

Main-Group Elements

From π -Bonded Gallapnictenes to Nucleophilic, Redox-Active Metal-Coordinated Pnictanides

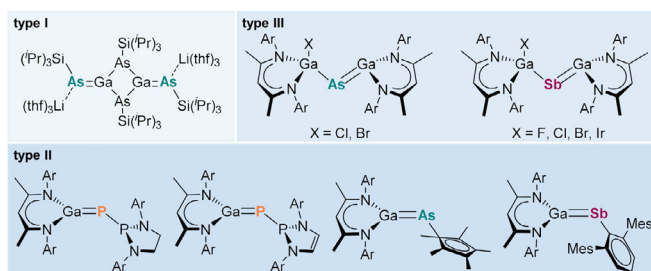
Julia Krüger, Christoph Wölper, and Stephan Schulz*

In memory of Professor Alan H. Cowley

Abstract: A comprehensive reactivity study of gallapnictenes $LGaEGa(Cl)L$ ($E = As, Sb$; $L = HC[C(Me)N(Ar)]_2$, $Ar = Dip = 2,6\text{-}i\text{-}Pr_2C_6H_3$) proved the nucleophilic character of the pnictogen and the electrophilic nature of the Ga atom. Reactions of $LGaEGa(Cl)L$ with imidazolium chloride $[IPrH][Cl]$ yielded $\{[LGa(Cl)]_2E^-\}\{IPrH^+\}$ ($E = As$ **1**, Sb **2**), and those with HCl and MeI gave pnictanes $[LGa(Cl)]_2EH$ ($E = As$ **5**, Sb **6**) and $L(I)GaE(Me)Ga(Cl)L$ ($E = As$ **7**, Sb **8**). Pnictanides **1** and **2** also react with $[H(OEt)_2][BAR^F_4]$ ($BAR^F_4 = B(C_6F_5)_4$) to **5** and **6**, while reactions with MeI yielded $[LGa(Cl)]_2EMe$ ($E = As$ **9**, Sb **10**). Single electron oxidation reactions of pnictanides **1** and **2** gave the corresponding radicals $[LGa(Cl)]_2E^\cdot$ ($E = As, Sb$).

Group 13/15 compounds with π -bonding contribution are well established for iminoboranes $RBNR'$ with strong $(2p-2p)\pi$ interaction^[1] and for kinetically and electronically stabilized compounds with $B-E$ ($E = P, As$)^[2] and $M-N$ double bonds ($M = Al, Ga, In$)^[3] whereas analogous compounds of heavier group 13 ($M = Al-Tl$) and group 15 elements ($E = P-Bi$) with $M-E$ π -bond are still rare ($M = Ga, E = P, As, Sb$). This is most likely caused by the inherent weakness of the π -bonds due to an ineffective $p(-p)\pi$ orbital overlap. Such compounds therefore tend to form head-to-tail adducts, yielding four- and six-membered rings.^[4] The first heavier group 13/15 π -bonded compound $[i-Pr_3SiAs(Li(thf)_3Ga-\mu-As(Si-Pr_3))]_2$ (type **I**, Scheme 1) was reported by Hänisch et al.^[5] and regarded as silyl derivative of the $[Ga_2As_4]^{6-}$ ion, which was previously observed in the ternary phase $Cs_6Ga_2As_4$.^[6]

Recently, Goicoechea et al. reported the synthesis of neutral phosphanyl-phoshagallenes with $Ga-P$ double bond (type **II**),^[7] while we established a general route to gallapnic-



Scheme 1. Structurally characterized gallapnictenes with $Ga-E$ π -bonding contribution of the heavier group 15 homologs ($E = As, Sb$; $Ar = Dip$).

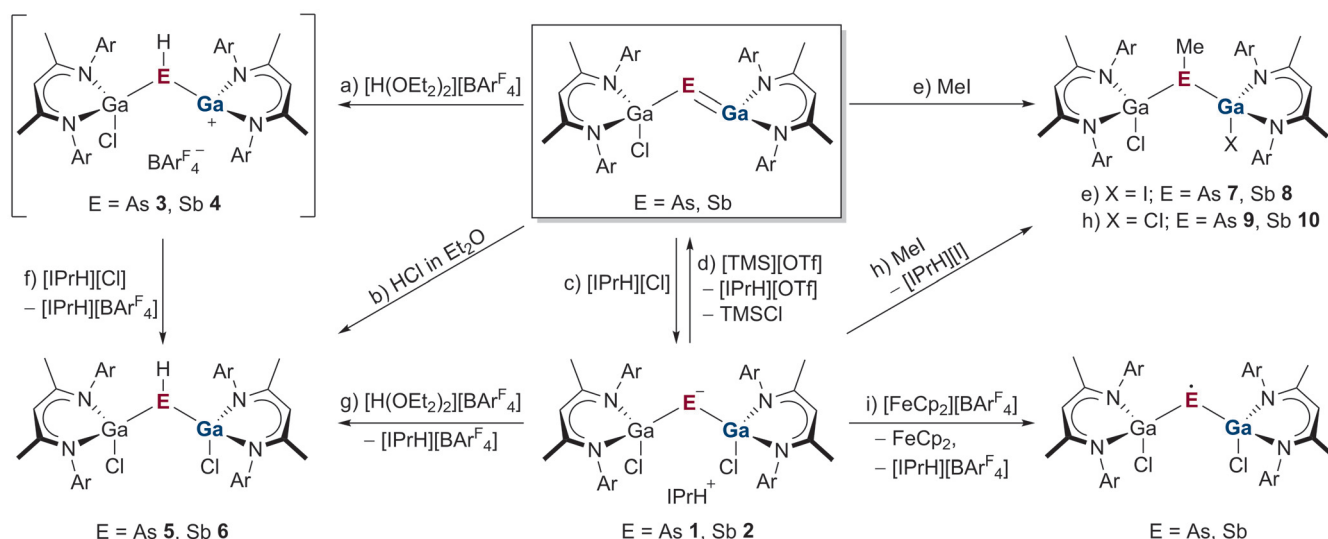
tenes $LGaEGa(X)L$ ($E = As, X = Cl, Br$; $E = Sb, X = F, Cl, Br, I$; type **III**)^[8] and $LGaER$ ($ER = AsCp^*, SbTer$; $Ter = 2,6\text{-}Mes_2C_6H_3$; $Mes = 2,4,6\text{-}Me_3C_6H_2$; type **II**)^[9] by reaction of gallanedyl LGa with pnictanes. While several compounds of types **II** and **III** were structurally characterized, their reactivity is almost unknown. Phosphanyl-phoshagallene $[(H_2C)_2(NAr)_2P]PGaL$ ($Ar = Dip$)^[7] (type **II**) reacted with small molecules (H_2, CO_2) like a frustrated Lewis pair in 1,3 position ($P-P-Ga$) rather than at the $P-Ga$ double bond due to the presence of the Lewis-basic phosphanyl group. Based on results from DFT calculations, the pnictogene atoms in $LGaEGa(Cl)L$ ($E = As, Sb$, type **III**) are expected to exhibit nucleophilic character, whereas the π -bonded Ga atom is electrophilic as indicated by the strongly polarized $Ga-E$ π -bonds (Ga 18%, As 84%; Ga 17%, Sb 83%) (Table S26) and the natural charges (Ga 1.27 e, As -1.00 e; Ga 1.12 e, Sb -0.71 e) (Table S25).^[18] To verify the computational results, we reacted both gallapnictenes with electrophilic and nucleophilic reagents.

In situ generated gallapnictenes $LGaEGa(Cl)L$ ($E = As, Sb$)^[8b,c] react with imidazolium chloride $[IPrH][Cl]$ to Ga-coordinated pnictanide anions $\{[LGa(Cl)]_2E^-\}\{IPrH^+\}$ in good yields ($E = As$ 77% **1**, Sb 72% **2**, Scheme 2c), proving the Lewis acidic character of the Ga atoms. Remarkably, the starting gallapnictenes were regenerated upon reactions of pnictanides **1** and **2** with trimethylsilyl triflate (Scheme 2d; Figure S27, S28). The nucleophilic character of the pnictogen atom in $LGaEGa(Cl)L$ was then proven in reactions with $[H(OEt)_2][BAR^F_4]$ at low temperature ($-78^\circ C$) (Scheme 2a). Unfortunately, the low stability of the likely formed cations $[LGaE(H)Ga(Cl)L]^+$ ($E = As$, **3**, Sb **4**) prevented their isolation, even though different counter anions ($Al[OC(CF_3)_3]_4^-$), solvents, and solvent mixtures (THF, Et_2O , CH_2Cl_2 , toluene, C_6FH_5 , C_6BrH_5 , $C_6F_2H_4$) were used. Never-

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Scheme 2. Synthesis of $\{[LGa(Cl)]_2E^-\}\{IPrH^+\}$ ($E = As\ 1, Sb\ 2$), $[LGaE(H)Ga(Cl)]$ ($E = As\ 5, Sb\ 6$), $L(I)GaE(Me)Ga(Cl)L$ ($E = As\ 7, Sb\ 8$), and $[LGa(Cl)]_2EMe$ ($E = As\ 9, Sb\ 10$).

theless, 1H NMR spectroscopic in situ monitoring of the reactions of $LGaEGa(Cl)L$ with $[H(OEt_2)_2][An]$ ($An = BARF_4^-, (Al[OC(CF_3)_3]_4)^-$) indicated the formation of the protonated, cationic species $[LGaE(H)Ga(Cl)]^+$ (Figure S33, S34) due to the occurrence of singlets at -1.09 ppm (As) and -3.77 ppm (Sb), which are in the typical regions for E–H groups.^[10] The intermediate protonation reaction was further proven by reaction of $[H(OEt_2)_2][BARF_4]$ with $LGaEGa(Cl)L$ at $-78^\circ C$ followed by immediate addition of $[IPrH][Cl]$ (Scheme 2 f; Figure S35, S36), yielding $[LGa(Cl)]_2EH$ (As 5 Figure S40, Sb 6 Figure 2). Pnictanes 5 and 6 also formed in reactions of gallapnictenes $LGaEGa(Cl)L$ with HCl in Et_2O (Scheme 2 b; Figure S31, S32), whereas comparable reactions with MeI (Scheme 2 e) yielded Me-substituted pnictanes $L(I)GaE(Me)Ga(Cl)L$ ($E = As\ 7$ Figure S42, Sb 8 Figure S43).

All attempts to deprotonate pnictanes 5 and 6 by reactions with strong nucleophiles $KN(SiMe_3)_2$, $LiN(i-Pr)_2$, and $n-BuLi$ to either regenerate the starting pnictanide anions $[LGa(Cl)]_2E^-$ or the gallapnictenes $LGaEGa(Cl)L$ failed.

While gallapnictenes were found to react both with nucleophiles and electrophiles, the pnictanide anions $\{[LGa(Cl)]_2E^-\}\{IPrH^+\}$ ($E = As\ 1, Sb\ 2$) were expected to react as strong nucleophiles due to the negatively charged pnictogen centers. This was confirmed in reactions of 1 and 2 with $[H(OEt_2)_2][BARF_4]$, which proceeded at $-78^\circ C$ with elimination of $[IPrH][BARF_4]$ and formation of pnictanes $[LGa(Cl)]_2EH$ (As 5, Sb 6) (Scheme 2 g), whereas Me-substituted pnictanes $[LGa(Cl)]_2EMe$ ($E = As\ 9, Sb\ 10$) were formed in reactions of 1 and 2 with MeI (Scheme 2 h). Moreover, cyclic voltammetry (CV) studies with compounds 1 and 2 (Figure S37) also showed reversible one-electron oxidation reactions, demonstrating that pnictanide anions also serve as one-electron oxidants. This was confirmed in subsequent reactions of 1 and 2 with $[FeCp_2][BARF_4]$, yielding the known pnictanyl radicals $[LGa(Cl)]_2E\cdot$ ($E = As, Sb$; Scheme 2 i, Figure S29, S30).^[9b,8a]

The 1H NMR spectra of compounds 1 and 2 show broad signals for the β -diketiminato ligands and expected resonances for the imidazolium cations ($IPrH^+$), while the 1H NMR spectra of 5 and 6 show resonances of the β -diketiminato ligands and the E–H groups (-1.32 (5); -3.59 ppm (6)). The IR spectra show absorptions bands at 2078 (5) and $1858\ cm^{-1}$ (6),^[10,11] confirming the formation of E–H moieties. The 1H NMR spectra of 7–10 exhibit resonances of the β -diketiminato and the Me ligands (0.04 (7), -0.35 (8), 0.04 (9), -0.32 ppm (10)), while the ^{13}C NMR spectra display signals for the Me groups at -8.5 (7) and -10.2 (9) ppm as well as at -28.2 (8) and -30.0 ppm (10).

The solid-state structures of the new compounds except compounds 3 and 4 were determined by single crystal X-ray diffraction.^[19] Suitable single crystals were obtained from THF solutions overlaid with benzene (1, 2) or from saturated n -hexane solutions (5–10) upon storage at ambient temperature. Compounds 1, 2 (Figure 1), 7 (Figure S42), 9 (Figure 2), and 10 (Figure S45) crystallize in the triclinic space group $P\bar{1}$, and compounds 5 (Figure S40), 6 (Figure 2), and 8 (Figure S43) in the monoclinic space group $P2_1/n$.^[12] The central bond lengths and bond angles of the Ga–E–Ga units in the pnictanide anions of compounds 1 and 2 largely differ

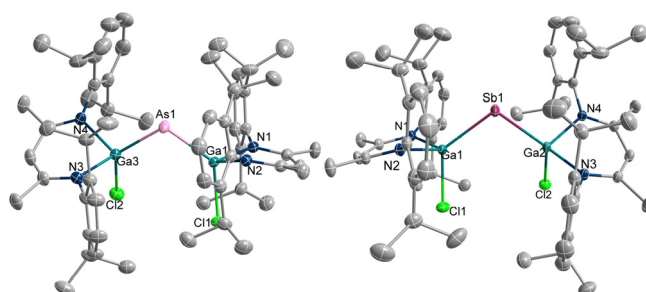


Figure 1. Molecular structure of the anions of 1 (left) and 2 (right).^[19] Ellipsoids set at 50% probability; hydrogen atoms and cations omitted for clarity.

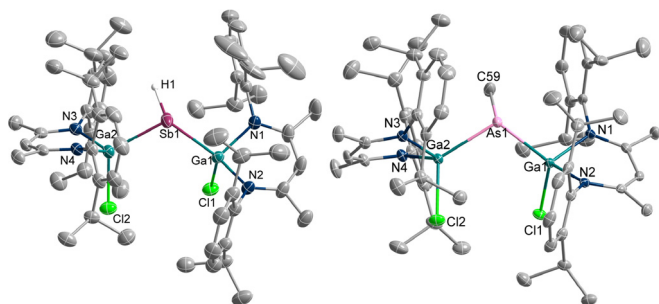


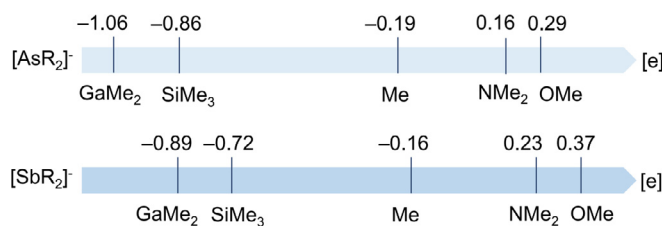
Figure 2. Molecular structure of **6** (left) and **9** (right).^[19] Ellipsoids set at 50% probability; hydrogen atoms except for Sb–H omitted for clarity. H1 is displayed as sphere of arbitrary radius.

from those in the corresponding gallapnictenes LGaEGa(Cl)L (E = As, Sb)^[9] and pnictanyl-centered radicals [LGa(Cl)]₂E[•],^[8a,13] which also contain twofold-coordinated pnictogen atoms.

The Ga–E bonds in **1** (2.3171(4) Å; 2.3197(4) Å) and **2** (2.5169(3) Å; 2.5186(3) Å) are significantly shorter than those of the neutral pnictanyl radicals [LGa(Cl)]₂E[•] (E = As 2.3983–(11) Å, 2.4085(14) Å;^[9b] Sb 2.5899(4) Å, 2.5909(3) Å^[8a]), but elongated compared to the Ga–E double bonds reported for gallapnictenes LGaEGa(Cl)L (E = As 2.2628(5) Å;^[8c] Sb 2.4629(2) Å^[8a]). In addition, Ga-coordinated dipnictenes [LGa(Cl)E]₂, which also contain twofold-coordinated pnictogen atoms, show longer Ga–E bonds (E = As 2.4217(6) Å; Sb 2.58178(19) Å)^[14] than the pnictanide anions **1** and **2**. They are comparable to the Ga–E bond lengths observed for pnictanes [LGa(Cl)]₂EH (**5** 2.4156(5) Å, 2.4000(6) Å; **6** 2.5669(3) Å, 2.5803(3) Å) as well as Me-substituted pnictanes L(X)GaE(Me)Ga(Cl)L **7–10** (**7** 2.3946(6) Å, 2.4232(6) Å; **8** 2.6118(6) Å, 2.6132(5) Å; **9** 2.4044(4) Å, 2.4134(4) Å; **10** 2.5837(7) Å, 2.6045(6) Å), respectively, which all contain threefold-coordinated pnictogen atoms. In addition, the Ga–Cl bonds in **1** (2.2548(7) Å, 2.2943(6) Å) and **2** (2.2611–(5) Å, 2.3012(5) Å) not only differ by almost 0.04 Å, but are also significantly longer than those in the neutral radicals [LGa(Cl)]₂E[•] (E = As 2.1967(10) Å, 2.2069 Å;^[9b] Sb 2.1623–(9) Å, 2.2028(7) Å^[8a]) and the pnictanes **5** (2.2320(6) Å, 2.2104(6) Å) and **6** (2.2161(6) Å, 2.2012(6) Å). Moreover, the Ga–E–Ga bond angles steadily increase from the pnictanide anions [LGa(Cl)]₂E[•] (**1** 107.377(15)°; **2** 104.534(9)°) over the neutral radicals [LGa(Cl)]₂E[•] (E = As 109.43(6)°, Sb 104.89(1)°) as well as the pnictanes [LGa(Cl)]₂EH (**5** 110.566–(13)°; **6** 107.412(10)°) and L(X)GaE(Me)Ga(Cl)L (**7** 110.14–(2)°; **8** 111.076(12)°; **9** 108.431(12)°; **10** 106.652(19)°) to the gallapnictenes LGaEGa(Cl)L (E = As 111.419(19)°; Sb 113.18(1)°).

The strong nucleophilic character of the pnictogene atom in the gallium-coordinated pnictanyl anions **1** and **2** renders these molecules promising candidates for small-molecule activation reactions as was recently demonstrated for anionic aluminum imides, which successfully reacted with H₂ and CO.^[15] We therefore became interested to get a deeper insight into the electronic structure of these metal-coordinated compounds, which, in contrast to well-known two-coordinated pnictanide anions R₂E[•] (E = As, Sb) con-

taining organyl, cyano, silyl, and phosphanyl substituents,^[16] are virtually unknown. To the best of our knowledge, only [[Th(Tren^{TIPS})]₂(μ-As)][K(15-crown-5)₂] (Tren^{TIPS} = N(CH₂CH₂NSi-Pr₃)₃) with Th–As multiple bond^[11c] and Ga-coordinated stibanide [L(Cl)GaSbB[N(Dip)CH]₂]-[K(crypt-222)]^[17] have been structurally characterized, which is probably caused by the weak metal–E bonds. Quantum chemical calculations (PBE0-D3BJ/def2-TZVP)^[18] on simple model compounds R₂E[•] (R = Me, Me₂N, MeO, Me₃Si, Me₂Ga) proved that the natural charge at the pnictogen center increases with increasing +I effect of the substituents, reaching its maximum with the electro-positive Ga-based substituents (Scheme 3, Table S22).



Scheme 3. Calculated natural charges [e] of group 15 elements (As, Sb) in [ER₂][•] (R = OMe, NMe₂, Me, SiMe₃, GaMe₂); PBE0-D3BJ/def2-TZVP level of theory.

We therefore studied the electronic structures of **1** and **2** in more detail by DFT calculations.^[18] The optimized structural parameters of **1'** and **2'** (**1'** and **2'** = calculated geometry of pnictanyl anions without counter cations) such as the Ga–E bond lengths (**1'** As–Ga 2.3198 Å, 2.3171 Å; **2'** Sb–Ga 2.5232 Å, 2.5375 Å) and Ga–E–Ga bond angles (**1'** Ga–As–Ga 108.21°; **2'** Ga–Sb–Ga 112.28°) are in good agreement with the experimental values from X-ray diffraction, although the Ga–Cl bond lengths (**1'** 2.2551 Å, 2.2545 Å; **2'** 2.2598 Å, 2.2586 Å) are almost equidistant, which can be attributed to the absence of the cation. The highest occupied molecular orbital (HOMO; Figure S46) mainly consists of the pnictogen p-orbital, and the Ga–E bonds are polarized towards the As and Sb atoms (**1'** P(As) = 69%, P(Ga) = 31%; **2'** P(Sb) = 59%, P(Ga) = 41%) (Table S26). The pnictogen centers in **1'** and **2'** show a high negative natural charge (**1'** –1.21 e; **2'** –0.93 e) (Table S25), hence both compounds are expected to react as strong nucleophiles as was experimentally proven in the protonation/methylation reactions of **1** and **2** with [H-(OEt)₂][BAR^F₄] and MeI, respectively. As already implied by the relatively short Ga–E bonds, **1** and **2** exhibit E–Ga π-bonding interactions as the Mayer bond orders (MBO) (**1** 1.28, 1.30; **2** 1.22, 1.23) (Table S23) and Wiberg bond indices (WBI) (**1** 1.12, 1.11; **2** 1.17, 1.17) (Table S24) reveal.

To summarize, the Ga–E double bonds in gallapnictenes LGaEGa(Cl)L (E = As, Sb) serve as electrophilic (Ga) and nucleophilic (E) centers, whereas pnictanides anions {[LGa(Cl)]₂E[•]}, which were formed in reactions of LGaEGa(Cl)L with imidazolium chloride, react as strong nucleophiles. In addition, they are one-electron oxidizers and react with [FeCp₂][BAR^F₄] to the corresponding pnictogen-centered radicals.

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Conflict of interest

The authors declare no conflict of interest.

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