

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Synthesis and Structures of Mononuclear and Dinuclear Gallium Complexes with α -Diimine Ligands: Reduction of Metal or Ligand?

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yanxia Zhao^{a*}, Yanyan Liu^a, Qian-Shu Li^b, Ji-Hu Su^c

Reduction of the dichloro gallium(III) α -diimine complex $[(L^{iPr})^{2-}GaCl_2]$ (**1**, $L^{iPr} = [(2,6\text{-}iPr_2C_6H_3)NC(Me)]_2$) by different equivalents of sodium metal afforded the gallium complexes $[(L^{iPr})^{2-}Ga^{II}(\mu_2\text{-Cl})_2Na(THF)_4]$ (**2**) and $[(Na(THF)_6)^+ \cdot (L^{iPr})^{2-}Ga-Ga(L^{iPr})^{2-}]$ (**3**). Interestingly, in complex **2** a Na^+Cl^- ion pair is incorporated, while compound **3** is an anionic digallium complex. Moreover, a cationic gallium complex with a tetrachlorogallium(III) counter anion, $[(LGaCl_2)^+ \cdot (GaCl_4)^-]$ (**4**), was accessed from the reaction of $GaCl_3$ with 0.5 equiv of ligand L^{iPr} . In contrast, reaction of $GaCl_3$ with the doubly reduced anion (Na_2L^{2-}) of the smaller α -diimine ligands L^{Me} ($[(2,6\text{-}Me_2C_6H_3)NC(Me)]_2$) or L^{Et} ($[(2,6\text{-}Et_2C_6H_3)NC(Me)]_2$) yielded the Ga–Ga-bonded complexes $[(L^{Et})^{2-}ClGa^{II}-Ga^{II}Cl(L^{Et})^{2-}]$ (**5**) and $[(L^{Me})^{2-}ClGa^{II}-Ga^{II}Cl(L^{Me})^{2-}]$ (**6**). Here L is the neutral α -diimine ligand, L^{2-} represents the monoanion, and L^{2-} is the dianionic form of the ligand. The complexes were characterized by X-ray diffraction and their electronic structures were studied by DFT computations.

Introduction

There is much interest in metal–metal-bonded compounds because of their novel structural and bonding features as well as specific reactivities¹. One effective method for synthesizing such dimetallic species is reductive coupling of high-valent metal complexes, which generally results in a lower (uncommon) formal oxidation state of the metal.² In these compounds the steric and electronic effects of the ligand play a key role in the stabilization of the low-valent and low-coordinate metal ions. The α -diimine agents are well-known ligands for both main group and transition metals.³ Moreover, such ligands are redox “noninnocent” and can be singly or doubly reduced to the monoanion and dianion, which have proven to be able to stabilize metal ions in a variety of oxidation states, thus leading to very interesting structures and properties.⁴ Using N-aryl-substituted α -diimine ligands, we have synthesized a series of dinuclear and mononuclear metal complexes by reduction of the metal halide precursors with alkali metals, from which interesting redox processes have

been observed.⁵

In the present work, we studied α -diimine gallium complexes. Organogallium compounds have been well established, and a number of gallium complexes derived from α -diimine ligands are known,⁶ including those with Ga–Ga bonds.⁷ Our goal is to study the effects of the noninnocence of α -diimine ligands on the structure and bonding of gallium complexes. In an effort to construct Ga–Ga-bonded compounds by reductive coupling of the $L^{2-}GaCl_2$ precursor (with accompanying elimination of NaCl), surprisingly, in compound **2** inclusion of the Na^+Cl^- ion pairs rather than elimination of NaCl salt has occurred. The similar Ga–Ga-bonded compound $[(dpp\text{-}bian)Ga-Ga(dpp\text{-}bian)]$ was also obtained by the reaction of $GaCl_3$ with reduced diimine ligands.^{7f} Herein, we report experimental and theoretical results of a series of gallium complexes, which display rich oxidation states of both gallium and α -diimine ligands. These include $[(L^{iPr})^{2-}Ga^{II}(\mu_2\text{-Cl})_2Na(THF)_4]$ (**2**), the anionic-cationic complexes $[(Na(THF)_6)^+ \cdot (L^{iPr})^{2-}Ga-Ga(L^{iPr})^{2-}]$ (**3**) and $[(LGaCl_2)^+ \cdot (GaCl_4)^-]$ (**4**), two Ga–Ga-bonded compounds, $[(L^{Et})^{2-}ClGa^{II}-Ga^{II}Cl(L^{Et})^{2-}]$ (**5**) and $[(L^{Me})^{2-}ClGa^{II}-Ga^{II}Cl(L^{Me})^{2-}]$ (**6**).

Results and Discussion

Synthesis and structures of complexes **2** and **3**.

The precursor $[(L^{iPr})^{2-}GaCl_2]$ (**1**)⁹ was prepared by the reaction of anhydrous $GaCl_3$ with $[NaL^{iPr}]$ (generated in situ from L^{iPr} and 1 equiv of sodium). Reduction of **1** with 1, 2, and 2.5 equiv

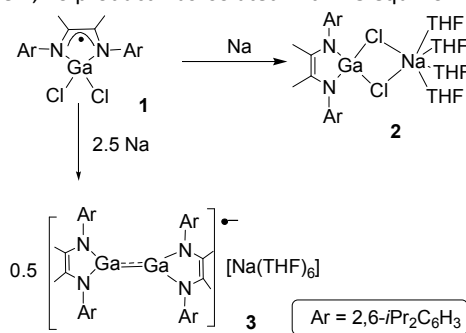
^aKey Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710127, China. E-mail: zhaoyx@nwu.edu.cn

^bCenter for Computational Quantum Chemistry, South China Normal University, Guangzhou 510631, China

^cDepartment of Modern Physics, University of Science and Technology of China, Hefei 230026, China

† Electronic supplementary information (ESI) available. Structure information and DFT calculations. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

of Na, respectively, led to the complexes **2**, digallane,⁸ and **3** (Scheme 1; no product was isolated with 1.5 equiv of Na).



Scheme 1. Synthesis of complexes **2** and **3**.

In these complexes, the monoanionic ligand in precursor **1** is further reduced to the dianion, as indicated by the C–N (1.430–1.435 Å) and C–C (1.334–1.349 Å) bond lengths of the C₂N₂ backbone.⁵ Correspondingly, the formal Ga^{III} ion is unchanged in **2** but is reduced to the Ga(+1.5) oxidation state in **3**, respectively. The solid state structures of the complexes were studied by X-ray crystal diffraction. Moreover, theoretical studies were performed at the B3LYP/6-31g* level to get deeper insights into their electronic structures.

[(L^{*i*Pr})²⁻Ga^{III}(μ₂-Cl)₂Na(THF)₄] (2). Upon uptake of 1 equiv of electrons, only the ligand (L^{*i*Pr})^{•-} in the precursor **1** was reduced to the dianion, and the Ga^{III} center remained intact in the mononuclear product [(L^{*i*Pr})²⁻Ga^{III}(μ₂-Cl)₂Na(THF)₄] (**2**) (Fig. 1). Notably, an “extra” Cl⁻ ion and a Na⁺ cation are included in the structure. The Ga atom sits in a tetrahedral environment containing the two N atoms of one bidentate ligand and two Cl⁻ ions. The two Cl atoms act as bridges between the Ga and Na atoms, and the sodium ion is further solvated by four THF molecules, thus forming a distorted octahedral geometry about the Na⁺ ion.

A simplified model [(L'Ga(μ₂-Cl)₂Na(H₂O)₄] (**2H**, L' = (PhNCH)₂), in which the 2,6-diisopropylphenyl groups were replaced by phenyl, Me groups on the central C₂N₂ moiety by H atoms, and THF by H₂O molecules, was used for DFT computations of complex **2** (Fig. S3 ESI[†]). The calculated Ga–Cl bond lengths (2.266 and 2.315 Å) are slightly longer than the X-ray data (2.214(1) and 2.208(1) Å) in **2**. Nevertheless, natural population analysis (NPA) shows a significant positive charge (1.56) on the Ga atom. This value compares well with that of **1H** (1.42), which features a formal oxidation state of +3 for Ga (Table S2 ESI[†]). On the other hand, the L' fragment accumulates more negative partial charges, from –0.46 (**1H**) to –1.31 (**2H**), thus indicating the reduction of the radical monoanionic α-diimine ligand into the dianion.

[(Na(THF)₆)⁺•[(L^{*i*Pr})²⁻Ga–Ga(L^{*i*Pr})²⁻]] (3). Addition of 2.5-fold Na to complex **1** in THF solution resulted in the one-electron-reduced product [(Na(THF)₆)⁺•[(L^{*i*Pr})²⁻Ga–Ga(L^{*i*Pr})²⁻]] (**3**), which is composed of a [Na(THF)₆]⁺ cation and a [LGaGaL]^{•-} radical anion (Fig. 2). The main structural backbone of the anionic part (Ga–Ga bond) is similar to that of the neutral digallane⁸; however, due to their different oxidation states,

there are significant differences between them. In the anion [(L^{*i*Pr})²⁻Ga–Ga(L^{*i*Pr})²⁻]^{•-} of **3**, each gallium ion is three-coordinate with two N atoms and the other Ga atom. The coordination geometry deviates severely from trigonal planar and can be described as “trigonal pyramidal” (the Ga atom is out of the GaN₂ plane by 2.47 Å). The Ga–N bond lengths of the anion (av. 1.903 Å) are somewhat shortened relative to those of the neutral digallane (1.924 Å)⁸.

Radical anionic digallanes have been reported previously.¹⁰ In complex **3**, the Ga–Ga distance (2.472(1) Å) is slightly longer than that in neutral digallane (2.455(1) Å), and is somewhat longer than those in the analogous anionic digallanes, [(*i*Pr₃C₆H₂)₂Ga–Ga(*i*Pr₃C₆H₂)₂]^{•-} (2.343(2) Å)^{10a} and [{(Me₃Si)₂CH}₂Ga–Ga{CH(SiMe₃)₂}]^{•-} (2.401(1) Å).^{10b} However, it is obviously shorter than the Ga=Ga double bond length in digallene Ar'GaGaAr' (2.6268(7) Å, Ar' = 2,6-(2,6-*i*Pr₂C₆H₃)₂C₆H₃).¹¹ Notably, it has been shown that the Ga=Ga double bonds can be significantly weaker than single bonds, and the compounds can easily dissociate to monomers in solution.¹²

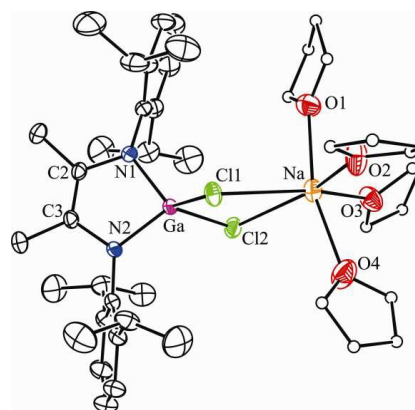


Fig. 1. Molecular structure of **2** (thermal ellipsoids are set at the 20% probability level; H atoms are omitted and C atoms of THF are drawn as smaller spheres for clarity). Selected bond lengths (Å) and angles (°): C2–N1 1.430(4), C3–N2 1.415(4), C2–C3 1.336(5), Ga–N1 1.860(2), Ga–N2 1.857(3), Ga–Cl1 2.214(1), Ga–Cl2 2.208(1), Na–Cl1 2.932(1), Na–Cl2 2.970(1); N1–Ga–N2 90.20(1), Cl1–Ga–Cl2 98.70(4), Cl1–Na–Cl2 69.29(4).

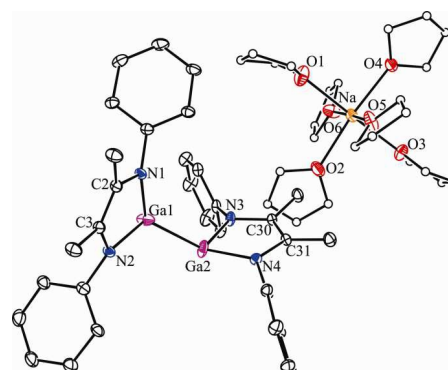


Fig. 2. Molecular structure of **3** (thermal ellipsoids are set at the 20% probability level; *i*Pr groups and H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): C2–N1 1.410(8), C3–N2 1.415(8), C2–C3 1.365(9), Ga1–N1 1.889(5), Ga1–N2 1.898(5), C30–N3 1.414(7), C31–N4 1.426(8), C30–C31 1.361(9), Ga2–N3 1.905(5), Ga2–N4 1.923(5), Ga1–Ga2 2.472(1); N1–Ga1–N2 87.10(2), N3–Ga2–N4 87.20(2).

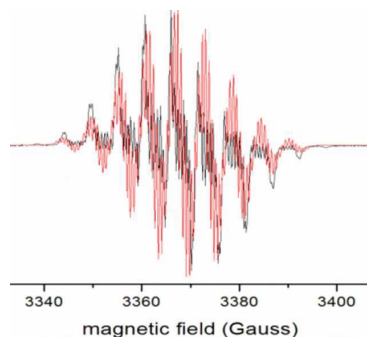
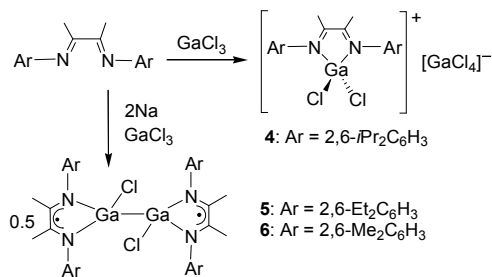


Fig. 3. EPR spectrum of complex **3** in THF at room temperature (black: experimental; red: simulated)

The EPR spectrum of compound **3** confirms its radical spin density is centered around Ga–Ga radical character (Fig 3), showing the expected paramagnetic signal similar to that reported for metal complexes that contain a one-electron Ga–Ga π -bond resulting from the overlap of two Ga 4p orbitals.¹⁰ With respect to the isotopic ^{69}Ga (60.1%) and ^{71}Ga (39.9%), the Ga–Ga is a complicated isotope composition of $^{69,69}\text{Ga}$, $^{69,71}\text{Ga}$, $^{71,69}\text{Ga}$ and $^{71,71}\text{Ga}$. For clarity, the $^{69,69}\text{Ga}$ and $^{71,71}\text{Ga}$ are used to in the EPR simulation. The hyperfine constants are $a(^{14}\text{N}) = 5.3$ G (four equivalent ^{14}N), $a(^{69}\text{Ga}) = 0.5\text{G}$ and $a(^{71}\text{Ga}) = 0.65$ G (two equivalent Ga). A contaminant signal of the ligand radical is overlapping therein with $a(^{14}\text{N}) = a(^1\text{H}) = 5.3$ G (two equivalent ^{14}N , and six equivalent ^1H) (Fig. S1 ESI[†]).

DFT computations were done for the Ga–Ga-bonded compound **3** by using a simplified model $[\text{L}^*\text{GaGaL}^*]^{2+}$ (**3H**) (Fig. S3 ESI[†]). The optimized structure is very close to that obtained from X-ray diffraction. The theoretical Ga–Ga distance (2.459 Å) compares with that for **3** (2.472(1)Å). The Wiberg bond index gives a Ga–Ga bond order of 0.84, which is marginally smaller than that calculated for neutral digallane (0.90). Previous calculations on a variety of model species with a Ga=Ga double bond, including HGaGaH, MeGaGaMe and PhGaGaPh, pointed to weak metal–metal bonding,¹³ which is consistent with literature reports on related digallenes that show relatively weak Ga–Ga bonding and a bond order significantly less than unity.¹¹ The natural charges on Ga (0.54 and 0.55) are much smaller than that in **1H** (1.42), **2H** (1.56). Moreover, there is a lot increase of the total negative charge on the α -diimine ligand L, from -0.461 (**1H**) to -1.010 (**3H**) (Table S2).



Scheme 2. Synthesis of complexes **4–6**.

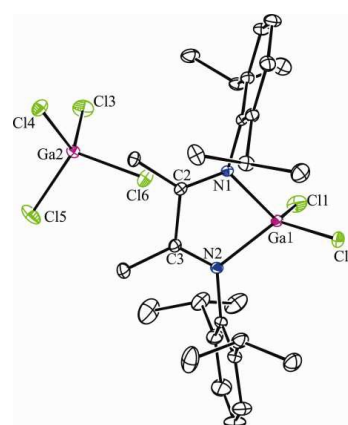


Fig. 4. Molecular structure of **4** (thermal ellipsoids are set at the 20% probability level; H atoms are omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): C2–N1 1.276(4), C3–N2 1.284(4), C2–C3 1.527(4), Ga1–N1 1.990(2), Ga1–N2 1.978(2), Ga1–Cl1 2.1126(8)2.113(1), Ga1–Cl2 2.1135(9)2.114(1), Ga2–Cl3 2.1920(8)2.192(1), Ga2–Cl4 2.1585(9)2.158(1), Ga2–Cl5 2.1632(9)2.163(1), Ga2–Cl6 2.1660(8)2.166(1); N1–Ga1–N2 82.43(1), Cl1–Ga1–Cl2 117.92(4).

Synthesis and structures of complexes **4–6**.

$[(\text{LGaCl}_2)^+\bullet(\text{GaCl}_4)^-]$ (**4**). The cationic gallium halide complex **4** with a $[\text{GaCl}_4]^-$ counter anion was obtained from the reaction of α -diimine ligand L^{Pr} and 2 equiv of GaCl_3 (Fig. 4). Similar compounds with $[\text{L}^*\text{GaCl}_2]^+$ cation and $[\text{GaCl}_4]^-$ anion are known for diimine, bisguanidine diphosphane and diarsane ligands.¹⁴ In the cationic part of **4**, the C–C (1.527(4) Å) and C–N (1.276(4) and 1.284(4) Å) bond distances of the central C_2N_2 core of α -diimine ligand are typical for the neutral form of the ligand.⁵ This is significantly different from the anionic $[\text{LGaCl}_2]^-$ complex in compound **2**, which contains a relatively stable dianion, $(\text{L}^{\text{Pr}})^{2-}$, in the enediamido ($\text{N}=\text{C}=\text{N}$) form. Thus, despite the same Ga^{III} center in both compounds, the difference of the redox forms of the ligand leads to the overall positive and negative charge of the complex in **2** and **4**. As a result, the Ga–N bond distances in **4** (1.990(2) and 1.978(2) Å) are considerably longer than those in **2** (1.860(2) and 1.857(3) Å), which are typical $\text{N}\rightarrow\text{Ga}$ donor–acceptor bond distances. The computed Ga–N (average 1.986 Å) bond lengths in **4** compare well with the experimental values, with an average bond order of 0.33 which is smaller than that in compound **2** (0.48). The N–Ga–N bond angle is more acute in **4** (82.43(1) $^\circ$) than in **2** (90.24(8) $^\circ$), while the Cl1–Ga–Cl2 angle (117.92(4) $^\circ$) is much larger than that in the latter (98.67(3) $^\circ$).

$[(\text{L}^{\text{Et}})^+\text{ClGa}^{\text{II}}-\text{Ga}^{\text{II}}\text{Cl}(\text{L}^{\text{Et}})^+]$ (**5**) and $[(\text{L}^{\text{Me}})^+\text{ClGa}^{\text{II}}-\text{Ga}^{\text{II}}\text{Cl}(\text{L}^{\text{Me}})^+]$ (**6**). In an attempt to prepare the similar $[\text{LGaCl}_2]$ precursors of the smaller ligands L^{Et} and L^{Me} , the ligand was treated with 1 equiv of Na (to generate the $[\text{NaL}]$ salt) and then reacted with GaCl_3 . However, neither $[(\text{L}^{\text{Et}})^+\text{GaCl}_2]$ nor $[(\text{L}^{\text{Me}})^+\text{GaCl}_2]$ (analogues of $[(\text{L}^{\text{Pr}})^+\text{GaCl}_2]$, **1**), was isolated. This might be due to the smaller steric effect of these two ligands that is unfavorable for the mononuclear complex. In contrast,

by direct reaction of GaCl_3 with the doubly reduced ligand $[\text{Na}_2\text{L}]$ (generated from **L** and 2 equiv of Na), the Ga–Ga-bonded complexes **5** and **6** were obtained.

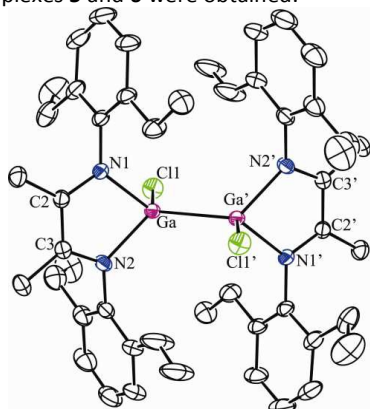


Fig. 5. Molecular structure of **5** (thermal ellipsoids are set at the 20% probability level; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): C2–N1 1.347(5), C3–N2 1.329(5), C2–C3 1.424(6), Ga–N1 1.956(3), Ga–N2 1.970(3), Ga–Ga' 2.444(1), Ga–Cl 2.211(1), N1–Ga–N2 83.01(4), Ga'–Ga–Cl 112.10(4). Symmetry code ('): $(-x, 2-y, -z)$.

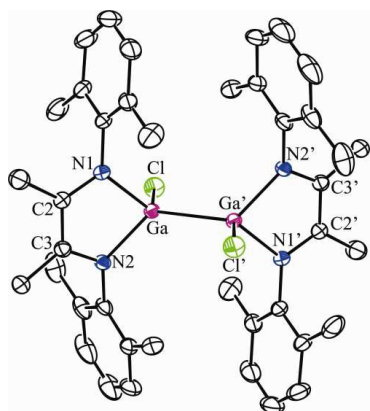


Fig. 6. Molecular structure of **6** (thermal ellipsoids are set at the 20% probability level; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): C2–N1 1.344(5), C3–N2 1.351(5), C2–C3 1.412(6), Ga–N1 1.958(3), Ga–N2 1.948(3), Ga–Ga' 2.424(1), Ga–Cl 2.218(1), N1–Ga–N2 83.62(4), Ga'–Ga–Cl 111.91(4). Symmetry code ('): $(1-x, -y, 1-z)$.

From the viewpoint of the electrons acquired by 1 equiv of **L** and GaCl_3 , it is interesting to compare the electronic structures of complexes **2** and **5/6**. In both cases two equivalents of electrons were transferred to $(\text{L} + \text{GaCl}_3)$, thus it is possible to elucidate the noninnocence of the ligand and metal ion, which might be competing during the reduction. As mentioned above, in complex **2** the Ga remains the +3 oxidation state, while the ligand is reduced to dianion. However, in **5** and **6**, both the structural feature (the C–C and C–N bond lengths of the C_2N_2 backbone) the ligand is monoanionic, and the metal center exists in the +2 oxidation state. Considering the different synthetic routes for **2** and **5/6**, it appears that the singly reduced α -diimine ligand in precursor **1** $[\text{L}^{\cdot-}\text{GaCl}_2]$ tends to be further reduced to dianion (in **2**) in the presence of Na, whereas the doubly reduced ligand $[\text{Na}_2\text{L}]$ could act as an electron donor and reduce the Ga^{III} to Ga^{II} (in **5**

and **6**). The Ga^{III} ion cannot form the Ga–Ga bond but the divalent Ga^{II} ion can by using the electron gained from reduction. These results clearly demonstrate the redox activity of α -diimine ligands, which makes them promising ligands for complexes with rich structures.

The two complexes (**5**, Fig. 5; and **6**, Fig. 6) are isostructural and are similar to the analogous diiodide and dibromide Ga complexes with related α -diimines (diazabutadienes, DAB), $[\text{Ga}(\text{DAB})_2]^{7b}$, $[\text{Ga}(\text{Ar-DAB})_2]$, and $[\text{Ga}(\text{tBu-DAB})_2]$.¹⁵ However, the dichloro analogues like **5** and **6** have not yet been reported before. Instead, a few organogallium complexes with terminal coordinated chloride ions have been obtained by using other supporting ligands such as N-heterocyclic carbenes, 1-aza-allyl, or β -diketonate ligands.¹⁶ The symmetry-related gallium centers adopt a distorted tetrahedral environment completed by one chelating ligand, one terminal Cl atom, and a Ga–Ga bond of 2.444(1) and 2.424(1) Å in **5** and **6**, respectively, which are in the normal range for Ga–Ga bond (2.391–2.576 Å) in compounds of the type $[\text{L}_2\text{Ga}_2\text{X}_2]$ (X = Cl, Br, I).^{15,16a,17} The mean Ga–N (1.963 Å) and Ga–Cl (2.211(1) Å) bond lengths in **5** are comparable to those in **6** (1.953 and 2.218(1) Å), and so are the N–Ga–N (83.01(4)° and 83.62(4)°) and Ga'–Ga–Cl (112.10(4)° and 111.91(4)°) angles. There are some minor structural differences between the two complexes. The dihedral angles between the central C_2N_2 moiety and the terminal aryl groups in complex **5** (84.6° and 85.0°) are somewhat smaller than those in **6** (88.4° and 88.5°), possibly due to the slightly smaller steric repulsion of the methyl groups in **7** than the ethyl analogue **5**.

Complexes **5** and **6** contain the monoanionic α -diimine ligands and are thus paramagnetic. Their ^1H NMR spectra in C_6D_6 display no accurate signals in the region corresponding to the ligand. Furthermore, the solid-state EPR spectrum of **5** (Fig. S2 ESI[†]) shows the expected ligand-centered paramagnetic signal at $g = 2.004$, which is consistent with related compounds containing radical anionic diimineligands.^{5d–g} The large singlet–triplet energy gap ($\Delta E_{\text{S-T}} = 13.98$ and 14.24 kcal mol⁻¹) calculated for **5** and **6** supports a triplet ground state. In the DFT computations on **5** and **6** (Fig. S3 ESI[†]), the fully optimized geometries are in reasonable agreement with the experimental structures. Natural bond orbital (NBO) analysis of **5** and **6** showed that the Wiberg bond index (WBI) of the Ga–Ga bond (0.79 and 0.80) is somewhat smaller than that in compounds digallane (0.90).⁸ The α -diimine fragment accumulates negative partial charges of -1.08 (**5**) and -1.08 (**6**). On the other hand, the NPA charge on the Ga atoms (1.08). The DFT-predicted bond dissociation energy, $E(\text{Ga-Ga})$, of 87.29 kcal mol⁻¹ for **5** is somewhat larger than that for **6** (70.11 kcal mol⁻¹).

Conclusions

Reduction of the gallium α -diimine complex $[(\text{L}^{\text{DPR}})^{\cdot-}\text{GaCl}_2]$ by sodium metal, or reaction of GaCl_3 with the in situ generated dianion $[\text{Na}_2\text{L}^{\text{Et/Me}}]$, occurred step-by-step with quantitative acquisition of electrons to form the Ga^{III} , Ga^{II} , and $\text{Ga}(\text{+1.5})$ compounds **2–6**. The

electronic structures of the products were studied by DFT computations. The results further demonstrated the noninnocence of α -diimine ligands that can lead to very rich structures and bonding modes. Further exploration of the reactivity of these compounds towards small molecules is underway.

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere using Schlenk or dry box techniques. Diethyl ether and tetrahydrofuran were dried by sodium/benzophenone and distilled under argon prior to use. The α -diimine ligands were prepared according to literature procedures.¹⁸ Anhydrous GaCl₃ was purchased from Alfa Aesar. Benzene-*d*₆ was dried over Na/K alloy. NMR spectra were recorded on a Mercury Plus-400 spectrometer in benzene-*d*₆. The EPR spectra of paramagnetic compounds **3** and **5** were recorded on a Bruker EMX-10/12 spectrometer at room temperature. Elemental analyses were performed with an Elementar VarioEL III instrument.

Synthesis of [(L^{ipr})²-Ga^{III}(μ_2 -Cl)₂Na(THF)₄] (2**):** Sodium (0.06 g, 2.61 mmol) was added to a suspension of **1** (0.27 g, 0.5 mmol) in THF (30 mL).⁹ The mixture was stirred for 1 d at room temperature and filtered. The filtrate was concentrated to about 5 mL and stored at ca. -20 °C for several days to yield the product as yellow crystals (0.24 g, 56%). M.p. 136 °C; ¹H NMR (400 MHz, C₆D₆, 25 °C, TMS): δ = 1.03 (d, 24H, *J* = 7.2 Hz, CH(CH₃)₂), 1.36 (THF), 1.60 (s, 6H, CCH₃), 3.09 (m, 4H, CH(CH₃)₂), 3.52 (THF), 6.96–7.11 ppm (m, 6H, *m*, *p*-ArH); ¹³C NMR (100.6 MHz, C₆D₆, 25 °C, TMS): δ = 15.2 (N-CCH₃), 23.8 (CH(CH₃)₂), 26.2 (CH(CH₃)₂), 26.4 (CH(CH₃)₂), 28.8 (THF), 68.4 (THF), 123.9 (*m*-C₆H₃), 124.2 (*p*-C₆H₃), 127.1 (*o*-C₆H₃), 143.4 (*i*-C₆H₃), 146.2 ppm (N-CCH₃); elemental analysis calcd (%) for C₄₄H₇₂Cl₂Ga₂NaO₄ (856.65): C, 61.69; H, 8.47; N, 3.27. Found: C, 61.88; H, 8.28; N, 3.06.

Synthesis of [(Na(THF)₆)⁺•((L^{ipr})²-Ga-Ga(L^{ipr})²)⁻] (3**):** Sodium (0.058 g, 2.5 mmol) was added to a suspension of **1** (0.55 g, 1.0 mmol) in THF (30 mL). The resulting mixture was stirred for 1 d and then filtered, and the filtrate was concentrated to about 5 mL and stored at ca. -20 °C for several days to yield the product as dark red crystals (0.456 g, 62%). EPR: *g* = 2.004; elemental analysis calcd (%) for C₈₀H₁₂₈Ga₂N₄NaO₆ (1404.29): C, 68.42; H, 9.19; N, 3.99. Found: C, 68.45; H, 8.96; N, 3.68.

Synthesis of [(LGaCl)⁺•(GaCl₄)⁻] (4**):** GaCl₃ (0.18 g, 1.0 mmol) was added to a toluene (30 mL) solution of α -diimine ligand L^{ipr} (0.20 g, 0.5 mmol) and the mixture was stirred for 2 d. The resulting mixture was filtered, and the filtrate concentrated to about 5 mL and stored at ca. -20 °C for several days to yield the product as red crystals (0.297 g, 70%). ¹H NMR (400 MHz, C₆D₆, 25 °C, TMS): 1.30 (m, 48H, CH(CH₃)₂), 2.00 (s, 12H, CCH₃), 3.85 (m, 8H, CH(CH₃)₂), 7.10–7.16 (m, 4H, *p*-ArH), 7.23 ppm (d, 8H, *J* = 7.2 Hz, *m*-ArH). ¹³C NMR (100.6 MHz, C₆D₆, 25 °C, TMS): δ = 15.9 (N-CCH₃), 24.0 (CH(CH₃)₂), 25.8 (CH(CH₃)₂), 26.9 (CH(CH₃)₂), 120.7 (*p*-C₆H₃), 122.8 (*m*-C₆H₃), 123.4 (*o*-C₆H₃), 147.0 (*i*-C₆H₃), 148.7 ppm (N-CCH₃); elemental analysis calcd (%) for C₂₈H₄₀Cl₆Ga₂N₂•C₇H₈(848.89): C, 49.52; H, 5.70; N, 3.30. Found: C, 49.05; H, 5.55; N, 5.80.

Synthesis of [(L^{Et})⁺-ClGa^{II}-Ga^{II}Cl(L^{Et})⁻] (5**):** Sodium metal (0.023 g, 1.0 mmol) was added to a stirred suspension of L^{Et} (0.17 g, 0.5 mmol) and GaCl₃ (0.09 g, 0.5 mmol) in THF (30 mL) and the mixture was stirred for 24 h at room temperature. All volatiles were then removed in vacuo, and the residue was extracted with toluene. The extract was filtered, concentrated to about 5 mL, and stored at ca. -20 °C for several days to yield dark red crystals (0.072 g, 32%). M.p.

180 °C; EPR (solid, 25 °C): *g* = 2.004; elemental analysis calcd (%) for C₄₈H₆₄Cl₂Ga₂N₄ (907.38): C, 63.53; H, 7.11; N, 6.17. Found: C, 63.62; H, 6.96; N, 6.24.

Synthesis of [(L^{Me})⁺-ClGa^{II}-Ga^{II}Cl(L^{Me})⁻] (6**):** Complex **6** was prepared following a similar procedure to complex **5**, by reduction of the mixture of L^{Me} (0.15 g, 0.5 mmol) and GaCl₃ (0.09 g, 0.5 mmol) with sodium metal (0.023 g, 1.0 mmol) in THF (30 mL). Dark-red crystals were isolated (0.075 g, 38%). M.p. 175 °C; elemental analysis calcd (%) for C₄₀H₄₈Cl₂Ga₂N₄ (795.16): C, 60.42; H, 6.08; N 7.05. found: C, 60.14; H, 6.28; N, 7.16.

X-ray crystal structure determination: Diffraction data for complexes **2–6** were collected on a Bruker SMART APEX II diffractometer at room temperature (293K) with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS¹⁹ was applied for all data. The structures were solved by direct methods using the SHELXS program.²⁰ All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on *F*² by the use of the program SHELXL.²⁰ The hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data have been deposited to the Cambridge Crystallographic Data Centre with reference numbers CCDC 697664(**2**), 1041744 (**3**), 1041745 (**4**), 998774 (**5**) and 998775 (**6**).

Density Functional Theory (DFT) Studies. The structure optimization and NBO bonding analysis of the complexes have been performed using the B3LYP method with the basis set 6-31G* by the Gaussian 09 program.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21402151) and Special Science Research Foundation of Education Committee of Shaanxi Province (14JK1736).

Notes and references

- (a) S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 1754–1757; (b) I. Resa, E. Carmona, E. Gutierrez-Puebla and A. Monge, *Science*, 2004, **305**, 1136–1138; (c) T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettingner, G. J. Long and P. P. Power, *Science*, 2005, **310**, 844–846; (d) J. Su, X.-W. Li, R. C. Crittendon and G. H. Robinson, *J. Am. Chem. Soc.*, 1997, **119**, 5471–5472; (e) K. A. Kreisel, G. P. A. Yap, O. Dmitrenko, C. R. Landis and K. H. Theopold, *J. Am. Chem. Soc.*, 2007, **129**, 14162–14163; (f) E. Carmona and A. Galindo, *Angew. Chem. Int. Ed.*, 2008, **47**, 6526–6536.
- (a) T. Pott, P. Jutzki, W. Kaim, W. W. Schoeller, B. Neumann, A. Stammler, H.-G. Stammler and M. Wanner, *Organometallics*, 2002, **21**, 3169–3172; (b) R. J. Baker, C. Jones, M. Kloth and D. P. Mills, *New. J. Chem.*, 2004, **28**, 207–213; (c) J. A. C. Clyburne, R. D. Culp, S. Kamepalli, A. H. Cowley and A. Decken, *Inorg. Chem.*, 1996, **35**, 6651–6655; (d) H. A. Jenkins, C. L. Dumaresque, D. Vidovic and J. A. C. Clyburne, *Can. J. Chem.*, 2002, **80**, 1398–1403.
- (a) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414–6415; (b) R. V. Belzen, H. Hoffmann and C. J. Elsevier, *Angew. Chem. Int. Ed.*, 1997, **36**, 1743–1745; (c) I. L. Fedushkin, A. A. Skatova, V. A. Chudakov and G. K. Fukin, *Angew. Chem. Int. Ed.*, 2003, **42**, 3294–3298; (d) E. S. Schmidt, A. Jockisch and H. Schmidbaur, *J. Am. Chem. Soc.*, 1999, **121**, 9758–9759; (e)

- T. Pott, P. Jutzi, B. Neumann and H.-G. Stammler, *Organometallics*, 2001, **20**, 1965–1967; (f) W. Kaim and W. Matheis, *J. Chem. Soc., Chem. Commun.*, 1991, 597–598.
4. (a) Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113–115; (b) I. L. Fedushkin, A. S. Nikipelov and K. A. Lysenko, *J. Am. Chem. Soc.*, 2010, **132**, 7874–7875; (c) P. L. Arnold, S. T. Liddle, J. McMaster, C. Jones and D. P. Mills, *J. Am. Chem. Soc.*, 2007, **129**, 5360–5361; (d) S. T. Liddle, J. McMaster, D. P. Mills, A. J. Blake, C. Jones and W. D. Woodul, *Angew. Chem. Int. Ed.*, 2009, **48**, 1077–1080; (e) M. Yamashita, Y. Suzuki, Y. Segawa and K. Nozaki, *J. Am. Chem. Soc.*, 2007, **129**, 9570–9571; (f) J. Shen, G. P. A. Yap, J.-P. Werner and K. H. Theopold, *Chem. Commun.*, 2011, **47**, 12191–12193.
5. (a) X.-J. Yang, J. Yu, Y. Liu, Y. Xie, H. F. Schaefer, Y. Liang and B. Wu, *Chem. Commun.*, 2007, 2363–2365; (b) Y. Liu, S. Li, X.-J. Yang, P. Yang and B. Wu, *J. Am. Chem. Soc.*, 2009, **131**, 4210–4211; (c) Y. Liu, Y. Zhao, X.-J. Yang, S. Li, J. Gao, P. Yang, Y. Xia and B. Wu, *Organometallics*, 2011, **30**, 1599–1606; (d) Q. Dong, X.-J. Yang, S. Gong, Q. Luo, Q.-S. Li, J.-H. Su, Y. Zhao, B. Wu, *Chem. Eur. J.*, 2013, **19**, 15240–15247; (e) X.-J. Yang, X. Fan, Y. Zhao, X. Wang, B. Liu, J.-H. Su, Q. Dong, M. Xu, and B. Wu, *Organometallics*, 2013, **32**, 6945–6949; (f) Y. Zhao, Y. Liu, L. Yang, J.-G. Yu, S. Li, B. Wu and X.-J. Yang, *Chem. Eur. J.*, 2012, **18**, 6022–6030.
6. (a) F. G. N. Cloke, G. R. Hanson, M. J. Henderson, P. B. Hitchcock and C. L. Raston, *J. Chem. Soc., Chem. Commun.* 1989, 1002–1003; (b) A. H. Cowley, D. S. Brown, A. Decken and S. Kamepalli, *Chem. Commun.*, 1996, 2425–2426; (c) R. J. Baker, C. Jones, D. P. Mills, D. M. Murphy, E. Hey-Hawkins and R. Wolf, *Dalton Trans.*, 2006, 64–72; (d) R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Angew. Chem., Int. Ed.*, 2003, **42**, 2660–2663; (e) C. Jones, A. Stasch and W. D. Woodul, *Chem. Commun.*, 2009, 113–115.
7. (a) T. Pott, P. Jutzi, W. W. Schoeller, A. Stammler, H.-G. Stammler, *Organometallics*, 2001, **20**, 5492–5494; (b) R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, *J. Chem. Soc., Dalton Trans.*, 2002, 3844–3850; (c) R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Organometallics*, 2004, **23**, 4811–4813; (d) D. S. Brown, A. Decken and A. H. Cowley, *J. Am. Chem. Soc.*, 1995, **117**, 5421–5422; (e) R. J. Baker, C. Jones, D. P. Mills, G. A. Pierce and M. Waugh, *Inorg. Chim. Acta*, 2008, **361**, 427–435; (f) I. L. Fedushkin, A. N. Lukoyanov, S. Y. Ketkov, M. Hummert and H. Mann, *Chem. Eur. J.*, 2007, **13**, 7050–7056.
8. Y. Zhao, Y. Liu, Z. Wang, W. Xu, B. Liu, J.-H. Su, B. Wu and X.-J. Yang, *Chem. Commun.*, 2015, 51, 1237–1239.
9. Y. Liu, S. Li, X.-J. Yang, Q.-S. Li, Y. Xie, H. F. Schaefer and B. Wu, *J. Organomet. Chem.*, 2011, 696, 1450–1455.
10. (a) X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon and P. P. Power, *Angew. Chem. Int. Ed.*, 1993, **32**, 717–719; (b) W. Uhl, U. Schütz, W. Kaim and E. Waldhö, *J. Organomet. Chem.*, 1995, **501**, 79–85.
11. N. J. Hardman, R. J. Wright, A. D. Phillips and P. P. Power, *Angew. Chem. Int. Ed.*, 2002, **41**, 2842–2844.
12. (a) N. J. Hardman, R. J. Wright, A. D. Phillips and P. P. Power, *J. Am. Chem. Soc.*, 2003, **125**, 2667–2679; (b) S. Li, X.-J. Yang, Y. Liu, Y. Zhao, Q.-S. Li, Y. Xie, H. F. Schaefer and B. Wu, *Organometallics*, 2011, **30**, 3113–3118.
13. N. Takagi, M. W. Schmidt and S. Nagase, *Organometallics*, 2001, **20**, 1646–1651.
14. (a) J. A. C. Clyburne, R. D. Culp, S. Kamepalli, A. H. Cowley and A. Decken, *Inorg. Chem.*, 1996, **35**, 6651–6655; (b) F. Cheng, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Inorg. Chem.*, 2007, **46**, 7215–7223; (c) M. Reinmuth, U. Wild, D. Rudolf, E. Kaifer, M. Enders, H. Wadepohl and H.-J. Himmel, *Eur. J. Inorg. Chem.*, 2009, 4795–4808.
15. R. J. Baker, R. D. Farley, C. Jones, D. P. Mills, M. Kloth and D. M. Murphy, *Chem. Eur. J.*, 2005, **11**, 2972–2982.
16. (a) B. Quillian, P. Wei, C. S. Wannere, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2009, 131, 3168–3169; (b) K. S. Klimek, C. Cui, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Organometallics*, 2000, **19**, 3085–3090; (c) O. T. Beachley, J. R. Gardinier and M. R. Churchill, *Organometallics*, 2000, **19**, 4544–4549.
17. (a) C. Jones, P. C. Junk, M. Kloth, K. M. Proctor and A. Stasch, *Polyhedron*, 2006, **25**, 1592–1600; (b) D. Rudolf, E. Kaifer and H.-J. Himmel, *Eur. J. Inorg. Chem.*, 2010, 4952–4961.
18. H. A. Zhong, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2002, **124**, 1378–1399.
19. G. M. Sheldrick, Program SADABS: Area-Detector Absorption Correction, 1996, University of Göttingen, Germany.
20. G. M. Sheldrick, SHELXS-97, SHELXL-97, Programs for Crystal Structure Analysis, 1997, University of Göttingen, Germany.

Synthesis and Structures of Mononuclear and Dinuclear Gallium Complexes with α -Diimine Ligands: Reduction of Metal or Ligand?

Yanxia Zhao^{a*}, Yanyan Liu^a, Qian-Shu Li^b, Ji-Hu Su^c

Graphical Abstract

A series of mononuclear and dinuclear gallium complexes with different oxidation states of the ligand and metal were obtained, and both monoanionic or dianionic ligand can be further reduced, in which reduction of the radical monoanionic α -diimine ligand into the dianion or of Ga (+3) into lower oxidation state Ga (+2) or Ga (+1.5).

