

Main-Group Elements

Monomeric β -Diketiminato Group 13 Metal Dipnictogenide Complexes with Two Terminal EH_2 Groups ($\text{E} = \text{P}, \text{As}$)Bin Li,^[a] Susanne Bauer,^[a] Michael Seidl,^[a] Alexey Y. Timoshkin,^[b] and Manfred Scheer^{*[a]}

Dedicated to Professor Jörg Sundermeyer on the occasion of his 60th birthday.

Abstract: The pnictogenyl Group 13 compounds $(\text{Dipp}_2\text{Nacnac})\text{M}[\text{E}(\text{SiMe}_3)_2\text{Cl}]$ and $(\text{Dipp}_2\text{Nacnac})\text{M}(\text{EH}_2)_2$ ($\text{Dipp}_2\text{Nacnac} = \text{HC}[\text{C}(\text{Me})\text{N}(\text{Ar})]_2$, Ar: Dipp = 2,6-*i*-Pr₂C₆H₃; M = Al, Ga, In; E = P, As) were successfully synthesized. The salt metathesis between $(\text{Dipp}_2\text{Nacnac})\text{MCl}_2$ and $\text{LiE}(\text{SiMe}_3)_2$ only led to monosubstituted compounds $(\text{Dipp}_2\text{Nacnac})\text{M}[\text{E}(\text{SiMe}_3)_2\text{Cl}]$ [E = P, M = Ga (1), In (2); E = As, M = Ga (3), In (4)], regardless of the stoichiometric ratios used. In contrast to the steric effect of the SiMe_3 groups in 1–4, the reactions of the corresponding halides with $\text{LiPH}_2\cdot\text{DME}$ (or KAsH_2) readily yielded the dipnictogenide compounds $(\text{Dipp}_2\text{Nacnac})\text{M}(\text{EH}_2)_2$ (E = P, M = Al (5), Ga (6), In (7); E = As, M = Al (8), Ga (9)), avoiding the use of flammable and toxic PH_3 and AsH_3 for their synthesis. The compounds 5–9 are the first examples of monomeric Group 13 diphosphanides and diarsanides in which the metal center is bound to two terminal PH_2 and AsH_2 groups, respectively. In contrast to the successful synthesis of the indium diphosphanide $(\text{Dipp}_2\text{Nacnac})\text{In}(\text{PH}_2)_2$, the reaction of $(\text{Dipp}_2\text{Nacnac})\text{InCl}_2$ with KAsH_2 led to an indium mirror due to the instability of the target product.

Pnictogenyl-substituted Group 13 metal compounds have emerged as an important type of molecules, having enormous potential to be used in material science of for example, nanoparticles,^[1] optoelectronic layers, or semiconductors.^[2] Moreover, the highly reactive EH_2 groups (E = N, P, and As) probably enable further substitution to obtain heterobimetallic species

containing $\text{M}-\text{E}(\text{H})-\text{M}'$ moieties. Given the Lewis acidity of the Group 13 metal center and the Lewis basicity of the EH_2 groups, these types of complexes readily undergo oligomerization to give dimers $(\text{R}_2\text{AlNH}_2)_2$ [R = SiMe_3 , $\text{N}(\text{SiMe}_3)_2$] and $[\text{Ph}^*\text{MH}(\text{NH}_2)]_2$ (M = Al, Ga, Ph^* = terphenyl ligands),^[3] trimers $(\text{R}_2\text{AlNH}_2)_3$ (R = CH_3 , *t*Bu),^[4] or pseudo oligomers $\text{Al}[\text{R}_2\text{Al}(\text{NH}_2)_2]_3$ (R = SiMe_3 , $\text{N}(\text{SiMe}_3)_2$) (A, B, C, Scheme 1).^[3b,5] Therefore, steric crowding is essential to isolate stable monomeric species with parent EH_2 substituents.^[6] In 2004, the first monomeric aluminum diamide supported by a β -diketiminato substituent was synthesized from the corresponding chloride derivative with NH_3 in the presence of an N-heterocyclic carbene (D, Scheme 1).^[7] Subsequently, the corresponding gallium diamide was obtained through a similar procedure.^[8] Nonetheless, no progress on its heavier analogues has been made until now. This is caused by the extreme flammability and toxicity of PH_3 and AsH_3 , respectively. To date, only very few of the heavier pnictogenyl Group 13 compounds with parent EH_2 (E = P, As) substituents have been reported. The lithium phosphanylalane $\text{LiAl}(\text{PH}_2)_4$ is known as the first aluminum phosphanide representing a convenient PH_2^- transfer reagent although it is only stable in ethereal solution.^[9] In 2000, Driess et al. reported the synthesis of diisobutyl(phosphanyl)alane $[\text{iBu}_2\text{AlPH}_2]_3$, which gives in situ in THF a monomolecular $\text{iBu}_2\text{Al}(\text{THF})\text{PH}_2$ species (E, Scheme 1).^[10] Power and co-workers reported phosphanyl alanes and -gallanes ring compounds stabilized by bulky terphenyl ligands (F, Scheme 1).^[3c,d] Previously, our group was able to obtain aluminum and gallium monophosphanide complexes $[(\text{CO})_5\text{W}]\text{PH}_2\text{MH}_2(\text{NMe}_3)$ (M = Al, Ga), which were prepared through H_2 elimination between $\text{Me}_3\text{N}\cdot\text{MH}_3$ (M = Al, Ga) and $\text{PH}_3[\text{W}(\text{CO})_5]$ (G, Scheme 1).^[11] Similarly, versatile oligomers can be obtained by using different conditions and different Lewis bases during the synthesis.^[12] Moreover, lithium arsanilalane $\text{LiAl}(\text{AsH}_2)_4$ was also synthesized by the reaction of LiAlH_4 with AsH_3 .^[13] In general, far less research has been made in arsanil (AsH_2) chemistry because of its toxicity, light sensitivity, and instability.

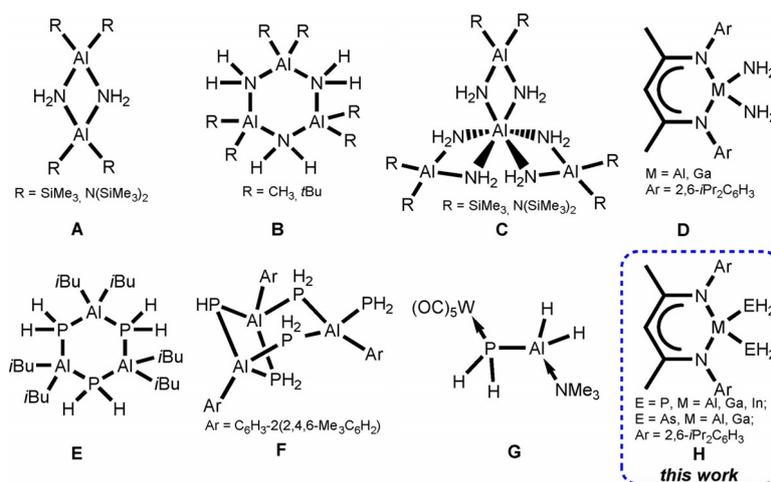
In addition to the aluminum and gallium diamide compounds (D, Scheme 1), the heavier analogues of Group 13 metal dipnictogenides are still unknown. Moreover, the preparation of pnictogenyl Group 13 compounds with an EH_2 moiety generally requires the pnictogen hydrogen compound SEH_3 , which, in addition to their flammability and toxicity, is invalid for stoichiometrically controlled reactions. Therefore, the quest for the stabilization of heavier Group 13 metal dipnictogenide species of type H is still open, and an appropriate

[a] Dr. B. Li, Dr. S. Bauer, Dr. M. Seidl, Prof. Dr. M. Scheer
Institut für Anorganische Chemie, Universität Regensburg
93040 Regensburg (Germany)
E-mail: manfred.scheer@chemie.uni-regensburg.de
Homepage: <https://www.uni-regensburg.de/chemistry-pharmacy/inorganic-chemistry-scheer/index.html>

[b] Prof. Dr. A. Y. Timoshkin
Institute of Chemistry, St. Petersburg State University
Universitetskaya emb. 7/9, 199037 St. Petersburg (Russia)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/chem.201903887>.

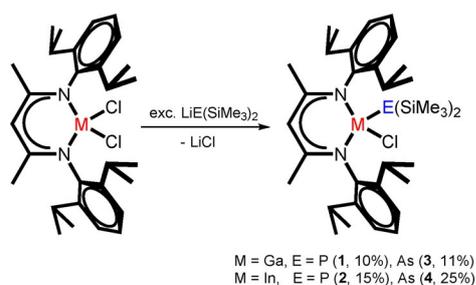
© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of Creative Commons Attribution NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.



Scheme 1. Selected examples of Group 13 metal pnictogenide compounds with EH_2 ($\text{E} = \text{N}, \text{P}$) substituents.

novel synthetic route should be developed. In 1993, Cowley prepared the base-stabilized phosphanyl- and arsanylalanes monomers $\text{Me}_3\text{N}\cdot\text{AlH}_2\text{E}(\text{Mes})_2$ ($\text{E} = \text{P}, \text{As}$; $\text{Mes} = 2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$) by metathesis reactions.^[14] More recently, we reported on the synthesis of Lewis base-stabilized pnictogenylboranes based on metathesis,^[15] demonstrating the feasibility of this type of reaction in the preparation of pnictogenyl metal compounds. In addition, the Lewis base-stabilized parent phosphanyl- and arsanylboranes $\text{H}_2\text{EBH}_2\cdot\text{Me}_3\text{N}$ ($\text{E} = \text{P}, \text{As}$) also were obtained by the alcoholysis of the corresponding $(\text{SiMe}_3)_2\text{EBH}_2\cdot\text{Me}_3\text{N}$ ($\text{E} = \text{P}, \text{As}$) with methanol,^[15g] which seems to be an alternative synthetic route. Herein, we report on the synthesis and characterization of first Group 13 metal diposphanide and diarsanide compounds through salt metathesis, in which the sterically bulky β -diketiminato ligand was employed for the stabilization of the target products.

Initially, we explored the approach of Group 13 metal dipnctogenide compounds with SiMe_3 substituents. Treatments of $(\text{Dipp}_2\text{Nacnac})\text{MCl}_2$ ($\text{Dipp}_2\text{Nacnac} = \text{HC}[\text{C}(\text{Me})\text{N}(\text{Ar})]_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$; $\text{M} = \text{Ga}, \text{In}$)^[16] with lithium bis(trimethylsilyl)phosphanide $[\text{LiP}(\text{SiMe}_3)_2]$ ^[17] or arsanide $[\text{LiAs}(\text{SiMe}_3)_2]$ ^[18] in toluene only gave the monosubstituted compounds **1–4**, respectively (Scheme 2). In **1–4**, one chlorine atom has been replaced by a $\text{P}(\text{SiMe}_3)_2$ or $\text{As}(\text{SiMe}_3)_2$ group. However, even by using an excess amount of the lithium pnictogenide reagents, it was not possible to substitute both chlorine atoms, which is attri-



Scheme 2. Synthesis of compounds **1–4**. Yields are given in parenthesis.

buted to the steric hindrance of the bulky β -diketiminato ligand as well as the size of trimethylsilyl groups. The compounds **1–4** are well soluble, for example in toluene. In the ^1H NMR spectra of **1–4**, characteristic resonances of the β -diketiminato ligand are observed, for example, the singlet at $\delta = 4.97$ ppm for **1** [**2**: 4.84, **3**: 4.93, and **4**: 4.81 ppm] corresponds to the γ -H in each compound. In addition, the ^1H NMR spectra of **1** and **2** also show a doublet at $\delta = 0.09$ and 0.02 ppm, respectively, with a $^3J_{\text{PH}}$ coupling constant of 4.6 Hz, corresponding to the trimethylsilyl groups. In comparison, the singlets assigned to the trimethylsilyl groups in the ^1H NMR spectra of **3** and **4** were observed at $\delta = 0.10$ and 0.07 ppm, respectively. Moreover, the $^{31}\text{P}\{\text{H}\}$ NMR spectra of **1** and **2** show a singlet at $\delta = -255.0$ and -252.9 ppm, respectively.

Single-crystal X-ray diffraction was carried out to confirm the structures of **1–4**. All four compounds crystallize in the monoclinic space group $P2_1/m$, the molecular structure of **1** is depicted in Figure 1. The metal center is in a tetrahedral coordination mode binding to a β -diketiminato ligand, a chlorine atom as well as a bis(trimethylsilyl)phosphanide or arsanide group, respectively. The N–M–N angles ($\text{M} = \text{Ga}, \text{In}$) in **1–4** were determined to $96.03(13)$ (**1**) and $95.95(9)^\circ$ (**3**) for the gallium

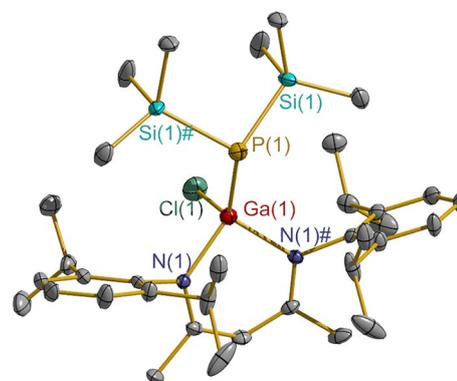
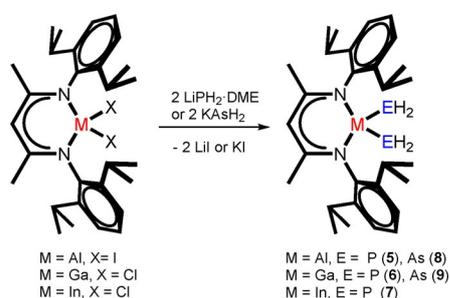


Figure 1. Molecular structure of **1** with thermal ellipsoids at 30% probability level. Carbon-bound hydrogen atoms are omitted for clarity.

compounds, and 90.33(10) (**2**) and 90.20(9)° (**4**) for the indium compounds. Compared with the N-M-N angles (M=Ga, In) in the starting materials (Dipp₂Nacnac)GaCl₂ (93.92(7)°) and (Dipp₂Nacnac)InCl₂ (92.5(1)°),^[16] respectively, the angles in **1–4** are significantly smaller, implying the steric effect of the substituents. The Ga–P bond length in **1** is 2.3310(9) Å, which is shorter than the In–P bond length in **2** (2.4806(8) Å). The Ga–As distance of 2.4196(4) Å in **3** is also shorter than the In–As distance in **4** (2.5632(3) Å).

Regardless of the steric hindrance, the above-mentioned results indicate the promising synthesis of pnictogenyl metal complexes through salt metathesis. Thus, we further investigated the targeted synthesis of metal dipnictogenides with two terminal EH₂ groups (E=P, As). The reaction of (Dipp₂Nacnac)MX₂ (X=I, M=Al; X=Cl, M=Ga, In)^[16,19] with two equivalents of LiPH₂·DME^[20] were carried out in diethyl ether or THF (Scheme 3). After workup, the expected metal di-



Scheme 3. Synthesis of compounds **5–9**.

phosphanides **5–7** were isolated in yields of 32, 34.3, and 1%, respectively. The quite low yield of isolated material for **7** is imputed to the extreme photosensitivity of indium compounds because the solution of **7** immediately became turbid upon exposure to light.

Compounds **5–7** are air and moisture sensitive and soluble in almost all common organic solvents. They were fully characterized by multinuclear NMR spectroscopy and X-ray diffraction. In the ¹H NMR spectra of **5–7**, typical resonances of β-diketimate backbones are observed. The resonances of γ-H are detected as a singlet at δ = 4.97 (**5**), 4.83 (**6**), and 4.75 ppm (**7**), which are comparable to those of (Dipp₂Nacnac)Al(NH₂)₂ (δ = 4.88 ppm)^[7] and (Dipp₂Nacnac)Ga(NH₂)₂ (δ = 4.76 ppm).^[8] Moreover, the ¹H NMR spectrum of **5** shows a doublet at δ = 0.74 ppm (*J*_{PH} = 172.0 Hz), which was assigned to the PH₂ moieties, whereas in the spectra of **6** and **7**, the signal splits into a doublet of doublets at δ = 1.03 ppm (¹*J*_{PH} = 175.7, ³*J*_{PH} = 5.1 Hz) for **6** and 0.90 ppm (¹*J*_{PH} = 168.0, ³*J*_{PH} = 4.6 Hz) for **7** (Table 1).

Complex	δ [ppm]	multiplicity	¹ <i>J</i> _{PH} [Hz]	³ <i>J</i> _{PH} [Hz]
5	0.74	d	172.0	Not observed
6	1.03	dd	175.7	5.1
7	0.90	dd	168.0	4.6

The AB spin systems in **6** and **7** are a result of the nonplanarity of the C₃N₂M ring, because the gallium and indium atoms are relatively oversized. The same coupling constants also were observed in the ³¹P NMR spectra. In contrast, singlets at δ = –273.4 (**5**), –262.1 (**6**), and –285.5 ppm (**7**) were detected in the ³¹P{¹H} NMR spectra, falling in the range of the typical resonances of terminal PH₂ groups.^[3d,10,12a] In addition, the LIFDI mass spectra of **5** and **6** show the most intense peak at *m/z* 477.3 and 519.4, respectively, assigned to the ionic fragment of [M⁺–PH₂]. However, mass spectroscopy could not be used for the characterization of **7** because of its light and air sensitivity.

The structures of **5–7** were further determined by single-crystal X-ray diffraction. Compounds **5** and **6** crystallize in the triclinic space group *P* $\bar{1}$, whereas **7** crystallizes in the monoclinic space group *P*2₁/*n*. The molecular structure of **5** is depicted in Figure 2 and those of **6** and **7** are included in the Support-

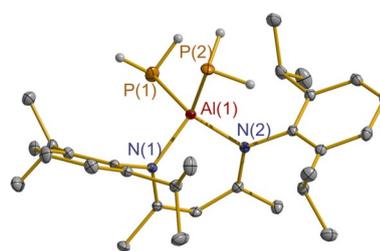


Figure 2. Molecular structure of **5** with thermal ellipsoids at 30% probability level. Carbon-bound hydrogen atoms were omitted for clarity.

ing Information. These three compounds are isostructural because their metal centers adopt a distorted-tetrahedral geometry in the coordination with two phosphorus and two nitrogen atoms, respectively. The phosphorus atoms adopt a pyramidal geometry with different orientations. The N-M-N angles (M=Al, Ga, In) decrease following the order of Group 13 as 97.47(**5**), 95.81(**6**), and 89.10(**6**)° (**7**). This indicates the nonplanarity of the C₃N₂M rings (M=Al, Ga, In), which is in agreement with the coupling in the ³¹P NMR spectra. In contrast, the P-M-P angles slightly increase in the sequence of 115.26(**2**) (**5**), 118.88(**19**) (**6**), and 122.55(**2**)° (**7**). In compound **5**, the Al–P bond lengths are 2.3474(**5**) and 2.3718(**5**) Å, thus being comparable to those containing parent PH₂ units in [((CO)₅W)H₂PAIH₂(NMe₃)_n] (*n* = 1, 2.367(**1**); *n* = 2, 2.432(**2**) Å),^[11,21] [((CO)₄Cr)H₂PAIH₂(NMe₃)] (2.383(**1**) Å),^[22] [((CO)₅WPH₂)(Me₃N)–AlPH(W(CO)₅)₂] (2.368(**6**) Å),^[12a] and [(Ar'Al)₃(μ-PH₂)₃(μ-PH)PH₂] [Ar' = C₆H₃-2,6(C₆H₂-2,4,6-Me₃)₂] (2.378(**2**) Å).^[3d] The Ga–P distances of **6** (2.3286(**5**) and 2.3532(**5**) Å) are close to those observed in [((CO)₅W)H₂PGaH₂(NMe₃)] (2.349(**2**) Å)^[11] and **1** (2.3310(**9**) Å), whereas **7** has slightly longer In–P bonds (2.5255(**7**) and 2.5052(**6**) Å) compared with that of **2** (2.4808(**8**) Å).

Furthermore, it was of interest if this synthetic procedure could also be used for the synthesis of the more sensitive bis-AsH₂-substituted derivatives. The treatment of (Dipp₂Nacnac)MX₂ (X=I, M=Al; X=Cl, M=Ga)^[16,19] with two equivalents of KAsH₂^[23] resulted in the new aluminum and gallium diarsanide complexes **8** and **9** (Scheme 3). However, the

reaction of $(\text{Dipp}_2\text{Nacnac})\text{InCl}_2$ with KAsH_2 led to an indium mirror as well as $[(\text{Dipp}_2\text{Nacnac})\text{H}]$ as the only product detectable by ^1H NMR spectroscopy,^[24] due to the high sensitivity, even though the compounds were handled in the absence of light. Compound **9** is also quite unstable in solution to give $[(\text{Dipp}_2\text{Nacnac})\text{H}]$, whereas the aluminum derivative **8** shows a higher stability. Similarly, the ^1H NMR spectra of **8** and **9** display characteristic signals for the β -diketiminate ligands such as the singlets for γ -H at $\delta=4.99$ and 4.86 ppm and the septets for CHMe_2 at $\delta=3.43$ and 3.44 ppm, respectively. In addition, the resonances for AsH_2 groups are observed as a singlet at $\delta=0.28$ and 0.65 ppm, respectively. In the LIFDI mass spectrum of **8**, the peak of the $[\text{M}^+-\text{AsH}_2]$ fragment is observed at m/z 521.2, whereas the EI mass spectrum of **9** shows not only the $[\text{M}^+-\text{AsH}_2]$ but also the $[\text{M}^+-2\text{AsH}_2]$ fragments at m/z 563.1(95) and 487.2(22), respectively.

Compound **8** was further characterized by single crystal X-ray diffraction and represents the first monomeric aluminum diarsanide that has been structurally characterized so far (Figure 3). Compound **8** crystallizes in the monoclinic space

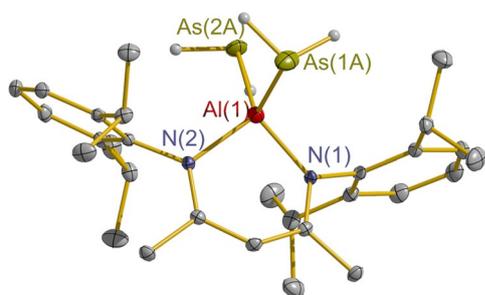


Figure 3. Molecular structure of **8** with thermal ellipsoids at 30% probability level. Carbon-bound hydrogen atoms and the distorted part of the AsH_2 units were omitted for clarity.

group $P2_1/n$, in which the fourfold-coordinated aluminum center is bound to a β -diketiminate ligand and two AsH_2 substituents. Both arsenic atoms adopt a pyramidal geometry, indicating the existence of the lone pairs of electrons. The $\text{N}(1)\text{-Al}(1)\text{-N}(2)$ angle in **8** ($97.77(4)^\circ$) is similar to those of **5** ($97.47(5)^\circ$) and $(\text{Dipp}_2\text{Nacnac})\text{Al}(\text{NH}_2)_2$ ($95.7(1)^\circ$).^[7] The average As-Al bond length of 2.474(3) Å in **8** is comparable to those observed in lithium arsanylalanate $[\text{Li}(\text{DME})_2]_2\text{-}[(\text{AlH}_2\text{AsR})_3\text{Li}(\text{DME})]$ ($\text{DME}=1,2\text{-dimethoxyethane}$) (av. 2.472(3) Å),^[13] whereas they are longer than the corresponding bond in **3** (2.4196(4) Å).

Computational DFT studies (see the Supplementary Information) indicate that the reactions leading to **1-4** and **5-9** are exergonic and that the formation of a solid salt is the driving force for the reaction. The computed thermodynamic data indicate that the stability of Group 13 metal diphosphanides and diarsanides decreases in the order $\text{Al} > \text{Ga} > \text{In}$. The processes of the decomposition of In-containing derivatives into indium metal with the formation of $[(\text{Dipp}_2\text{Nacnac})\text{H}]$, E_4 , and H_2 as by-products are exergonic at room temperature by 10 and 53 kJ mol^{-1} for $\text{E}=\text{P}$ or As , respectively, which is in agreement

with the experimentally observed low stability of **7** and the absence of its diarsanide analog.

The analysis of the electronic structure reveals that the HOMOs of **5-9** are essentially lone pairs of electrons located at pnictogen atoms. Thus, **5-9** can potentially serve as bidentate Lewis bases. However, the large E-M-E angles ($115\text{-}123^\circ$, see above), which are unfavorable for the formation of 4-membered cycles, suggest that such compounds could be rather bridging than chelating ligands.

In summary, we provided a smooth synthetic route to metal phosphanide and arsenide compounds through salt-metathesis reactions and a series of β -diketiminate ligand-stabilized pnictogenyl Group 13 complexes $(\text{Dipp}_2\text{Nacnac})\text{M}[\text{E}(\text{SiMe}_3)_2]\text{Cl}$ ($\text{E}=\text{P}, \text{As}$; $\text{M}=\text{Ga}, \text{In}$) and $(\text{Dipp}_2\text{Nacnac})\text{M}(\text{EH}_2)_2$ ($\text{E}=\text{P}, \text{M}=\text{Al}, \text{Ga}, \text{In}$; $\text{E}=\text{As}, \text{M}=\text{Al}, \text{Ga}$) have been synthesized. The utilization of alkali-metal pnictides ($\text{LiE}(\text{SiMe}_3)_2$, LiPH_2 , and KAsH_2) avoids the use of flammable and toxic PH_3 and AsH_3 for their synthesis. Due to steric hindrance, reactions of $\text{LiE}(\text{SiMe}_3)_2$ ($\text{E}=\text{P}$ and As) with the corresponding metal chlorides only led to monosubstituted products **1-4**. When using $\text{LiPH}_2\text{-DME}$ and KAsH_2 as starting materials, the monomeric Group 13 diphosphanides and diarsanides **5-9** were obtained. For the first time, these complexes contain two terminal PH_2 and AsH_2 groups, respectively. Notably, the reaction of $(\text{Dipp}_2\text{Nacnac})\text{InCl}_2$ with KAsH_2 led to an indium mirror and $[(\text{Dipp}_2\text{Nacnac})\text{H}]$ due to the intrinsic instability, implying the high photolability of such species. The good solubility and stability of aluminum diphosphanide and diarsanide compounds promise an interesting subsequent reactivity pattern, which is in the focus of current investigations. Moreover, the rather low stability of the M-E bonds might result in potential PH_2 and AsH_2 transfer reagents.^[25]

Acknowledgements

The authors thank the DFG for comprehensive support in the project Sche 384/35-1. A.Y.T. is grateful to the SPSU grant 12.65.44.2017.

Conflict of interest

The authors declare no conflict of interest.

Keywords: beta-diketiminate ligands • diarsanides • diphosphanide • group 13 metals • main-group elements

[1] J. A. Jegier, W. L. Gladfelter, *Coord. Chem. Rev.* **2000**, 206–207, 631–650.

[2] a) A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, 110, 4023–4078; b) A. M. Priegert, B. W. Rawe, S. C. Serin, D. P. Gates, *Chem. Soc. Rev.* **2016**, 45, 922–953; c) H. Sahin, S. Cahangirov, M. Topsakal, E. Bekaroglu, E. Akturk, R. T. Senger, S. Ciraci, *Phys. Rev. B* **2009**, 80, 155453; d) S. Schulz, *Coord. Chem. Rev.* **2001**, 215, 1–37; e) R. A. Fischer, J. Weiß, *Angew. Chem. Int. Ed.* **1999**, 38, 2830–2850; *Angew. Chem.* **1999**, 111, 3002–3022; f) R. L. Wells, W. L. Gladfelter, *J. Cluster Sci.* **1997**, 8, 217–238; g) A. C. Jones, P. O'Brien in *CVD of Compound Semiconductors*, VCH, Weinheim, **1997**; h) D. A. Neumayer, J. G. Ekerdt, *Chem. Mater.* **1996**, 8, 9–25; i) M. L. Hitchman, K. F. Jensen in *Chemical vapor deposition: principles and applications*, Elsevier, London,

- 1993; j) A. J. Downs in *Chemistry of aluminium, gallium, indium and thallium*, Blackie, Glasgow, 1993.
- [3] a) J. F. Janik, E. N. Duesler, R. T. Paine, *Inorg. Chem.* **1987**, *26*, 4341–4345; b) K. J. L. Paciorek, J. H. Nakahara, L. A. Hoferkamp, C. George, J. L. Flippen-Anderson, R. Gilardi, W. R. Schmidt, *Chem. Mater.* **1991**, *3*, 82–87; c) Z. Zhu, X. Wang, Y. Peng, H. Lei, J. C. Fettinger, E. Rivard, P. P. Power, *Angew. Chem. Int. Ed.* **2009**, *48*, 2031–2034; *Angew. Chem.* **2009**, *121*, 2065–2068; d) C. E. Melton, J. W. Dube, P. J. Ragoon, J. C. Fettinger, P. P. Power, *Organometallics* **2014**, *33*, 329–337.
- [4] L. V. Interrante, G. A. Sigel, M. Garbaskas, C. Hejna, G. A. Slack, *Inorg. Chem.* **1989**, *28*, 252–257.
- [5] J. F. Janik, E. N. Duesler, R. T. Paine, *Inorg. Chem.* **1988**, *27*, 4335–4338.
- [6] P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3504.
- [7] V. Jancik, L. W. Pineda, J. Pinkas, H. W. Roesky, D. Neculai, A. M. Neculai, R. Herbst-Irmer, *Angew. Chem. Int. Ed.* **2004**, *43*, 2142–2145; *Angew. Chem.* **2004**, *116*, 2194–2197.
- [8] V. Jancik, L. W. Pineda, A. C. Stückl, H. W. Roesky, R. Herbst-Irmer, *Organometallics* **2005**, *24*, 1511–1515.
- [9] A. E. Finholt, C. Helling, V. Imhof, L. Nielsen, E. Jacobson, *Inorg. Chem.* **1963**, *2*, 504–507.
- [10] M. Driess, C. Monsé, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1091–1094.
- [11] a) U. Vogel, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2001**, *40*, 4409–4412; *Angew. Chem.* **2001**, *113*, 4541–4544.
- [12] a) M. Bodensteiner, U. Vogel, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2009**, *48*, 4629–4633; *Angew. Chem.* **2009**, *121*, 4700–4704; b) M. Bodensteiner, A. Y. Timoshkin, E. V. Peresypkina, U. Vogel, M. Scheer, *Chem. Eur. J.* **2013**, *19*, 957–963.
- [13] M. Driess, K. Merz, H. Pritzkow, R. Janoschek, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2507–2510; *Angew. Chem.* **1996**, *108*, 2688–2691.
- [14] D. A. Atwood, L. Contreras, A. H. Cowley, R. A. Jones, M. A. Mardones, *Organometallics* **1993**, *12*, 17–18.
- [15] a) O. Hegen, C. Marquardt, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2017**, *56*, 12783–12787; *Angew. Chem.* **2017**, *129*, 12959–12963; b) U. Vogel, P. Hoemensch, K.-C. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2003**, *9*, 515–519; c) C. Marquardt, O. Hegen, M. Hautmann, G. Balázs, M. Bodensteiner, A. V. Virovets, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2015**, *54*, 13122–13125; *Angew. Chem.* **2015**, *127*, 13315–13318; d) O. Hegen, J. Braese, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2019**, *25*, 485–489; e) O. Hegen, A. V. Virovets, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2018**, *24*, 16521–16525; f) K.-C. Schwan, A. Y. Timoshkin, M. Zabel, M. Scheer, *Chem. Eur. J.* **2006**, *12*, 4900–4908; g) C. Marquardt, A. Adolf, A. Stauber, M. Bodensteiner, A. V. Virovets, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2013**, *19*, 11887–11891.
- [16] M. Stender, B. E. Eichler, N. J. Hardman, P. P. Power, J. Prust, M. Noltemeyer, H. W. Roesky, *Inorg. Chem.* **2001**, *40*, 2794–2799.
- [17] G. Fritz, W. Hölderich, *Z. Anorg. Allg. Chem.* **1976**, *422*, 104–114.
- [18] G. Becker, G. Gutekunst, H. J. Wessely, *Z. Anorg. Allg. Chem.* **1980**, *462*, 113–129.
- [19] C. M. Cui, H. W. Roesky, H. G. Schmidt, M. Noltemeyer, H. J. Hao, F. Cimpoesu, *Angew. Chem. Int. Ed.* **2000**, *39*, 4274–4276; *Angew. Chem.* **2000**, *112*, 4444–4446.
- [20] H. Jacobs, K. M. Hassiepen, *Z. Anorg. Allg. Chem.* **1985**, *531*, 108–118.
- [21] U. Vogel, K.-C. Schwan, M. Scheer, *Eur. J. Inorg. Chem.* **2004**, 2062–2065.
- [22] U. Vogel, A. Y. Timoshkin, K.-C. Schwan, M. Bodensteiner, M. Scheer, *J. Organomet. Chem.* **2006**, *691*, 4556–4564.
- [23] W. C. Johnson, A. Pechukas, *J. Am. Chem. Soc.* **1937**, *59*, 2068–2071.
- [24] J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese, S. D. Arthur, *Organometallics* **1997**, *16*, 1514–1516.
- [25] CCDC 1917287, 1917288, 1917289, 1917290, 1917291, 1917292, 1917293, and 1917294 (1–8) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Manuscript received: August 24, 2019

Accepted manuscript online: August 28, 2019

Version of record online: October 4, 2019