

First Dinuclear Copper/Gallium Complexes: Supporting Cu⁰ and Cu^I Centres by Low-Valent Organogallium Ligands**

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Abstract: The synthesis and structural characterisation of low-valent dinuclear copper(I) and copper(0) complexes supported by organogallium ligands has been accomplished for the first time by the reductive coordination reaction of [GaCp*] (Cp* = pentamethylcyclopentadienyl) and [Ga(ddp)] (ddp = HC(CMeNC₆H₃-2,6-*i*Pr₂)₂, 2-diisopropylphenylamino-4-diisopropylphenylimino-2-pentene) with readily available copper(II) and copper(I) precursors. The treatment of CuBr₂ and Cu(OTf)₂ (OTf = CF₃SO₃) with [Ga(ddp)] under mild conditions resulted in elimination of [Ga(L)₂(ddp)] (L = Br, OTf) and afforded the novel galliu-

m(I)/copper(I) compounds [(ddp)-GaCu(L)]₂ (L = Br (**1**), OTf (**2**)). The single-crystal X-ray structure determinations of **1** and **2** reveal that these molecules are composed of {(ddp)GaCu(L)} dimeric units, with planar Cu^I-Ga^I four-membered rings and short Cu^I...Cu^I distances, with **2** exhibiting the shortest Cu^I...Cu^I contact reported to date of 2.277(3) Å. The all-gallium coordinated dinuclear [Cu₂(GaCp*)(μ-GaCp*)₃Ga(OTf)₃] (**3**) is

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formed when Cu(OTf)₂ is combined with [GaCp*] instead of [Ga(ddp)]. Notably, in the course of this redox reaction Lewis acidic Ga(OTf)₃ is formed, which coordinates to one of the electron-rich copper(0) centres. Compound **3** is suggested as the first case of a structurally characterised complex of copper(0). By changing the copper(II) to a copper(I) source, that is, [Cu(cod)]₂[(OTf)] (cod = 1,5-cyclooctadiene), the salt [Cu₂(GaCp*)(μ-GaCp*)₂][(OTf)₂] (**4**) is formed, the cationic part of which is related to previously described isoelectronic dinuclear d¹⁰ complexes of the type [M₂(GaCp*)₃] (M = Pd, Pt).

Introduction

The recent upsurge in the field of main group chemistry has resulted in significant developments in the aspects of both

fundamental research and potential applications, with a special focus on stabilizing unusual bonding situations in molecules.^[1] Recent striking examples on this subject include novel bonds between main group elements stabilized at low-valence state, such as [(L)Mg–Mg(L)] (L = [(Ar)NC(NR')₂N(Ar)][−]; Ar = 2,6-diisopropylphenyl, R' = isopropyl), [(L)E=E(L)] (E = BH, Si, Ge, P, As; L = NHC=:C{N(2,6-*i*Pr₂C₆H₃)CH₂}₂ or :C{N(2,4,6-Me₃-C₆H₂)CH₂}₂) and the [Ga(ddp)]-stabilized dibismuthene, [(R)(ddp)GaBi=BiGa(ddp)(R)] (R = OTf, OC₆F₅; ddp = HC(CMeNC₆H₃-2,6-*i*Pr₂)₂).^[2–5] Another impressive case in this area is the isolation of the neutral “aromatic” Ga₆ octahedral cluster, [Ga₆(Mes)₄(L)₂] through the reduction of [GaCl₂(Mes)L] with potassium (L = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, Mes = 2,4,6-Me₃C₆H₂).^[6] All these complexes, clusters and reaction strategies were achieved by the use of nitrogen heterocyclic carbenes (NHC) or heavier main group metal NHC analogues as versatile ligands and reaction partners, which provide the desired electronic and steric requirements.

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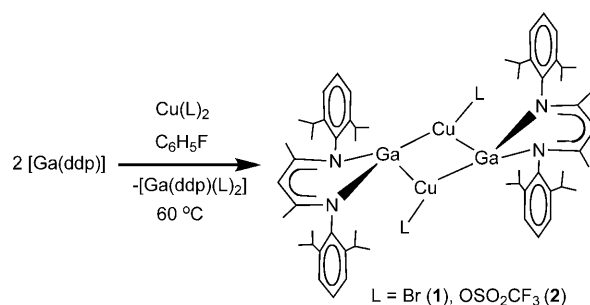
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On the other hand, the stabilizing effect of the pentamethylcyclopentadienyl group (Cp*) on low-valent Group 13 metals has been very well established since the pioneering work reported in the early nineties by Schnöckel, Jutzi, Uhl, and Roesky.^[7–15] The coordination chemistry of the NHC-analogous low-valent Group 13 carbenoid ligands L=ER to transition metals has also been systematically investigated (E=Al, Ga, In; R=bulky substituents, that is, Cp*, ddp).^[16] During this time, a variety of neutral and cationic transition-metal complexes containing ER ligands have been synthesized, in particular those of the late transition metals in oxidation state zero (d⁸–d¹⁰), with [Ni(In{C(SiMe₃)₃})₄]^[17] as the first homoleptic low-valent Group 13 metal/transition metal complex. In the case of [GaCp*]₄, the preparation of [Ni(GaCp*₄)]^[18] as the prototype, and some isoelectronic congeners such as [Zn(GaCp*₄)]²⁺ involving cationic metal centres, have been synthesized and characterised over the years.^[19] Note the somewhat related coordination chemistry of the bulky anionic diazabutadiene gallanates [Ga{[N(Ar)C(R)]₂}]⁻ (R=CH₃, H). This latest work has, however, chiefly focused on the more electropositive main group and lanthanide metals, such as Mg, Ca, Sm, Eu, Yb, Nd, Tm, and U, in addition to Rh and the coinage metals, and typically involves salt elimination reactions.^[20–23] In contrast, the coordination chemistry of neutral ER ligands is primarily based on substitution reactions of other weakly bonded neutral ligands, such as olefins or acetonitrile, by ER. The chemical properties of transition metal [ECp*] as well as [E(ddp)] complexes have been documented in several reaction types including bond activation, insertion reactions, redox reactions, and access to unprecedented compounds, that is, [Mo(ZnCp*₃(ZnMe)₉], to a large extent due to the special properties of the soft binding and transferable Cp* group.^[24–28] Those developments bear the potential of linking the coordination and cluster chemistry of metal-rich molecules of the kind discussed above with materials science in a new way. In particular, the soft chemical syntheses of M/E Hume–Rothery phases (NiAl, NiGa, PtGa, CuAl, CuGa, etc.) as colloidal nanoparticles or as powder materials were achieved by using combinations of all-hydrocarbon precursors of [M(L)_n] and ER, or by employing tailored single source precursors with direct, preformed M–E bonds.^[29] It is worth noting that gallium and zinc are neighbours in the periodic table and share various aspects of their molecular and intermetallic solid-state chemistry. For example, α-, β-, γ-Cu/Zn colloids, “nano-brass”, were obtained from [CuCp(L)] with [ZnCp*₂] as precursors, which is quite similar to the selective synthesis of θ-CuE₂ (E=Al, Ga) and Cu_{1-x}Al_x intermetallic phases from [CuCp(L)] and [ECp*] (L=PMe₃, CNtBu).^[30] Evidently, the success of this organometallic precursor chemistry for intermetallic materials depends on the knowledge of the underlying coordination chemistry of ER. Within this wider context of research, we were led to investigate the organometallic Cu/Ga molecular coordination chemistry with particular emphasis on oligonuclear Cu_aGa_b-type complexes or clusters, which ideally should be homoleptic and feature the Cu in a formally low oxidation state.

The formation of Cu–Ga bonds can be achieved by two different reaction schemes, namely 1) the salt elimination reaction of anionic gallium(I) heterocycles with suitable late-transition-metal complexes,^[23] and 2) the reaction of cationic transition-metal compounds containing weakly bonded acetonitrile ligands with [GaCp*].^[31] Nevertheless, just three examples of Cu–Ga bond interactions in molecular compounds have been reported, including [Cu(GaCp*₄)]⁺[BAR^F]⁻ (BAR^F=[B{C₆H₃(CF₃)₂]₄), which features Cu^I.^[23,31] Interestingly, the formation of oligonuclear Cu_aGa_b (b ≥ a ≥ 2) complexes or clusters has not been observed so far. It should be noted that, to the best of our knowledge, there is no example of a (homoleptic) copper(0) complex [Cu_a(L)_b] (L=arbitrary neutral ligand). In contrast, the literature on dimeric and polynuclear copper complexes with copper(I) or copper(II) is very rich, and it has been established that the ligand system plays an important role in these systems, for example, N-heterocyclic carbenes as well as bulky ligands such as phosphines and pyrazolylborates.^[32–34] Through the preparation of the Ag^I compound [Ag₂(GaCp*₃)(μ-GaCp*₂)]⁺[OTf]₂⁻, we were able to illustrate that [GaCp*] also has the ability to stabilize dinuclear compounds of soft cationic d¹⁰ coinage metal centres without immediate reduction to the metal by ER.^[31] Below we report on related dinuclear complexes, formally assigned as copper(I) and copper(0) compounds, which were obtained by the reaction of [GaCp*] and [Ga(ddp)] with copper(II) and copper(I) precursors. We will address effects on the reaction behaviour as a function of changing the ligand system of both components, at the copper source and at the GaR species.

Results and Discussion

Synthesis and characterisation of [(ddp)GaCu(L)]₂ (L = Br (1), OTf (2)): Mild reduction of the copper(II) compound CuBr₂ with two equivalents of [Ga(ddp)] in fluorobenzene at 60 °C afforded the [Ga(ddp)]-supported copper(I) dimer **1** through the reductive elimination of [GaBr₂(ddp)] in good yields. Likewise, the reaction of Cu(OTf)₂ and [Ga(ddp)] gave the almost isostructural molecule **2** in good yields (Scheme 1). Notably, the reaction of the copper(I) compound Cu(OTf)-toluene or CuBr with [Ga(ddp)] under various conditions resulted in the formation of [Ga(L)₂(ddp)]



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

(L=Br, OTf) and a grey solid, but no pure Cu/Ga mixed metal product was isolated. The new compounds **1** and **2** are stable under inert atmosphere for several days. The colourless crystals of the triflate derivative **2**, however, slowly turned black when they were stored under inert gas atmosphere for more than two weeks. Compound **1** is insoluble in most solvents, but freely soluble in THF. Compound **2** decomposes immediately when it is dissolved in polar coordinating or non-coordinating organic solvents, such as THF, benzene or fluorobenzene, even at low temperature, to produce a grey solid and [Ga(OTf)₂(ddp)] (Supporting Information, Figures S5–S8).

Compound **1** has been characterised by ¹H NMR and ¹³C NMR spectroscopy, elemental analysis, and single-crystal X-ray techniques. The ¹H NMR spectrum of single crystals of **1** gave resonance peaks associated with the ddp ligand and some hexane which was included as solvent in the crystal lattice. The γ -CH proton of the ddp ligand in **1** resonates at δ =5.48 ppm in the ¹H NMR spectrum, whereas the γ -CH carbon appears at δ =94.49 ppm in the ¹³C NMR spectrum. Compound **2** has been characterised by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction techniques. Elemental analysis results compare well with the calculated values. The presence of a monodentate triflate ligand, covalently linked to the copper(I) centres in **2**, was evidenced by IR spectroscopy (1381(s) and 1211(s) cm⁻¹).^[35] Colourless single crystals of **1** suitable for X-ray analysis were obtained at room temperature from fluorobenzene/THF/hexane mixtures. Molecule **1** crystallized in the monoclinic space group *P*2₁/*c* with a solvent molecule hexane in the lattice. Molecule **1** can be regarded as a CuBr dimer, stabilized by two bridging [Ga(ddp)] ligands. Due to the poor structural data of **1**, a further structural discussion is not undertaken here; however, the structural identity and close similarity to **2** is substantiated by the data (see Supporting Information).

The colourless crystals of **2** suitable for X-ray measurement were grown at room temperature in fluorobenzene/hexane mixtures. Compound **2** crystallizes in the triclinic space group *P*1̄. The solid-state structure of **2** is shown in Figure 1, which can be considered as largely isostructural with **1**. The molecular core is composed of a Cu₂Ga₂ four-membered ring, which is almost perfectly planar. Both the OTf oxygen atoms attached to the Cu centres in the molecule lie in the Cu₂Ga₂ plane, and the ddp backbone is almost perpendicular to this plane. Interestingly, **2** exhibits the shortest Cu...Cu contact in molecular compounds to the best of our knowledge. The Cu...Cu distance is 2.277(3) Å, and is about 0.03 Å shorter than the known copper(I) dimer, [(N(2,6-*i*Pr₂-C₆H₃)CH)₂Cu(H)]₂, which has a very short Cu^I...Cu^I distance of 2.3059(11) Å.^[36] It is 0.117 Å longer than the Cu^I...Cu^I distance calculated for [(CuH)₂] (2.16 Å) and is nearly comparable with that of the Cu₂ molecule in the gas phase (2.22 Å).^[37] The Ga...Cu distances in **2** are not equal (2.4212(18) Å for Ga(1)...Cu(1) and 2.4997(3) Å for Ga(1)...Cu(1)#). Thus, molecule **2** can be considered as two strongly associated monomers

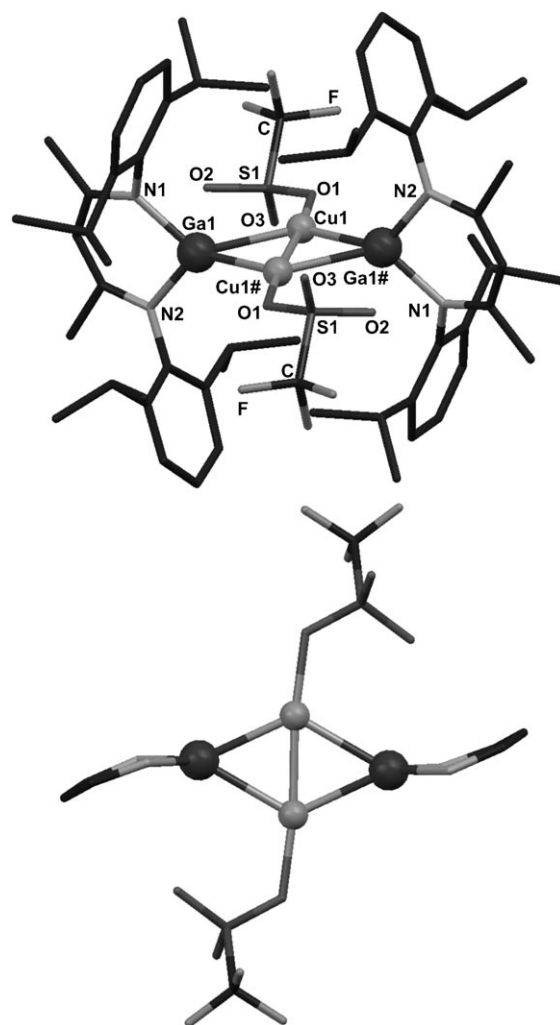
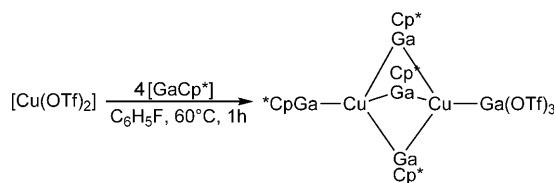


Figure 1. Molecular structure of **2**. H atoms attached to carbon are omitted for clarity. The solid line between the two copper atoms illustrates the short metal–metal contact and not the real bonding situation. Selected bond lengths [Å] and angles [°] for **2**: Cu(1)–Cu(1)# 2.277(3), Ga(1)–Cu(1) 2.4212(18), Ga(1)–Cu(1)# 2.4997(3), Cu(1)–O(1) 1.942(8), Ga(1)–N(1) 1.936(10), Ga(1)–N(2) 1.939(9), Cu(1)–Ga(1)–Cu(1)# 55.10(6), Cu(1)#–Cu(1)–Ga(1) 64.20(7), Ga(1)–Cu(1)–Ga(1)# 124.90(6), Cu(1)#–Cu(1)–Ga(1)# 60.70(6), O(1)–Cu(1)–Cu(1)# 173.9(2), O(1)–Cu(1)–Ga(1) 121.7(2), O(1)–Cu(1)–Ga(1)# 113.4(2), N(1)–Ga(1)–N(2) 96.0(4), N(1)–Ga(1)–Cu(1) 126.5(2), N(2)–Ga(1)–Cu(1) 129.1(4), N(1)–Ga(1)–Cu(1)# 125.2(3), N(2)–Ga(1)–Cu(1)# 124.5(3).

[(ddp)GaCu(OTf)] in the solid state. The Ga...Cu distances in **2** are considerably longer than the Ga...Cu distances found in the few related Cu–Ga reference compounds, which contain terminal Ga ligands only: [(L)Cu...Ga(R)] (2.3066(6) Å and 2.2807(5) Å with R={N(C₆H₃-2,6-*i*Pr₂)CH)₂, L={N(2,4,6-Me₃-C₆H₂)CH)₂C and L={N(2,6-*i*Pr₂-C₆H₃)CH)₂C, respectively) and [Cu(GaCp*)₄][BAR^F] (2.3517(5) and 2.3496(5) Å) (BAR^F=[B(C₆H₃(CF₃)₄)₄]).^[23,31] The sum of the angles (359.98°) around copper provides trigonal planar geometry. The coordination environment around each copper atom is completed by one OTf and two Ga centres. The Ga(1)–Cu–Ga(1)# (124.90(6)°), Ga(1)–Cu–

O(1) (121.7(2)°) and O(1)–Cu–Ga(1)# (113.4(2)°) angles are close to 120°. The Cu(1)⋯O(1) distance (1.942(8) Å) in **2** indicates the presence of (polar) covalently linked triflate at the copper centre. Moreover, the SO₃ moiety of the triflate ligand shows no donor–acceptor interaction with the gallium centre. The molecular packing of **2** depicts the presence of intermolecular C–F⋯H–C(aryl) and intramolecular C–F⋯H–C(*i*Pr) interactions, which leads to the chain-like arrangements (Supporting Information, Figure S3). As expected, molecule **2** shows shorter Ga⋯N distances (Ga⋯N(1), 1.936(10) Å and Ga⋯N(2), 1.939(9) Å) and a larger N(1)–Ga–N(2) angle (96.0(4)°) as a result of coordination of the Ga to the Cu centre compared to free [Ga(ddd)] (Ga⋯N, 2.0528(14) and 2.0560(13) Å; N–Ga–N, 87.53(5)°).^[38–40]

Synthesis and characterisation of [Cu₂(GaCp*)(μ-GaCp*)₃Ga(OTf)₃] (3) and [Cu₂(GaCp*)₃(μ-GaCp*)₂][OTf]₂ (4): The reaction of the copper(II) compound Cu(OTf)₂ with four equivalents of GaCp* leads to the formation of the unusual compound [(Cp*Ga)Cu(μ-GaCp*)₃Cu[Ga(OTf)₃] (**3**) (Scheme 2).



Scheme 2. Synthesis of **3**.

Compound **3** is stable under an inert gas atmosphere for several weeks at –30°C. The ¹H NMR spectrum of **3** in [D₈]THF shows only one signal at δ = 2.03 ppm for the protons of the C₅Me₅ rings, that is, terminal and bridging [GaCp*] moieties are not distinguished, whereas the ¹H NMR measurement in [D₈]THF at –60°C shows two signals in a 1:3 ratio at δ = 1.99 and δ = 2.06 ppm, which indicates a fluxional process of the [GaCp*] ligands in solution. The ¹³C NMR spectrum does not show any unusual features and displays one set of signals at δ = 9.75 ppm for (GaC₅Me₅) and δ = 115.46 ppm for (GaC₅Me₅). It should be noted that the OTf atoms were not detected in the ¹³C NMR spectrum under the standard conditions of the routine measurements. The ¹⁹F NMR spectrum shows one signal at δ = –78.8 ppm. Suitable crystals of **3** were obtained by slow diffusion of *n*-hexane into a fluorobenzene solution at room temperature. It crystallizes in the monoclinic space group *P*2₁/*n*. The central Cu atoms are surrounded by three bridging GaCp* ligands and one terminally bonded GaCp* ligand on one side, and one Ga(OTf)₃ group on the other (Figure 2). The coordination angle of the terminal Ga ligands toward the Cu central atoms is nearly linear (177.17(4)° for Ga(1)–Cu(1)–Cu(2) and 178.91(4)° for Cu(1)–Cu(2)–Ga(5)). The Ga⋯Cp*_{centroid} distance (1.972 Å) of the terminal ligand is slightly elongated in comparison to the bridging Ga⋯Cp*_{centroid} units (average distance 1.892 Å),

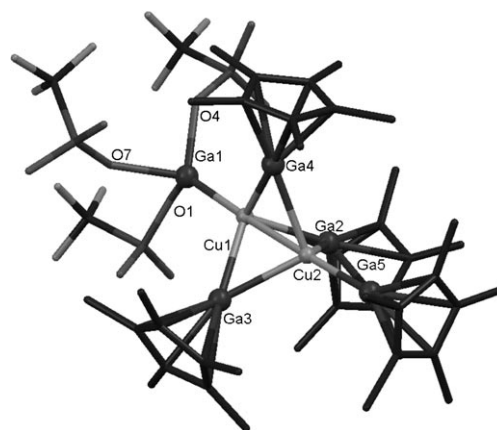


Figure 2. Molecular structure of **3**. H atoms attached to carbon are omitted for clarity. The solid line between the two copper atoms illustrates the short metal–metal contact and not the real bonding situation. Selected bond lengths [Å] and angles [°] for **3**: Cu(1)⋯Cu(2) 2.3236(8), Cu(1)⋯Ga(1) 2.2906(8), Cu(1)⋯Ga(2) 2.4011(8), Cu(1)⋯Ga(3) 2.4131(9), Cu(1)⋯Ga(4) 2.4120(9), Cu(2)⋯Ga(5) 2.3268(8), Cu(2)⋯Ga(2) 2.5044(9), Cu(2)⋯Ga(3) 2.4837(9), Cu(2)⋯Ga(4) 2.4883(8), Ga(1)⋯O(1) 1.993(3), Ga(1)⋯O(4) 1.969(3), Ga(1)⋯O(7) 1.964(4), Ga(2)⋯Cp*_{centroid} 1.879, Ga(3)⋯Cp*_{centroid} 1.896, Ga(4)⋯Cp*_{centroid} 1.902, Ga(5)⋯Cp*_{centroid} 1.972, Ga(1)–Cu(1)–Cu(2) 177.17(4), Cu(1)–Cu(2)–Ga(5) 178.91(4), Cu(1)–Ga(4)–Cu(2) 56.59(2), O(1)–Ga(1)–Cu(1) 121.58(11), O(1)–Ga(1)–O(7) 91.96(15), Cu(1)–Ga(4)–Cp*_{centroid} 150.95, Cu(2)–Ga(5)–Cp*_{centroid} 177.63.

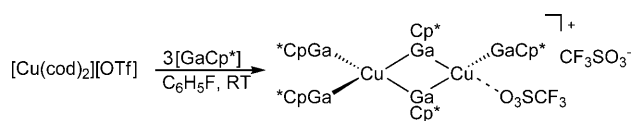
which is in contrast to the homoleptic dimeric compound [Pt₂(GaCp*)₅].^[41] The Cu⋯Cu distance (2.3236(8) Å) is longer than **2** (2.277(3) Å). The average Cu(1)⋯GaCp*_{bridging} bond length (2.409 Å) is slightly shorter than the average Cu(2)⋯GaCp*_{bridging} distance (2.492 Å). The Cu(2)⋯GaCp*_{terminal} bond (2.3268(8) Å) is much shorter than all Cu⋯GaR_{bridging} (R = Cp* and ddp) distances in **2** (av 2.460 Å) and **3** (av 2.451 Å). Note that all these Cu⋯Ga bonds are, as expected, somewhat longer with respect to compounds [(L)Cu–Ga(R)] (2.2807(5) and 2.3066(6) Å; R = {N(C₆H₃-2,6-*i*Pr₂)CH}₂; L = {N(2,4,6-Me₃-C₆H₃)CH}₂C and {N(2,6-*i*Pr₂-C₆H₃)CH}₂C), and [Cu(GaCp*)₄][BAR^F] (av = 2.3517(5) Å), which bear terminal Ga ligands only.^[23,31] Interestingly, the Cu(1)⋯Ga(1) distance of 2.2906(8) Å involving the Ga(OTf)₃ group is significantly shorter than all the other Cu⋯GaCp* distances of **3**, and of the cation [Cu(GaCp*)₄]⁺.^[31] These structural comparisons also support the treatment of **3** as a Lewis acid/base adduct^[26,42–44] with Ga(OTf)₃ as the (evident) Lewis acid very well, in agreement with numerous quantum chemical calculations on related transition metal/Group 13 metal complexes, revealing more or less polarized covalent donor–acceptor bonds with M(δ–) and Ga(δ+).^[45,51] We therefore suggest assigning the formal oxidation states copper(0) and gallium(I) to the (neutral) structural fragment [Cu₂(GaCp*)₄] of **3**, at least for heuristic reasons.

A likely mechanism of the formation of **3** is a redox reaction with [GaCp*] as the gallium(I) reductant of the copper(I) starting compound, which is evidently supported by the formation of Ga(OTf)₃ as a gallium(III) species as one distinct and coordinatively trapped by-product of this pro-

cess (including Cp* transfer products). The electrophilic centre of Ga(OTf)₃ acts as a strong Lewis acid, and coordinates at the vacant pyramidal Cu site of the dinuclear fragment [(Cp*Ga)Cu(μ-GaCp*)₃Cu], which is nucleophilic and acts as the Lewis base. The composition and the structure of **3** suggest that a fully homoleptic compound [(Cp*Ga)Cu(μ-GaCp*)₃Cu(GaCp*)] with an additional GaCp* donor ligand instead of the Ga(OTf)₃ acceptor is likely to be too electron-rich to be stable. Note the electron count of 32 for such a hypothetical species [Cu₂(GaCp*)₅] in comparison to its existing isostructural [M₂(GaCp*)₅] (M = Pd, Pt) congeners, which exhibit an electron count of 30.^[41] Whether **3** should be addressed as a Cu/Ga complex or a ligand-supported metal cluster may depend on the point of view. Nevertheless, quantum chemical calculations and a molecular orbital analysis are definitely necessary for the understanding and identification of the details including charge distributions, but this is beyond the scope of this work and will be published separately.

Treatment of **3** with excess GaCp* did not yield [Cu₂(GaCp*)₅]. We are thus led to the conclusion that Lewis acid/base interactions Cu⁰→Ga^{III} are stronger than Cu^I←Ga^I and Cu⁰←Ga^I interactions. This situation may also contribute to the inaccessibility of [Cu₂(GaCp*)₅] under the conditions of the synthesis of **3**. Further reactions to replace the Ga(OTf)₃ ligand by weaker Lewis acids like GaMe₃, achieving an all-hydrocarbon shell around the metal core, were not successful due to the low stability of the products, which was indicated by the colour change of the red solution at the beginning of the reaction to black–grey even at –40 °C over a period of a few minutes. The isolation and identification of pure reaction products has failed so far.

Whereas the reaction of Cu(OTf)·toluene with [GaCp*] does not afford any pure product suitable for characterisation, the 1,5-cyclooctadiene ligand-stabilized starting compound [Cu(cod)₂][OTf] undergoes quite a smooth reaction with [GaCp*] in fluorobenzene to yield compound **4**, of empirical composition [Cu₂(GaCp*)₅][OTf]₂ (Scheme 3).



Scheme 3. Synthesis of **4**.

The ¹H NMR spectrum of **4** in [D₈]THF at room temperature reveals one signal at δ = 2.04 ppm for the protons of the C₅Me₅ rings. The ¹³C NMR spectrum does not show any unusual features in terms of the expected signals. The ¹⁹F NMR spectrum shows one signal at δ = –78.4 ppm. These features indicate fluxional behaviour of **4** in solution, quite similar to that observed for **3** and the previously described silver analogue [Ag₂(GaCp*)₅(μ-GaCp*)₂][OTf]₂.^[31] Suitable crystals of **4** for X-ray measurements were obtained by slow diffusion of *n*-hexane into a fluorobenzene solution

at room temperature. It crystallizes in the monoclinic space group *P*2₁/*n*. The central Cu atoms are bridged by two [GaCp*] ligands. One copper atom, namely Cu(2) in the structure, binds to two terminally coordinating GaCp* ligands, and the other one, Cu(1), is coordinated by only one [GaCp*] ligand as well as one triflate ligand, resulting in a tetrahedral environment for both copper centres. This structural motif is exactly the same as in the analogue [Ag₂(GaCp*)₅(μ-GaCp*)₂][OTf]₂.^[31] It is worth noting that the single-crystal X-ray analysis showed a disordered structure that could not be sufficiently refined, so that only the connectivity of the heavy atoms, Ag and Ga in particular, in the solid-state structure were clearly determined.

Now, the Cu⋯Cu distance (2.5247(12) Å) is much longer than those contacts found for **2** (2.277(3) Å) and **3** (2.3238(7) Å). The Cu⋯GaCp*_{bridging} distances range between 2.4232(1) Å and 2.4572(11) Å and are, as expected, elongated compared to the Cu⋯GaCp*_{terminal} distances (average value 2.389 Å), as observed in the case of compound **3** and the related distances in [M₂(GaCp*)₅].^[16,41,46] As usual, the Ga⋯Cp*_{centroid} distance (1.991 Å) of the terminal ligand is slightly elongated in comparison to the bridging Ga⋯Cp*_{centroid} units (average distance 1.968 Å). In contrast to compound **3**, the Cu⋯GaCp*_{terminal} distance is slightly longer than the average Cu⋯Ga bond length in the homoleptic cation [Cu(GaCp*)₄]⁺ (2.351 Å) and the other known mononuclear Cu⋯Ga complexes.^[23,31]

Evidently, the comparison of the composition and structural features of **3** and **4** (Figures 2 and 3) with the related isoelectronic neutral compounds [M₂(GaCp*)₅] (M = Pd, Pt)

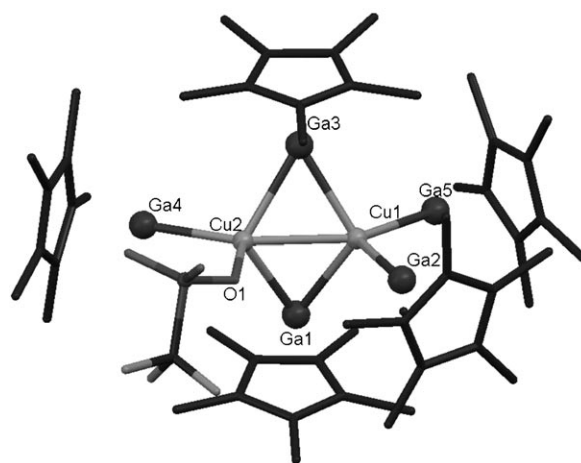


Figure 3. Molecular structure of the cationic part of **4**. H atoms attached to carbon and the OTf counterion are omitted for clarity. The solid line between the two copper atoms illustrates the short metal–metal contact and not the real bonding situation. Selected bond lengths [Å] and angles [°] for **4**: Cu(1)⋯Cu(2) 2.5247(12), Cu(1)⋯Ga(3) 2.4292(10), Cu(2)⋯Ga(3) 2.4572(11), Cu(1)⋯Ga(1) 2.4232(10), Cu(2)⋯Ga(1) 2.4430(11), Cu(1)⋯Ga(5) 2.3900(12), Cu(1)⋯Ga(2) 2.3886(12), Cu(2)⋯Ga(4) 2.4010(13), Cu(2)⋯O(1) 2.075(5), Ga(1)⋯Cp*_{centroid} 1.924, Ga(2)⋯Cp*_{centroid} 1.997, Ga(3)⋯Cp*_{centroid} 2.011, Ga(4)⋯Cp*_{centroid} 1.995, Ga(5)⋯Cp*_{centroid} 1.982, Ga(4)–Cu(2)–O(1) 108.25(15), Cu(2)–Ga(3)–Cp*_{centroid} 130.29, Cu(2)–Ga(3)–Cu(1) 62.22(3), Ga(2)–Cu(1)–Ga(5) 108.55(5), Cu(1)–Ga(2)–Cp*_{centroid} 171.71, Cu(2)–Ga(4)–Cp*_{centroid} 172.89.

is interesting.^[16,41,46] The hypothetical, dicationic species $[\text{Cu}_2(\text{GaCp}^*)_5]^{2+}$ exhibits an electron count of 30, similarly to $[\text{M}_2(\text{GaCp}^*)_5]$ and the neutral fragment $[\text{Cu}_2(\text{GaCp}^*)_4]$ discussed above in the case of **3**. It should be noted here that the isoelectronic $[\text{Ni}_2(\text{GaCp}^*)_5]$ is still the missing link in the whole series. The solid-state structure of **4**, and likewise the Ag congener mentioned before, can be viewed as the trapping of one of the intermediate structures of electronically saturated, 30-electron, fluxional $[\text{M}_2(\text{GaCp}^*)_5]^{2+}$ ($\text{M} = \text{Cu}, \text{Ag}$), by coordinating a triflate ligand to one electrophilic M^{I} site upon crystallisation from solution (note that this feature is absent for **3**, which bears more electron-rich copper centres). By choosing an appropriate, bulky, and very weakly coordinating anion other than triflate, it might be possible to stabilise the naked dication $[\text{M}_2(\text{GaCp}^*)_5]^{2+}$ ($\text{M} = \text{Cu}, \text{Ag}$) in the solid-state structure. However, we have failed so far to isolate and characterise such products in pure form.

A note on copper–copper interactions: Revealing the nature of the copper(I)–copper(I), $d^{10}\text{--}d^{10}$ interaction has been a challenging task for last two decades. This particular theme has been thoroughly investigated with the aid of theoretical calculations and experimental evidence by Cotton et al. and others.^[47–49] It is important to note that the copper(I)–copper(I) interaction may exist without covalent metal–metal bonding,^[49] but one cannot rule out the arguments that support the presence of such $\text{Cu}^{\text{I}}\cdots\text{Cu}^{\text{I}}$ bonds.^[48,49] Note that explicit $\text{Cu}^0\cdots\text{Cu}^0$ bonds have not been characterised in molecules so far. Apart from this dispute, we restrict ourselves to pointing out the following findings about the $\text{Cu}\cdots\text{Cu}$ contacts in our new compounds: 1) a shortest $\text{Cu}\cdots\text{Cu}$ (2.277(3) Å) contact is achieved for **2** due to the small bite angle of the bridging $[\text{Ga}(\text{ddp})]$ ligand; 2) the different $\text{Cu}\cdots\text{Cu}$ distances observed for **2** and **3** can be attributed to the steric bulk as well as the σ -donor/ π -acceptor nature of the ligands;^[47] 3) compound **3** and the hypothetical parent fragment $[\text{Cu}_2(\text{GaCp}^*)_4]$ may be an interesting object for theoretical studies in comparison and may represent the first case of a copper(0) complex.

A note on the significance of oxidation states: We would like to point out that the assignment of valence and oxidation states in coordination chemistry is primarily of heuristic value, needs to be done in a self-consistent way, and requires awareness that it may be meaningless for understanding the physical and especially bonding properties of the molecules.^[50]

Conclusion

We have investigated the stabilization of novel copper dimers with short $\text{Cu}\cdots\text{Cu}$ distances in both (formal) oxidation states copper(I) and as well copper(0) by employing the somewhat “exotic” bridging $[\text{Ga}(\text{R})]$ ligands ($\text{R} = \text{Cp}^*, \text{ddp}$). The $[\text{Ga}(\text{R})]$ component behaves as both a selective reduc-

ing agent and a supporting ligand. Interestingly, the selective synthesis of the copper(I) dimers $[\{(\text{RGa})\text{CuX}\}_2]$ (**1**, **2**) requires the combination of $[\text{Ga}(\text{ddp})]$ with CuX_2 ($\text{X} = \text{Br}, \text{OTf}$). The delicate competition between coordination, insertion, and redox processes is further illustrated by the reaction of $\text{Cu}(\text{OTf})_2$ with $[\text{GaCp}^*]$, which leads to the formation of the quite unusual compound $[(\text{Cp}^*\text{Ga})\text{Cu}(\mu\text{-GaCp}^*)_3\text{Cu}\{\text{Ga}(\text{OTf})_3\}]$ (**3**). This Lewis acid/base adduct contains the fluxional, neutral, 30-electron fragment $\{\text{Cu}_2(\text{GaCp}^*)_4\}$, and is suggested as the first example of a copper(0) complex or cluster. Evidently, the formation of $\text{Ga}(\text{OTf})_3$ takes place in situ by a redox reaction, in which copper(II) is reduced to copper(0), and some gallium(I) is oxidized to gallium(III). In contrast, copper(I) complexes of the type $[\text{Cu}_2(\text{GaR})_5][\text{OTf}]_2$ (**4**) were accessible only with the sterically much less crowded $\text{R} = \text{Cp}^*$ and by choosing a copper(I) starting compound $[\text{Cu}(\text{cod})_2][\text{OTf}]$, which avoids any Cu/Ga redox reaction. Taken together, our new results show promise for extending the coordination chemistry of neutral, carbenoid Group 13 ligands ER beyond Group 10, to achieve oligonuclear cationic or even neutral compounds $[\text{M}_a\{\text{E}(\text{R})\}_b]^m$ ($m \geq 0$; $\text{M} \supset \text{group} \geq 11$; $b \geq a \geq 2$), which will be interesting as intermediates or starting precursors for the soft chemical synthesis of larger M/E intermetallic clusters or nanoparticles.

Experimental Section

General remarks: All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glove-box techniques. Hexane was dried using an MBraun Solvent Purification System. Fluorobenzene was dried by an alumina column under a dry atmosphere. The final H_2O content in all solvents was checked by Karl Fischer titration, and did not exceed 5 ppm. $[\text{Ga}(\text{ddp})]^{[12]}$ and $[\text{GaCp}^*]^{[51,52]}$ were prepared as previously described. $[\text{Cu}(\text{cod})_2][\text{OTf}]$ was prepared as previously described using $\text{Cu}^{\text{I}}(\text{OTf})\text{-toluene}$ instead of $\text{Cu}^{\text{I}}(\text{OTf})\text{-benzene}$.^[53] 2,6-Diisopropylaniline (Aldrich), 2,4-pentanedione (Aldrich), gallium (Aldrich), potassium hydride (Acros), iodine (Aldrich), Cu^{II} triflate (ABCR), $\text{Cu}^{\text{I}}(\text{OTf})\text{-toluene}$ (ABCR), $\text{Cu}^{\text{I}}\text{Br}$ (ABCR), and $\text{Cu}^{\text{II}}\text{Br}_2$ (ABCR) were purchased from commercial sources. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr University Bochum. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer in $[\text{D}_8]\text{THF}$ at 298 K. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. Chemical shifts are described in parts per million, downfield shifted from TMS, and are consecutively reported as position (δ_{H} or δ_{C}), relative integral, multiplicity (s = singlet, d = doublet, $sept$ = septet, m = multiplet), coupling constant (J in Hz) and assignment. IR measurements (KBr pellet) were carried out on a Bruker Alpha-P Fourier transform spectrometer.

X-ray crystallography: Crystals of **1**, **2**, **3** and **4** were obtained from mixtures of fluorobenzene/THF/*n*-hexane (**1**) at -30°C or fluorobenzene/*n*-hexane (**2**, **3** and **4**) at RT. The X-ray diffraction intensities were collected on an Oxford Xcalibur2 diffractometer with a Sapphire2 CCD. The crystal structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.^[54] The crystals were coated with a perfluoropolyether, picked up with a glass fibre, and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final R values are provided in Table S1 (Supporting Information). Molecules **1–4** were refined with distance restraints and restraints for the anisotropic displacement parameters. A co-crystallized fluorobenzene molecule was found in molecules **2**, **3** and **4** to be severely

disordered in each case, and could not be modelled reasonably. Thus, its contributions were removed from the diffraction data using PLATON/SQUEEZE.^[55,56] The Cp* ligands in **4** C₆H₅F are affected by disorder and show partially large displacement parameters. The Cp* ligand attached to Ga(2) was described by a split model and treated as a rigid group. Rigid bond restraints and restraints toward isotropy were applied to the carbon atoms. The non-coordinating [OTf]⁻ ion shows rotational disorder about the C–S axis. The opposite oxygen and fluorine atoms were refined with equal equivalent displacement parameters, respectively. Fluorine atoms were restrained toward isotropy. CCDC-766992 (**2**), 766993 (**3**), and 766994 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Complex 1: Fluorobenzene (2 mL) was added to a mixture of [Ga(dpp)] (0.1 g, 0.206 mmol) and CuBr₂ (0.023 g, 0.103 mmol) at RT under vigorous stirring. The clear yellow solution turned to cloudy brown when it was heated at 60 °C for 1 h. THF (1 mL) was added to this solution, stirred for 15 min, filtered, layered with hexane (6 mL) and stored at RT to afford colourless crystals of **1** after 24 h. Yield: 31% (based on CuBr₂); ¹H NMR ([D₈]THF, 250 MHz): δ = 7.28–7.21, 7.11–7.08 (m, 12H, Ar CH), 5.48 (s, 2H, γ-CH), 3.17 (sept, 8H, CH(Me)₂), 1.69 (s, 12H, CH₃), 1.29 (s, 8H, hexane-CH₂), 1.05 (d, 48H, CH(Me)₂), 0.92–0.83 ppm (m, 6H, hexane-CH₃); ¹³C NMR ([D₈]THF, 62.8952 MHz): δ = 161.95 (C(Dipp)-N), 143.09 (CMe), 141.66 [o-C(Dipp)], 126.04 [p-C(Dipp)], 123.73 [m-C(Dipp)], 94.49 (γ-C), 30.8 (hexane-CH₂), 29.06 (CHMe₂), 23.47 (CMe), 23.3 (hexane-CH₂), 20.91 (CHMe₂), 17.1 ppm (hexane-CH₃); elemental analysis calcd (%) for C₅₈H₈₂Cu₂Br₂Ga₂N₄·hexane (1347.84): C 57.03, H 7.18, N 4.16; found: C 57.11, H 7.18, N 4.15.

Complex 2: Fluorobenzene (2.5 mL) was added to a mixture of [Ga(dpp)] (0.1 g, 0.206 mmol) and Cu(OTf)₂ (0.037 g, 0.103 mmol) under vigorous stirring at RT. The reaction mixture was heated at 60 °C for 1 h, during which the clear pale yellow solution became brown-yellow and slightly turbid. At this stage the solution was brought to RT, filtered, and layered with hexane (0.5 mL), to afford colourless crystals of **2** at RT over a period of 12 h. Yield: 63% (based on Cu(OTf)₂). Compound **2** slowly decomposed at RT in the absence of mother liquid under inert atmosphere or when it was dissolved in organic solvents. Thus, the detailed study of molecule **2** was not successful. Elemental analysis calcd (%) for C₆₀H₈₂Cu₂F₆Ga₂N₄O₆S₂ (1400.00): C 51.48, H 5.90, N 4.00, S 4.58; found: C 51.73, H 5.87, N 3.87, S 4.52; IR: ν̄ = 2962, 2926, 2868, 1528, 1460, 1440, 1381, 1362, 1318, 1296, 1255, 1228, 1211, 1164, 1103, 1055, 1019, 936, 863, 798, 757, 631, 573, 531, 515, 440 cm⁻¹.

Complex 3: [GaCp*] (0.357 g, 1.742 mmol) was added to a solution of Cu(OTf)₂ (0.150 g, 0.415 mmol) in fluorobenzene (5 mL). The reaction mixture was heated at 60 °C for 1 h, then the solvent was reduced in vacuo, and the residue was washed with *n*-hexane and dried in vacuo to give a colourless solid. Yield: 0.385 g (63%). Recrystallisation of the crude product by slow diffusion of *n*-hexane into a solution of **3** in fluorobenzene gave colourless single crystals. ¹H NMR ([D₈]THF, 250 MHz): δ = 2.03 ppm (s, 60H, GaCp*); ¹³C NMR ([D₈]THF, 62.8952 MHz): δ = 115.46 (GaC₃Me₅), 9.75 ppm (GaC₃Me₅); ¹⁹F NMR ([D₈]THF, 235.3 MHz): δ = -78.8 ppm (CF₃SO₃); elemental analysis calcd (%) for C₄₅H₆₀F₉S₃O₉Cu₂Ga₃ (1457.81): C 35.40, H 4.15, S 6.58; found: C 35.65, H 4.16, S 6.31; IR: ν̄ = 1593, 1480, 1456, 1417, 1384, 1329, 1308, 1262, 1232, 1189, 1162, 1018, 998, 799, 754, 685, 631, 572, 513 cm⁻¹.

Complex 4: [GaCp*] (0.388 g, 1.093 mmol) was added to a suspension of [Cu(cod)]₂[OTf] (0.150 g, 0.350 mmol) in fluorobenzene (5 mL), whereupon the suspension became a yellow solution. The reaction mixture was stirred at room temperature for 1 h, then the solvent was reduced in vacuo, and the residue was washed with *n*-hexane and dried in vacuo to give a colourless solid. Yield: 0.354 g (70%). Recrystallisation of the crude product by slow diffusion of *n*-hexane into a solution of **4** in fluorobenzene gave colourless single crystals. ¹H NMR ([D₈]THF, 250 MHz): δ = 2.04 ppm (s, 60H, GaCp*); ¹³C NMR ([D₈]THF, 62.8952 MHz): δ = 112.2 (GaC₃Me₅), 7.1 ppm (GaC₃Me₅); ¹⁹F NMR ([D₈]THF, 235.3 MHz): δ = -78.4 ppm (CF₃SO₃); elemental analysis calcd (%) for C₅₂H₇₅F₉S₂O₆Cu₂Ga₅ (1443.98): C 43.21, H 5.23, S 4.43; found: C 43.85, H

5.47, S 4.14; IR: ν̄ = 1480, 1451, 1420, 1384, 1305, 1268, 1230, 1203, 1157, 1015, 799, 756, 687, 632, 589, 571, 513 cm⁻¹.

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