

The Role of London Dispersion Interactions in Ga-Substituted Dipnictenes

Lijuan Song,[#] Juliane Schoening,[‡] Christoph Wölper,[‡] Stephan Schulz,^{*,‡} and Peter R. Schreiner^{*,#}

[#]Institute of Organic Chemistry, Justus Liebig University, Heinrich-Buff-Ring 17, D-35392 Giessen, Germany and Center for Materials Research (LaMa), Justus Liebig University, Heinrich-Buff-Ring 16, 35392 Giessen, Germany

[‡]Institute for Inorganic Chemistry and Center for Nanointegration Duisburg-Essen (Cenide), University of Duisburg-Essen, Universitätsstr. 5-7, D-45117 Essen, Germany.

ABSTRACT: We report the synthesis and structural characterization of Ga-substituted diarsene $[L(OEt)GaAs]_2$, which is an exemplary case of a Ga-substituted dipnictene of the general type $[L(X)Ga]_2E_2$ ($L=C[C(Me)N(2,6-i-Pr_2-C_6H_3)]_2$, $X = F, Cl, Br, I, NMe_2, OEt$, $E = As, Sb, Bi$). We examined this extended series of compounds computationally and found that attractive London dispersion interactions between the substituents on the N,N' -chelating β -diketiminato ligands as well as pnictogen- π interactions between the group 15 metal center and the ligand are a key factor for the stability and the electronic structures of such types of complexes.

INTRODUCTION

The synthesis and structural characterization of low-valent and low-coordinated main group metal complexes in the last four decades has provided a detailed understanding of the electronic properties and the nature of the chemical bonding in heavy main group element compounds.¹ For instance, the chemical bonding in compounds of heavy group 13 to group 15 elements with multiple bonds differs fundamentally from those of their lighter congeners – boron, carbon, and nitrogen – resulting in significantly different structures, i.e., *trans-bent* orientations of heavier ethylene and acetylene congeners.²

Since the initial reports on the first stable stannylene by Lappert et al.,³ disilene by West et al.,⁴ and diphosphene by Yoshifuji et al.,⁵ respectively, a large number of *kinetically stabilized* complexes have been synthesized by using sterically demanding organic substituents such as (substituted) cyclopentadienyls, terphenyls or N,N' -chelating β -diketiminates and amidinates, respectively.⁶ The bulky substituents occupy the space surrounding a reactive metal atom, which prevents decomposition or transformation reactions of the metal complexes. The bulk also causes repulsive Pauli exchange interactions between the electron clouds of the substituents, which typically results in bond length and angle distortions. In recent years, the principle of *electronic stabilization* was introduced for the successful preparation of such complexes. Coordination of strong σ -donating Lewis bases, in particular N -heterocyclic carbenes (NHC)⁷ and cyclic alkyl(amino)carbenes (cAAC),⁸ has resulted in the stabilization of unforeseen complexes, including those adopting the formal oxidation state zero.⁹

While the role of sterically demanding substituents and Lewis bases for the stabilization of low-coordinate and low-valent main group metal complexes is well established, the

stabilizing effect of London dispersion (LD) interactions, which constitute the attractive part of the van der Waals potential, was only recognized in recent years.¹⁰ Their importance for the stability as well as reactivity of organic, inorganic, and metal organic compounds has been largely ignored, but with the development of suitable quantum mechanical methods,¹¹ the decisive role of LD for the stabilization of sterically crowded hydrocarbon compounds and ligands has been recognized.¹² More recently, the effect of LD on the physical and chemical properties as well as on the structures of organometallic and inorganic molecules was also emphasized.^{10c,13,14} LD typically occurs between the C–H moieties in sterically bulky ligands, as was shown, for instance, for the chemical bonding in Lappert's classical stannylene, which was recently re-evaluated.¹⁵ In addition, the structure-defining role of metal–metal interactions, in particular, between easily polarizable heavy main group metals and semimetals of group 13 to group 16, as well as metal–ligand interactions was also reported.¹⁶

Owing to our interest in the synthesis, reactivity, and structure of low valent main group metal complexes, we recently started to investigate reactions of monovalent gallanediyls LGa with group 15 metal complexes EX_3 ($E = P-As$, $X = \text{halide, amide, alkyl, alkoxide}$). These reactions typically proceed with activation of the $E-X$ bond and yields compounds with unusual bonding properties, including $Ga=E$ double bonds ($E = As, Sb$) as well as group 15 metal centered radicals $[L(X)Ga]_2E\cdot$ ($E = Sb, Bi$, respectively).¹⁷ In addition, reactions of EX_3 with two equivalents of LGa gave general access to a group of Ga-substituted dipnictenes $[L(X)Ga]_2E_2$ ($X = \text{halide, } NR_2, OEt$; $E = As, Sb, Bi$),¹⁸ whose solid state structures were determined by single crystal X-ray diffraction, whereas the nature of the $As=As$, $Sb=Sb$, and $Bi=Bi$ double bonds was investigated by quantum chemical computa-

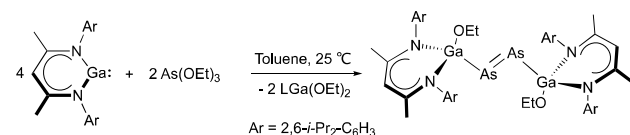
tions, including atoms in molecules (AIM), electron localization function (ELF), and natural bond orbital (NBO) analyses.¹⁹ The complexes were regarded as kinetically stabilized by the presence of the very bulky 2,6-*i*-Pr₂-C₆H₃ substituent, and we became further interested in examining the role of these bulky ligands on the stability of the complexes in more detail and to identify any stabilizing and structure-defining roles of LD interactions.

Herein we report the synthesis and structural characterization of the Ga-substituted diarsene [L(OEt)GaAs]₂ and describe the results of systematic DFT computations based at the BP86/def2-SVP level of theory with and without dispersion corrections (D3(BJ)) for ten complexes of the desired type [L(X)GaE]₂ (X = halide, NR₂, OR; E = As-Bi).²⁰

RESULTS AND DISCUSSION

Synthesis. The reaction of two equivalents of LGa with As(OEt)₃ proceeds with elimination of LGa(OEt)₂ and subsequent formation of [L(OEt)Ga]₂As₂, which was isolated in 11% yield and spectroscopically and structurally characterized.

Scheme 1. Synthesis of [L(OEt)Ga]₂As₂



[L(OEt)Ga]₂As₂ shows the expected resonances due to the β -diketiminato ligand in the ¹H and ¹³C NMR spectra. The ¹H NMR spectrum of [L(OEt)Ga]₂As₂ in benzene-*d*₆ shows two septets and four doublets for the magnetically inequivalent *i*-Pr groups of the β -diketiminato ligand, a single resonance for the γ -CH and the methyl groups of the C₃N₂M ring, as well as a triplet and quartet for the ethoxy group. The ¹³C NMR spectrum shows the expected resonances of the β -diketiminato groups and is similar to the analogously-substituted distibene [L(OEt)Ga]₂Sb₂.^{16b}

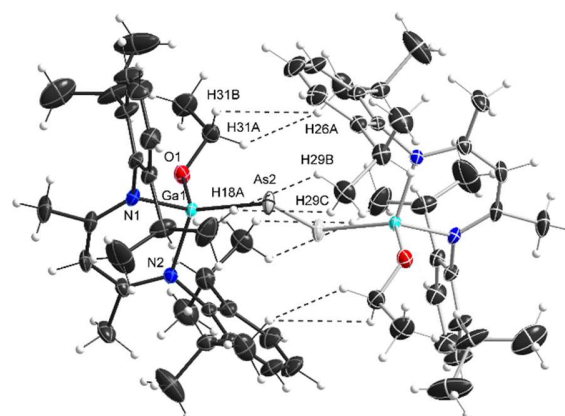


Figure 1. Solid state structure of [L(OEt)Ga]₂As₂. Pale parts are generated by symmetry. Displacement ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: Ga(1)–O(1) 1.8240(11), Ga(1)–N(2) 1.9494(12), Ga(1)–N(1) 1.9723(12), Ga(1)–As(2) 2.4283(3), As(2)–As(2)′ 2.2498(3), O(1)–Ga(1)–N(2) 100.15(5), O(1)–Ga(1)–N(1) 105.55(5), N(2)–Ga(1)–N(1) 95.56(5), O(1)–Ga(1)–As(2) 120.80(4), N(2)–Ga(1)–As(2) 118.76(4), N(1)–Ga(1)–As(2) 112.37(4), C(31)–O(1)–Ga(1) 124.22(10), As(2)′–As(2)–Ga(1) 95.841(12). Intramolecular H⋯H contacts below 3.0 Å are indicated by dashed lines: H(31A)⋯H(26A)′ 2.27, H(18A)⋯H(29B)′ 2.63, H(18A)⋯H(29C)′ 2.64, H(31B)⋯H(26A)′ 2.79.

Single crystals of [L(OEt)Ga]₂As₂ were grown from a solution in toluene upon storage for 48 h at –30 °C (Figure 1). [L(OEt)Ga]₂As₂ crystallizes in the orthorhombic space group *Pbca* with four independent molecules in the asymmetric unit, i.e., the molecule is placed on a center of inversion as is typically observed for gallium-substituted dipnictenes [L(X)Ga]₂E₂ (E = As–Bi, X = NR₂, OR, halide). The molecule shows a *trans-bent* conformation with a Ga–As–As angle of 95.841(12)°. The gallium atom is coordinated in a distorted tetrahedral way with angles from 95.56(5)° to 124.22(10)° and therefore is off the best plane of the N₂C₃ backbone (0.4971(17) Å) as was typically observed in these types of complexes. There are a few intramolecular H⋯H contacts below 3.0 Å, pointing to attractive LD interactions between the ligands. The As=As bond length matches well

Table 1. Selected bond lengths [Å] and angles [°] of selected diarsenes^[a]

	As=As [Å]	X–As [Å] ^[b]	As–As–X [°]	N–Ga–N [°]
[L(OEt)Ga] ₂ As ₂	2.2498(3)	2.4283(3)	95.841(12)	95.56(5)
(Me ₃ Si) ₂ CHAs=As(2,4,6- <i>t</i> Bu ₃ C ₆ H ₂) ^{21a}	2.224(2)	1.946(10), 1.976(10)	99.9(3), 93.6(3)	-
2,6-Mes ₂ H ₃ C ₆ As=AsC ₆ H ₃ -2,6-Mes ₂ ^{21b}	2.276(3)	1.963(13)	98.5(4)	-
2,6-Trip ₂ H ₃ C ₆ As=AsC ₆ H ₃ -2,6-Trip ₂ ^{21b}	2.285(3)	1.986(7), 1.980(7)	96.4(2), 107.8(2)	-
[L(Cl)Ga] ₂ As ₂	2.2556(6)	2.3957(5)	92.69(2)	96.98(9)
[L(Ga(Cl))As=As[Ga(NMe) ₂ L] ²⁴	2.2554(8)	2.4217(6)	95.23(3)	95.28(12)
[L(NMe ₂)Al] ₂ As ₂	2.2707(4)	2.4554(7), 2.4501(7)	95.64(2), 95.69(2)	94.91(9), 94.51(8)

^[a] 10 hits were found in the Cambridge Structural Database for diarsenes with twofold-coordinated As atoms of the general type X-As=As-X (X = "Any"). The As=As bond lengths range from 2.219 to 2.358 Å (mean 2.270 Å, standard deviation 0.043 Å). ^[b] X = Al, Ga, C.

with that of previously reported diarsenes XAs=AsX (X = C, Al, Ga) containing twofold-coordinated As atoms²¹ as well as with those reported for [L(NMe₂)Ga]₂As₂ and [L(Cl)Ga]₂As₂, respectively (Table 1).^{18a} In marked contrast, the N-heterocyclic carbene (NHC) stabilized diarsenic molecule [L:As-As:L] (L:=C{N(2,6-*i*-Pr₂-C₆H₃)CH₂}) shows a significantly elongated As-As single bond (2.442(1) Å).²² However, oxidation of [L:As-As:L] with GaCl₃ yielded the radical cation [L:As-As:L]⁺ as well as the dication [L:As-As:L]²⁺, which showed significantly shorter As-As bonds of 2.332(3) Å and 2.2803(5) Å, respectively, indicating As=As double bond character.²³ The WBI = 1.79 also indicates a double bond in [L(OEt)Ga]₂As₂. Furthermore, the computed IR spectrum (Figure S7) agrees well with the experimental spectrum (Figure S4).

Quantum chemical computations. To investigate the influence of LD on the structures of the dipnictenes, we compared the structures optimized with and without the D3-BJ dispersion correction and compared the optimized structures with the crystal structure ([L(Cl)Ga]₂As₂, Figure 2).^{16b, 18, 25} The structure without LD corrections deviates significantly (and much more than expected from packing forces^{12c}) from the crystal structure, especially when focusing on the central metals and the ligands. The structure including LD corrections shows excellent agreement with the crystal structure; key structural parameters are collected in Table S2. This finding is generally true, as structures inclusive of dispersion often show very small deviations from their crystal structures. For example, in [L(Cl)Ga]₂As₂, the computed Ga-As bond is in excellent agreement with the crystal structure (0.4% deviation), and the As=As bond is only 2.2% longer than the experimental value. On the other hand, the computations without dispersion yield much longer Ga-As bonds (3.2% deviation), which also leads to a larger distance between the ligands across the central E=E bonding moiety, which is essentially unaffected.

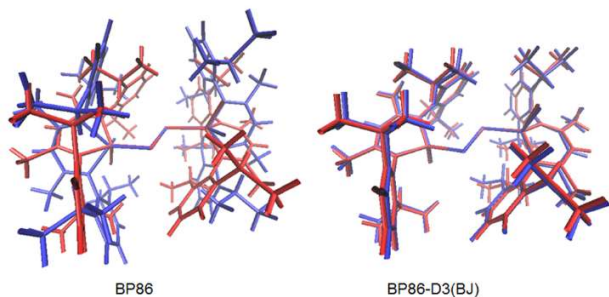


Figure 2. Comparison of the optimized [L(Cl)Ga]₂Sb₂ (without and with dispersion corrections, blue) with the X-ray crystal structure (red).

We established that the LD correction is indispensable to obtain accurate structures. Further support for this conclusion comes from a non-covalent interaction (NCI) analysis²⁶ of [L(Cl)Ga]₂As₂ that shows very significant differences in the non-covalent interactions between the structures computed with and without dispersion corrections (Figure 3).

As LD constitutes the major part of non-covalent interactions in this case, significant dispersion interactions between substituent groups of ligands and between the metal center and the ligand were observed in the LD-corrected structure. The ligand-ligand interactions are also apparent from the short H...H contacts across the central E=E moiety (Figure 4).²⁷ As a consequence, the LD-corrected structure pulls the ligands together and leads to a more compact structure.

To evaluate the LD energy contributions in Ga-substituted dipnictenes upon changing the metal and the X group, we set up an homodesmotic reaction (equation 1),²⁸ this approach has been applied before to discern the role of dispersion.^{12b} The assumption hereby is that the D3(BJ) correction captures most of the dispersion contributions so that computing such error-cancelling reactions should indeed bring the magnitudes of the dispersion interactions to the fore. The reaction of tetra-aryl-substituted dipnictenes with tetra-phenyl-substituted dipnictenes leads to a product with one ligand substituted by aryl groups. The reaction energy was calculated with and without LD corrections (Figure 5). Without LD corrections, the reaction energies are negative, indicating that the tetra-aryl-substituted dipnictenes are energetically unfavorable, which does not reflect the experimental results. Indeed, the situation *reverses* when LD corrections are included. The tetra-aryl-substituted dipnictenes are now favored (E=Sb, X=NMe₂, the slightly negative LD energy is within the expected computational error). This energy evaluation also supports the stabilizing effect of LD in the Ga-substituted dipnictenes [L(X)Ga]₂E₂(L=C{C(Me)N(2,6-*i*-Pr₂-C₆H₃)})₂.

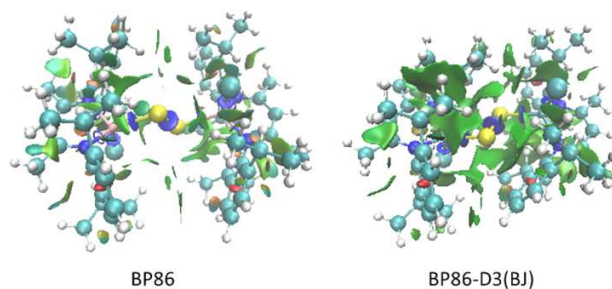


Figure 3. Non-covalent interaction (NCI) plots ($s = 0.5$ au, $-0.1 < r < +0.1$ au) of [L(Cl)Ga]₂Sb₂. Red: repulsion; blue: attraction, green: non-covalent interactions.

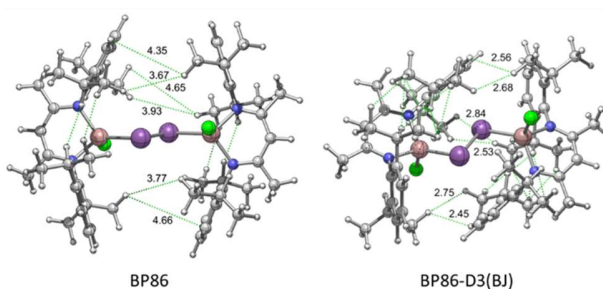


Figure 4. Short inter- and intra-ligand H...H contacts based on

$[\text{L}(\text{Cl})\text{Ga}]_2\text{Sb}_2$ computed without and with dispersion corrections (the short intra-ligand $\text{H}\cdots\text{H}$ contacts below 3.0 Å are indicated by green dashed lines, the short inter-ligand $\text{H}\cdots\text{H}$ contacts below 3.0 Å in the dispersion corrected structure are listed and the corresponding distances are shown in Å).

The magnitude of the LD energy depends on the metal center and the X group. For instance, the LD correction of $[\text{L}(\text{Cl})\text{Ga}]_2\text{As}_2$ amounts to 4.2 kcal mol⁻¹, while that of

$[\text{L}(\text{Cl})\text{Ga}]_2\text{Sb}_2$ is only 2.9 kcal mol⁻¹. This relates to the size of the metal center: The smaller As atom has a shorter As–Ga bond of 2.396 Å, leading to a more compact structure as compared to $[\text{L}(\text{Cl})\text{Ga}]_2\text{Sb}_2$ with a longer Sb–Ga bond of 2.582 Å, thereby favoring closer $\text{H}\cdots\text{H}$ inter-ligand contacts. However, in the presence of the same metal center, e.g., Sb, the dispersion energy changes only slightly (by 0.8 kcal mol⁻¹) with varying halide substituent.

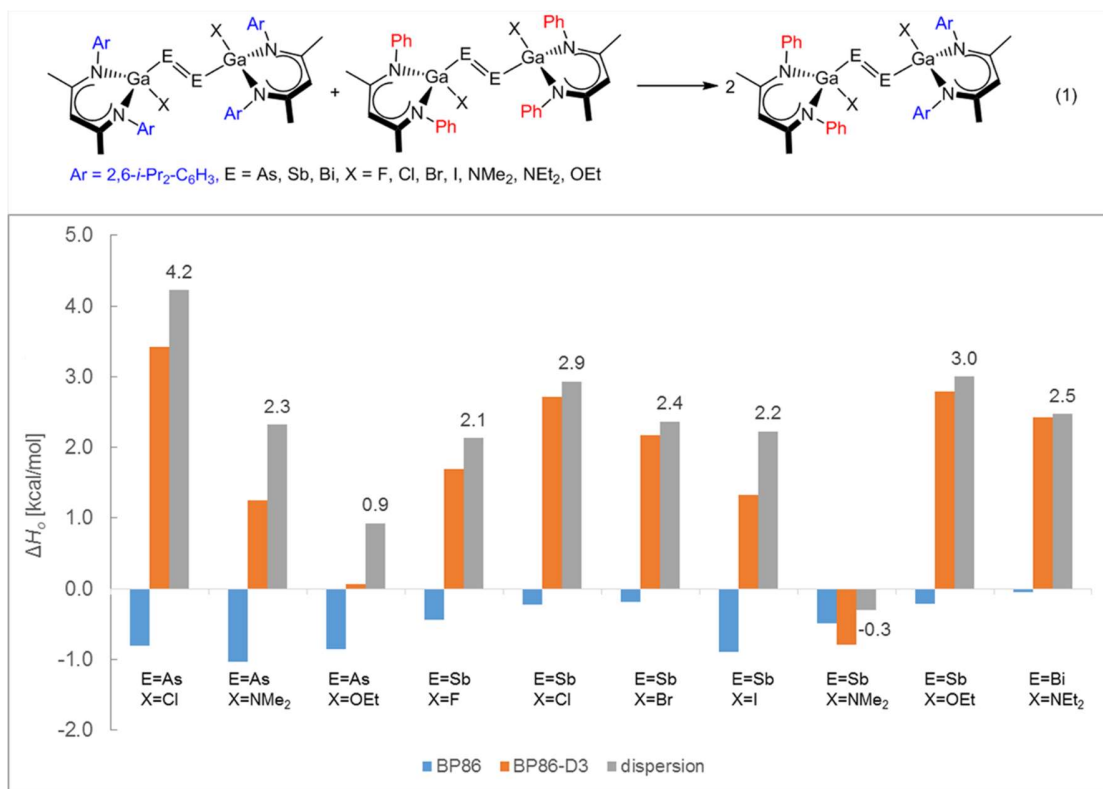


Figure 5. Reaction enthalpies ΔH_0 of homodesmotic eq. 1 with and without dispersion corrections and the dispersion energies (in gray) of Ga-substituted dipnictenes.

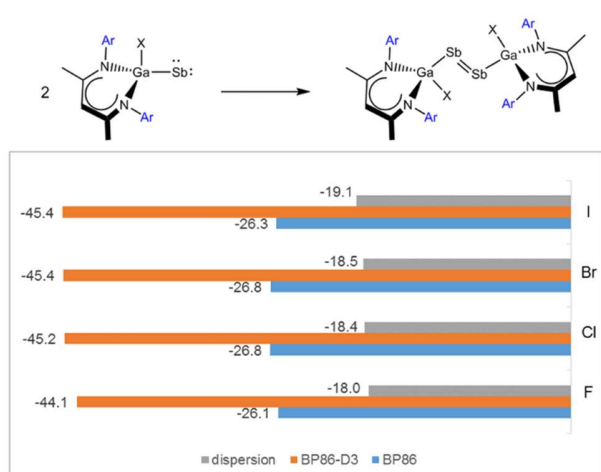


Figure 6. Dimerization enthalpies ΔH_0 (kcal mol⁻¹) with and without dispersion corrections and the dispersion energy (in gray) of Ga-substituted distibenes with different halides.

To investigate the influence of the halide substituent on LD in detail, we compared the dimerization energies of the

$[\text{L}(\text{X})\text{Ga}]_2\text{Sb}_2$ (X=F, Cl, Br, I) complexes (Figure 6) with and without dispersion, which was proposed as a key step in the reaction mechanism.^{17b} The dispersion energy is large and increases only slightly with increasing size of X from F to I (from 18.0 to 19.1 kcal mol⁻¹), which is, however, within computational error. A direct estimation of the dispersion energy between Ar substituents was also carried out by DFT-D3 (Figure S8). In agreement with the homodesmotic equation (1), there is a subtle decrease in dispersion energy from As to Bi. On the other hand, the dispersion energy is essentially unaltered for varying halide as well as NMe₂ and OEt. Therefore, the influence of the halide and other substituents on the amount of the dispersion correction is rather small.

The LD interactions involve both metal–ligand and ligand–ligand participation. The metal–ligand interactions involve dispersive type pnictogen– π interactions, whose strength is related to the metal–arene distance,²⁸ while the ligand–ligand interaction depends largely on the number and distance of $\text{H}\cdots\text{H}$ contacts. As illustrated in Figure 7 in the top row, with the same metal Sb, the Sb–arene distances from X = Cl to I vary only by 0.051 Å and 0.052 Å. Again, the shortest

H...H distances are very similar (2.448–2.505 Å) with the nearly unaltered Ga–Sb and Sb=Sb bonds, which correlates well with the unaffected dispersion energies. However, when changing the metal from As to Bi (Figure 7 bottom row, X = NMe₂ or NEt₂), the dispersion energy is influenced by the pnictogen- π interactions. The metal-arene distances and the shortest H...H distances are similar in the case of arsenic and antimony, although the Ga–E and E=E bond lengths increase with the size of the group 15 atoms (Ga–E bond: 2.411–2.693 Å; E=E bond: 2.295–2.832 Å). In contrast, the dispersion energy of the alkoxide-substituted

complex (X = OEt) increases due to the shorter metal-arene distance (Figure S9). In the bismuth complex, the stronger bismuth- π interaction as indicated by the shortened distances and the strengthened ligand interactions (H...H distance of 1.998 Å) was found to overcompensate the lower stability of the core structure. Although the correlation between pnictogen-arene distances and dispersion interactions is observed, one should notice that the change on dispersion energy is rather subtle.

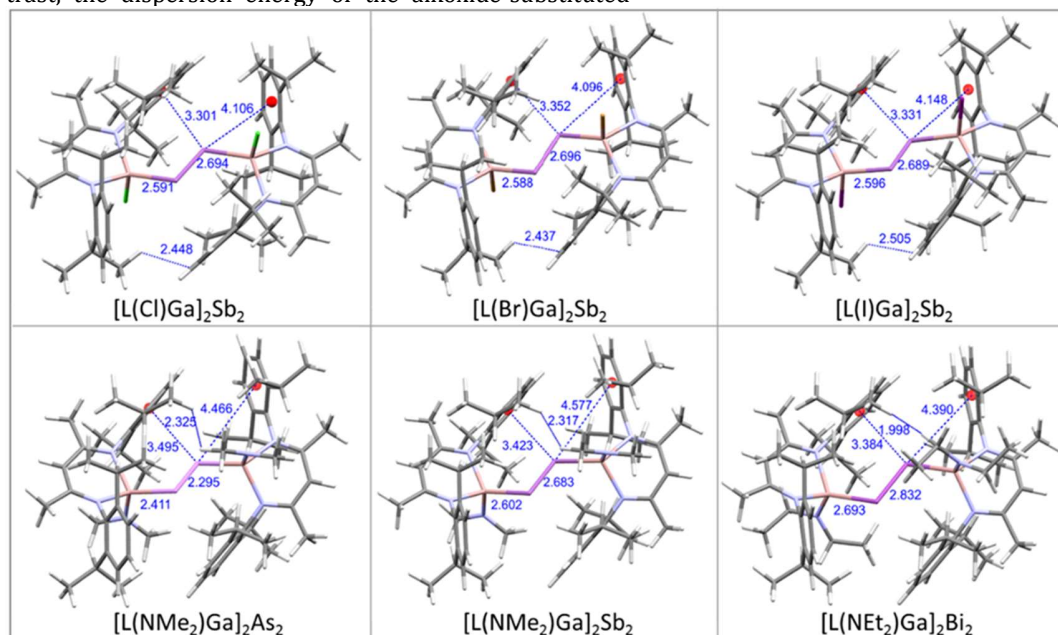


Figure 7. Selected bond lengths, metal- π distances, and the shortest H...H distance between different ligands [Å] from the computed Ga-substituted dipnictenes.

While the LD energy is not much affected by the X substituent and the pnictogen center, the steric bulk introduced by the aryl groups plays a key role. This was studied by varying the substituent on the N,S,N'-chelating β -diketiminato ligand (Ar (= 2,6-*i*-Pr₂-C₆H₃), Ph, Cy, *t*Bu, *i*Pr, Me, H; Figure 8). The bulky and polarizable substituents act as dispersion energy donors (DEDs).^{11b} As can be seen, the dispersion corrections have a significant effect on the reaction energies. The stability of dipnictenes decreases with decreasing size of the DEDs upon inclusion of dispersion corrections. The LD energy decreases significantly from aryl to phenyl substitution (from 19.1 to 13.7 kcal mol⁻¹), whereas the dispersion energy varies only by 1.8 kcal mol⁻¹ from *t*Bu to sterically less-demanding substituents (*i*Pr, Me, H). Obviously, the strength of the inter-ligand dispersion interactions decreases with decreasing size of the substituents, which is also reflected by the shortest inter-ligand H...H distance, which is significantly elongated in case of the *t*Bu-substituted complex (3.88 Å). The dispersion interactions mainly originate from antimony- π interactions (Figure S10). Including such interactions, the *t*Bu-substituted complex is also stable, but the dimerization energy is about 11.0 kcal mol⁻¹ lower compared to the Ar-substituted complex. Therefore, the stability of the Ga-substituted dipnictenes depends largely on the dispersion interaction introduced by the bulky ligand, and the other part comes from the intrinsic

stability of the inner core. The sterically demanding aryl substituent (2,6-*i*-Pr₂-C₆H₃) thus can be considered as a good dispersion energy donor that can achieve strong dispersion interactions through ligand-ligand and metal-ligand interactions.

To further study the electronic effect of the halide substituents on the electronic structure of the dipnictenes, the NBO charge and Wiberg Bond Indices (WBI) were analyzed (Table S3 and Table S4). Dispersion corrections were

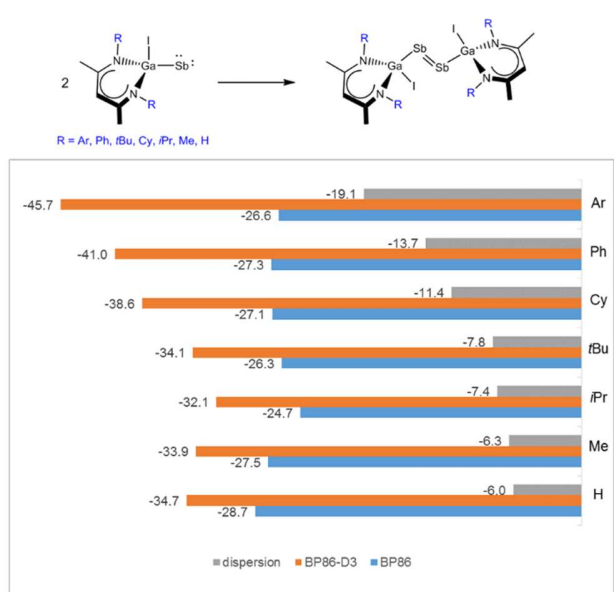


Figure 8. Dimerization enthalpies ΔH_0 (kcal mol⁻¹) with and without LD corrections and the dispersion energy (in gray) of $[L(I)Ga]_2Sb_2$ with different substituents on the ligands.

found to have only a slight influence on the charge distributions, whereas a noticeable influence on the WBI, especially on E=E bond, was observed. The distibenes show a decreasing charge distribution on X (q_X from -0.65 to -0.36) with decreasing electronegativity from F to I, which also leads to lower positive charges on the connected Ga atoms (q_{Ga} from $+1.29$ to $+0.89$) and decreasing Ga–Sb bond polarity. The Sb=Sb bond also show diminished charge (q_{Sb} from -0.13 to -0.05), which lowers the repulsion between negative charges and thus shortens the Sb=Sb bond length. The same bond polarity trend was also observed from As to Sb. The dispersion correction leads to smaller WBI of the E=E bond, whose stability is influenced by the ligands.

CONCLUSIONS

The synthesis of $[L(OEt)GaAs]_2$ through the reaction of $As(OEt)_3$ and two equivalents of LGa demonstrates the viability of this reaction pathway for the synthesis of Ga-substituted dipnictenes of the general type $[L(X)Ga]_2E_2$ ($L=C[C(Me)N(2,6-i-Pr_2-C_6H_3)]_2$, $X=F, Cl, Br, I, NMe_2, OEt, E=As, Sb, Bi$). $[L(OEt)GaAs]_2$ was structurally characterized by single crystal X-ray diffraction and its structure was examined computationally together with an extended series of previously reported compounds of the desired type. Computational studies indicate that the stabilities and electronic structures of Ga-substituted dipnictenes $[L(X)Ga]_2E_2$ ($L=C[C(Me)N(2,6-i-Pr_2-C_6H_3)]_2$, $X=F, Cl, Br, I, NMe_2, E=As, Sb, Bi$) are strongly influenced by attractive LD interactions between the substituents on the N, N' -chelating β -diketiminato ligands and by pnictogen– π interactions between the metal center and the ligand. The dispersion corrections are as large as 19 kcal mol⁻¹. The pnictogen atom only shows a subtle effect on the strength of the dispersion interaction by pnictogen– π interactions. The X group almost exclusively changes the bond polarity and bond order, and thus the structural parameters of the inner core, while it hardly affects the magnitude of the LD contributions. This demon-

strates that DEDs can significantly stabilize unusual structures and that DEDs should be employed as a key tool for the design of new inorganic structural motifs.

COMPUTATIONAL DETAILS

All computations were performed with the Gaussian09 Program.³⁰ Geometries were optimized in the gas phase at the BP86-D3(BJ)/def2-SVP level of theory.²⁰ Default effective core potentials were used for Sb and Bi atoms replacing 28 and 60 electrons including the treatment of relativistic effects (ECP28MDF and ECP60MDF). Frequency computations were performed for each optimized structure to verify the stationary points as minima. Geometry optimizations were also carried out without the empirical dispersion correction (DFT-D3(BJ)) as a reference to evaluate dispersion energies.^{11a} All energies discussed are enthalpies at 298 K and 1 atm in kcal mol⁻¹. The NBO and WBI analyses were performed at BP86-D3/def2-SVP as implemented in Gaussian09.³¹ Non-covalent interaction (NCI) analyses were performed with the NCIPLOT program.²⁶

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed using Schlenk-line and glove-box techniques under purified argon atmosphere. Toluene and hexane were obtained after passing these solvents through activated alumina columns on an MBraun Solvent Purification System. Deuterated NMR solvents were dried over potassium, purified by distillation, stored over activated molecular sieves (4 Å) and degassed prior to use. Karl Fischer titration of the dry solvents show values less than 2 ppm. LGa^{32} was prepared according to literature methods, whereas $SbBr_3$ and SbI_3 were obtained from commercial sources. $As(OEt)_3$ was prepared by a literature method.³³

Instrumentation. 1H (300 MHz) and $^{13}C\{^1H\}$ (75.5 MHz) NMR spectra (δ in ppm) were recorded using a Bruker Avance DPX-300 spectrometer and the spectra were referenced to internal C_6D_5H (1H : $\delta = 7.154$; ^{13}C : $\delta = 128.39$). Microanalysis was performed at the Elemental Analysis Laboratory of the University of Duisburg-Essen. The IR spectrum was recorded with an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The spectrometer was placed in a glovebox to allow measurement in inert gas atmosphere. The melting point was measured using a Thermo Scientific 9300 apparatus.

Synthesis of $[L(EtO)Ga]_2As_2$. LGa (150 mg, 0.308 mmol) and $As(OEt)_3$ (32.35 mg, 26.7 μ L, 0.154 mmol) were dissolved in 0.5 mL of C_6D_6 and stirred at ambient temperature for 2 d. Evaporation of the solvent yielded a light-green solid, which was dissolved in *n*-hexane (0.5 mL) and stored at room temperature. Light-green crystals of $[L(EtO)Ga]_2As_2$ were formed within five days. M. p. 208 °C. Yield 20 mg (0.015 mmol, 11%). Anal. Calcd. for $C_{62}H_{92}N_4O_2Ga_2As_2$: C, 61.30; H, 7.63; N, 4.61. Found: C, 61.20; H, 7.88; N, 4.59%. 1H NMR (C_6D_6 , 300 MHz, 25 °C): δ 1.12 (d, 24 H, $^3J_{H-H} = 6.8$ Hz, $CH(CH_3)_2$), 1.38 (d, 12 H, $^3J_{H-H} = 6.8$ Hz, $CH(CH_3)_2$), 1.42 (t, $^3J_{H-H} = 6.6$ Hz, 6 H, OCH_2CH_3), 1.42 (d, 12 H, $^3J_{H-H} = 6.6$ Hz, $CH(CH_3)_2$), 1.68 (s, 12 H, $ArNCCH_3$), 3.09 (sept, $^3J_{H-H} = 6.9$ Hz, 4 H, $CH(CH_3)_2$), 3.87 (q, $^3J_{H-H} = 6.7$ Hz, 4 H, OCH_2CH_3), 4.06 (sept, $^3J_{H-H} = 6.9$ Hz, 4 H, $CH(CH_3)_2$), 4.86 (s, 2 H, $\gamma-CH$), 7.14–6.92 (m, 12 H, ArH). ^{13}C NMR (C_6D_6 , 75 MHz, 25 °C): δ 21.4 (OCH_2CH_3), 24.0 ($NCCH_3$), 25.1, 25.1 ($CH(CH_3)_2$), 25.4, 26.0, 28.1, 29.4 ($CH(CH_3)_2$), 62.7 (OCH_2CH_3), 97.4 ($\gamma-CH$), 124.4, 125.0, 127.3, 142.5, 143.2, 145.7 (ArC), 169.1 ($NCCH_3$). IR (neat): ν 3064, 2961, 2924, 2866, 2704, 1552, 1524, 1436, 1394, 1317, 1259, 1175, 1106, 1061, 1019, 938, 905, 861, 792, 757, 603, 524, 438 cm⁻¹.

Single crystal X-ray diffraction. Crystallographic data of $[L(EtO)Ga]_2As_2$ were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (MoK_α radiation, $\lambda = 0.71073$ Å) at

100(2) K and are summarized in Table S1 (SI). The structure was solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2017).³⁴ Absorption correction was performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups.

The crystallographic data of $[L(EtO)Ga]_2As_2$ (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1875976. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

ASSOCIATED CONTENT

Supporting Information

A CIF file giving X-ray crystallographic data of $[L(EtO)Ga]_2As_2$, 1H NMR spectra of $[L(EtO)Ga]_2As_2$ as well as spectroscopic details (1H , ^{13}C NMR; IR), and crystallographic details of $[L(EtO)Ga]_2As_2$.

The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

*prs@uni-giessen.de

*stephan.schulz@uni-due.de

Notes

The authors declare no competing financial interests.

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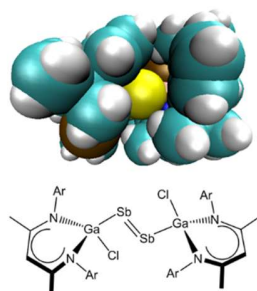
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