A general route to metal-substituted dipnictenes of the type \([L(X)M]_2E_2\) (\(M = \text{Al, Ga}; E = \text{As, Bi}; X = \text{halide, amide}\))

Lars Tuscher,[a] Christoph Helling,[a] Christoph Wölper,[a] Walter Frank,[b] Anton S. Nizovtsev,[c,d,e] and Stephan Schulz*[a]

Abstract: Two equivalents of \(L_X = \text{HC}[(\text{Me})N(2,6-\text{Pr}_2\text{C}_6\text{H}_4)]_2\) react with \(PX_3\) (\(X = \text{Cl, Br}\)) with insertion into two \(P-X\) bonds and formation of \([L(X)Ga]_2PX\) (\(X = \text{Cl or Br}\)), whereas the analogous reaction with \(AsCl_3\) occurred with twofold insertion and subsequent elimination of \(L\) to form \([L(As)Ga]_2\). Analogous reactions were observed in the reactions with \(Me_2NAsCl_2\), yielding the unsymmetrically-substituted diarsane \([L(Cl)Ga]_2AsCl_2\) (3). Analogous findings were observed in the reactions with \(Me_2NAsCl_2\), yielding the unsymmetrically-substituted diarsane \([L(Cl)Ga]_2AsCl_2\) (4). The reaction of \(As(NMe_2)_3\) with \(LGA\) gave \([L(Me_2N)Ga]_2AsCl_2\) (5) after heating at 165 °C for 5 days, whereas the analogous reaction with \(L\) gave \([L(Me_2N)Ga]_2AsCl_2\) (6) after heating at only 80 °C for 1 day. Finally, two equivalents of \(L\) reacted with \(Bi(\text{NMe}_2)_3\) to \([L(\text{Et}_3\text{N})Ga]_2Bi\] (7). 1 - 7 were characterized by NMR spectroscopy \((^{1}H, ^{13}C, ^{11}B, ^{31}P\) elemental analysis and single crystal X-ray diffraction \((\text{except 1 and 5})\). The bonding situations in 4, 6 and 7 were analyzed by quantum chemical calculations.

Introduction

Monovalent group 13 diyl \(LM\) (\(M = \text{Al, Ga}; L = \text{HC}[(\text{Me})N(2,6-\text{Pr}_2\text{C}_6\text{H}_4)]_2\)) containing an \(N,N\)-chelating \(\eta^4\)-diketiminate ligand exhibit bifunctional properties due to the presence of an electron lone pair, which render these molecules rather Lewis basic, and also electron-accepting character. They therefore act as nucleophiles, i.e., in coordination chemistry, but also show electrophilic reactivity, and this unique reactivity has led to several applications in synthetic inorganic chemistry, in particular in the activation of small molecules.\[1\] Despite their structural analogy, the electronic structure of monovalent \(L\) and \(L\) Al GAs slightly differs. Both show sp-like hybridized, doubly occupied HOMOs and \(\pi^*\)-like LUMOs localized at the C-N unit of the ligand. The empty metal p- orbitals in both compounds are the LUMO+1. Quantum chemical calculations revealed that the singlet-triplet energy gap (Al: 34.3–45.7 kcal/mol; Ga: 51.7–55.5 kcal/mol) as well as the HOMO-LUMO separation (Al: 75.76 kcal/mol; Ga: 96.24 kcal/mol) in \(L\) is smaller than in \(L\).[2] In addition, \(L\) and \(L\) display somewhat different chemical reactivity. The chemistry of \(L\) Al is smaller than in \(L\).

We recently started to investigate reactions of \(LM\) (\(M = \text{Al, Ga, In}) with distibines \(R_2\) \(\text{Bi}\) \((R = \text{Me, Et})\) occurred with insertion of \(LM\) into the \(\text{Bi-C}\) bond, whereas the analogous reactions with the \(\text{Bi}\) \((R = \text{Me, Et})\) occurred with insertion of \(LM\) into the \(\text{Sb-C}\) bond.

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[1]"
In order to prove if Ga-coordinated dihydrides of the type \([L(X)Ga]_2E_2\) (\(E = P, Bi\)) are generally accessible by reaction of two equivalents of LM with group 15 complexes \(EX_3\), we systematically investigated reactions of LM with halide- and amide-substituted phosphines, arsines and bismuthines \(EX_3\). These reactions proceeded with formation of the double insertion products \([L(X)Ga]EX\), which is stable in case of the reactions with \(PX_3\) \((X = Cl, Br)\), or with subsequent elimination of \(LGaX_2\) and formation of Ga-substituted dihydrides containing As=As and Bi=Bi double bonds. The solid state structures of the compounds were determined by single crystal X-ray diffraction, and their bonding situation was further analyzed in detail by quantum chemical calculations.

### Results and Discussion

The reactions of two equivalents of LGa with \(PX_3\) \((X = Cl, Br)\) in toluene at ambient temperature occurred with insertion of LGa into two P-X bonds and formation of the stable Ga-coordinated phosphines \([L(X)Ga]PX\) \((X = Cl, Br)\), which were isolated as pale green (1) and pale yellow crystalline solids (2) after workup (Scheme 1). Similar twofold insertion reactions of a germylene in the P-Cl bonds of \((Me_2N)_2PCl\) have recently been reported. In contrast, no reaction was observed for the analogous reaction of LGa with \(P(NMe_2)Cl\) even at high reaction temperatures up to 125 °C and prolonged reaction times (24 h) in toluene.

![Scheme 1. Synthesis of 1 and 2.](image)

In contrast, the reactions of two equivalents of LGa with AsCl\(_2\) and \(As(NMe_2)Cl\) occurred with elimination of \(LGaCl_2\) and \(LGa(As(NMe_2)Cl)\), respectively, as was confirmed by \(^1\)H NMR spectroscopy (Figure S23) and subsequent formation of the corresponding Ga-substituted diarsenes \([L(Cl)Ga]_2AS_2\) (3) and \([L(Me_2N)Ga]_2As_2\) (5), while the analogous reaction with \(Me_2NASCl\) yielded \([L(Cl)Ga]As=As(Ga(AsMe_2)LL)\) (4). In order to identify the reaction mechanism, the in situ \(^1\)H NMR spectrum of this reaction (Figure S24) was compared with \(^1\)H NMR spectra of isolated samples of \(LGaCl_2\) and \(LGa(AsMe_2)Cl\) and with an in situ \(^1\)H NMR spectrum of the reaction of \(LGaCl_2\) with one eq. of \(As(NMe_2)Cl\), which shows three resonances of the backbone C-H moiety indicating the presence of \(LGaCl_2\), \(LGa(AsMe_2)Cl\) and a third product, most likely \(LGa(Cl)As(AsMe_2)Cl\). Comparison of the backbone C-H resonances in these spectra clearly shows that LGa reacts with \(Me_2NASCl\) with elimination of equal amounts of \(LGaCl_2\) and \(LGa(Cl)As(AsMe_2)Cl\) and that the formation of \(LGa(AsMe_2)Cl\) can be excluded. In addition, the \(^1\)H NMR spectrum neither shows the formation of \([L(Cl)Ga]_2As_2\) (3) nor \([L(Me_2N)Ga]_2As_2\) (5).

The influence of the substituent on the reactivity of the arsines can clearly be seen, since the reaction of LGa with \(AsCl_2\) and \(Me_2NASCl\) occurred smoothly at ambient temperature within minutes, whereas with \(As(NMe_2)Cl\) required much harsher reaction conditions and the formation of the corresponding diarsene \([L(Me_2N)Ga]_2As_2\) was only finished after heating the solution up to 165 °C for five days (Fig. S22). In contrast, the analogous reaction with \(AlCl_3\) yielded \([L(Me_2N)Al]_2As_2\) (6) after heating at 80 °C for one day, clearly demonstrating the higher reduction potential of \(AlCl_3\) compared to \(GaCl_3\) (Scheme 2).

![Scheme 2. Synthesis of 3-6.](image)

Finally, the reactions of LGa with several Bi amides were studied (Scheme 3). While the reaction of two equivalents of LGa with \(Bi(NMe_2)Cl\) only yielded Bi metal and \(LGa(As(NMe_2)Cl)\) (as confirmed by \(^1\)H NMR spectroscopy, Figure S23) even at low temperatures, with that sterically more pronounced \(Bi(NEt_2)Cl\) gave \([L(Et_2N)Ga]Bi_2\) (7) in good yields. \([L(Et_2N)Ga]Bi_2\) (7) was formed at milder reaction conditions (25 °C, 4 days) compared to the diarsene \([L(Me_2N)Ga]_2As_2\) (5), which clearly results from the weaker Bi-N bond compared to the As-N bond. It should further be mentioned that the analogous reaction of LGa with \(Sb(NMe_2)Cl\) required heating at 60 °C in the absence of any solvents for seven days, whereas the reaction with the sterically less hindered \(Sb(NMe_2)Cl\) proceeded already very slowly at ambient temperature, but is finished after heating to 75 °C for 24 h. In contrast, no reaction between LGa and the sterically more demanding \(Sb(NEt_2)Cl\) was observed, even after prolonged heating at 120 °C. Analogous trends were observed for the reactions of two equivalents of LGa with \(ECl_3\) \((E = As, Sb, Bi)\). The reaction with \(AsCl_3\) occurred at ambient temperature, whereas with \(SbCl_3\) is finished within minutes already at 0 °C. In contrast, the reaction with \(BiCl_3\) occurred slowly at ambient temperature with formation of elemental bismuth as well as \(LGaCl_3\), but we could not prove if this reaction proceeds via formation of an thermally unstable dibismuthene \([L(Cl)Ga]Bi_2\) or if BiCl\(_3\) is directly reduced to Bi. However, these experimental findings clearly reveal the strong influence of the strength of the diarsene bond on the reaction rate.
E-X (X = Cl, N) bond as well as the steric demand of the amido (NR$_2$) substituent.

Isolated 1 – 7 are thermally stable and can be stored in a glove box under Ar atmosphere for several months. The thermal stability of the compounds differ significantly. 1, 2, 4 and 6 melt without decomposition at 222 °C (2), 239 °C (4) and 275 °C (6), while 3 and 7 decomposes at 255 °C (3) and 120 °C (7), respectively, without melting.

**Solution-phase characterization.** 1 and 2 dissolve moderately in benzene, toluene and hexane, whereas 3 - 7 dissolve poorly in benzene and toluene and are insoluble in hexane. The $^1$H NMR spectrum of 1 and 2 in toluene-d$_8$ show the expected septetts and doubletts for the IPr groups of the $\beta$-diketiminate ligand as well as single resonances of the γ-CH and two methyl groups of the $\beta$-diketiminate ligand (Table 1). These findings are confirmed by the $^{13}$C NMR spectrum, which only shows the expected resonances of the $\beta$-diketiminate groups. The $^{31}$P NMR spectra of 1 and 2 show single resonances at 0.52 (1) and -42.9 ppm (2), which prove the formation of a phosphine rather than a diphosphene. Diphosphenes of the type R$_2$P$_2$[20] and metal-substituted diphosphenes such as [(P$_2$DPDI)IrCO]$_2$(μ-P$_2$) (PDI = pyridine-diketimine) and [(silox)$_2$M$_2$($\mu$-η$_3$-P$_2$)] (M = Nb, Ta) typically exhibit resonances between 440 and 550 ppm.[11] Heating a solution of [L(Cl)Ga]$_2$PCI (1) in toluene-d$_8$ at 125 °C for 5 d resulted in the formation of several new phosphorous species, but the decomposition of a phosphene was excluded due to the lack of any resonances in the typical range. However, two new triplets at -187.4 and -338.1 ppm ($J_{PP} = 140$ Hz) in the $^{31}$P NMR spectrum (Figure S25), which appear in the typical range for tetraphosphacyclobutanes R$_2$P$_4$[22] show the formation of [L(Cl)Ga]$_2$PCI as was previously observed for [L(Cl)Ga]$_2$Sb$_2$.[14] In addition, the in situ $^1$H NMR spectrum of [L(Cl)Ga]$_2$Sb$_2$ show the formation of LGaCl$_2$ as by-product as was also observed for the formation of [L(Cl)Ga]$_2$Sb$_2$.

The $^1$H NMR spectra of 3 to 7 are very similar and each show two septetts and four doubletts for the magnetically inequivalent IPr groups of the $\beta$-diketiminate ligand as was previously observed for the corresponding distibenes [L(X)Ga]$_2$Sb$_2$ (X = Cl, NMe$_2$).[14] while the γ-CH and two methyl groups of the C$_2$N$_2$M ring exhibit only single resonances. The $^{13}$C NMR spectra of 1, 2, 3 and 6 show the expected 15 resonances of the $\beta$-diketiminate groups, whereas unsymmetrical 4 shows only 29 of the expected 30 resonances of the $\beta$-diketiminate groups (Figure S13) and two additional resonances of the NMe$_2$ group. The resonance at 24.8 ppm appears with twofold intensity, indicating an overlap of two signals, which is supported by the fact that only 7 resonances instead of eight are observed for the IPr groups.

1 - 4 and 6 are stable in toluene solutions and don't show any kind of decomposition up to temperatures of 80 °C. A solution of 7 in toluene also doesn't show any sign of light sensitivity and can be stored for weeks at ambient temperature without decomposition, whereas it decomposes gradually at elevated temperatures even in the dark with precipitation of Bi metal and formation of unidentified reaction products.

**Solid state structures.** The molecular structures of 2-2ClH$_2$. 3, 4, 6 and 7 were determined by single crystal X-ray diffraction. Single crystals were obtained from saturated solutions in toluene upon storage at -30 °C for 3 days (2), at 0 °C (3) or at room temperature for 2 days (7) and 3 days (4 and 6). 2-2ClH$_2$ crystallizes in the monoclinic space group $P2_1$/c with the molecule and two distorted toluene molecules in general positions (Figure 1). Since the central P–Br unit is disordered over three positions with the atomic displacement parameters of the corresponding atoms still large, a meaningful quantitative discussion of this part of the molecule is not feasible. The Ga-Br bond lengths (Table 2) of the three disordered units slightly differ. The Ga atoms adopt distorted tetrahedral coordination spheres and the $\beta$-diketiminate ligands deviate from planarity as is typical for LGaX fragments.

![Scheme 3. Synthesis of 7.](image-url)

**Table 1.** $^1$H NMR chemical shifts of 1 - 4, 6 and 7.$^a$

<table>
<thead>
<tr>
<th></th>
<th>γ-CH</th>
<th>CHMe$_2$</th>
<th>CHMe$_2$</th>
<th>CMe</th>
<th>NR$_2$</th>
</tr>
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<tbody>
<tr>
<td>1$^a$</td>
<td>4.81</td>
<td>3.55, 3.22</td>
<td>1.21, 1.18</td>
<td>0.98</td>
<td>1.46</td>
</tr>
<tr>
<td>2$^a$</td>
<td>4.87</td>
<td>3.63, 3.24</td>
<td>1.25, 1.20</td>
<td>0.98</td>
<td>1.47</td>
</tr>
<tr>
<td>3$^a$</td>
<td>4.85</td>
<td>3.77, 2.90</td>
<td>1.35, 1.24</td>
<td>1.09, 0.97</td>
<td>1.61</td>
</tr>
<tr>
<td>4$^a$</td>
<td>4.87, 4.72</td>
<td>3.77, 3.54</td>
<td>1.31, 1.21</td>
<td>1.13, 1.02</td>
<td>1.63</td>
</tr>
<tr>
<td>6$^a$</td>
<td>4.92</td>
<td>3.53, 2.93</td>
<td>1.28, 0.99</td>
<td>0.96</td>
<td>1.60</td>
</tr>
<tr>
<td>7$^a$</td>
<td>4.74</td>
<td>2.77, 4.07</td>
<td>1.05, 1.11</td>
<td>1.28, 1.39</td>
<td>1.58</td>
</tr>
</tbody>
</table>

$^a$ NMR spectra of 5 couldn't be recorded due to its poor solubility in organic solvents; [b] in toluene-d$_8$; [c] in benzene-d$_6$. 

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The metal-substituted diarsene \([\text{L(Cl)Ga}]_2\text{As}_2\) (3) crystallizes monoclinic with space group \(P2_1/n\), while \([\text{L(Cl)Ga}]_2\text{As}=\text{As}[\text{Ga(NMe}_2\text{)L}]\) (4) and \([\text{L(Me}_2\text{N})\text{Al}]_2\text{As}_2\) (6) crystallize in the triclinic space group \(P-1\) (Figures 2 - 4). 3 and 4 are located on centers of inversion.

Since the point group symmetry of the molecule of 4 does not match the site symmetry, the Cl and NMe\(_2\) substituents are superimposed. Refinement in a space group of lower symmetry did not yield an acceptable model.
The dibismuthene \([L(\text{EtN})\text{Ga}]=\text{Bi}_2\) (7) crystallizes in the monoclinic space group \(P2_1/n\) and is also placed on a center of inversion (Figure 5).

**Figure 5.** Molecular structure of \([L(\text{EtN})\text{Ga}]=\text{Bi}_2\) in the crystal of 7. H-atoms and the minor occupied carbon atom positions of the disordered ethyl group at N3 were omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level and the symmetry generated part of the molecule is depicted in pale colors (symmetry operation 1-x, 1-y, -z).

Compared to the analogous distibene structures \([L(X)\text{Ga}]=\text{Bi}_2\) (X = Cl, NMe2, NMeEt),\(^{[14]}\) neither changing M (Al, Ga) nor E (As, Sb, Bi) strongly influences the overall conformation of the molecule. The As atoms in \([L(\text{Cl})\text{Ga}]=\text{As}_2\) (3), \([L(\text{Cl})\text{Ga}]=\text{As}=\text{As}(\text{NMe}_2)\text{L}\) (4) and \([L(\text{Me}_2\text{N})\text{Al}]=\text{As}_2\) (6) are slightly further off the plane formed by the ligands’ backbones (offset from best plane of the backbones: 0.195(6) Å (3), 0.4097(13) Å (4), 0.4503(8) and –0.5168(8) Å (6), 0.0192(23) Å (7)). The As=As bond lengths in 3 (2.2556(6) Å), 4 (2.2554(8) Å) and 6 (2.2707(4) Å) are comparable to those reported for diarsines of the general type RAs=AsR (2.219 - 2.358 Å; mean bond length 2.271 Å),\(^{[23]}\) but shorter compared to the heavier congeners \([L(X)\text{Ga}]=\text{Bi}_2\) (X = Cl, NMe2, NMeEt) and \([L(\text{EtN})\text{Ga}]=\text{Bi}_2\) (2.8132(5) Å). In addition, the E-E bond distances in 3 - 7 are shorter than the sum of the calculated atomic radii \([1.21 \text{ (As)}, 1.40 \text{ (SB), 1.51 \text{ (Bi)}],^{[28]} 1.31 \text{ (As), 1.46 \text{ (Sb), 1.50 \text{ (Bi)}]},^{[28]} \text{ most likely due to the lower coordination number (c.n. 2) of 3 - 7 compared to the calculated values (c.n. 3).}

The Bi-Bi bond length in \([L(\text{EtN})\text{Ga}]=\text{Bi}_2\) (7) matches well with those of \([L(\text{RO})\text{Ga}]=\text{Bi}_2\) \([R = \text{CF}_3, \text{CF}_2\text{Cl}, \text{CF}=\text{C} (\text{R} = \text{CF}_3, \text{CF}=\text{C} (\text{R} = \text{CF}_3)]^{[23]}\) and other dibismuthenes found in the CSD database (2.796 - 2.893 Å; mean bond length 2.831 Å).\(^{[31]}\) However, the Ga-Bi (2.7061(6) Å) and Ga-N1/2 bonds (av. 2.006 Å) in 7 are slightly elongated compared to those in \([L(\text{RO})\text{Ga}]=\text{Bi}_2\) \([R = \text{CF}_3, \text{CF}=\text{C}\text{Ga-Bi}\text{2.693}(5)\text{Å}, \text{av. Ga-N}\text{1.952Å}, \text{SO}\text{CF}_3=\text{Ga-Bi}2.655(1)\text{Å}, \text{av. Ga-N}\text{1.928Å}],\) which can be attributed to the weaker electron-withdrawing nature of the NEt2 group in \([L(\text{EtN})\text{Ga}]=\text{Bi}_2\) (7) compared to the OR groups in \([L(\text{RO})\text{Ga}]=\text{Bi}_2\).

### Quantum chemical calculations

The bonding situations in 4, 6 and 7 were analyzed by using a number of quantum chemical techniques to gain further insight into the chemical bonding within the \(\text{M}_2\text{E}_2\) \((\text{M} = \text{Al, Ga; E} = \text{As, Bi})\) skeletons and also to compare the results with those observed in \([L(X)\text{Ga}]=\text{Bi}_2\) \((X = \text{Cl, NMeEt})^{[14]}\). All calculated bond lengths within the \(\text{M}_2\text{E}_2\) cores (BP86-D3/def2-SVP level of theory)\(^{[27–31]}\) Tables S2–S4) are in good agreement with the corresponding experimental values \(\Delta r = 0.01–0.05 \text{ Å}\).

As predicted by atoms in molecules (AIM), electron localization function (ELF), and natural bond orbital (NBO) analyses,\(^{[32–35]}\) the E–E bonds in 4, 6 and 7 are covalent (Tables S2–S4, Figures 6–8), in accordance to reported computational data for pnictogen-containing species.\(^{[36]}\)

### Table 2. Comparison of bond lengths (Å) and angles (°) in 2, 3, 4, 6 and 7.

<table>
<thead>
<tr>
<th></th>
<th>2(^{[1]})</th>
<th>3(^{[3]})</th>
<th>4(^{[1]})</th>
<th>6(^{[1]})</th>
<th>7(^{[1]})</th>
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</thead>
<tbody>
<tr>
<td>E-E</td>
<td>2.2556(6)</td>
<td>2.2554(8)</td>
<td>2.2707(4)</td>
<td>2.8132(5)</td>
<td></td>
</tr>
<tr>
<td>M-E</td>
<td>2.388(5)</td>
<td>2.3957(5)</td>
<td>2.4217(6)</td>
<td>2.4554(7)</td>
<td>2.4501(7)</td>
</tr>
<tr>
<td>M-X</td>
<td>2.3550(4)</td>
<td>2.2247(8)</td>
<td>2.1909(9)</td>
<td>1.802(2)</td>
<td>1.806(2)</td>
</tr>
<tr>
<td>M-NL</td>
<td>1.947(2)</td>
<td>1.987(2)</td>
<td>1.938(2)</td>
<td>1.974(3)</td>
<td>1.918(2)</td>
</tr>
<tr>
<td>M-E-E</td>
<td>2.388(5)</td>
<td>2.3954(6)</td>
<td>2.4217(6)</td>
<td>2.4554(7)</td>
<td>2.4501(7)</td>
</tr>
</tbody>
</table>

\(^{[1]}\) 4 = Ga, X = Br; \(^{[3]}\) 3 = Ga, X = Cl/NMe; \(^{[1]}\) 4 = Al, X = NMe; \(^{[1]}\) 4 = Ga, X = NMe; \(^{[1]}\) 4 = Ga, X = NEt; \(^{[2]}\) 2th and 3rd component of the disordered part, note that P-Br bond lengths are restrained to be equal; N1 = N of the L ligand.
respectively. and V(As,As) basins are indicated by white, yellow, and black arrows, respectively. Moreover, multiple bonding between pnictogen centers is observed for these complexes. Indeed, NBO analysis finds two-center two-electron \( \sigma_{E,E} \) and \( m_{E,E} \) bonds with occupation numbers (ON) varying from 1.9 to 2.0 |e| (Tables S2–S4) and ELF distribution reveals two disynaptic V(E,E) basins in \( [\text{V(Ga,As)}] = 1.1–1.3; \) Figures 6–8). Thus, 4 and 6 possess As=As double bonds, whereas 7 contains a Bi=Bi double bond. Additionally, each E atom from 4, 6 and 7 has one electron lone pair (Tables S2–S4), as calculated by NBO analysis (ON=1.9–2.0 |e|) and ELF (\( \langle \tilde{\rho}(\text{Sb}) \rangle = 2.8–3.0 \) e; Figures 6–8).

Conclusions

In summary, reactions of LGa with phosphorus, arsenic and bismuth halides and amides were studied, revealing clear trends in the reactivity as well as different reaction pathways. The reaction of LGa with PX3 (X = Cl, Br) stopped after twofold insertion into the P-X bonds and formation of [L(X)Ga]3PX (X = Cl, Br), whereas the analogous reactions with AsCl3, Me2NAsCl2 and As(NMe2)3 further proceeded with elimination of LGaX2 (X = Cl, NMe2) and subsequent formation of the corresponding diarsenes \( [\text{L(Cl)Ga}]; \) 3, \( [\text{L(Cl)Ga}]; \) 2 and \( [\text{L(Cl)Ga}]; \) 4 (4), and \( [\text{L(Me2N)Ga}]; \) 5 (5). The reaction of LGa with As(NMe2)3 required very harsh conditions (165 °C, 5 d), whereas the reaction with stronger \( \sigma \)-donor and stronger reducing agent LAl already proceeded at 80 °C and yielded \( [\text{L(Cl)Al}]; \) 6 after 1 day. Finally, the reactions of LGa with Bi(NEt3)3 also occurred with insertion and elimination of LGa(NEt3) and formation of the corresponding Ga-substituted dibismuthene \( [\text{L(Et3N)Ga}]; \) 7 (2, 3, 4, 6 and 7 were structurally characterized by single crystal X-ray diffraction and the bonding situation, which was investigated by quantum chemical calculations, clearly revealed the double bond character within these complexes.

Experimental Section

General Procedures. The reactions were performed in purified argon atmosphere using standard Schlenk and glove-box techniques. Solvents were dried using a MBraun Solvent Purification System and carefully degassed. Karl Fischer titration of the dry solvents show values less than 3 ppm. Deuterated NMR solvents were stored over activated molecular sieves (4 Å) and degassed prior to use. LGa,[23] LAl,[24] As(NMe2)3,[143] and...
Bi(NEt₃)₃Cl were prepared according to literature methods and Me₃AsCl₂ was prepared by a ligand exchange reaction of As(NMe₂)₂ with two equivalents of AsCl₃. Pb₂& and AsCl₃ were obtained from commercial sources and purified prior to use by distillation or sublimation.

Instrumentation. The 'H (300, 500 & 600 MHz), ¹³C(CH₃)(D₅) (75.5, 125 & 150 MHz) and ³¹P NMR (200 MHz) spectra (6 in ppm) were recorded using a Bruker Avance DPX-300 or Bruker Avance III HD spectrometer and the spectra were referenced to internal C₆D₆ (δ = 7.154; ¹³C = 128.39) and C₆D₆Cl₂ (δ = 2.00; ¹³C = 20.40). Microanalyses were performed at the elemental analysis laboratory of the University of Duisburg-Essen. IR spectra were measured in an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The melting points were measured using a Thermo Scientific 9300 apparatus.

Synthesis of [L(Br)Ga]Cl₂ (1). LGa (250 mg, 0.513 mmol) and PC₁₂ (35.22 mg, 22.43 μL, 0.256 mmol) were dissolved in 2 mL of toluene and stirred for 24 h, during which the color of the reaction solution changed from yellow to reddish brown. The solution at -30 °C for 3 days yielded pale green solid of 2. Yield 16.9 mg (6.45 %). Anal. Calcd. for C₆H₁₂N₃GaBr·C₆H₆: C, 66.64; H, 6.85; N, 4.50. Found: C, 66.64; H, 6.85; N, 4.50. %.

Synthesis of [L(Ga)]Cl₂ (2). LGa (100 mg, 0.205 mmol) and PC₁₂ (27.77 mg, 9.74 μL, 0.103 mmol) were dissolved in 0.5 mL of toluene-d₈ in a J-Yong NMR tube and stirred for 24 h, during which the color of the reaction solution changed from yellow to dark orange. Storage of the solution at -30 °C for 3 days yielded pale yellow crystals of 3. Yield 6.64; N, 4.50. Found: C, 56.10; H, 6.71; N, 4.71 %.

Synthesis of [L(AsCl₃)]GaCl₃ (3). A solution of LGa (20 mg, 0.103 mmol) and Me₃AsCl₂ (19.06 mg, 0.106 μL, 0.103 mmol) was dissolved in 0.5 mL of toluene-d₈ in a J-Yong NMR tube and stirred for 4 h at 80 °C. The color of the reaction solution changed from yellow to red and a red solid precipitated, which was isolated by filtration and recrystallized in toluene, yielding red brown crystals of 4. M. p. 239 °C. Yield 11.4 mg (43.8 %). Anal. Calcd. for C₆H₁₃N₃AsGaCl₃·C₆H₆: C, 59.85; H, 5.82. Found: C, 60.06; H, 7.40; N, 6.04 %.

Synthesis of [L(AsCl₃)]GaCl₃ (5). A solution of LGa (100 mg, 0.205 mmol) and Me₃AsCl₂ (19.06 mg, 0.106 μL, 0.103 mmol) was dissolved in 0.5 mL of toluene-d₈ in a J-Yong NMR tube and stirred for 24 h at 80 °C. The color of the reaction solution changed from yellow to red and a red solid precipitated, which was isolated by filtration and recrystallized in toluene, yielding red brown crystals of 4. M. p. 239 °C. Yield 43.2 mg (34.8 %). Anal. Calcd. for C₆H₁₃N₃AsGaCl₃·C₆H₆: C, 59.85; H, 5.82. Found: C, 60.06; H, 7.40; N, 6.04 %.

Instrumentation. The 'H (300, 500 & 600 MHz), ¹³C(CH₃)(D₅) (75.5, 125 & 150 MHz) and ³¹P NMR (200 MHz) spectra (6 in ppm) were recorded using a Bruker Avance DPX-300 or Bruker Avance III HD spectrometer and the spectra were referenced to internal C₆D₆ (δ = 7.154; ¹³C = 128.39) and C₆D₆Cl₂ (δ = 2.00; ¹³C = 20.40). Microanalyses were performed at the elemental analysis laboratory of the University of Duisburg-Essen. IR spectra were measured in an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The melting points were measured using a Thermo Scientific 9300 apparatus.

Synthesis of [L(Ga)]Cl₂ (2). LGa (100 mg, 0.205 mmol) and PC₁₂ (3.53 mmol) were dissolved in 2 mL of toluene and stirred for 24 h, during which the color of the reaction solution changed from yellow to dark orange. Storage of the solution at -30 °C for 3 days yielded pale yellow crystals of 3. Yield 6.64; N, 4.50. Found: C, 56.10; H, 6.71; N, 4.71 %.

Synthesis of [L(AsCl₃)]GaCl₃ (3). A solution of LGa (20 mg, 0.103 mmol) and Me₃AsCl₂ (19.06 mg, 0.106 μL, 0.103 mmol) was dissolved in 0.5 mL of toluene-d₈ in a J-Yong NMR tube and stirred for 4 h at 80 °C. The color of the reaction solution changed from yellow to red and a red solid precipitated, which was isolated by filtration and recrystallized in toluene, yielding red brown crystals of 4. M. p. 239 °C. Yield 11.4 mg (43.8 %). Anal. Calcd. for C₆H₁₃N₃AsGaCl₃·C₆H₆: C, 59.85; H, 5.82. Found: C, 60.06; H, 7.40; N, 6.04 %.

Synthesis of [L(AsCl₃)]GaCl₃ (5). A solution of LGa (100 mg, 0.205 mmol) and Me₃AsCl₂ (19.06 mg, 0.106 μL, 0.103 mmol) was dissolved in 0.5 mL of toluene-d₈ in a J-Yong NMR tube and stirred for 24 h at 80 °C. The color of the reaction solution changed from yellow to red and a red solid precipitated, which was isolated by filtration and recrystallized in toluene, yielding red brown crystals of 4. M. p. 239 °C. Yield 43.2 mg (34.8 %). Anal. Calcd. for C₆H₁₃N₃AsGaCl₃·C₆H₆: C, 59.85; H, 5.82. Found: C, 60.06; H, 7.40; N, 6.04 %.
were washed with hexane (2x 1 mL) to afford 7 in a pure form. M. p. 120 °C (dec). Yield 0.083 g (65 %). Anal. Calc. for C_{6}H_{10}BrAl_{2}As_{2}N_{4}. M. 1127.23, pale yellow crystal, (0.401 x 0.327 x 0.040 mm); triclinic, space group P-1; a = 10.7453(7) Å, b = 15.6159(10) Å, c = 18.2991(12) Å; α = 84.315(3)°, β = 89.408(3)°, γ = 79.142(3)°; V = 3000.6(3) Å³; Z = 2; μ = 1.186 mm⁻¹; ρcalcd = 1.248 g cm⁻³; 72834 reflections (Rp = 0.3064 ), 18296 unique (Rw = 0.0426); 673 parameters; largest max/min in the final difference Fourier synthesis 1.86 e Å⁻³ -0.874 e Å⁻³, max/min. transmission 0.750.56; RRF of 4, 6 and CDDC-57551 (7). Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: Main group elements • Subvalent compounds • Bond activation reaction


[50] G. M. Sheldrick, SHELXL-2014, Program for the Refinement of Crystal Structures University of Göttingen, Göttingen (Germany) 2014 (see also:
LGa reacted with PX₃ with formation of [L(X)Ga]₂PX (X = Cl₁, Br₂), whereas reactions with AsCl₃, Me₂NAsCl₂, As(NMe₂)₃ and Bi(NEt₂)₃ yielded Ga-substituted dipnictenes [L(Cl)Ga]₂As₂ (3), [L(Cl)Ga]₁As₁Ga₂(NMe₂)₁L₁ (4), [L(Me₂N)Ga]₂As₂ (5) and [L(Cl)Ga]₂Bi₂ (7). The stronger reductant LAl reacted with As(NMe₂)₃ under milder conditions with formation of [L(Me₂N)Al]₂As₂ (6). Quantum chemical calculations revealed the bonding situation within 4, 6 and 7.