ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2023, 59, 1353

Received 24th November 2022,
Accepted 20th December 2022

DOI: 10.1039/d2cc06377h

rsc.li/chemcomm

How long are Ga⇆Ga double bonds and Ga–Ga single bonds in dicationic gallium dimers?†

Antoine Barthélemy, Harald Scherer, Hanna Weller and Ingo Krossing *

Syntheses and characterization of two salts [(L)GaGa(L)][*pf*]$_2$ ([*pf*]$^-$ = [Al(OR^F)$_4$]$^-$; R^F = C(CF$_3$)$_3$) are reported. They include the first dicationic digallene [(L)Ga⇆Ga(L)]$^{2+}$ (L = CDP^{Ph} = C(PPh$_3$)$_2$) and a digallane [(L)Ga–Ga(L)]$^{2+}$ (L = [NacNac^{Mes}]$^-$). The CDP^{Ph}-supported digallene dication includes a *trans*-bent [L–GaGa–L]$^{2+}$ bond that is analogous to neutral R–GaGa–R molecules and related to Robinson's famous "Digallyne" [R–GaGa–R]$^{2-}$. The dicationic digallane [(L)Ga–Ga(L)]$^{2+}$ is analogous to the widely used "Jones magnesium dimer", but includes a very short Ga^{II}–Ga^{II} single bond.

An understanding of the nature and strength of covalent bonds is at the heart of chemistry. Using the standard notion of bond strengths and lengths, a single bond should be longer and weaker than a double or triple bond. Yet, more generally and following the Carter–Goddard–Malrieu–Trinquier model, the different binding modes in formally doubly bonded R$_x$E=ER$_x$ systems depend on the energy difference between singlet and triplet state of the two fragments: ER$_x$.[1,2] For most substituents R and elements E, the singlet state is energetically more favourable than the respective triplet state.[3] Thus, formal double bonds between heavier elements are better described as two dative bonds "R$_x$E⇆ER$_x$" between filled s-orbitals and empty p-orbitals of two singlet carbene-analogue fragments.[1,4–6] In this respect, group 13 elements are somewhat notorious.[7,8] Several compounds exhibit unusual **GaGa** bonds and have triggered fundamental discussions about the nature of covalent bonds and the concept of bond orders in general.[7–11] The digallium bonding in such compounds is illustrated in Fig. 1, *i.e.* digallanes, formal digallenes and digallynes. Note that only the incorporation of Na$^+$ ions into the cluster core in Robinson's formal digallyne Na$_2$[Ar*GaGaAr*], one of the most discussed organometallic compounds,[7,8,11,12] impedes Coulomb explosion into two [Ar*Ga]$^-$ anions.

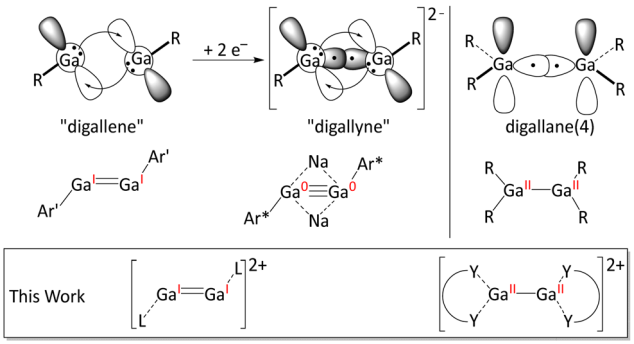


Fig. 1 Non-classical formal double bonds between two R–Ga^I fragments (digallene; top left), two-electron reduction, giving a formal digallyne (top middle),[1,4–6] structures of known digallenes[14] (Ar′ = 2,6-(Dipp)$_2$C$_6$H$_3$; Ar* = 2,6-(Tripp)$_2$C$_6$H$_3$) and digallynes.[11,14,15] The structures of neutral digallanes (top right) and of the cationic compounds presented herein are also shown (R = alkyl, aryl, amido; L = CDP^{Ph}; Y = N donor groups).

In this work, we show that Ga–Ga single and formal double bonds form within dications (Fig. 1). Ion pairing is avoided by using the weakly coordinating anion [*pf*]$^-$ = [Al{OC(CF$_3$)$_3$}$_4$]$^-$.[13]

Syntheses and molecular structures. The Ga$^+$ source used in this work is [Ga(PhF)$_2$][*pf*].[16] Upon addition of a mesityl-substituted β-diketiminate ([NacNac^{Mes}]$^-$) ligand, Ga$^+$ disproportionates, giving the dicationic digallane [{Ga(NacNac^{Mes})}$_2$][*pf*]$_2$·1.5*o*DFB ([**1**][*pf*]$_2$·1.5*o*DFB) (eqn (1)) which is isostructural to neutral Mg^I dimers.[17] Eqn (2) shows that the dicationic digallene [{Ga(CDP^{Ph})}$_2$][*pf*]$_2$ ([**2**][*pf*]$_2$) forms with the neutral ligand L = hexaphenylcarbodiphosphorane (CDP^{Ph})[18] as electron-rich, four-electron ligand, under conservation of the oxidation state of Ga. Obviously, [NacNac^{Mes}]$^-$ is more strongly

Institut für Anorganische und Analytische Chemie and Freiburger Materialforschungszentrum (FMF), Universität Freiburg, Albertstr. 21, Freiburg 79104, Germany. E-mail: krossing@uni-freiburg.de

† Electronic supplementary information (ESI) available. CCDC 2220000–2220002. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d2cc06377h

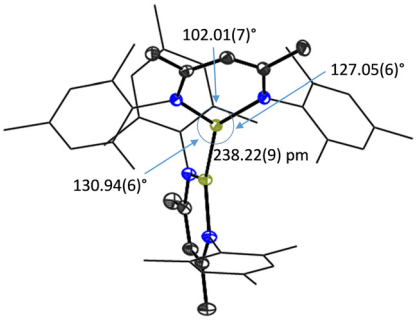


Fig. 2 Molecular structure of $\mathbf{1}^{2+}$ in [**1**][*pf*]$_2$·1.5*o*DFB. Only one of the two crystallographically independent 1^{2+} units is shown. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability level, the mesityl groups are shown as a wireframe model (black: C; blue: N; beige: Ga).

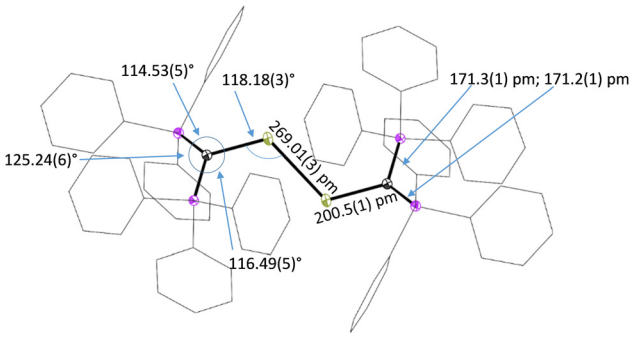
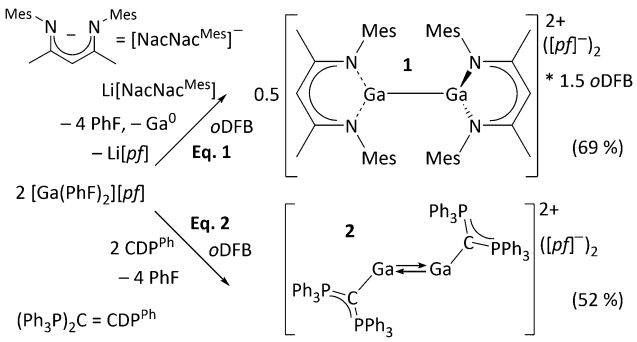


Fig. 3 Molecular structure of $\mathbf{2}^{2+}$ in [**2**][*pf*]$_2$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability level, the phenyl groups are shown as a wireframe model (black: C; purple: P; beige: Ga).

coordinating than neutral CDP^{Ph}, inducing disproportionation of metastable Ga^{+}[19] (characterization in ESI†).‡



The molecular structure of the ecliptic dication $\mathbf{1}^{2+}$ is shown in Fig. 2. Despite several NacNacGa compounds being known,[20] $\mathbf{1}^{2+}$ is the first featuring a Ga–Ga bond. The intact dimer $\mathbf{1}^{2+}$ exists in solution, as confirmed by DOSY NMR experiments (see ESI†). This is in line with quantum chemical calculations, which suggest that the dissociation is both endergonic in the gas phase and in *o*DFB (see below, eqn (5). Application of [In(PhF)$_2$][*pf*] in the reaction leading to $\mathbf{2}^{2+}$ yielded [In(CDP^{Ph})][*pf*] including a monomeric complex cation. However, the synthesis was not reproducible and the crystal structure is only discussed in the ESI.† In contrast to $\mathbf{1}^{2+}$, DOSY NMR experiments did not allow to clarify whether $\mathbf{2}^{2+}$ dissociates in solution (see ESI†). Its centrosymmetric molecular structure is displayed in Fig. 3. To the best of our knowledge, $\mathbf{2}^{2+}$ is the first isolated Ga^{I}–CDP complex. The structure contains a Ga$_2$-dumbbell and a coplanar C^{CDP}–Ga–Ga–C^{CDP} moiety. Each Ga atom is coordinated by one CDP^{Ph} ligand in a *trans*-bent fashion that is typical for non-classical formal double bonds.[3–6,9]

Comparison with neutral digallanes and digallenes. The main structural parameters of the digallane $\mathbf{1}^{2+}$ and digallene $\mathbf{2}^{2+}$ are compared with related neutral species in Table 1. The correlation between Ga–Ga bond length and formal bond order is rather poor, underpinning the difficulty to assign bond orders in such compounds. The average Ga–Ga bond length in $\mathbf{1}^{2+}$ (238.22(9) pm) is remarkably short and only comparable to those in neutral five-membered Ga^{II} NHC dimer analogues, *e.g.* [Ga^{II}{[N(Dipp)C(Me)]$_2$}]$_2$ (236.34(9) pm)[21] or [Ga^{II}{[N(^{t}Bu)CH]$_2$}]$_2$ (233.3(1) pm).[22] The Ga–Ga bond in the singly bonded $\mathbf{1}^{2+}$ is only slightly longer than that in Robinson's formal digallyne[22] and significantly shorter than in other digallanes(4). This is somewhat surprising, since Coulomb repulsion should lead to a bond lengthening in the dicationic dimer. Neutral dimers [{M(NacNac)}$_2$] are also known for M = Zn^{I},[23] and M = Mg^{I}.[24] Ga^{II} is isoelectronic to Zn^{I} and, ignoring the filled d orbitals, analogous to Mg^{I}. The Mg–Mg bond length in [{Mg^{I}(NacNac^{Mes})}$_2$], is almost 43 pm longer[24] than the Ga–Ga bond in $\mathbf{1}^{2+}$. The positive charge residing on Ga, leading to contracted orbitals and, in addition, d-block contraction probably account for the shorter bonds. Accordingly, the corresponding Zn^{I} dimer [{Zn^{I}(NacNac^{Mes})}$_2$] has a similar M–M bond length (238.13(8) pm[23]) to the gallium dimer. However, the dihedral angle in the Ga dimer (84.65(8)°) is even higher than in the respective Zn (45.0(1)°) and Mg dimer (43.94(7)°).

The Ga–Ga distance in $\mathbf{2}^{2+}$ is longer than in a neutral digallene (entry 8 in Table 1), probably as a result of Coulomb repulsion between the positively charged [Ga(CDP^{Ph})]$^+$ fragments. The putative digallynes display shorter Ga–Ga bonds, due to the influence of the bridging Na atoms and the additional electrons in bonding orbitals (Fig. 1). In addition, the digallene in entry 3, stabilized by silyl- and NHC ligands,[25] has a Ga–Ga distance similar to the Ga–Ga distance in putative digallynes, possibly due to the donation of electron density of the NHC-ligands into a Ga–Ga-bonding orbital.

The digallene dimer in entry 10 displays the longest Ga–Ga bond of the compounds presented in Table 1.[28]

Calculated thermodynamics. Eqn (3) and (4) include the formation energetics of $\mathbf{2}^{2+}$ and its (hypothetical) indium-analogue, which in our experiments remained monomeric in the solid state. The CDP^{Ph} complexation is favourable to the monocation (eqn (3)). Dimerization in eqn (4) is slightly favourable, but only in a polar *o*DFB solution (ε_r = 13.38;[29] RI-BP86(D3BJ)/def2-TZVPP).

$$[M^{I}(PhF)_2]^+ + CDP^{Ph} \rightarrow [M^{I}(CDP^{Ph})]^+ + 2PhF \quad (3)$$

Ga: $\Delta_r H_{(g)} = -174$; $\Delta_r G_{(g)} = -208$ kJ mol^{-1}

In: $\Delta_r H_{(g)} = -153$; $\Delta_r G_{(g)} = -190$ kJ mol^{-1}

Table 1 Structural comparison of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ with related neutral Ga-dimers (NHC = :C(N{^{i}Pr}CMe)$_2$; tmp = 2,2,6,6-tetramethylpiperidino)

Entry[a]	Compound	d_{Ga-Ga} [pm]	d_{E-Ga} [pm]	E–Ga–Ga angle [°]	Ref.
$1_{Ga\equiv Ga}$	Na_2[Ar*GaGaAr*]	231.9(3), 232.4(1)	204(2) av. (E = C) 204.1(5) av. (E = C)	131.0(4) av. (E = C) 131.07(17) av. (E = C)	11 and 15
2_{Ga-Ga}	[HC(^{t}Bu)N]$_2$GaGa[N(^{t}Bu)CH]$_2$	233.3(1)	183.8(6) av. (E = N)	134.8(2) av. (E = N)	22
$3_{Ga=Ga}$	[(^{t}Bu$_2$MeSi)(NHC)GaGa(NHC)(SiMe^{t}Bu$_2$)]	234.1(3)	209.7(4) (E = C)	110.99(13) (E = C) 125.88(17) (E = Si)	25
$4_{Ga\equiv Ga}$	Na_2[Ar′GaGaAr′]	234.7(1)	205.9(5) (E = C)	130.7(1) (E = C)	14
5_{Ga-Ga}	[(NacNac^{Mes})GaGa(NacNac^{Mes})]$^{2+}$ ($\mathbf{1}^{2+}$)	238.22(9)	184.68(18) av. (E = N)	128.99(6) av. (E = N)	This work
6_{Ga-Ga}	(tmp)$_2$GaGa(tmp)$_2$	252.5(1)	190.1(4) av. (E = N)	120.7(1) av. (E = N)	26
7_{Ga-Ga}	[(Me$_3$Si)$_2$HC]$_2$GaGa[CH(SiMe$_3$)$_2$]$_2$	254.1(1)	199.5(7) av. (E = C)	122.0(2) av. (E = N)	27
$8_{Ga=Ga}$	[Ar′GaGaAr′]	262.68(7)	202.5(3) (E = C)	123.16(7) (E = C)	14
$9_{Ga=Ga}$	[(CDP^{Ph})GaGa(CDP^{Ph})]$^{2+}$ ($\mathbf{2}^{2+}$)	269.01(3)	200.52(9) (E = C)	118.18(3) (E = C)	This work
$10_{Ga=Ga}$	Ph$_2$P(DippN)$_2$GaGa(NDipp)$_2$PPh$_2$	278.73(12)	207.9(2) av. (E = N)	107.70(6) av. (E = N)	28

[a] Includes as subscript the formally (!) assigned GaGa bond order of the respective compound.

$$2\left[M^{I}(CDP^{Ph})\right]^{+} \rightarrow \left[(CDP^{Ph})M^{I} \leftrightarrows M^{I}(CDP^{Ph})\right]^{2+} \quad (4)$$

$$\text{Ga: } \Delta_r H_{(g)} = +6;\ \Delta_r G_{(g)} = +72;\quad \Delta_r G_{(o\text{DFB})} = -39 \text{ kJ mol}^{-1}$$

$$\text{In: } \Delta_r H_{(g)} = +26;\ \Delta_r G_{(g)} = +95;\quad \Delta_r G_{(o\text{DFB})} = -18 \text{ kJ mol}^{-1}$$

tIn agreement with the experiments, DFT calculations suggest that the Ga^{II}–Ga^{II} single bond in $\mathbf{1}^{2+}$ is stronger by *ca.* 200 kJ mol^{-1} compared to the formal $Ga^{I}\leftrightarrows Ga^{I}$ double bond in $\mathbf{2}^{2+}$ (see eqn (4) and (5), in line with previous calculations that point to a bond order below unity for neutral digallenes.[14,30]

$$2\left[Ga^{II}(NacNac^{Mes})\right]^{+} \rightarrow \mathbf{1}^{2+} \quad (5)$$

$$\Delta_r H_{(g)} = -186;\ \Delta_r G_{(g)} = -119,\ \Delta_r G_{(o\text{DFB})} = -251 \text{ kJ mol}^{-1}$$

Bonding in the dicationic digallane and digallene. QTAIM charges δ of selected atoms in $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, bond path ellipticities (ε_{BCP}), electron densities on bond critical points (ρ_{BCP}) and the Ga–Ga Wiberg bond indices (WBI), are summarized in Table 2. Both, ρ_{BCP}(Ga–Ga) and WBI, are higher for $\mathbf{1}^{2+}$ compared to $\mathbf{2}^{2+}$. Additionally, the HOMO-LUMO gap is significantly higher in $\mathbf{1}^{2+}$ (2.6 *vs.* 2.1 eV; RI-BP86(D3BJ)/def2-TZVPP), again indicating a stronger Ga–Ga bond. The QTAIM charge of +1.09 on the formal Ga^{II} atoms suggests significant delocalization of the positive charge over the ligand in $\mathbf{1}^{2+}$. This, along with the contracted s and p orbitals in the dication, presumably accounts for the surprisingly short Ga–Ga bond. Ellipticity ε_{BCP} and WBI unequivocally classify the Ga–Ga bond as a single bond. By contrast, the bonding situation in the dicationic digallene is amazingly complex (resonance forms in Fig. 4, frontier orbitals in ESI†). The C^{CDP}–Ga bonds can either be described as purely dative bonds (forms **IV** and **VII** in Fig. 4), leaving the positive charge on the Ga-centres, or as covalent bonds, formally shifting the positive charge to the ligand (forms **I**, **V**, **VI**).

Invoking covalent double bonds between C^{CDP} and Ga formally leaves a negative charge on the Ga atoms (forms **II** and **III**). Interestingly, the C^{CDP}–Ga distance in $\mathbf{2}^{2+}$ is short at 200.6(1) pm and is even shorter than the covalent $C^{terphenyl}$–Ga bond in the first neutral digallene (202.5(3) pm).[14] This

Table 2 QTAIM charges, electron densities, bond path ellipticities and WBIs for selected atoms and bonds in $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ (RI-BP86(D3BJ)/def2-TZVPP). For $\mathbf{2}^{2+}$, the gas phase-optimized structure and the scXRD structure (values in parentheses) were analyzed[a]

Property	$\mathbf{2}^{2+}$	Property	$\mathbf{1}^{2+}$	$\mathbf{2}^{2+}$
δ^+(P) / [e]	2.60 (2.63)	δ^+(Ga) / [e]	1.09	0.52 (0.51)
δ^-(C^{CDP}) / [e]	−2.06 (−2.07)			
ρ_{BCP}(C^{CDP}–Ga) / [e Å^{-3}]	0.610 (0.664)	ρ_{BCP}(Ga–Ga) / [e Å^{-3}]	0.508	0.182 (0.283)
ε_{BCP}(C^{CDP}–Ga)	0.119 (0.107)	ε_{BCP}(Ga–Ga)	0.000	0.061 (0.100)
WBI (C^{CDP}–Ga)	0.410 (0.438)	WBI (Ga–Ga)	0.872	0.604 (0.814)

[a] For reasoning, see section 8.4 in ESI.

indicates partial transfer of the positive charge to the CDP ligands as evident from entry 1 in Table 2 and is further supported by the nearly trigonal planar coordination mode around C^{CDP} ($\sum_{\text{bond angles}}(C^{CDP})$ = 356.26(6)°). The simplified picture of a central sp^2-hybridized C^{CDP} atom and a delocalization of the positive charge along the P–C^{CDP}–P axis as in form **I** would explain the observation. However, the calculated QTAIM charge on C^{CDP} is negative at about −2 (Table 2 and forms **IV**–**VII**). This suggests that the C^{CDP}–Ga bond also exhibits considerable electrostatic character, accounting for the surprisingly short C^{CDP}–Ga bond. In fact, EDA-NOCV analysis confirms that the orbital-based and electrostatic contributions are equally important to describe the C^{CDP}–Ga bond (see ESI†). The C–Ga bond in $\mathbf{2}^{2+}$ has a WBI less than unity, underlining the contribution of resonance forms **IV** and **VII**. Additionally, ε_{BCP}(C^{CDP}–Ga) of *ca.* 0.11 (Table 2) and the EDA-NOCV analysis of [Ga(CDP^{Ph})]$^+$ indicate that both the σ- and the π-electron pairs of C^{CDP} contribute to the formation of the C^{CDP}–Ga bond (forms **II**, **III** and **V**–**VII**). Thus, the bonding situation in $\mathbf{2}^{2+}$ needs to be described by multiple resonance forms but is best visualized by resonance forms **V**–**VII**.

The non-classical double bond character of the GaGa bond in $\mathbf{2}^{2+}$ is clearly confirmed by an EDA-NOCV analysis: The HOMO of $\mathbf{2}^{2+}$ has pronounced Ga lone pair character (see ESI†) and accordingly EDA-NOCV analysis suggests that the most important interaction between the Ga atoms is the reciprocal donation of lone pair electron density into an empty 4p orbital. The resulting deformation

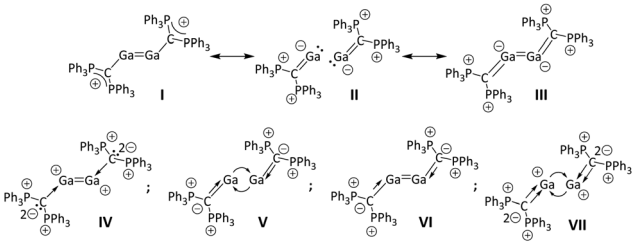


Fig. 4 Limiting resonance forms **I–III** and arrow-based descriptions **IV–VII** of $\mathbf{2}^{2+}$.

densities $\Delta\rho_{(1)-(2)}$ for the interaction between the $[Ga(CDP^{Ph})]^+$ fragments are shown in Fig. S-63 (ESI†).

In summary, we demonstrated that formation of single and formally double **GaGa** bonds is possible in dimeric, dicationic gallium compounds. Coulomb explosion can be prevented by employing electron rich ligands and the weakly coordinating $[pf]^-$ anion. $\mathbf{1}^{2+}$ is a dicationic digallane with very short **GaGa** bond, isostructural to a Jones Mg dimer. $\mathbf{2}^{2+}$ is the first dicationic digallane: Its bonding situation is complicated and has to be described by multiple resonance forms, best **V–VII**. It also represents the first univalent gallium-carbodiphosphorane-complex.

The authors acknowledge support by the Fonds of the Chemical Industry, the DFG in normal procedure, the state of Baden-Württemberg through bwHPC and the DFG through grant no. INST 40/467-1 and 575-1 FUGG (JUSTUS1 and 2 cluster).

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ In *o*DFB solutions of $\mathbf{2}^{2+}$, we reproducibly observed the formation of *ca*. 12% $[H–CDP^{Ph}]^+$. The amount of protonated ligand is solvent-dependent. We suggest that the super basic ligand and Ga^+ initiate intra-or intermolecular C–H bond activation of the ligand (see ESI†).

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