NHC-stabilized Parent Arsanylalanes and -gallanes

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Dedicated to Professor Wolfgang Kaim on the occasion of his 70th birthday

Abstract: The synthesis and characterization of the unprecedented compounds IDipp-EH2AsH2 (E = Al, Ga; IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) are reported, the first monomeric, parent representative of an arsanylane and arsanylgallane, respectively, stabilized only by a LB (LB = Lewis Base). They are prepared by a salt metathesis reaction of KAsH3 with IDipp-EH2Cl (E = Al, Ga). The H2-elimination pathway through the reaction of AsH3 with IDipp-EH2 (E = Al, Ga) was found to be a possible synthetic route with some disadvantages compared to the salt metathesis reaction. The corresponding organo-substituted compounds IDipp-GaH2AsPh2 (1) and IDipp-AH2AsPh2 (2) were obtained by the reaction of KAsPh2 with IDipp-pEH2Cl (E = Al, Ga). The novel branched parent compounds IDipp-EH2(EH2)2 (E = Al, Ga; E = P, As) were synthesized by salt metathesis reactions starting from IDipp-EHCl2 (E = Al, Ga). Supporting DFT computations give insight into the different synthetic pathways and the stability of the products.

Introduction

The chemistry of group 13/15 compounds is an active research field and has influenced many areas of chemistry. For instance, unsaturated compounds of the type H2E=EH2 (E = Group 13 element, E = Group 15 element) are isoelectronic to alkenes. They are of interest as starting materials for semiconducting applications[1] or as precursor for composite 13/15 materials.[2] In comparison to aminoboranes LB·BR2NR2·LA (LB = Lewis base, LA = Lewis acid) the chemistry of the heavier group 13/15 element analogs is rarely investigated. The few known compounds of arsanylanes and -gallanes LB·[E'RnAsR2]n·LA (E = Al, Ga) exist as dimers,[3] trimers (n = 3),[4] or LB/LA-stabilized monomers depending on the steric demands of the organic substituents,[5] the parent compounds of these precursors are of particular interest for improving the current MOCVD process which involves the reaction of trimethylgallium with the toxic gas AsH3 at elevated temperatures. In contrast to the phosphorus analog E=EH2(EH2)2 (E = Al, Ga), for which we recently succeeded in the synthesis of the first only LB-stabilized parent compounds IDipp-EH2PH2 (E = Al, Ga; IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidine),[6] the heavier arsenic analogs exhibit a higher lability of the Ga–As/Al–As bond, which is why they have so far only been studied by theoretical methods.[7] In fact, because of their toxicity, light sensitivity, and tendency to decompose, as well as the unsuitable NMR activity of the As nucleus, the handling and characterization of such compounds are hampered by numerous difficulties. Moreover, only a few examples of stable primary arsines, such as (2,6-Tipp2C6H3)AsH2 (Tipp = 2,4,6-iPr3C6H2), TriptAsH2 (Tript = tribenzobarrelene),[8] or NMe2-BH2AsH2 containing bulky or special substituents have so far been reported. Therefore, the question arises whether compounds containing AsH2 bound to alanes and gallanes can be synthesized. In any case, a stabilization via a LB and a LA or at least via a LB alone would be needed if organic substitution at the As and the Al and Ga atoms, respectively, was to be avoided. Even from this perspective, it is astonishing that only parent arsanylorboranes exist as LA/LB-stabilized molecules. No LA/LB-stabilized arsanylanes or -gallanes have been reported yet, only their phosphanyl analogs,[9] which reflects the
specific lability of the corresponding E–As bonds (E = Al, Ga).

Herein, we report the synthesis and characterization of the first monomeric parent compound of an arsanylgallane, IDipp-GaH₂AsH₂ (3), and an arsanylalane, IDipp-AlH₂AsH₂ (4), as well as their organo-substituted analogs IDipp-E₂H₃AsPh₂ (E = Ga, Al), only stabilized by a LB. The initially formed unprecedented side products IDipp-E₂H₃-(E₈H₂)₃ (E = Al, Ga; E = As, P; 5-8) could be synthesized and characterized on a selective route.

Results and Discussion

The organo-substituted compounds IDipp-GaH₂AsPh₂ (1) and IDipp-AlH₂AsPh₂ (2) can be synthesized by the reaction of IDipp-E₂H₃Cl (E = Ga, Al) with KAsPh₂ dioxide in Et₂O at −80°C [Eq. (1)]. Compound 1 was isolated at −30°C as colorless crystals in a yield of 63% and 2 as pale yellow blocks in a yield of 52%.

In the solid state, 1 and 2 can be stored at ambient temperatures in an inert atmosphere for more than two months without decomposition. The molecular ion peak of 1 is detected at m/z 688.2142 in the mass spectrum (LIFDI-MS). The LIFDI-MS spectrum of 2 shows a fragment peak of IDipp due to decomposition of 2 during the ionization process. The ¹H NMR spectra of 1 and 2 show a broad singlet at δ = 4.28 ppm for the GaH₃ moiety in 1 and a broad singlet at δ = 3.95 ppm for the AlH₃ moiety in 2, respectively. The ¹³C NMR spectrum of 2 reveals a broad singlet at δ = 126.5 ppm, which partially overlaps with the signal of the NMR sample head and the NMR tube material.

The structures of 1 and 2, determined by single-crystal X-ray analysis, are depicted in Figure 2 and Figure S35 (cf. S1), respectively. The Al–As bond in 2 shows a length of 2.4929(4) Å and is therefore slightly longer than the Al–As bond (2.485(2) Å) in tmp₂AlAsPh₃ [15] (tmp = 2,2,6,6-tetramethylpiperidinium). Compound 1 reveals a Ga–As bond length of 2.4659(5) Å, which is in good agreement with the sum of the usual E–C single bonds and are similar to the Ga–C bond length in IDipp-GaH₃PCy_3 (2.090(2) Å, Cy = cyclohexyl) and to the Al–C bond (2.056(2) Å) bond length in IDipp-AlH₂PH₃ [7] respectively. The C1-Ga-As angle of 1 (109.33(8)°) is in good agreement with the C1-Al-As angle in 2 (109.53(3)°).

For the synthesis of the parent compounds IDipp-GaH₂AsH₂ (3) and IDipp-AlH₂AsH₂ (4), two different routes were used [Eq. (2)]. Similarly to the substituted analogs, compounds 3 and 4 are accessible by a salt metathesis reaction between IDipp-E₂H₃Cl (E = Al, Ga) and KAsH₂ at −80°C in THF (route 1). Furthermore, 3 and 4 can be synthesized by H₂-elimination reactions of IDipp-E₂H₃ (E = Al, Ga) and AsH₃ (route 2). For this purpose, an excess of AsH₃ is condensed onto a solution of IDipp-E₂H₃ in toluene at −70°C and stirred for 3 days at this temperature. Unfortunately, 3 and 4 were formed only in minor amounts via route 2 according to ¹H NMR spectroscopic monitoring (Figure S1 and S2). The low yield of these H₂-elimination reactions is obviously caused by the applied temperature of −70°C, which significantly slows down the exergonic reaction between IDipp-E₂H₃ and AsH₃ but was needed throughout the reaction to keep AsH₃ condensed (see below, Table 1, process 1). Compound 3 can be isolated at −30°C in a crystalline yield of 39% via route 1. In the mass spectrum
Table 1: Thermodynamic characteristics of studied reactions (gas phase compounds if not noted otherwise).\textsuperscript{[4]}

| Entry | Process | \( \Delta H_{298} \) | \( \Delta S_{298} \) | \( \Delta G_{298} \) | \( E' = \text{Al} \) | \( \Delta S_{298} \) | \( \Delta G_{298} \) |
|-------|---------|----------------------|------------------|----------------------|---------------------|------------------|----------------------|
| 1     | IDipp·E'\text{H}_2 + \text{AsH}_3 \rightarrow \text{H}_2 + \text{IDipp·E'\text{H}_2\text{AsH}_3} | -27.6 | -26.3 | -19.7 | -29.2 | -26.3 | -21.4 |
| 2     | IDipp·E'\text{H}_2\text{Cl} + \text{KAsH}_2 \rightarrow \text{KCl}_2 + \text{IDipp·E'\text{H}_2\text{AsH}_3} | -11.2 | -61.9 | 7.2 | -15.7 | -60.6 | 2.3 |
| 3     | IDipp·E'\text{H}_2\text{Cl} + \text{KAsH}_2 \rightarrow \text{KCl}_2 + \text{IDipp·E'\text{H}_2\text{AsH}_3} | -227.7 | -179.8 | -174.1 | -261.9 | -182.8 | -207.4 |
| 4     | IDipp·E'\text{H}_2\text{Cl} + \text{KAsH}_2 \rightarrow \text{KCl}_2 + \text{IDipp·E'\text{H}_2\text{AsH}_3} | -97.2 | 98.6 | -126.6 | -134.2 | 96.7 | -163.1 |
| 5     | IDipp·E'\text{H}_2\text{Cl} + \text{KAsH}_2 \rightarrow \text{KCl}_2 + \text{IDipp·E'\text{H}_2\text{AsH}_3} | 65.4 | 76.5 | 42.6 | 52.9 | 75.4 | 30.4 |
| 6     | IDipp·E'\text{H}_2\text{Cl} + \text{KAsH}_2 \rightarrow \text{KCl}_2 + \text{IDipp·E'\text{H}_2\text{AsH}_3} | 44.5 | 70.3 | 23.6 | 33.8 | 75.1 | 11.4 |
| 7     | IDipp·E'\text{H}_2\text{Cl} + \text{KAsH}_2 \rightarrow \text{KCl}_2 + \text{IDipp·E'\text{H}_2\text{AsH}_3} | -23.0 | -43.3 | -10.1 | -25.4 | -39.0 | -13.8 |
| 8     | IDipp·E'\text{H}_2\text{Cl} + \text{KAsH}_2 \rightarrow \text{KCl}_2 + \text{IDipp·E'\text{H}_2\text{AsH}_3} | -13.0 | -38.5 | -1.6 | -11.9 | -40.6 | 0.2 |
| 9     | IDipp·E'\text{H}_2\text{Cl} + \text{KAsH}_2 \rightarrow \text{KCl}_2 + \text{IDipp·E'\text{H}_2\text{AsH}_3} | -46.8 | -354.8 | -362.8 | -536.0 | -343.8 | -433.5 |
| 10    | IDipp·E'\text{H}_2\text{Cl} + \text{KAsH}_2 \rightarrow \text{KCl}_2 + \text{IDipp·E'\text{H}_2\text{AsH}_3} | -461.8 | -367.9 | -352.1 | -535.9 | -352.9 | -430.7 |

\[\text{[a]}\] Standard enthalpies \( \Delta H_{298} \) and standard Gibbs energies \( \Delta G_{298} \) in kJ mol\(^{-1}\), standard entropies \( \Delta S_{298} \) in J mol\(^{-1}\) K\(^{-1}\). B3LYP/def2-TZVP level of theory.

(LIFDI-MS) the molecular ion peak of 3 is detected at \( m/z \) 535.1239 [M–H]\(^+\). The \(^1\)H NMR spectrum of 3 in CD\(_3\) shows a triplet at \( \delta = -0.18 \) ppm (\( J_{\text{HH}} = 3.68 \) Hz) for the AsH\(_2\) moiety and a broad singlet at \( \delta = 4.31 \) ppm for the GaH\(_2\) moiety. Compound 3 co-crystallizes with the starting material IDipp·GaH\(_2\)Cl (for more information see SI). The structure of 3 in solid state is shown in Figure 3. With a distance of 2.4503(12) \( \text{Å} \) the Ga–As bond length in 3 is between the Ga–As bond lengths in 1 (2.4659(5) \( \text{Å} \)) and (r-Bu),GaAs(r-SMe)\(_2\) (2.433 \( \text{Å} \))\(^{[25]}\) and (r-Bu)\(_2\)GaAs(r-Bu)\(_2\) (2.466 \( \text{Å} \)).\(^{[26]}\) The Ga–Cl bond in 3 (2.0476(17) \( \text{Å} \)) reveals the repulsion between the NHCl and the phenyl groups in 1. Since the H substituents at the As atom had to be restrained, no statement about the conformation of 3 can be made. The C1-Ga-As angle in 3 (107.99(6)\(^\circ\)) is slightly smaller compared to the substituted analog 1 (109.25(3)\(^\circ\)) and to the phosphorus derivative IDipp-GaH\(_2\)PH\(_2\) (109.19(5)\(^\circ\)).\(^{[7]}\)

IDipp·AlH\(_2\)AsH\(_2\) (4) can be isolated at \(-30^\circ\)C as colorless plates in a yield of 40% via route 1. The LIFDI-MS spectrum of 4 only shows the fragment ion peak of IDipp\(^-\) due to the decomposition of 4 during the ionization process. The \(^1\)H NMR spectrum of 4 in CD\(_3\) reveals a triplet at \( \delta = -0.47 \) ppm (\( J_{\text{HH}} = 3.23 \) Hz) for the AsH\(_2\) moiety and a broad singlet at \( \delta = 4.1 \) ppm for the AlH\(_2\) moiety. In the \(^1\)H NMR spectrum, besides a side product IDipp·AlH\(_2\)AsH\(_2\) (5) can be detected as two doublets of doublets at \( \delta = -0.15 \) ppm and \( \delta = -0.04 \) ppm, respectively, for the AsH\(_2\) moieties (\( J_{\text{HH}} = 12.59 \) Hz, \( J_{\text{HH}} = 2.80 \) Hz). The signals for these two AsH\(_2\) moieties split in two separated signals because of the prochirality of the entities. The \(^27\)Al NMR spectrum of 4 shows a broad signal at \( \delta = 133.5 \) ppm which is partly superimposed with the signal of the NMR sample head and the NMR tube material. Compound 4 (Figure 4) crystallizes in the monoclinic space group \( \text{I2/a} \) and co-crystallizes with IDipp·AlH\(_2\)AsH\(_2\) (5) (for more information, see SI). The Al–As distance in 4 is in the range of 2.399(6)–2.473(4) \( \text{Å} \). The Al–C bond length (2.060(2) \( \text{Å} \)) is very similar to the \( \text{Al}–\text{As} \) distance in 4 (2.399(6)–2.473(4) \( \text{Å} \)).

The formation of IDipp·AlH\(_2\)AsH\(_2\) (5) as a side product led us to the question if the selective synthesis of compounds of the type IDipp·E'H\(_2\)AsH\(_3\) (\( E' = \) Al, Ga) was possible, and indeed we were able to synthesize 5 and IDipp·GaH\(_2\)AsH\(_2\) (\( E' = \) Ga, As).

Figure 3. Molecular structure of 3 in the solid state; thermal ellipsoids at 50% probability.\(^{[20]}\) Selected bond lengths [\( \AA \)] and angles [\( \text{\textdegree} \)]: Ga-As 2.4503(12), Ga-C1 2.0476(17), C1-Ga-As 107.99(6).

Figure 4. Molecular structure of 4 in solid state (part 1); thermal ellipsoids at 50% probability.\(^{[20]}\) Selected bond lengths [\( \AA \)] and angles [\( \text{\textdegree} \)]: Al-As 2.399(6), C1-Al 2.060(2), C1-Al-As 107.83(17)–114.3(2).
Compounds 5 and 6 crystallize as colorless thin needles at –30°C in a yield of 42% and 36%, respectively. The LIFDI-MS spectrum of 5 shows a fragment ion peak of IDipp⁺ due to decomposition of 5 during the ionization process. In the mass spectrum of 6 (LIFDI-MS) the molecular ion peak is detected at m/z 611.6067 [M+H]+. Solutions of 5 show a strong tendency towards decomposition. The 1H NMR spectrum of 5 in [D₆]toluene at –80°C reveals two doublets of doublets at δ = –0.09 ppm and δ = 0.14 ppm (JᵢH₁H₂ = 12.40 Hz, JᵢH₁H₃ = 2.71 Hz) for the two AsH₃ moieties, a broad singlet at δ = 4.82 ppm for the AlH moiety, as well as the formation of IDippH₂ and free IDipp as decomposition products. In the 1H NMR spectrum of 6 in C₆D₆, the signals for the AsH₂ moieties and the GaH moiety are shifted downfield to δ = 0.20, 0.38 (JᵢH₁H₂ = 12.77 Hz, JᵢH₁H₃ = 3.46 Hz), and δ = 5.09 ppm compared to 5.

Compounds 5 and 6 crystallize from concentrated n-hexane solutions as very thin colorless plates. Because of the thinness of the crystals the single-crystal X-ray analysis of 6 was only possible to a theta range of 47°. Nevertheless, it was possible to solve the structure and prove the framework of the heavy atoms of 6 (see Figure S42). Compound 5 co-crystallizes with 6% of the starting material IDipp·AlHCl₂ (see Figure S41). Compounds 5 and 6 crystallize in the monoclinic space group P2₁/a. The molecular structure of 5 in solid state is depicted in Figure 5. The E'–As distances in 5 and 6 are in the range of 2.451(4)–2.511(6) Å (5) and 2.442(19)–2.462(2) Å (6), respectively, and therefore similar to the Al–As bonds in (Dipp₂Nacnac)Al(AsH₃)₂ (Dipp₂Nacnac = HC[C(Me)N–(Ar)]₂, Ar = 2,6-Pr₂C₆H₄).[18] The E'–Cl bond lengths (Al–Cl = 2.066(3) Å, Ga–Cl = 2.064(9) Å) are not heavily affected by the presence of a second AsH₃ moiety compared to 3 (2.0476(17) Å) and 4 (2.060(2) Å), respectively. The Cl–E'–As angles are 114.24(9)° and 114.38(10)° for 5 as well as 111.7(2)° and 113.3(2)° for 6.[17]

Interestingly, during the synthesis of the phosphorus analog IDipp·E'H₃P₃H (E' = Al, Ga) by the reaction of IDipp·E'H₃Cl with NaPH₃ we did not find any sign for the formation of IDipp·E'H₃(PO)(THF)₂ (E' = Al, Ga) as a side product.[17] A possible pathway for the formation of 5 as a side product in the arsenic case is the formation of the reaction product IDipp·E'H₃AsH₃ with in situ formed AsH₃ in an H₃-elimination reaction. Computations confirm that this route is possible in the arsenic case (Table 1, process 7) while it is more unlikely for phosphorus (Table 1, process 8), which agrees with our experimental observations.

Similar to 5 and 6, we were able to synthesize the parent branched compounds IDipp-GaH(PH₂)₂ (7) and IDipp-AlH·(PH₂)₃ (8) selectively by the salt metathesis reaction of IDipp·E'H₃Cl and NaPH₂ in Et₂O (Table 1, process 9). Compounds 7 and 8 can be isolated at –30°C in a yield of 57% and 48%, respectively. The 1H NMR spectrum of 7 in C₆D₆ shows a doublet which splits into multiplets at δ = 0.54 ppm (JᵢH₁H₂ = 175 Hz) for the PH₂ moieties and a broad singlet at δ = 4.81 ppm for the GaH moiety. In the 1H NMR spectrum of 8 in [D₆]toluene at –80°C the PH₂ moieties can be detected at δ = 0.42 ppm (JᵢH₁H₂ = 175.4 Hz) as a doublet of multiplets. The AlH moiety can be detected as a broad singlet at δ = 4.56 ppm. The 31P NMR spectra of 7 and 8 show a triplet of multiplets at δ = –255.4 ppm (7, JᵢP₁P₂ = 175 Hz, JᵢP₁P₃ = 18.17 Hz, JᵢP₁P₄ = –270.8 ppm) and 8, JᵢP₁P₂ = 175.4 Hz, JᵢP₁P₃ = 15.48 Hz, respectively. Due to the prochirality of the PH₂ groups in 7 and 8 the signals in the 1H and 31P NMR spectra reveal a fine splitting which could not be resolved. Like 5, solutions of 8 show a strong tendency towards decomposition. Compounds 7 and 8 crystallize in the monoclinic space group P2₁/a. The molecular structures of 7 and 8 in solid state are shown in Figure 6 and Figure S44, respectively. The E'–P bonds are shorter compared to the arsenic analogs with 2.3437(10)–2.3574(9) Å (7) and 2.3075(10)–2.3418(9) Å (8). The E'–Cl bond lengths are again not affected by the change from arsenic substituents to phosphorus substituents on the E' atom. The Ga–Cl bond length is 2.075(3) Å and the Al–Cl bond length is 2.066(2) Å. The Cl–E'–P angles (112.38(7)° and 113.68(7)° for 7, 112.04(6)° and 113.91(6)° for 8) are comparable to the Cl–E'–As angles in the arsenic analogs 5 and 6.

Computational studies indicate that the salt elimination route via solid potassium chloride formation is highly exothermic and exergonic both for the parent and the substituted compounds, which could be experimentally verified by the synthesis of 1–4. (Table 1, process 3 and 4). The hydrogen elimination route via the reaction of IDipp·E'H₃
with AsH₃ (Table 1, process 1) is exothermic and at 298 K exergonic by about 20 kJ mol⁻¹, but slightly endergonic (2–7 kJ mol⁻¹) for the reaction with diphenylarsine (Table 1, process 2), which reflects that compounds 1 and 2 could not be accessed via route 2. Compounds 1–4 are predicted to be stable with respect to IDipp dissociation with formation of (E’H₂AsH₂)ₖ polymers, which were modeled by the formation of the trimer[14] (Table 1, process 5 and 6). The interaction of IDipp-EH₁AsH₂ with an arsine formed in situ (Table 1, process 7) is also exergonic (Al: –10.1 kJ mol⁻¹, Ga: –13.8 kJ mol⁻¹) and may explain the formation of 5 as a side product during the synthesis of IDipp-AH₁AsH₂ via route 1. In contrast, a similar reaction for the phosphorus analogs (Table 1, process 8) is energetically less favored and has Gibbs energies close to zero at 298 K. Nevertheless, computations show that route 1 is an even more exergonic reaction for the synthesis of branched pnictogenylalanes and -gallanes than for the synthesis of the linear compounds (Table 1, process 9 and 10). This is confirmed by the synthesis of the unique molecules IDipp-EH₁(EH₂)₃ (5: Al, 6: Ga) and IDipp-EH₁(PH₂)₃ (7: Ga, 8: Al) via route 1.

Conclusion

The results show that, regardless of the rather low E’–As bond stability (E’ = Al, Ga), we succeeded in the synthesis of the first monomeric parent arsanylalanes and -gallanes stabilized only by a LB. Besides the synthesis of the organo-substituted arsenic derivatives by salt metathesis, it was shown that the monomeric parent compounds can be obtained by salt metathesis and H₂-eliminations, respectively. However, the latter method is incomplete, so that the first one is preferred. Furthermore, in contrast to the synthesis of the corresponding phosphorylalanes and -gallanes, the As derivatives exhibit a different reactivity and form the branched side products IDipp-EH₁(AsH₂)₃ (E’ = Al, Ga), obviously by AsH₃-caused substitution reactions. This kind of alkane-like branched parent derivatives had been unknown before and subsequently the double substituted parent compounds IDipp-EH₁(EH₂)₃ (E’ = Al, Ga; E = As, P) could be selectively synthesized by salt metathesis reactions. They may serve as chelating ligands in coordination chemistry, which is currently being investigated. The monomeric compounds IDipp-EH₁AsH₂ (E’ = Al, Ga) represent unprecedented parent arsanylalanes and -gallanes without any prior sterical stabilization by a substituent but by a LB. In further studies, the focus will be on their reaction behavior towards cate- nation and as precursor for CVD processes to obtain Group 13/15 materials.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alanes · arsenic · gallanes · group 13/15 compounds · Lewis bases

[1] a) J. D. Masuda, A. J. Hoshkin, T. W. Graham, C. Beddick, M. C. Fermin, N. Etkin, D. W. Stephan, Chem. Eur. J. 2006, 12, 8696–8707; b) R. A. Fischer, J. Weiβ, Angew. Chem. Int. Ed. 1999, 38, 2830–2850; Angew. Chem. 1999, 111, 3002–3022; c) R. L. Wells, W. L. Gladfelser, J. Cluster Sci. 1997, 8, 217–238; d) A. C. Jones, P. O’Brien, in CVD of Compound Semiconductors: Precursor Synthesis Development and Applications, VCH, Weinheim, 1996.
[2] a) S. Schulz, Coord. Chem. Rev. 2001, 215, 1–37; b) S. Schulz, Adv. Organomet. Chem. 2003, 49, 225–317; c) B. Neumuller, E. Irvani, Coord. Chem. Rev. 2004, 248, 817–834; d) A. Y. Timoshkin, Coord. Chem. Rev. 2005, 249, 2094–2131; e) T. J. Clark, K. Lee, I. Manners, Chem. Eur. J. 2006, 12, 8634–8648; f) A. Stautz, A. P. Soto, I. Manners, Angew. Chem. Int. Ed. 2008, 47, 6212–6215; Angew. Chem. 2008, 120, 6308–6311.
[3] a) G. E. Coates, J. Graham, J. Chem. Soc. 1963, 233–237; b) D. E. Heaton, R. A. Jones, K. B. Kidd, A. H. Cowley, C. M. Nunn, Polyhedron 1988, 7, 1901–1908; c) R. L. Wells, A. T. McPhail, T. M. Speer, Organometallics 1992, 11, 960–963.
[4] a) O. T. Beachley, G. E. Coates, J. Chem. Soc. 1965, 3241–3247.
[5] a) E. K. Byrne, L. Parkany, K. H. Theopold, Science 1988, 241, 332–334; b) K. T. Higa, C. George, Organometallics 1990, 9, 275–277; c) D. A. Atwood, L. Contreras, A. H. Cowley, R. A. Jones, M. A. Mardones, Organometallics 1993, 12, 17–18.
[6] a) M. R. Leys, Chemtronics 1987, 2, 155–164; b) G. B. String-fellow, Rep. Prog. Phys. 1982, 45, 469–525.
[7] M. A. K. Weinhart, A. S. Lisovenko, A. Y. Timoshkin, M. Scheer, Angew. Chem. Int. Ed. 2020, 59, 5541–5545; Angew. Chem. 2020, 132, 5586–5590.
[8] A. Y. Timoshkin, Phosphorus Sulfur Silicon Relat. Elem. 2001, 168, 275–280.
[9] M. Brynda, Coord. Chem. Rev. 2005, 249, 2013–2034.
[10] a) C. Marquardt, A. Adolf, A. Stauber, M. Bodenstein, A. V. Virovets, A. Y. Timoshkin, M. Scheer, Chem. Eur. J. 2013, 19, 11887–11891; b) U. Vogel, P. Hoemensh, K.-Ch. Schwan, A. Y. Timoshkin, M. Scheer, Chem. Eur. J. 2003, 9, 515–519; c) U.
[11] A. Hock, L. Werner, C. Luis, U. Radius, *Dalton Trans.* **2020**, *49*, 11108–11119.

[12] K. Knabel, I. Krossing, H. Noth, H. Schwenk-Kircher, M. Schmidt-Amelunxen, T. Seifert, *Eur. J. Inorg. Chem.* **1998**, *1095–1114*.

[13] P. Pyyskö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186–197.

[14] C. G. Pitt, K. T. Higa, A. T. McPhail, R. L. Wells, *Inorg. Chem.* **1986**, *25*, 2483–2484.

[15] A. M. Arif, B. L. Benac, A. H. Cowley, R. Geerts, R. A. Jones, K. B. Kidd, J. M. Power, S. T. Schwab, *J. Chem. Soc. Chem. Commun.* **1986**, *1543–1545*.

[16] a) 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; b) B. Li, S. Bauer, M. Seidl, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2019**, *25*, 13714–13718.

[17] Due to the limited quality of the X-ray structure analysis the bond lengths of 6 might deviate a bit.

[18] C. Marquardt, O. Hegen, A. Vogel, A. Stauber, M. Bodensteiner, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2018**, *24*, 360–363.

[19] Deposition Numbers 2035397 (for 1), 2035398 (for 2), 2035399 (for 3), 2035340 (for 4), 2035341 (for 5), 2035342 (for 6), 2035343 (for 7), and 2035344 (for 8) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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The first parent arsanylalanes and -gallasses stabilized only by a Lewis base were synthesized. These compounds are accessible via a salt metathesis reaction of LB·E'HCl and KAsH₂ and a H₂ elimination reaction between LB·E'H₃ and AsH₃, respectively. In addition, the unprecedented branched compounds IDipp·E'H(EH₂)₂ (E' = Al, Ga; E = As, P) could be obtained.