

Phosphanylalanes and Phosphanylgallanes Stabilized only by a Lewis Base

Michael A. K. Weinhart, Anna S. Lisovenko, Alexey Y. Timoshkin, and Manfred Scheer*

Dedicated to Professor Reinhold Tacke on the occasion of his 70th birthday

Abstract: The synthesis and characterization of the first parent phosphanylalane and phosphanylgallane stabilized only by a Lewis base (LB) are reported. The corresponding substituted compounds, such as IDipp-GaH₂PCy₂ (**1**) (IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene) were obtained by the reaction of LiPCy₂ with IDipp-GaH₂Cl. However, the LB-stabilized parent compounds IDipp-GaH₂PH₂ (**3**) and IDipp-AlH₂PH₂ (**4**) were prepared via a salt metathesis of LiPH₂·DME with IDipp-E'H₂Cl (E' = Ga, Al) or by H₂-elimination reactions of IDipp-E'H₃ (E' = Ga, Al) and PH₃, respectively. The compounds could be isolated as crystalline solids and completely characterized. Supporting DFT computations gave insight into the reaction pathways as well as into the stability of these compounds with respect to their decomposition behavior.

In current main-group chemistry, the development of new synthetic routes to functional materials is an important topic. In this context, unsaturated compounds, such as H₂EE'H₂ (E = Group 15 element, E' = Group 13 element) are interesting as they are isoelectronic to hydrocarbons, such as ethene in the given example. Owing to the polarity of the bond between the Group 13 and the Group 15 atom, different reactivity and functionalities compared to hydrocarbons can be observed. Therefore they are studied, for example, as single-source precursors for binary and composite Group 13/15 materials for micro- and optoelectronic devices,^[1] as well as in the fabrication of semiconducting materials, layered and

inorganic materials.^[1,2] Apart from H₂NBH₂, which could be isolated in an Ar matrix,^[3] it was only possible to study the parent compounds of the type H₂EE'H₂ by DFT calculations,^[4] because of their instability monomeric compounds are unstable with respect to polymerization due to the existing donor and acceptor orbitals and their high tendency to H₂ eliminations. Therefore, a combination of a donor (Lewis base = LB) and an acceptor (Lewis acid = LA) was needed for the electronic stabilization of these compounds.^[5] For boron-based systems, various synthetic routes^[6] and different types of stabilization (types **A** and **B**, Figure 1)^[7] as well as

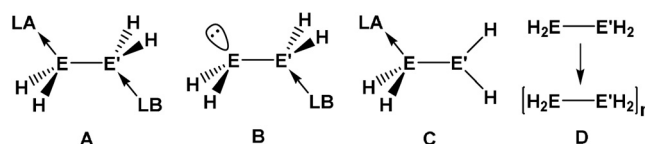


Figure 1. Different types of stabilization of the parent compounds of the pentelyltrielanes.

their reactivity^[8] and polymerization^[9] (type **D**) were investigated. With regard to the heavier analogues Al and Ga, the current research is more focused on the use as FLPs (frustrated Lewis pairs)^[10] and in solid-state chemistry.^[11] In the context of the parent compounds, up to now we have only succeeded in stabilizing type **A** compounds.^[5] In contrast to the corresponding boron derivatives, it has so far not been possible to make type **B** compounds except for organo substituted compounds such as, dmap·AlMe₂P(SiMe₃)₂ (dmap = 4-dimethylaminopyridine).^[12] Moreover, LA/LB-stabilized phosphanylalanes and -gallanes of type **A** have a strong tendency to have a pentacoordinate environment at the Group 13 element atom, and therefore readily undergo H₂-elimination reactions to form polymers. Depending on the solvent, the reaction temperatures and the used LB, we were able to control the polymerization process and isolate and characterize different oligomers, as for instance the dimer **A1**, the trimer **A2** and other four-membered ring species, such as **A3** (Figure 2).^[13] Still the question arises, if it is possible to avoid the formation of these oligomers and, moreover, stabilize for the first time type **B** compounds. One way could be to prevent a pentacoordinate environment at the Group 13 element by using a bulky but also strong donating LB.^[14]

Herein, we report the synthesis and characterization of different substituted phosphanylalanes and -gallanes stabilized only by a LB as well as the first Lewis base stabilized parent phosphanylalane and -gallane (type **B**).

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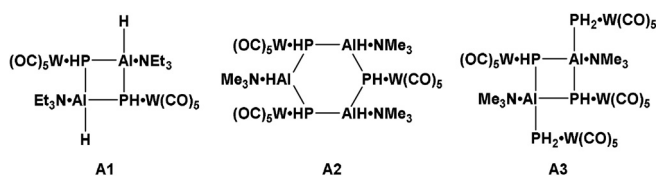


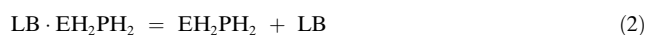
Figure 2. Different oligomeric products of the reaction between $\text{PH}_3 \cdot \text{W}(\text{CO})_5$ and $\text{AlH}_3 \cdot \text{NMe}_3/\text{AlH}_3 \cdot \text{NEt}_3$.

To select the most promising LB for the stabilization, quantum chemical computations were carried out for several Lewis bases: NMe_3 , Py, dmap and IDipp (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene). One of the decomposition pathways of the Lewis base stabilized compounds $\text{LB} \cdot \text{E}'\text{H}_2\text{PH}_2$ is the LB elimination with the formation of $(\text{E}'\text{H}_2\text{PH}_2)_n$ polymers ($\text{E}' = \text{Al}, \text{Ga}$). We modeled the oligomer formation [Eq. (1)], as the trimer was shown to be a good energetic model compound for the stability studies of long-chain oligomers.^[15]



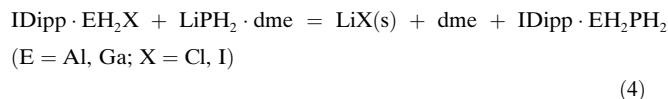
Quantum chemical computations indicate that, in terms of stabilization with respect to the oligomer formation [Eq. (1)], the order of Lewis bases is $\text{NMe}_3 < \text{Py} < \text{dmap} < \text{Dipp}$ (Table 1) with IDipp providing the best energetic stabilization. Note that decomposition of $\text{PH}_2\text{GaH}_2 \cdot \text{NMe}_3$ and $\text{PH}_2\text{GaH}_2 \cdot \text{Py}$ is predicted to be exergonic even at room temperature, whereas $\text{PH}_2\text{GaH}_2 \cdot \text{IDipp}$ is expected to be stable even in boiling toluene ($\Delta G_{383}^\circ = 14.2 \text{ kJ mol}^{-1}$).

Kinetic stability with respect to LB elimination depends on the activation energy of the dissociation [Eq. (2)]. Since complex formation proceeds without energy barrier, the standard enthalpy of the complex dissociation can be taken as an estimation of the activation energy.



The enthalpies of processes of complex dissociation increase in the order $\text{NMe}_3 < \text{Py} < \text{dmap} < \text{IDipp}$ (Table S4), indicating the increase in kinetic stabilization. Thus, the N-heterocyclic carbene IDipp provides the best energetic stabilization both from a thermodynamic and a kinetic point of view.

After identifying the IDipp as the prominent LB, we considered the thermodynamic favorability of possible synthetic pathways leading to $\text{LB} \cdot \text{EH}_2\text{PH}_2$. Two alternative pathways toward the parent phosphanylalanes and -gallanes stabilized only by a LB were regarded [Eqs. (3) and (4)].



As can be seen from the data in Table 1, reactions of $\text{IDipp} \cdot \text{MH}_3$ with phosphine are exothermic and slightly exergonic for both Al and Ga. Thus, the H_2 elimination synthetic pathway is thermodynamically allowed in this case. In contrast, the reaction with PHCy_2 instead of phosphine is both endothermic and endergonic and is thermodynamically prohibited. These data are in good agreement with the experimental observations: the reaction proceeds in the case of PH_3 , but not in case of PHCy_2 (see below).

In contrast, the alternative metathesis pathway is highly exothermic and exergonic and thermodynamically allowed in all cases (ΔG_{298}° values for Equation (4) are in the range -140 – -208 kJ mol^{-1} , see Table S6 for details). The formation of solid LiX (X = Cl, I) is a driving force for the metathesis reaction.

Lewis acidity trends: From the results of the quantum chemical computations, we can evaluate the influence of the substituent R in the Lewis acid EH_2R on its Lewis acidity with respect to IDipp as a reference Lewis base. For both aluminum and gallium, the stability of the complexes decreases in the order $\text{Cl} > \text{I} > \text{H} > \text{PH}_2 > \text{PCy}_2$. For the same R substituent, the aluminum complexes are more stable compared to the gallium analogues. The overall order of the stability of complexes with IDipp with respect to the dissociation is $\text{AlH}_2\text{Cl} > \text{AlH}_2\text{I} > \text{AlH}_3 > \text{AlH}_2\text{PH}_2 > \text{GaH}_2\text{Cl} > \text{GaH}_2\text{I} > \text{GaH}_3 > \text{AlH}_2\text{PCy}_2 > \text{GaH}_2\text{PH}_2 > \text{GaH}_2\text{PCy}_2$. Thus, compounds bearing PCy_2 substituents are the weakest with respect to the dissociation by means of the liberation of IDipp (Table S5).

The IDipp stabilized compound $\text{IDipp} \cdot \text{GaH}_2\text{PCy}_2$ (**1**; Cy = cyclohexyl) can be synthesized by the reaction between $\text{IDipp} \cdot \text{GaH}_2\text{Cl}$ and LiPCy_2 in Et_2O at -30°C . Crystals of **1** can be isolated in a yield of 55% at -30°C . As a solid, **1** is stable at ambient temperatures in an inert atmosphere. The

Table 1: Thermodynamic characteristics of gas-phase reactions.^[a]

Process	E = Al			E = Ga		
	ΔH_{298}°	ΔS_{298}°	ΔG_{298}°	ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
$\text{PH}_2\text{EH}_2 \cdot \text{NMe}_3 = 1/3 (\text{PH}_2\text{EH}_2)_3 + \text{NMe}_3$	13.7	40.4	1.7	0.6	37.6	-10.6
$\text{PH}_2\text{EH}_2 \cdot \text{Py} = 1/3 (\text{PH}_2\text{EH}_2)_3 + \text{Py}$	17.8	25.6	10.2	1.1	26.4	-6.8
$\text{PH}_2\text{EH}_2 \cdot \text{dmap} = 1/3 (\text{PH}_2\text{EH}_2)_3 + \text{dmap}$	36.1	33.8	26.0	15.7	31.0	6.5
$\text{PH}_2\text{EH}_2 \cdot \text{IDipp} = 1/3 (\text{PH}_2\text{EH}_2)_3 + \text{IDipp}$	52.1	78.5	28.7	40.7	69.0	20.1
$\text{IDipp} \cdot \text{MH}_3 + \text{PH}_3 = \text{H}_2 + \text{IDipp} \cdot \text{MH}_2\text{PH}_2$	-16.0	-39.0	-4.3	-14.6	-36.7	-3.7
$\text{IDipp} \cdot \text{MH}_3 + \text{PHCy}_2 = \text{H}_2 + \text{IDipp} \cdot \text{MH}_2\text{PCy}_2$	25.9	-81.1	50.1	23.5	-82.3	48.0

[a] Standard enthalpies ΔH_{298}° and standard Gibbs energies ΔG_{298}° in kJ mol^{-1} , standard entropies ΔS_{298}° in $\text{J mol}^{-1} \text{K}^{-1}$. B3LYP/def2-TZVP level of theory.

molecular ion peak of **1** can be detected at m/z 656.337 in the mass spectrum (LIFDI-MS). Its ^1H NMR spectrum shows a doublet at $\delta = 4.04$ ppm ($^2J_{\text{PH}} = 7.91$ Hz) for the GaH_2 -moiety. The ^{31}P NMR spectrum of a solution of **1** in C_6D_6 shows a broadened singlet at $\delta = -56.13$ ppm that is upfield shifted compared to the compound $[\{\text{H}_2\text{Ga}(\mu\text{-PCy}_2)\}_3]$ ($\delta = -32.7$ ppm).^[16] This shift results because of the stabilization from the NHC which increases the shielding of the phosphorus atom.

The X-ray structure analysis of **1** (Figure 3) shows a P–Ga bond length of 2.3724(6) Å that is shorter than the Ga–P bond in $\text{IMes}\cdot\text{GaEt}_2\text{P}(\text{H})\text{SirBuPh}_2$ (Ga–P = 2.4051(2) Å,

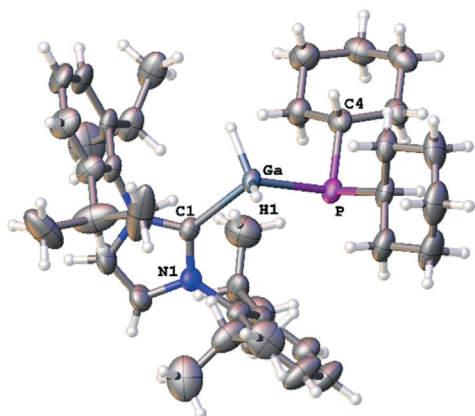


Figure 3. Molecular structure of **1** in the solid state. Selected bond lengths [Å] and angles [°]: Ga–P 2.3724(6), Ga–C1 2.090(2); H1–Ga–P–C4 125.6, C1–Ga–P 112.34(5). See Supporting Information for crystallographic details and all CCDC numbers.

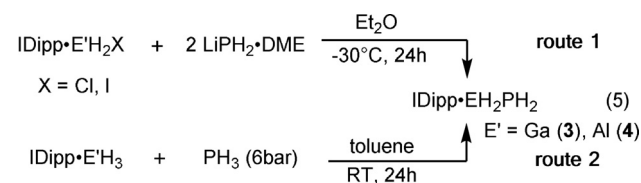
$\text{IMes} = 1,3$ -Bis-(2,4,6-trimethylphenyl)imidazole-2-ylidene) characterized by von Hähnisch et al. because of less bulkier substituents on the phosphorus atom and the Ga atom, respectively.^[17] Likewise, the Ga–C1 bond in **1** (2.090(2) Å) is shorter, too, compared to $\text{IMes}\cdot\text{GaEt}_2\text{P}(\text{H})\text{SirBuPh}_2$ (Ga– $\text{C}_{\text{NHC}} = 2.1254(7)$ Å) because of the stronger donation by IDipp as opposed to IMes. The conformation of **1** is an eclipsed one with a torsion angle of H1–Ga–P–C4 = 125.6° (Figure 3). The C1–Ga–P angle of **1** (112.34(5)°) is much wider than in $\text{IMes}\cdot\text{GaEt}_2\text{P}(\text{H})\text{SirBuPh}_2$ ($\text{C}_{\text{NHC}}\text{-Ga-P} = 99.1(2)^\circ$) because of the steric demand of the isopropyl-moiety of the IDipp.

Reactions between $\text{IDipp}\cdot\text{GaH}_3$ and PHCy_2 were performed in toluene at -30°C , room temperature and 100°C for 24 hours. In neither of these reactions the formation of compound **1** could be identified, supporting the results of the previously discussed computations (Table 1).

The Al analogue $\text{IDipp}\cdot\text{AlH}_2\text{PCy}_2$ (**2**) is accessible by the reaction between $\text{IDipp}\cdot\text{AlH}_2\text{Cl}$ and LiPCy_2 in Et_2O at -30°C . Numerous attempts to crystallize **2** failed because of its extreme sensitivity towards hydrolysis. The ^1H NMR spectrum of crude **2** in C_6D_6 shows IDippH as the major component which cannot be separated due to similar solubility. None the less it was possible to assign compound **2** to the signals in the ^1H NMR spectrum as a minor component. The ^{31}P NMR spectrum of **2** in C_6D_6 shows

a singlet at -66.24 ppm (Figure S12) that is upfield shifted compared to **1**. This is consistent with the spectra of **3** and **4** in which the signal for the Al analogue is likewise shifted upfield (see below).

In contrast to the substituted phosphanylalanes and -gallanes, the NHC-stabilized parent compounds can be synthesized via two different routes [Eq. (5)].



Route 1 is on the lines of the synthesis of the substituted compounds (**1** and **2**), a reaction between $\text{IDipp}\cdot\text{E}'\text{H}_2\text{Cl}$ ($\text{E}' = \text{Ga, Al}$) and the parent phosphanide $\text{LiPH}_2\cdot\text{DME}$ in Et_2O at -30°C . The other synthesis is the H_2 -elimination route between $\text{IDipp}\cdot\text{E}'\text{H}_3$ and PH_3 (6 bar) in toluene at room temperature (route 2), which was not possible for the substituted derivatives.

Compound **3** ($\text{IDipp}\cdot\text{GaH}_2\text{PH}_2$) can be isolated at -30°C in a crystalline yield of 67% via route 1 and of 23% via route 2. It can be stored at ambient temperatures under an inert atmosphere without showing any decomposition. The molecular ion peak of **3** was detected at m/z 493.205 (LIFDI-MS). The ^1H NMR spectrum of **3** shows a broad singlet at $\delta = 4.21$ ppm for the GaH_2 moiety and a doublet of triplets at $\delta = 0.54$ ppm ($^1J_{\text{PH}} = 170.8$ Hz, $^3J_{\text{HH}} = 3.68$ Hz) for the PH_2 moiety. The ^{31}P NMR spectrum reveals a triplet of triplets at $\delta = -277.10$ ppm ($^1J_{\text{PH}} = 170.8$ Hz, $^2J_{\text{PH}} = 19.05$ Hz). The molecular structure of **3** (Figure 4) shows a P–Ga bond (2.3373(6) Å) which is slightly shorter than in **1** (2.3724(6) Å) as well as the Ga–C1 bond (2.0507(2) Å, **1**: 2.090(2) Å). In contrast to **1**, which has an eclipsed conformation, compound **3** has a staggered conformation (torsion angle of H1–Ga–P–H3 = 164.1°) because of the less-bulky H substituents on the phosphorus atom, which results in a smaller C1–Ga–P angle as well (109.19(5)°).

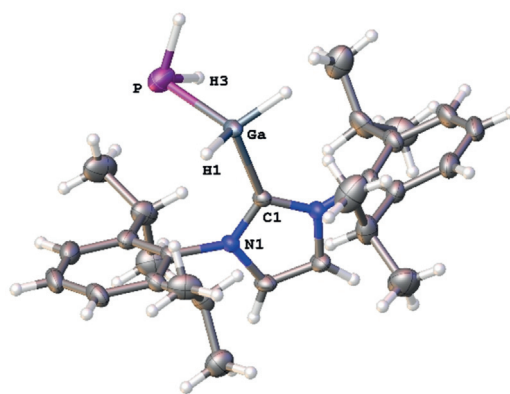


Figure 4. Molecular structure of **3** in the solid state. Selected bond lengths [Å] and angles [°]: Ga–P 2.3373(6), Ga–C1 2.0507(2); H1–Ga–P–H3 164.1°, C1–Ga–P 109.19(5).

The aluminum analogue IDipp-AlH₂PH₂ (**4**) can also be synthesized via salt metathesis and H₂ elimination reactions. Compound **4** can be isolated as a colorless crystalline solid at –30 °C in 55% yield (route 1) and 20% yield (route 2), respectively. This reveals that the H₂ elimination route is less efficient in comparison with the salt elimination reaction. Compound **4** can be stored under an inert atmosphere at room temperature without showing any decomposition. The LIFDI-MS and FD-MS spectrum does not show a molecular ion peak due to decomposition during the ionization process. The ¹H NMR spectrum of **4** reveals a broad singlet at $\delta = 3.64$ ppm for the AlH₂ moiety and a triplet of triplets at $\delta = 0.22$ ppm (¹J_{PH} = 169.6 Hz, ³J_{H,H} = 3.09 Hz) for the PH₂ moiety. The ³¹P NMR spectrum of **4** shows a triplet of triplets at $\delta = -285.7$ ppm (¹J_{PH} = 169.6 Hz, ²J_{PH} = 18.7 Hz) which is upfield shifted compared to **3**.

The P–Al bond in **4** (2.3131(10) Å; Figure 5) is slightly shorter than the P–Al bond in [(CO)₅W]H₂PAIH₂·NMe₃] (2.377(1) Å).^[5] The Al–C1 (2.056(2) Å) bond length is in good agreement with the Ga–C1 bond in **3** (2.0507(2) Å). The C1–Al–P angle (113.17(7)°) is slightly wider than the C1–Ga–P angle in compound **3** (109.19(5)°) and the C1–Ga–P angle in **1** (112.34(5)°). It was not possible to freely refine the H substituents on the phosphorus atom and therefore it is not possible to provide any information about the torsion angle and the conformation of **4**.

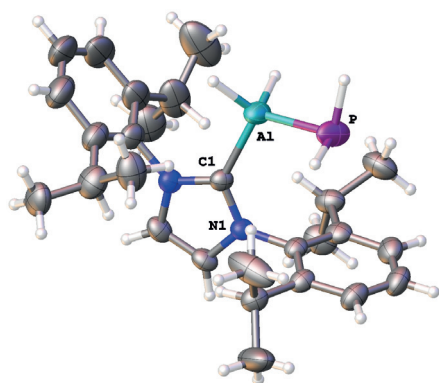


Figure 5. Molecular structure of **4** in the solid state. Selected bond lengths [Å] and angles [°]: Al–P 2.3131(10), Al–C1 2.056(2), C1–Al–P 113.17(7). The H atoms at the P atom were restrained at fixed positions.

The results have shown for the first time that it is possible to synthesize monomeric phosphanylalanes and phosphanylgallanes stabilized only by a Lewis base if a strong donating and sterically demanding LB is used. In addition to the derivatives, which are organosubstituted on the P atom, also the parent compounds were isolated representing the unprecedented examples of only LB-stabilized parent phosphanylalanes and -gallanes. While the parent compounds can be synthesized via salt metathesis and H₂ elimination, the organosubstituted compounds can only be accessed via a salt metathesis reaction. The energetic differences in the reaction pathways and the different stability of these complexes were computed by DFT methods. Moreover, the salt

elimination route was applied for the first time to access stabilized phosphanylalanes and phosphanylgallanes. Further investigations will be directed at using the novel compounds as precursors for CVD-processes to obtain Group 13/15 materials.

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Conflict of interest

The authors declare no conflict of interest.

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