz): δ = –0.42 (br. t, $^1J_{B,H}$ = 133 Hz, BH_2), –18.27 (br. s, $B(C_6F_5)_3$) ppm. $^{11}B\{^1H\}$ NMR: δ = –0.4 (br. s, BH_2), –18.27 (br. s, $B(C_6F_5)_3$) ppm. ^{19}F NMR (C_6D_6, 25 °C, 282.4 MHz): δ = –130.8 (br. s, 6 F, *o*-F), –157.52 (t, $^3J_{F,F}$ = 20.8 Hz, 3 F, *p*-F), –164.03 (m, 6 F, *m*-F) ppm. EI-MS (70eV, 180 °C): *m*/*z* (%) = 512 (100) $[(C_6F_5)_3B]^+$, 168 (52) $[C_6F_5H]^+$, 58 (64) $[NMe_3–H]^+$. Raman (Solid): $\tilde{\nu}$ = 3027 (s, CH), 2973 (s, CH), 2956 (s, CH), 2871 (s, CH), 2471 (br. m, BH), 2433 (s, PH), 2394 (vs, PH), 1647 (s, CF), 1377 (m), 975 (br. m), 850 (s), 595 (m), 581 (s), 490 (s), 472 (m), 448 (s), 394 (s) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3026 (s, CH), 2962 (s, CH), 2925 (m, CH), 2853 (w, CH), 2463 (s, BH), 2433 (s, BH), 2394 (w, PH), 2324 (vw, PH), 1647 (vs, CF), 1601 (w), 1518 (vs), 1464 (vs), 1376 (s), 1281 (s), 1130 (s), 1110 (vs), 1085 (s), 1071 (w, sh), 982 (s), 966 (s), 868 (m), 826 (m), 784 (s), 772 (s), 736 (m), 709 (m), 674 (s), 670 (s, sh), 624 (m), 575 (m), 472 (br. m) cm^{-1}. $C_{21}H_{13}B_2F_{15}NP$ (616.9): calcd. C 40.88, H 2.12, N 2.27; found C 41.25, H 2.38, N 2.28.

Synthesis of $(C_6F_5)_3GaPH_2BH_2NMe_3$ (2): $(C_6F_5)_3GaOEt_2$ (356 mg, 0.552 mmol) is added to a solution of $PH_2BH_2NMe_3$ (0.058 mg, 0.552 mmol) in toluene (25 mL). After stirring for 18 h, the solution is concentrated to ca. 4 mL in vacuo. Colourless crystals of **2** are obtained by slow diffusion of *n*-hexane into this solution at room temperature. Yield 401 mg (97%). ^1H NMR (C_6D_6, 25 °C, 300 MHz): δ = 1.48 (s, 9 H, $N(CH_3)_3$), 2.85 (br. d, $^1J_{P,H}$ = 318 Hz, 2 H, PH_2) ppm. ^{31}P NMR (C_6D_6, 25 °C, 121.5 MHz): δ = –161.13 (br. t, $^1J_{P,H}$ = 321.8 Hz, PH_2) ppm. $^{31}P\{^1H\}$ NMR: δ = –161.14 (s, PH_2) ppm. ^{11}B NMR (C_6D_6, 25 °C, 128.4 MHz): δ = –10.94 (br. s, BH_2) ppm. $^{11}B\{^1H\}$ NMR: δ = –10.81 (br. s, BH_2) ppm. ^{19}F NMR (C_6D_6, 25 °C, 282.4 MHz): δ = –122.7 (d, $^3J_{F,F}$ = 18.5 Hz, 6 F, *o*-F), –154.4 (t, $^3J_{F,F}$ = 19.6 Hz, 3 F, *p*-F), –161.9 (m, 6 F, *m*-F) ppm. EI-MS (70 eV): *m*/*z* (%) = 570 (21) $[[(C_6F_5)_3Ga]^+]$, 403 (43) $[[(C_6F_5)_2Ga]^+]$, 168 (100) $[[C_6F_5H]^+]$, 105 (12) $[[PH_2BH_2NMe_3]^+]$. IR (KBr): $\tilde{\nu}$ = 3026 (s, CH), 2961 (s, CH), 2925 (m, CH), 2853 (br. m, CH), 2454 (s, BH), 2424 (s, BH), 2374 (br. m, PH), 2318 (m, PH), 1643 (vs, CF), 1613 (w), 1556 (w, sh), 1511 (vs), 1467 (vs), 1445 (m, sh), 1411 (m), 1363 (s), 1268 (s), 1243 (m), 1160 (s), 1126 (s), 1066 (vs), 1015 (m), 960 (vs), 863 (s), 798 (m), 756 (m), 740 (w), 720 (w), 700 (m), 608 (m), 490 (m) cm^{-1}. $C_{21}H_{13}BF_{15}GaNP$ (675.8): calcd. C 37.32, H 1.94, N 2.07; found C 37.21, H 2.01, N 2.02.

Synthesis of $(C_6F_5)_3GaPPhH_2$ (3): $PhPH_2$ (0.852 mL, 0.853 g, 7.75 mmol) is added slowly to a solution of $(C_6F_5)_3GaOEt_2$ (5 g, 7.75 mmol) in toluene (70 mL) at 0 °C. After stirring the solution for 18 h at room temperature the solvent is removed in vacuo and the residue is washed with *n*-hexane (3 × 20 mL) leaving $(C_6F_5)_3GaPPhH_2$ as a white powder. Single crystals of **3** can be obtained by recrystallisation from a mixture of toluene and *n*-hexane as colourless prisms. Yield 5.06 g (91%). ^1H NMR (C_6D_6, 25 °C, 400 MHz): δ = 4.53 (d, $^1J_{P,H}$ = 369 Hz, 2 H, PH_2), 6.65–6.85 (m, 5 H, Ph) ppm. ^{31}P NMR (C_6D_6, 25 °C, 162 MHz): δ = –81.44 (t, $^1J_{P,H}$ = 369 Hz, PH_2) ppm. $^{31}P\{^1H\}$ NMR: δ = –81.44 (s, PH_2) ppm. ^{19}F NMR (C_6D_6, 25 °C, 376.5 MHz): δ = –122.89 (d, $^3J_{F,F}$ = 17 Hz, 6 F, *o*-F), –151.73 (t, $^3J_{F,F}$ = 20 Hz, 3 F, *p*-F), –160.46 (m, 6 F, *m*-F) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, 75.5 MHz): δ = 129.19 (d, $^3J_{C,P}$ = 9 Hz, *m*-C (C_6H_5)), 130.74 (s, *p*-C (C_6H_5)), 133.79 (d, $^2J_{C,P}$ = 12 Hz, *o*-C (C_6H_5)), 137.42 (br. d, $^1J_{C,F}$ = 250 Hz, *p*-C, $Ga(C_6F_5)_3$), 142.06 (br. d, $^1J_{C,F}$ = 254 Hz, *m*-C, $Ga(C_6F_5)_3$), 148.97 (br. d, $^1J_{C,F}$ = 235 Hz, *o*-C, $Ga(C_6F_5)_3$) ppm. EI-MS (70 eV, toluene): *m*/*z* (%) = 570 (15) $[Ga(C_6F_5)_3]^+$, 168 (100) $[C_6F_5H]^+$. IR (KBr): $\tilde{\nu}$ = 3067 (m, CH), 2968 (w, CH), 2916 (w, CH), 2880 (w, CH), 2405 (m, PH), 2323 (m, PH), 1639 (s, CF), 1613 (w), 1576 (w), 1555 (w, sh), 1510 (vs), 1468 (vs), 1443 (s, sh), 1365 (s), 1271 (s), 1221 (m), 1127 (m), 1086 (s, sh), 1068 (vs), 1024 (m), 999 (m), 962 (vs), 844 (s), 799 (m), 738 (s), 719 (w), 691 (m), 611 (m), 582 (w), 491 (m), 460 (w), 412 (m) cm^{-1}. $C_{24}H_7F_{15}GaP$ (681): calcd. C 42.33, H 1.04; found C 42.17, H 1.12.

Synthesis of $(C_6F_5)_3BPPhHBH_2NMe_3$ (4): To a solution of $(C_6F_5)_3BPPhH_2$ (298 mg, 0.479 mmol) in toluene (25 mL), *n*BuLi (0.3 mL, 0.48 mmol) is added slowly at 0 °C. After stirring the solution at room temperature for 1 h, $ClBH_2NMe_3$ (51 mg, 0.475 mmol) is added and the solution is stirred overnight at room temperature. Filtration of the reaction mixture over a bed of Celite followed by concentration of the filtrate to ca. 2 mL and layering with *n*-hexane yields **4** as colourless prisms. Yield 266 mg (81 %). ^{1}H NMR (C_6D_6, 25 °C, 400 MHz): δ = 1.33 (s, 9 H, $N(CH_3)_3$), 5.44 (dm, $^1J_{P,H}$ = 353 Hz, 1 H, PH), 6.8–7.0 (m, 5 H, C_6H_5) ppm. ^{31}P NMR (C_6D_6, 25 °C, 162 MHz): δ = –51.5 (d, $^1J_{P,H}$ = 352 Hz, PH) ppm. ^{31}P{^{1}H} NMR: δ = –51.5 (s, PH) ppm. ^{11}B NMR (C_6D_6, 25 °C, 128.4 MHz): δ = –14.66 (br. s, $(C_6F_5)_3B$), –10.83 (br. s, BH_2) ppm. ^{11}B{^{1}H} NMR: δ = –14.66 [s, $(C_6F_5)_3B$], –10.83 (s, BH_2) ppm. ^{19}F NMR (C_6D_6, 25 °C, 376.5 MHz): δ = –128.15 (s, 6 F, *o*-F), –158.25 (t, $^3J_{F,F}$ = 20 Hz, 3 F, *p*-F), –164.45 (t, $^3J_{F,F}$ = 19 Hz, 6 F, *m*-F) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 100.6 MHz): δ = 52 ppm. 96 (d, $^3J_{C,P}$ = 4.8 Hz, $N(CH_3)_3$), 128.73 (d, $^3J_{C,P}$ = 9.2 Hz, *m*-C, C_6H_5), 130.75 (d, $^4J_{C,P}$ = 2.7 Hz, *p*-C, C_6H_5), 133.52 (d, $^2J_{C,P}$ = 5.9 Hz, *o*-C, C_6H_5), 137.56 (br. d, $^1J_{C,F}$ = 248 Hz, *p*-C, $Ga(C_6F_5)_3$), 140.03 (br. d, $^1J_{C,F}$ = 231 Hz, *m*-C, $Ga(C_6F_5)_3$), 148.7 (br. d, $^1J_{C,F}$ = 242 Hz, *o*-C, $Ga(C_6F_5)_3$) ppm. FI/FD-MS (toluene): *m/z* (%) = 512 (100), $[(C_6F_5)_3B]^+$, 361.5 (26), $[M^+ - 2\ C_6F_5]$). IR (KBr):[22] $\tilde{\nu}$ = 3079 (br. m, CH), 3028 (s, CH), 3010 (s, CH), 2954 (s, CH), 2924 (w, b, CH), 2846 (s, CH), 2462 (s, BH), 2419 (s, BH), 1645 (vs, CF), 1602 (w), 1518 (vs), 1469 (vs), 1409 (m), 1382 (s), 1372 (w, sh), 1317 (w), 1284 (s), 1158 (m), 1129 (s), 1094 (vs), 1025 (m), 980 (vs), 849 (s, br), 789 (s), 773 (m), 759 (s), 744 (m), 705 (m), 677 (s), 605 (m), 575 (m), 502 (m), 468 (m), 430 (m), 419 (w) cm^{-1}. $C_{27}H_{17}B_2F_{15}NP$ (693.00): calcd. C 46.79, H 2.47, N 2.02; found C 46.96, H 2.52, N 1.98.

Synthesis of $(C_6F_5)_3GaPPhHBH_2NMe_3$ (5): *n*BuLi (0.3 mL, 0.48 mmol) is added dropwise to a solution of $(C_6F_5)_3GaPPhH_2$ (327 mg, 0.48 mmol) in toluene (25 mL) at 0 °C. The solution is stirred for 1 h at room temperature and then $ClBH_2NMe_3$ (52 mg, 0.484 mmol) is added. After filtration through Celite, the solution is concentrated to ca. 2 mL and layered with *n*-hexane. Crystals of **5** are obtained as colourless prisms which are washed with *n*-hexane (3 × 20 mL). Yield 311 mg (86 %). ^{1}H NMR (C_6D_6, 25 °C, 400 MHz): δ = 4.53 (br. d, $^1J_{P,H}$ = 328 Hz, 1 H, PH), 1.34 (s, 9 H, $N(CH_3)_3$), 6.8–6.9 (m, 5 H, C_6H_5) ppm. ^{31}P NMR (C_6D_6, 25 °C, 162 MHz): δ = –77.9 (br. d, $^1J_{P,H}$ = 328 Hz, PH) ppm. ^{31}P{^{1}H} NMR: δ = –77.9 (br. s, PH) ppm. ^{11}B NMR (C_6D_6, 25 °C, 128.4 MHz): δ = –9.69 (br. m, BH_2) ppm. ^{11}B{^{1}H} NMR: δ = –9.69 (br. s, BH_2) ppm. ^{19}F NMR (C_6D_6, 25 °C, 376.5 MHz): δ = –121.9 (d, $^3J_{F,F}$ = 17 Hz, 6 F, *o*-F), –154.4 (t, $^3J_{F,F}$ = 20 Hz, 3 F, *p*-F), –161.94 (m, 6 F, *m*-F) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 25 °C, 100.6 MHz): δ = 52.58 (d, $^3J_{C,P}$ = 4.9 Hz, $N(CH_3)_3$), 129.03 (d, $^3J_{C,P}$ = 10 Hz, *m*-C, C_6H_5), 129.9 (s, *p*-C, C_6H_5), 132.36 (d, $^2J_{C,P}$ = 8 Hz, *o*-C, C_6H_5), 137.37 (br. d, $^1J_{C,F}$ = 252 Hz, *p*-C, $Ga(C_6F_5)_3$), 141.4 (br. d, $^1J_{C,F}$ = 250 Hz, *m*-C, $Ga(C_6F_5)_3$), 149.39 (br. d, $^1J_{C,F}$ = 235 Hz, *o*-C, $Ga(C_6F_5)_3$) ppm. FI/FD-MS (toluene): *m/z* = 750 (1 %, $[M^+ - H]$), 570 (100 %, $[(C_6F_5)_3Ga]^+$). IR (KBr):[22] $\tilde{\nu}$ = 3065 (w, CH), 3014 (br. s, CH), 2958 (br. s, CH), 2926 (w, CH), 2451 (br. s, BH), 2416 (br. s, BH), 2318 (w, PH), 1639 (vs, CF), 1612 (w), 1556 (w), 1510 (vs), 1484 (m, sh), 1464 (vs), 1446 (s, sh), 1412 (m), 1361 (s), 1328 (w), 1267 (s), 1243 (m), 1155 (m), 1126 (s), 1076 (vs), 1066 (vs), 1016 (m), 959 (vs), 887 (w), 857 (m), 818 (w), 794 (m), 745 (m), 720 (w), 701 (w, sh), 695 (m), 660 (w), 609 (m), 582 (w), 490 (m) (cm^{-1}) cm^{-1}. $C_{27}H_{17}BF_{15}GaNP$ (751.9): calcd. C 43.13, H 2.28, N 1.86; found C 42.76, H 2.22, N 1.86.

Crystal Structure Analyses: The crystal structure analyses of **1**, **3**, **4** and **5** (Table 2) were performed on a STOE IPDS diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The crystal structure analysis of **2** was performed on an Oxford Diffraction Gemini Ultra

Table 2. Crystallographic data for compounds **1**–**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{21}F_{15}H_{13}B_2PN$	$C_{21}F_{15}H_{13}GaPBN$	$C_{24}F_{15}H_7GaP$	$C_{27}H_{17}F_{15}B_2PN$	$C_{27}H_{17}F_{15}GaPBN$
Formula mass [g mol^{-1}]	616.91	675.82	680.99	693.01	751.92
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
Collection temp. [K]	100(1)	123(1)	123(1)	173(1)	173(1)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a [Å]	9.5020(19)	9.8314(5)	7.6898(7)	9.0723(8)	14.0153(14)
b [Å]	11.544(2)	11.6007(6)	10.9916(10)	14.5892(9)	12.6649(8)
c [Å]	11.592(2)	11.98837(16)	14.1418(12)	21.3383(18)	17.2272(15)
α [°]	70.93(3)	70.792(7)	84.309(11)	90	90
β [°]	76.51(3)	75.442(7)	89.773(11)	93.773(11)	95.067(11)
γ [°]	77.44(3)	77.731(4)	77.249(11)	90	90
V [Å^3]	1157(4)	1236.6(2)	1159.89(19)	2818.2(4)	3045.9(5)
Z	2	2	2	4	4
$D_{calcd.}$ [g cm^{-3}]	1.774	1.815	1.95	1.633	1.64
μ [mm^{-1}]	0.254	1.303	1.39	0.218	1.068
$F(000)$	612	664	664	1384	1488
2 θ range	3.78–54.08	6.20–58.04	4.56–53.7	3.38–51.64	3.60–51.72
Index ranges	$-11 \le h \le 12$	$-11 \le h \le 13$	$-9 \le h \le 9$	$-11 \le h \le 11$	$-17 \le h \le 17$
	$-14 \le k \le 14$	$-15 \le k \le 15$	$-13 \le k \le 13$	$-17 \le k \le 17$	$-15 \le k \le 15$
	$-14 \le l \le 14$	$-16 \le l \le 15$	$-17 \le l \le 17$	$-26 \le l \le 26$	$-21 \le l \le 21$
Reflections collected	8413	14488	12608	21292	29999
Independent reflections	4688	5537	4609	5374	5850
Goodness-of-fit on F^2	0.942	1.094	1.078	0.844	0.942
R_{int}	0.0714	0.0210	0.0283	0.0462	0.043
Parameters	380	376	378	439	427
R_1[a] [$I > 2s(I)$]	0.0485	0.0293	0.0247	0.0366	0.0324
wR_2[b] (all data)	0.1309	0.0797	0.0644	0.0893	0.0838
max./min. $\Delta\rho$ [e·Å^{-3}]	0.255/–0.494	0.515/–0.459	0.415/–0.233	0.313/–0.203	0.454/–0.293

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$. [b] $wR_2 = \sqrt{\Sigma[w(F_0^2 - F_c^2)^2]}/\sqrt{\Sigma[w(F_0^2)^2]}$.

diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods with the program SHELXS-97,[23a] and full-matrix least-squares refinement on F^2 in SHELXL-97[23b] was performed with anisotropic displacements for non-H atoms. 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 could be localised by residual electron density and freely refined. CCDC-630846 (for **1**), -630849 (for **2**), -630847 (for **3**), -630850 (for **4**), and -630848 (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.

Acknowledgments

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

---

[1] a) R. T. Paine, H. Nöth, *Chem. Rev.* **1995**, *95*, 343–379; b) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3503.

[2] a) T. L. Allen, W. H. Fink, *Inorg. Chem.* **1992**, *31*, 1703–1705; b) T. L. Allen, A. C. Scheiner, H. F. Schaefer, *Inorg. Chem.* **1990**, *29*, 1930–1936; c) M. B. Coolidge, W. T. Borden, *J. Am. Chem. Soc.* **1990**, *112*, 1704–1706.

[3] a) R. I. Wagner, F. F. Caserio, *J. Inorg. Nucl. Chem.* **1959**, *11*, 259; b) A. B. Burg, *J. Inorg. Nucl. Chem.* **1959**, *11*, 258.

[4] a) H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough, I. Manners, *Angew. Chem.* **1999**, *111*, 3540–3543; *Angew. Chem. Int. Ed.* **1999**, *38*, 3321–3323; b) H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 6669–6678.

[5] J.-M. Denis, H. Forintos, H. Szelke, L. Toupet, T.-N. Pham, P.-J. Madec, A.-C. Gaumont, *Chem. Commun.* **2003**, *1*, 54–55.

[6] U. Vogel, P. Hoemensch, K.-C. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2003**, *9*, 515–519.

[7] K.-C. Schwan, A. Y. Timoskin, M. Zabel, M. Scheer, *Chem. Eur. J.* **2006**, *12*, 4900–4908.

[8] F. Thomas, S. Schulz, H. Mansikkamaeki, M. Nieger, *Organometallics* **2003**, *22*, 3471–3477.

[9] K.-C. Schwan, Ph. D. Thesis, University of Regensburg, **2006**.

[10] W. E. Pier, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345–354; K. Ishihara, H. Yamamoto, *Eur. J. Org. Chem.* **1999**, 527–538.

[11] E. Mayer, *Inorg. Chem.* **1971**, *10*, 2259–2262.

[12] Usually, to synthesise the LA phosphane adducts, PH_3 was bubbled through a solution of the corresponding Lewis acid. Whereas Lewis base-free $B(C_6F_5)_3$ can be used as the starting material to synthesise $B(C_6F_5)_3PH_3$, $Ga(C_6F_5)_3$ is only available as a diethyl ether adduct, which hinders the preparation of $Ga(C_6F_5)_3PH_3$ in an acceptable yield per time scale.

[13] J. L. W. Pohlmann, F. E. Brinckmann, *Z. Naturforsch. Teil B* **1965**, *20*, 5–11.

[14] M. Westerhausen, T. Rotter, Ch. Pfaller, A. N. Kneifel, A. Schulz, *Inorg. Chim. Acta* **2005**, *358*, 4253–4260.

[15] C. Janiak, *J. Chem. Soc. Dalton Trans.* **2000**, 3885–3896.

[16] J. H. Williams, *Acc. Chem. Res.* **1993**, *26*, 593–598.

[17] J. C. Collings, K. P. Roscoe, E. G. Robins, A. S. Batsanov, L. M. Stimons, J. A. K. Howard, S. J. Clark, T. B. Marder, *New J. Chem.* **2002**, *26*, 1740–1746.

[18] A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1966**, *5*, 218–225.

[19] D. C. Bradley, M. B. Hursthouse, M. Motevalli, Z. Dao-Hong, *J. Chem. Soc. Chem. Commun.* **1991**, *1*, 7–8.

[20] G. E. Ryschkewitsch, J. W. Wiggins, *Inorg. Synth.* **1970**, *12*, 116–126.

[21] K. Bourumeau, A.-C. Gaumont, J.-M. Denis, *J. Organomet. Chem.* **1997**, *529*, 205–213.

[22] The assignment of the P–H stretching frequencies was difficult, because the CO_2 vibration frequencies, which occur in the same region, could not be completely excluded due to the spectrometer settings.

[23] a) G. M. Sheldrick, *SHELXS-97*, University of Göttingen, **1996**; b) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**.

Received: December 13, 2006