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Synthesis and Structure of New Compounds with Zn–Ga Bonds: Insertion of the Gallium(I) Bisimidinate Ga(DDP) into Zn–X (X = CH_3, Cl) and the Homoleptic Complex Cation $[Zn(GaCp^*)_4]^{2+}$†

Andreas Kempter, Christian Gemel, Thomas Cadenbach, and Roland A. Fischer*

Anorganische Chemie II, Organometallics & Materials, Ruhr-Universität Bochum,
D-44780 Bochum, Germany

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Insertion reactions of the low-valent group 13 bisimidinate ligand Ga(DDP) {DDP = 2-[(2,6-diisopropylphenyl)-amino]-4-[(2,6-diisopropylphenyl)imino]-2-pentene} into Zn–Me and Zn–Cl bonds are reported. The reaction of $ZnMe_2$ with 2 equiv of Ga(DDP) yields the double-insertion product $[\{(DDP)GaMe\}_2Zn]$ (**1**), whereas the insertion of Ga(DDP) into the Zn–Cl bond of $ZnCl_2$ in tetrahydrofuran (THF) leads to the monoinsertion product $[\{(DDP)GaCl\}ZnCl(THF)_2]$ (**2**). Treatment of **2** with Na[BAr^F] results in the salt $[\{THF\cdot Ga(DDP)\}Zn(THF)(\mu\text{-}Cl)]_2[BAr^F]_2$ (**3**), with two Cl atoms bridging the Zn centers. The structural features of the Zn–Ga-bonded compounds **1**–**3** were compared with related complexes and in particular with the compound $[Zn(GaCp^*)_4][BAr^F]_2$ (**4**), which was synthesized by the reaction of $ZnMe_2$, $[H(OEt_2)_2][BAr^F]$, and GaCp* in fluorobenzene. The complex cation $[Zn(GaCp^*)_4]^{2+}$ of **4** relates to previously reported d^{10} analogues $[M(GaCp^*)_4]$ (M = Ni, Pd, Pt). All new compounds were fully characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray diffraction analysis.

1. Introduction

A continuous motif in metal−organic coordination chemistry has been exploring the bonding of the heavier group 13 and 14 elements E to p-, d-, and f-block metal fragments ML_n featuring direct M−E bonds.[1] The availability of neutral as well as anionic nucleophilic carbenoid group 13 organyls $[E^IR]^a$ (R = bulky organic group; $a = 0, -1$)[1−4] as free ligands boosted the research on the synthesis and reactivity of their complexes with late transition metals (Fe,[5,6] Ru,[7] Co,[8,9] Rh,[10,11] Ni,[12−15] Pd,[2,16−18] Pt[2,14,18] Cu, Ag,[19] and Au[20,21]) during the past decade. For example, the neutral NHC analogue (NHC = nitrogen heterocyclic carbene) gallium(I) bisimidinate ligand [Ga(DDP)] {DDP = 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]-2-pentene} stabilizes low-coordinated, very electron-rich d^{10} M^0 centers (Ni,[13] Pd, and Pt[2]), which allow typical oxidative addition reactions of hydrogen, organosilanes, and benzene. Similarly, the anionic congeners to [Ga(DDP)], namely, the five-membered heterocycle $[Ga\{[N(Ar)C(H)]_2\}]^-$ (Ar = 2,6-${}^iPr_2C_6H_3$), have been introduced as NHC analogue ligands

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† Organo group 13 complexes of transition metals. XLVIII. Part XLVII: Reference 13.

* To whom correspondence should be addressed. E-mail: roland.fischer@rub.de. Fax: (+49)234 321 4174.

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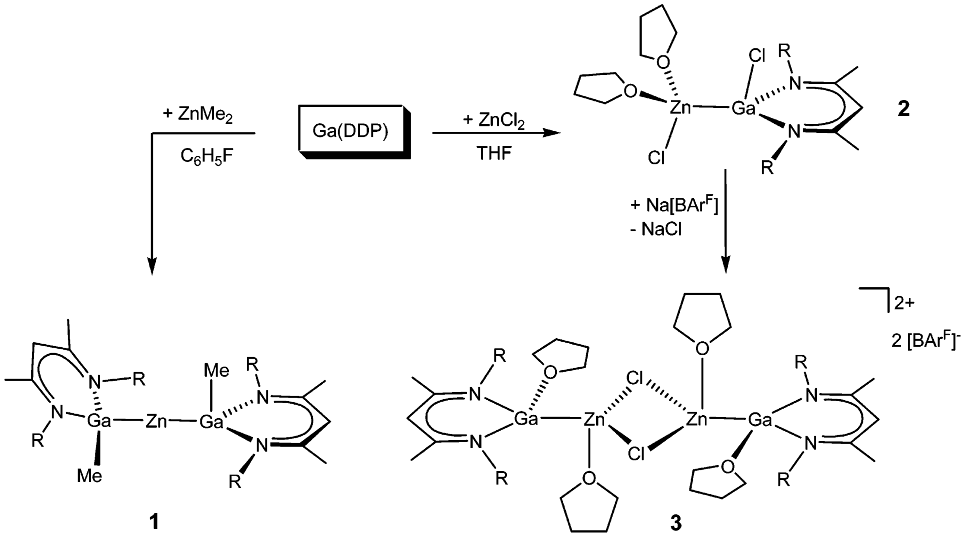
Scheme 1. Synthesis of Compounds **1**−**3** ($R = 2,6\text{-}{}^{i}Pr_2C_6H_3$)



by Jones et al.[4−6,9,15,19,22−26] The M−E bonding in all of these compounds has been extensively studied by quantum chemical methods on various levels of theory.[27−29] In general, one should note that the M−E bond is dominated by electrostatic effects, leading to M(δ^-) and E(δ^+) polarization due to the very strong σ-donor properties of the $[E^{I}R]^{a}$ ligands.[30] The π(M−E) back-bonding is typically rather weak, and its contribution to the bonding heavily depends on the particular types of σ/π donor/acceptor properties of the supporting group R. As an extreme case, the complex cation $[GaPt(GaCp^*)_4]^+$ may be quoted here. This complex features a naked Ga^+ cation in a terminal position bonded to the 18-electron closed-shell $[Pt(GaCp^*)_4]$. The calculations point toward equally strong electrostatic and covalent σ and π *acceptor* interactions but without any σ-donor influence caused by the remaining lone pair at the Ga^{I} center.[31,32] Looking at the large number of M−E complexes of these types of ligands reported to date, the elements of the Zn group, Zn, Cd, and Hg, have so far remained elusive. Two examples with very short Hg−In interactions are known,[33] whereas no molecular complexes of Hg and Cd with the lighter group 13 ligands $[Al^{I}R]^{a}$ or $[Ga^{I}R]^{a}$ have been isolated and characterized so far. Most recently, however, Jones et al. communicated on the salt elimination reaction of $[Ga\{[N(Ar)C(H)]_2\}]^-$ with N,N-chelated zinc chloride complexes to give the very first examples of compounds featuring a Zn−Ga bond.[23] This report prompted us to present here our results on the synthesis and structural characterization of some related new compounds with Zn−Ga bonds, namely, $[\{(DDP)GaMe\}_2Zn]$ (**1**), $[\{(DDP)GaCl\}ZnCl(THF)_2]$ (**2**), $[\{THF\cdot Ga(DDP)\}Zn(THF)(\mu\text{-}Cl)]_2[BAr^F]_2$ (**3**), and $[Zn(GaCp^*)_4][BAr^F]_2$ (**4**) (THF = tetrahydrofuran; $[BAr^F] = [B\{C_6H_3(CF_3)_2\}_4]$).

2. Results and Discussion

Using the *anionic* five-membered heterocycles of the type $[Ga\{[N(Ar)C(H)_2\}]^-$ as ligands evidently implies the substitution of halides from appropriate metal precursors via salt elimination reactions resulting in neutral complexes with three-coordinated Ga centers.[4,19,23,24] In addition, the substitution of weakly bound neutral ligands such as olefins is possible, leading to anionic complexes.[14] Also, the insertion of $[Ga\{[N(Ar)C(H)_2\}]^-$ into metal−halide bonds is observed but invariably leads to the elimination of the paramagnetic Ga^{II} dimers.[34] In contrast to that, the related *neutral* six-membered heterocycle [Ga(DDP)] typically inserts into metal-halide bonds to give neutral complexes with a M−Ga−X motif (X = halide), and four-coordinated Ga^{I} centers, as we have recently reported for Rh^{I} [10] as well as Au^{I} [20] complexes. The formally anionic fragment $[Ga(Cl)(DDP)]^-$ coordinated to a formally cationic metal center can thus be viewed as being isolobal to phosphanes PR_3 or arsanes AsR_3 with similar bonding properties and a four-coordinated ligator atom.

2.1. Insertion Reaction of [Ga(DDP)] into Zn−CH$_3$ and Zn−Cl Bonds. The reaction of [Ga(DDP)] with Me_2Zn in a ratio of 2:1 in fluorobenzene at room temperature gives

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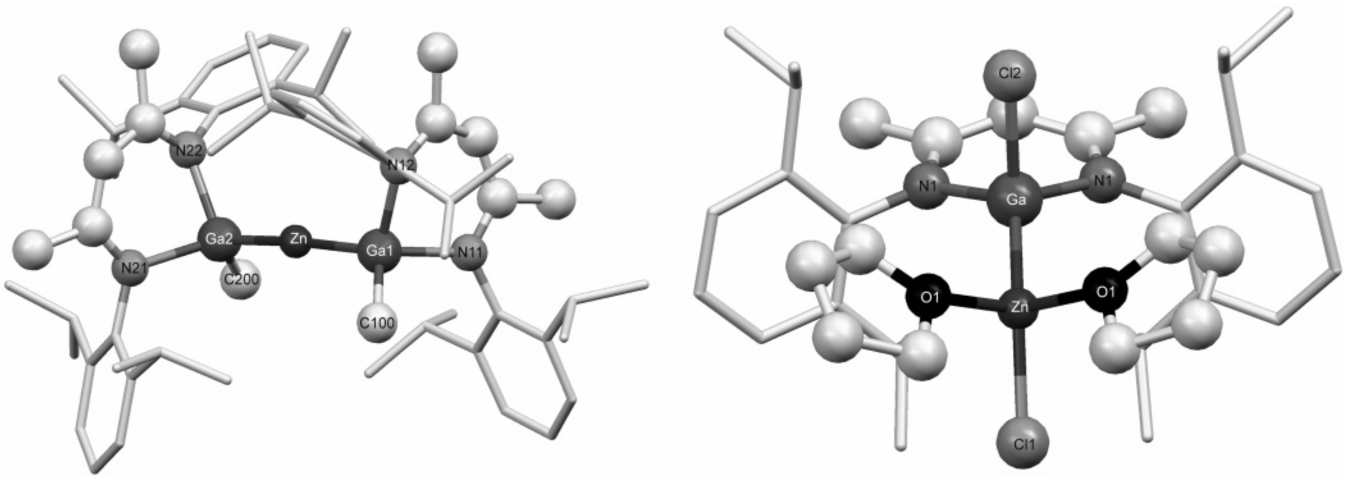

Figure 1. Mercury plots of **1** (left) and **2** (right). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) of **1**: Zn1−Ga1 2.4631(7), Zn1−Ga2 2.4609(7), Ga1−C100 1.995(3), Ga2−C200 1.984(4), Ga1−N11 2.027(3), Ga1−N12 2.012(3), Ga2−N21 2.027(3), Ga2−N22 1.998(3), N11−C3 1.322(4), N12−C1 1.327(4), N21−C32 1.325(4), N22−C30 1.323(4); Ga1−Zn1−Ga2 173.61(2), N11−Ga1−N12 90.86(11), N21−Ga2−N22 91.18(12), Zn1−Ga1−C100 121.14(10), Zn1−Ga2−C200 122.00(11); C100−Ga1−Ga2−C200 93.4. Selected bond lengths (Å) and angles (deg) of **2**: Ga−Zn 2.3920(6), Zn−O1 2.098(2), Zn−Cl1 2.2016(14), Ga−Cl2 2.2820(10), Ga−N1 1.965(2), N1−C1 1.335(3); N1−Ga−N1* 94.18(13), Zn−Ga−Cl2 111.31(3), Cl1−Zn−Ga 138.07(4), O1−Zn−O1* 87.26(17); Cl1−Ga−Zn−Cl1 180.0.

the insertion product **1** as orange-red crystals in yields of around 80% (Scheme 1). Compound **1** was found to be air-sensitive in solution as well as in the solid state but can be stored in an inert gas atmosphere for several weeks without decomposition. The compound is well soluble in common aprotic organic solvents like hexane, THF, or benzene. Several attempts to remove the methyl groups of **1** by protonation with $[H(OEt_2)_2][BAr^F]$ in fluorobenzene aiming at methane elimination and thus leading to the salt $[\{(DDP)Ga\}_2Zn][BAr^F]_2$ as a potential product were not successful. Instead, the deposition of a gray, obviously metallic precipitate was observed. Because no well-defined products could be isolated and characterized, no further attempts to optimize the conditions were undertaken.

The ^1H NMR spectrum of **1** in $CDCl_3$ at room temperature displays one set of signals for the DDP ligand, with a reduced (C_s) symmetry (e.g., two signals for the ^iPr-CH protons, indicative of a lack of rotation around the C−N bond of the aryl group). The $^iPr-CH_3$ protons give rise to four distinct doublet signals at 1.28, 1.24, 1.22, and 1.09 ppm, whereas a signal at −0.45 ppm can be assigned to the protons of the methyl groups bound to the Ga atoms. The ^{13}C NMR spectrum is in good agreement with these results. Deep-orange-red crystals of **1** suitable for single-crystal X-ray analysis were obtained by crystallization from *n*-hexane at −30 °C overnight. The molecular structure of **1** in the solid state is shown in Figure 1 (left). In addition, Figure 1 (right) shows the molecular structure of **2**, the synthesis and characterization of which are discussed below.

Compound **1** shows a linear two-coordination of the central Zn atom by the Ga atoms [Ga−Zn−Ga = 173.61(2)°] with equal Ga−Zn bond distances of 2.4631(7) and 2.4609(7) Å. These bond lengths are significantly longer than those in $[\{^iPr_2NC[N(Ar)]_2\}ZnGa\{[N(Ar)C(H)]_2\}]$ [2.3230(7) Å] but comparable to those in $[(tmeda)Zn\{Ga\{[N(Ar)C(H)]_2\}\}_2]$ [Ar = 2,6-$^iPr_2C_6H_3$; 2.4491(17) and 2.4307(17) Å].[23] In general, the M−E bond distances can vary over quite a large range depending on the coordination number at the group 13 metal, and the distance does not simply reflect the bond order. In the course of the reaction, the [Ga(DDP)] ligand inserts into the Zn−Me bond, giving a distorted tetrahedral geometry at the Ga center. The {MeGa(DDP)} moieties are oriented perpendicular to each other (torsion angle C100−Ga1−Ga2−C200: 93.4°) to minimize steric strain in the complex. Averaging to 1.99 Å, the Ga−Me bond distances are distinctly longer than those in $[Me_2Ga(DDP)]$ (av 1.75 Å)[35] but more similar to that of [(Me)(Cl)Ga(DDP)] [1.956(2) Å],[36] the observation of which can be interpreted as an effect of the lower oxidation state and thus less electrophilic character of the Ga atom in **1**. The Ga−N bond distances of 1.998(3)−2.027(3) Å are in agreement with that explanation and are only slightly shorter than that in free [Ga(DDP)] (av 2.054 Å)[37] but similar to that found in [{(DDP)Ga}Au{Ga(DDP)Cl}] [1.984(6) Å for the {Ga(DDP)Cl} moiety].[20]

In contrast to the insertion of [Ga(DDP)] into the Zn−C bond of $ZnMe_2$, the reaction of $ZnCl_2$ with [Ga(DDP)] in a THF solution does not give the congener of **1**, namely, the compound $[\{(DDP)GaCl\}_2Zn]$. Rather, the compound **2** is obtained in quite good yields even in the case of a larger excess of [Ga(DDP)] (Scheme 1). The presence of the coordinating solvent THF instead of fluorobenzene may favor the formation of Zn−THF adducts and thus four-coordinated Zn species. The increased steric bulk of the DDP ligand (cone angle of ca. 270°) in comparison with $[Ga\{[N(Ar)C(H)]_2\}]^-$ (cone angle of ca. 180°) is likely to disfavor the formation of $[\{(DDP)GaCl\}_2Zn(THF)_2]$ as the hypothetical double-insertion product, which, however, would compare with the known a four-coordinated compound [(tmeda)Zn{Ga{[N(Ar)C-

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(H)]$_2$}}$_2$].[23] Several attempts to react $ZnCl_2$ with [Ga(DDP)] in fluorobenzene as a very polar, inert but noncoordinating solvent did not give any isolable products. Thus, the solvent-free congeners to **2** and **3** (vide infra) remain a synthetic challenge. Compound **2** is soluble in THF, Et_2O, or $CHCl_3$ and can be stored in the solid state in an inert gas atmosphere for several days without decomposition. The ^1H NMR spectrum of **2** in $CDCl_3$ shows one signal for the DDP-backbone proton at 5.27 ppm as well as signals indicating a C_{2v} symmetry around the {Ga(DDP)} moiety, which is not in accordance with the solid-state structure discussed below. Obviously, the chloro ligands exchange fast in solution, leading to coalescence of the DDP signals. However, even at low temperature (−60 °C), no significant splitting of the signals could be observed.

Pale-yellow prismatic crystals of **2** were grown by storing the solution at −30 °C overnight. The molecular structure of **2** in the solid state is shown in Figure 1 (right). Compound **2** crystallizes in the monoclinic space group $P2_1/m$, with only half of the molecule in the elemental cell and the THF ligand at the Zn being disordered, showing two THF moieties rotated by around 65.6°. The Zn atom is coordinated in a distorted tetrahedral geometry by two THF molecules, the chloro fragment, and the {ClGa(DDP)} fragment. The Zn−Cl bond [2.2016(14) Å] is slightly longer than those in the parent compound [$(THF)_2ZnCl_2$] [2.176(2) and 2.184(2) Å][38] but is well in the range for other Zn−Cl bonds reported in the literature. The same is true for the Zn−O bond distance, which is 2.098(2) Å in **2** and slightly longer than those in [$(THF)_2ZnCl_2$] [2.009(5) and 2.016(5) Å]. Interestingly, the Ga−Zn bond distance of 2.3920(6) Å is slightly shorter than that in **1** [2.4609(7) Å] and is well shortened with respect to four-coordinated Zn complex [(tmeda)Zn{Ga{[N(Ar)C(H)]$_2$}}$_2$] [2.4491(17) and 2.4307(17) Å] but significantly longer than that in [{^{i}Pr$_2$NC[N(Ar)]$_2$}ZnGa{[N(Ar)C(H)]$_2$}] [2.3230(7) Å], which features three-coordinated Zn.[23] These results indicate that the difference in the Zn−Ga bond length can be attributed to steric interactions of the coordinated group 13 ligands rather than being primarily related to the Zn coordination numbers, as was previously suggested for the five-membered heterocycle complexes.[23] The two Cl atoms, the Ga atom, and the Zn atom are coplanar (torsion angle Cl−Ga−Zn−Cl: 180°), with the Cl atoms being in the trans position to each other. Whereas the Ga−Cl bond distance [2.2820(10) Å] is significantly longer than those in [(DDP)$GaCl_2$] [2.218(1) and 2.228(1) Å],[35] it is similar to those in other L_nM[Ga(DDP)Cl] complexes such as [(Ph_3P)Au{Ga(DDP)Cl}] [2.290(2) Å], [{(DDP)Ga}Au{Ga(DDP)Cl}] [2.2837(16) Å],[20] or [(COE)(benzene)Rh{(DDP)GaCl}] [2.321(2) Å],[10] respectively (COE = cyclooctene). The comparably long Ga−Cl distance is in good agreement with the fluxional behavior of the chloro ligand observed in solution.

2.2. Cationic Complex with Zn−Ga Bonds. When **2** is reacted with 1 equiv of Na[BAr^F] in THF or fluorobenzene, no color change or precipitation took place. However, on storing the solution overnight at −30 °C, colorless needles of [{THF•Ga(DDP)}Zn(THF)(μ-Cl)]$_2$[BAr^F]$_2$ (**3**) were obtained in 72% yield (Scheme 1). No further reaction was observed upon the addition of another 1 equiv of Na[BAr^F] to **3**. Compound **3** can be stored in an inert gas atmosphere for several days without decomposition and was found to be soluble only in polar solvents such as THF or fluorobenzene but not in hexane or toluene, which matches with the ionic nature of the product. Again, the ^1H NMR spectrum of **3** in fluorobenzene at room temperature shows only one set of signals for a C_{2v}-symmetric {Ga(DDP)} moiety. This is in agreement with a fast exchange of the axially coordinated THF molecule, further supported by two broad signals for the THF ligands observed at 3.51 and 1.53 ppm, respectively. Similar NMR features were previously reported for the Au compound [{(DDP)Ga•THF}$_2$Au][BAr^F], which also shows only signals for a {Ga(DDP)} moiety in a C_{2v}-symmetric coordination.[20]

Colorless needles, suitable for single-crystal X-ray diffraction analysis could be obtained by cooling a saturated solution of **3** in fluorobenzene to −30 °C overnight. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with half of the molecule in the asymmetric unit. The molecular structure of **3** is depicted in Figure 2 and consists of a planar Zn_2Cl_2 core, with the two Cl atoms bridging the Zn centers. The Zn atoms show a distorted tetrahedral environment. The Zn−Cl bond distances are 2.3520(16) Å (Zn−Cl) and 2.3652(18) Å (Zn−Cl*), similar to those found in the halide-bridged complexes [{$Me_3Si)_3Si$}Zn(THF)(μ-Cl)]$_2$ (2.36 and 2.40 Å) or [{$(Me_3Si)_3Ge$}Zn(THF)(μ-Cl)]$_2$ (2.36 and 2.40 Å).[39] Whereas the Zn−Ga [2.3960(11) Å] bond distance is similar to those found in **2** [2.3920(6) Å] and therefore in between those found for [(tmeda)Zn{Ga{[N(Ar)C(H)]$_2$}}$_2$] [2.4491(17) and 2.4307(17) Å] and for [{^{i}Pr$_2$NC[N(Ar)]$_2$}-ZnGa{[N(Ar)C(H)]$_2$}] [2.3230(7) Å],[23] the Zn−O bond distance [2.021(4) Å] is slightly shorter than that in **2** [2.098(2) Å] but comparable to [$(THF)_2ZnCl_2$] [2.009(5) and 2.016(5) Å].[38] Similar to the situation discussed at [{(DDP)Ga•THF}$_2$Au][BAr^F],[10] the electrophilicity of the Ga center increases according to the coordination to the metal center. This is reflected in the weak coordination of a THF molecule to each Ga atom *perpendicular* to the least-squares plane of the heterocycle. The behavior of the Ga center of the {Ga(DDP)} moiety to act as a Lewis acid if a Lewis base approaches from above the ring plane corresponds well with the theoretical findings of Reiher and Sundermann.[29] The THF moieties coordinated to Zn and Ga are perpendicularly oriented to each other (torsion angle O−Ga−Zn−O: 90.08°), with the Ga−O bond distance in **3** [2.098(2) Å] being slightly shorter than that in [{(DDP)Ga•THF}$_2$Au][BAr^F] (av 2.16 Å).[10]

In contrast to [Ga(DDP)], [GaCp*] does not react with Me_2Zn in either THF or fluorobenzene. However, when [$H(OEt_2)_2$][BAr^F] and Me_2Zn were previously mixed in a 2.1 mole ratio at −30 °C and the resulting colorless solution, presumably containing solvated Zn^{2+} cations and/or [Zn^{2+}]-

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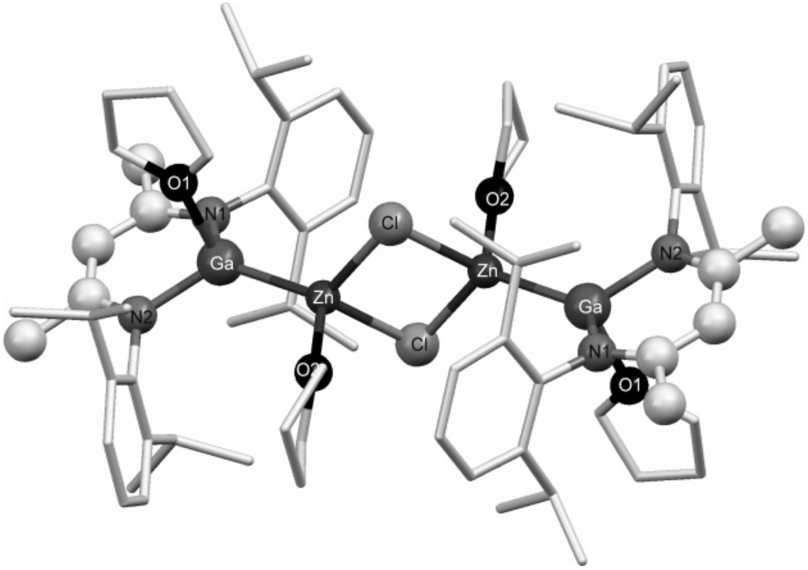
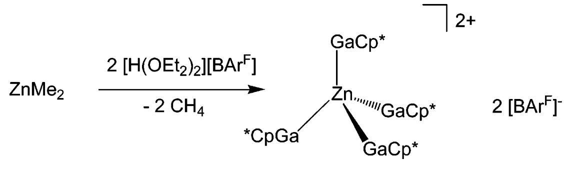


Figure 2. Mercury plot of **3**. H atoms and $[BAr^F]^-$ anions are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga−N1 1.926(5), Ga−N2 1.942(5), Ga−O1 2.105(4), Ga−Zn 2.3960(11), Zn−O2 2.021(4), Zn−Cl1 2.3520(16), Zn−Cl1* 2.3652(18), N1−C1 1.332(7), N2−C3 1.320(7); N1−Ga−N2 96.8(2), O1−Ga−Zn 107.43(13), Cl1−Zn−Cl1* 92.96(6), O2−Zn−Ga 116.13(12); O1−Ga−Zn−O2 90.07(18).

Scheme 2. Synthesis of Compound **4**



$[BAr^F]_2$ ion aggregates, was warmed to room temperature and then GaCp* added, colorless crystals of **4** could be obtained by slow diffusion of hexane into the concentrated solution overnight (Scheme 2). It should be noted that no reaction was observed when using $[Zn(Otf)_2]$ (Otf = $CF_3SO_3^-$) as the alternative Zn source. Besides the signals for the $[BAr^F]^-$ anion, the ^1H NMR spectrum of **4** in CD_2Cl_2 at room temperature expectedly shows only one signal for the coordinated GaCp* moieties at 2.03 ppm, which is in agreement with a presumably dynamic and highly symmetric homoleptic compound with η^5 coordination of the Cp* rings in solution. The molecular structure of **4** in the solid state is shown in Figure 3.

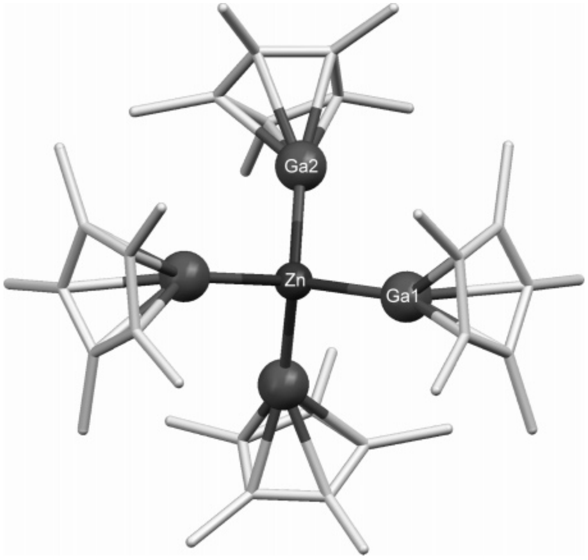


Figure 3. Mercury plot of the homoleptic complex cation $[Zn(GaCp^*)_4]^{2+}$ of **4**. H atoms and $[BAr^F]^-$ anions are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn−Ga1 2.4036(6), Zn−Ga2 2.4111(6), Ga1−Cp*$_{centroid}$ 1.861, Ga1−Cp*$_{centroid}$ 1.850; Ga1−Zn−Ga2 107.440(18), Ga1*−Zn−Ga2 108.510(17), Ga2−Zn−Ga2* 111.18(3), Ga1−Zn−Ga1* 113.80(3).

Compound **4** crystallizes in the monoclinic space group *C*2/*c*, with some CF_3 groups of the $[BAr^F]$ anion being slightly disordered. The Zn atom is coordinated by four Ga atoms in a distorted tetrahedral fashion. In contrast to the previously reported homoleptic complexes $[M(GaCp^*)_4]$ (M = Ni, Pd, and Pt),[40,41] which exhibit nearly *ideal* tetrahedral Ga−M−Ga angles of around 109°, the Ga−Zn−Ga angles in **4** vary from 107.44 to 113.80°, possibly because of packing effects of the $[BAr^F]^-$ anion in the unit cell. The Zn−Ga bond distances are 2.4036(6) and 2.4111(6) Å; these distances are shorter than those in **1** [2.4609(7) Å] or [(tmeda)Zn{Ga{[N(Ar)C(H)]$_2$}}$_2$] [2.4491(17) and 2.4307(17) Å] but comparable to the ones in **2** [2.3920(6) Å] or **3** [2.3960(11) Å]. The Cp*$_{centroid}$−Ga distances range between 1.850 and 1.861 Å and are thus significantly shortened in comparison to the corresponding distance of the free [(η^5-Cp*)Ga] (2.08 Å)[42] and the complexes $[M(GaCp^*)_4]$ [M = Ni (2.00 Å), Pd (2.02 Å), and Pt (1.99 Å)].[40,41] Similar Cp*$_{centroid}$−Ga distances are found in [Cp*GaFe(CO)$_4$] (1.86 Å)[43] or [$(C_6F_5)_3$BGaCp*] (1.865 Å), for example.[44] This shortened Cp*$_{centroid}$−Ga distance indicates the increased electrostatic interaction and the strong σ donation of the Ga

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lone pair to the Zn^{2+} cation. The Cp* moieties are nearly symmetrically η^5-bonded to the Ga centers [Ga1−C bond distances 2.197(4)−2.225(4) Å; Ga2−C bond distances 2.203(4)−2.236(4) Å], but a substantial deviation from linearity is observed for the $Cp^*_{centroid}$−Ga−Zn vectors (165° and 170°). This deviation is known for other [M(GaCp*)] (M = Ni, Pd, and Pt) complexes and is caused by repulsive intramolecular interactions between the Cp* methyl groups of different Cp*Ga ligands (cone angle ∼ 112°).

3. Conclusion

We have successfully synthesized and structurally characterized several new examples of compounds with Zn−Ga bonds by insertion of the bulky bisimidinate Ga(DDP) into Zn−Me and Zn−Cl bonds. Thus, the reaction of $ZnMe_2$ with [Ga(DDP)] yields the insertion product $[\{(DDP)GaMe\}_2Zn]$ (**1**), with two {MeGa(DDP)} moieties coordinating to the Zn center. Compound **1** exhibits a perpendicular orientation of the {MeGa(DDP)} moieties in the solid state, which is explained by the steric bulk of the DDP ligand. The complex $[\{(DDP)GaCl\}Zn(Cl)(THF)_2]$ (**2**), synthesized by the reaction of $ZnCl_2$ with [Ga(DDP)] in THF, only shows a single insertion of one [Ga(DDP)] moiety into one Zn−Cl bond. In contrast to the related reaction with the anionic five-membered heterocycle $[Ga\{[N(Ar)C(H)]_2\}]^-$, the Cl remains coordinated at the Ga center and allows subsequent substitution reactions. Thus, salt elimination of **2** with $Na[BAr^F]$ yields the cationic complex $[\{THF{\cdot}Ga(DDP)\}Zn(THF)(\mu\text{-}Cl)]_2[BAr^F]_2$ (**3**). The rather strong electrophilicity of the coordinated Ga center of the [Ga(DDP)] ligand in cationic complexes becomes visible by the axial coordination of THF molecules to each Ga center in **3**. Additionally, the reaction of Me_2Zn with $[H(OEt_2)_2][BAr^F]$ and [GaCp*] yield in the compound $[Zn(GaCp^*)_4][BAr^F]_2$ (**4**), featuring the homoleptic complex cation $[Zn(GaCp^*)_4]^{2+}$, which represents the Zn analogue of the well-known neutral homoleptic complexes $[M(GaCp^*)_4]$ (M = Ni, Pd, and Pt). This example nicely illustrates the Lewis base bonding properties of [GaCp*] to metal cations similar to those of classical Werner-type complexes such as $[Zn(NH_3)_4]^{2+}$.

4. Experimental Section

4.1. Methods and Techniques. All manipulations were carried out in an atmosphere of purified Ar using standard Schlenk and glovebox techniques. Hexane, Et_2O, toluene, and THF were dried using an mBraun Solvent Purification System, and fluorobenzene and benzene were dried by passing through a column filled with activated Al_2O_3. Deuterated solvents ($CDCl_3$ and C_6D_6) are used as received, dried over an activated molecular sieve (4 Å), and degassed by bubbling dried Ar through the solvents. The final H_2O content in all solvents was checked by Karl Fischer titration and did not exceed 5 ppm. The starting compounds [Ga(DDP)],[37] GaCp*,[8] $[H(OEt_2)_2][BAr^F]$,[45] and $Na[BAr^F]$[46,47] ($[BAr^F] = [B\{C_6H_3\text{-}(CF_3)_2\}_4]$) were prepared and purified according to literature methods. Solutions of Me_2Zn were prepared by dissolving an appropriate amount of the commercially available (Fluka) and as-received alkyl in hexane or C_6H_5F. $ZnCl_2$ was purchased from Riedel-de-Haen and used as received. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr-Universität Bochum. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer (^1H NMR, 250.1 MHz; ^{13}C NMR, 62.9 MHz) in C_6D_6 at 298 K, if not stated otherwise. Chemical shifts are given relative to tetramethylsilane and were referenced to the solvent resonances as internal standards.

All crystal structures were measured on an Oxford Excalibur 2 diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods using *SHELXS-97* and refined against F^2 on all data by full-matrix least squares with *SHELXL-97*. Details to the data collection, structure solutions, and refinements of the new compounds **1**−**4** are available as Supporting Information (see below).

4.2. Synthetic Procedures and Analytical Data. $[\{(DDP)GaMe\}_2Zn]$ (1). A sample of [Ga(DDP)] (200 mg, 0.41 mmol) was dissolved in 5 mL of fluorobenzene at room temperature. A volume of 1.66 mL of a 0.25 M solution of $ZnMe_2$ in fluorobenzene was added slowly. The reaction mixture turned to deep-orange and was stirred for an additional 1 h at room temperature. The solvent was removed in vacuo, and the orange-yellow solid was redissolved in ca. 2 mL hexane. Cooling the solution to −30 °C overnight gave deep-orange-red crystals of **1** in 178 mg yield (81%). ^1H NMR ($CDCl_3$, 25 °C): δ 7.28−7.13 (m, 12H, Ar), 5.24 (s, 2H, γ-CH), 3.55 (sept, 4H, C*H*(Me)$_2$, J_{HH} = 6.72 Hz), 3.07 (sept, 4H, C*H*(Me)$_2$, J_{HH} = 6.85 Hz), 1.85 (s, 12H, CH_3), 1.28 (d, 12H, CH(*Me*)$_2$, J_{HH} = 7.02 Hz), 1.24 (d, 12H, CH(*Me*)$_2$, J_{HH}= 6.93 Hz), 1.22 (d, 12H, CH(*Me*)$_2$, J_{HH} = 6.57 Hz), 1.09 (d, 12H, CH(*Me*)$_2$, J_{HH} = 6.78 Hz), −0.49 (s, 6H, Ga*Me*). ^{13}C NMR ($CDCl_3$, 25 °C): δ 169.3 (*C*N), 145.7 (*C*Me), 142.7 (Ar), 139.7 (Ar), 127.1 (Ar), 124.9 (Ar), 123.5 (Ar), 97.1 (γ -C), 28.9 (*C*HMe$_2$), 27.7 (CH*Me*$_2$), 26.8 (C*Me*), 24.8 (C*Me*), 24.1 (CH*Me*$_2$). 23.7 (CH*Me*$_2$), 23.7 (CH*Me*$_2$), 1.0 (Ga*Me*). Elem anal. Calcd (found) for $C_{60}H_{88}Ga_2N_4Zn$: C, 67.34 (69.69); H, 8.29 (8.57); N, 5.24 (5.06).

A typical experimental approach to remove the methyl groups of **1** was as follows: 100 mg (0.093 mmol) of **1** was dissolved in 5 mL of C_6H_5F, and $[H(OEt_2)_2]$[BArF] (100 mg, 0.093 mmol) was added at room temperature. After the resulting solution was stirred for 2 min, a gray/black insoluble precipitate formed. Additionally, performing the reaction at lower temperature (−30 °C) did not change the outcome of the reaction.

$[\{(DDP)GaCl\}Zn(Cl)(THF)_2]$ (2). Samples of $ZnCl_2$ (55 mg, 0.41 mmol) and [Ga(DDP)] (200 mg, 0.41 mmol) were dissolved in 5 mL of THF at room temperature. The pale-yellow solution was stirred for 1 h, the solvent was reduced to ca. 2 mL, and the mixture was then stored at −30 °C overnight. Big colorless prismatic crystals of **2** were obtained in 250 mg yield (79%). ^1H NMR ($CDCl_3$, 25 °C): δ 7.34−7.20 (m, 6H, Ar), 5.27 (s, 1H, γ -CH), 3.83 (br t, 8H, THF), 3.24 (sept, 4H, C*H*(Me)$_2$, J_{HH}= 6.78 Hz), 1.90 (br., 14 H, overlapping signal of THF and CH_3), 1.33 (d, 12H, CH(*Me*)$_2$, J_{HH} = 6.70 Hz), 1.18 (d, 12H, CH(*Me*)$_2$, J_{HH} = 6.84 Hz). ^{13}C NMR ($CDCl_3$, 25 °C): δ 171.5 (*C*N), 144.4 (*C*Me), 137.9 (Ar), 127.9 (Ar), 124.5 (Ar), 97.1 (γ -C), 68.7 (THF), 28.5 (THF), 25.5 (C*Me*), 25.1 (C*Me*), 24.8 (CH*Me*$_2$), 23.9 (CH*Me*$_2$). Elem anal. Calcd (found) for $C_{37}H_{57}Cl_2GaN_2O_2Zn$: C, 57.87 (57.89); H, 7.48 (7.56); N, 3.65 (3.98).

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[{(DDP)Ga·THF}Zn(Cl)(THF)]$_2$[BAr^F]$_2$ (3). A mixture of 100 mg of **2** (0.127 mmol) with 1 equiv of Na[Bar^F] (100 mg, 0.127 mmol) in THF or fluorobenzene was stirred at room temperature for 1 h. By cooling the colorless solution to −30 °C overnight, colorless needles of **3** were obtained in 72% yield (173 mg). ^{1}H NMR (7:1 C_6H_5F/C_6D_6, 25 °C): δ 8.33 (br, 16H, BAr^F), 7.63 (s, 8H, BAr^F), 7.36−6.50 (overlying signals of FPh and aromatic protons, not interpretable), 5.24 (s, 2H, γ-CH), 3.51 (br s, 16H, THF), 2.78 (sept, 8H, C*H*Me$_2$, J_{HH} = 6.76 Hz), 1.60 (s, 12H, C*CH*$_3$), 1.53 (br m, 16H, THF), 1.16 (d, 24H, CH*Me*$_2$, J_{HH} = 6.82 Hz), 1.09 (d, 24H, CH*Me*$_2$, J_{HH} = 6.81 Hz). ^{13}C NMR (7:1 C_6H_5F/C_6D_6, 25 °C): Because of the large ^{13}C NMR signals for the solvent, no assignment of the ^{13}C NMR signals of the aromatic carbons of this sample could be done. δ 98.7 (γ-C), 68.5 (THF), 28.5 (C*H*Me$_2$), 25.5 (THF), 25.1 (C*Me*), 23.9 (CH*Me*$_2$), 23.5 (CH*Me*$_2$). Elem anal. Calcd (found) for $C_{138}H_{138}B_2Cl_2F_{48}Ga_2N_4O_4Zn_2$: C, 51.94 (52.08); H, 4.36 (4.35); N, 1.76 (1.66).

[Zn(GaCp*)$_4$][BAr^F]$_2$ (4). A sample of 200 mg of [H(OEt$_2$)$_2$][BAr^F] (0.198 mmol) was dissolved in 5 mL of C_6H_5F and cooled to −30 °C. After the addition of 0.1 mL of a 2 M solution of Me$_2$Zn in toluene under vigorous stirring, the solution was warmed to room temperature and an excess of [GaCp*] (4.5 equiv, 182 mg, 0.89 mmol) was added. After the reaction mixture was stirred for ca. 30 min, the solvent was reduced to approximately 2 mL. Diffusion of ca. 10 mL of hexane overnight gave colorless crystals of **4**. Yield: 196 mg (76%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.73 (br t, 16H, BAr^F), 7.57 (br s, 8H, BAr^F), 2.03 (s, 60H, Cp*). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 163.5 (q, J = 50 Hz, BAr^F), 135.4 (BAr^F), 129.5 (q, J = 31.5 Hz, BAr^F), 127.3 (BAr^F), 123.3 (C_5Me_5), 118.1 (BAr^F), 10.0 (C_5Me_5). Elem anal. Calcd (found) for $C_{104}H_{84}B_2F_{48}Ga_4Zn$: C, 47.83 (47.38); H, 3.24 (3.51).

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Supporting Information Available: Crystallographic data file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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