

NHC-Induced Dismutation of Gallium–Zinc Bonds

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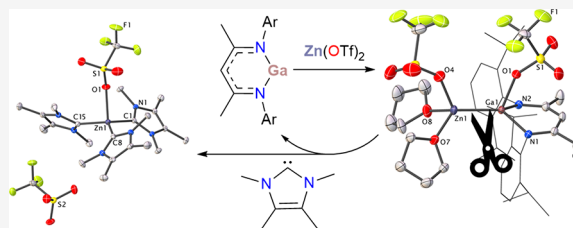
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ABSTRACT: The insertion of gallium(I) reagent $[(\text{BDI})\text{Ga}^{\text{I}}]$ (**I**, BDI = $\text{HC}\{\text{C}(\text{CH}_3)\text{Ndipp}\}_2$; $\text{dipp} = 2,6\text{-di-isopropyl-phenyl}$) into $\text{Zn}^{\text{II}}\text{-X}$ bonds ($\text{X} = \text{OTf}, \text{Cl}$) to provide gallyl zinc complexes $[(\text{BDI})\text{Ga}(\text{X})\text{-Zn}(\text{X})\text{L}_2]$ (**1** – **3**; $\text{L}_2 = \text{thf}_2, \text{tmeda}$; $\text{tmeda} = N,N,N',N'$ -tetramethylethylenediamine) is readily reversed by ligand substitution with an N-heterocyclic carbene (NHC), regenerating **I** and eliminating $(\text{NHC})_n\text{ZnX}_2$ via ‘dismutation’ of the Ga–Zn bond. The dative Ga→Zn interaction present in $[(\text{BDI})\text{Ga}\cdot\text{Zn}(\text{Cl})(\text{tmeda})][\text{BAR}^{\text{F}}_4]$ (**4**; $\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2$) is similarly disrupted by the addition of NHC. $[(\text{BDI})\text{Ga}(\text{X})\text{Zn}(\text{X})\text{L}_2]$ complexes also react as a ‘masked’ source of **I**, as demonstrated by reactions with Et_3NHCl and $\text{B}(\text{C}_6\text{F}_5)_3$, which yield the respective literature compounds $[(\text{BDI})\text{Ga}(\text{H})\text{Cl}]$ and $[(\text{BDI})\text{Ga}\cdot\text{B}(\text{C}_6\text{F}_5)_3]$.



Subhalides of gallium such as Ga_2X_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) undergo comproportionation and disproportionation (synonym: dismutation) depending on the availability of donor ligands or solvent. While the relative stability of monovalent gallium and closed-shell trivalent gallate anions favors the mixed-valence formulation $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{X}_4]$, Lewis bases promote comproportionation and formation of digallane species $[(\text{L})\text{X}_2\text{Ga-GaX}_2(\text{L})]$ with a covalent $\text{Ga}^{\text{II}}\text{-Ga}^{\text{II}}$ σ -bond.^{1–4} Organometallic digallanes are well-known to be prone to disproportionation into gallium(III) and gallium(0) or gallium(I) species.^{5–9} Zinc(I) dimers, which are formally isoelectronic to digallanes, contain a $\text{Zn}^{\text{I}}\text{-Zn}^{\text{I}}$ bond, which is remarkably robust toward oxidants and Brønsted acids^{10–12} but may be kinetically activated by judicious choice of ligand and/or desymmetrization to introduce polarity to the Zn–Zn bond.^{11,13–17} On the other hand, while examples of heteronuclear Ga–M and Zn–M bonds are numerous, the reactivity of such species—which may similarly benefit from a degree of polarization—has not been thoroughly studied.

The gallium(I) complex, $[(\text{BDI})\text{Ga}]$ (**I**, BDI = $\text{HC}(\text{C}(\text{CH}_3)\text{N}(2,6\text{-iPr-C}_6\text{H}_3)_2)$)¹⁸ inserts into E–X bonds ($\text{E} = \text{Al}, \text{P}, \text{Sb}, \text{Bi}, \text{Sn}, \text{Ge}, \text{Si}, \text{Zn}$, etc.) to provide access to a plethora of compounds involving Ga–E σ -bonds, some of which display unusual reactivity.^{19–25} Maron, Okuda, and co-workers reported the reaction of **I** with cationic aluminum dihydride $[(\text{tmeda})\text{AlH}_2(\text{OEt}_2)][\text{BAR}^{\text{Me}}_4]$ (TMEDA = N,N,N',N' -tetramethylethylenediamine; $\text{Ar}^{\text{Me}} = \text{C}_6\text{H}_3\text{-3,5-(CH}_3)_2$) to form $[(\text{BDI})\text{Ga}(\text{H})\text{-Al}(\text{H})(\text{tmeda})][\text{BAR}^{\text{Me}}_4]$ (**II**) with a covalent Al–Ga bond (Scheme 1a).²⁶ Addition of excess THF to **II** or ligand substitution with two equiv of N-heterocyclic carbene $\text{C}\{\text{N}(\text{CH}_3)\text{C}(\text{CH}_3)\}_2$ (IME_4) resulted in the elimination of $[(\text{tmeda})\text{AlH}_2(\text{thf})_2]^+$ or $[(\text{IME}_4)_2\text{AlH}_2]^+$ to regenerate **I**.²⁶ In a subsequent advance, zinc hydride cation $[(\text{tmeda})\text{ZnH}(\text{OEt}_2)][\text{BAR}^{\text{F}}_4]$ ($\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2$) was

shown to react with **I** to provide a Ga–Zn species $[(\text{BDI})\text{Ga}(\text{H})\text{Zn}(\text{tmeda})][\text{BAR}^{\text{F}}_4]$ (**III**), which reversibly splits dihydrogen across the metal–metal bond (Scheme 1b).²⁷

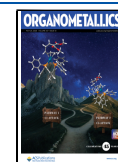
We aimed to explore the potential for similar reactivity in heterobimetallic complexes derived from simple zinc salts instead of the synthetically elaborate zinc hydride cation and BAR^{F}_4 anion. To this end, $\text{Zn}(\text{OTf})_2$ was added to a THF solution of **I** without or with TMEDA and then heated at 60 °C overnight to yield the respective bimetallic triflate complexes $[(\text{BDI})\text{Ga}(\text{OTf})\text{Zn}(\text{OTf})\text{L}_2]$ ($\text{L}_2 = \text{thf}_2$ (**1**), tmeda (**2**); Scheme 2), which crystallized directly from the filtered and cooled reaction mixture. Chloride derivative $[(\text{BDI})\text{Ga}(\text{Cl})\text{Zn}(\text{Cl})(\text{tmeda})]$ (**3**) was prepared by ligand substitution of Fischer’s THF-ligated derivative $[(\text{BDI})\text{Ga}(\text{Cl})\text{Zn}(\text{Cl})(\text{thf})_2]$ (**IV**)²⁵ with TMEDA and isolated as a colorless microcrystalline solid after recrystallization from hot toluene. Attempts to prepare a coordinatively unsaturated cation via chloride abstraction of **3** with $\text{Na}[\text{BAR}^{\text{F}}_4]$ ²⁸ in diethyl ether were unsuccessful. Instead, compound **I** was reacted with a zinc chloride cation “ $[(\text{tmeda})\text{ZnCl}][\text{BAR}^{\text{F}}_4]$ ”, prepared *in situ* by protonolysis of ethylzinc chloride with $[(\text{tmeda})\text{H}][\text{BAR}^{\text{F}}_4]$ in THF-*d*₈,²⁹ to provide $[(\text{BDI})\text{Ga}\cdot\text{Zn}(\text{Cl})(\text{tmeda})][\text{BAR}^{\text{F}}_4]$ (**4**). Compound **4** was isolated as a colorless crystalline solid after layering the concentrated reaction solution with *n*-hexane. Compounds **1** – **4** were characterized by X-ray crystallography, NMR spectroscopy, and elemental microanalysis and are indefinitely stable in the solid state when

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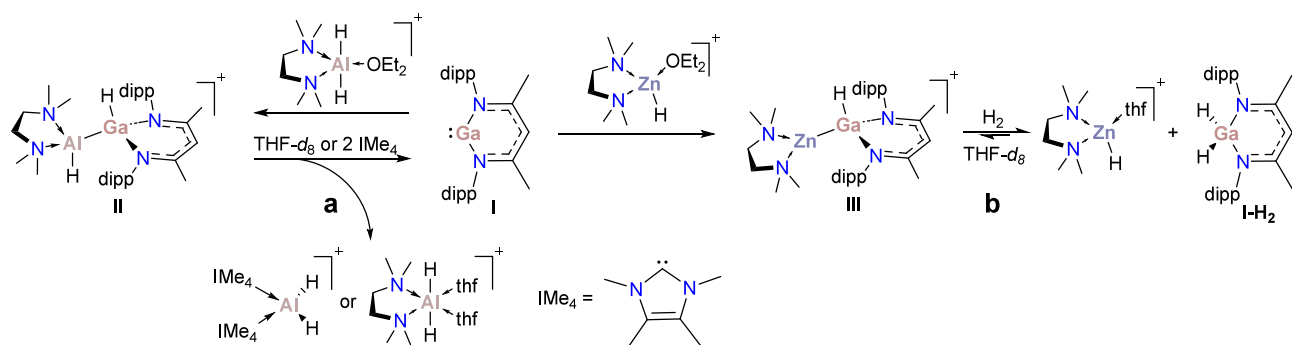
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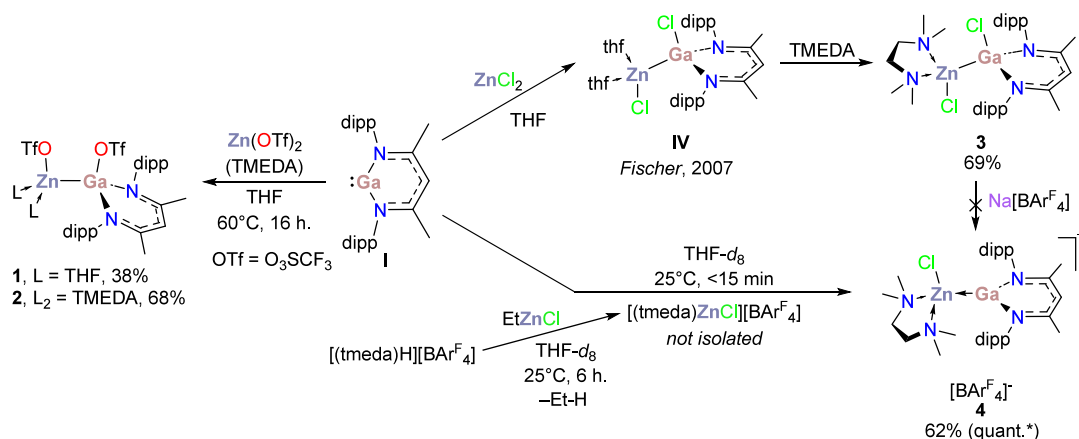
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Scheme 1. a) Base-Induced Dismutation of Al–Ga Complex II; b) Reversible Splitting of Dihydrogen across Ga–Zn Bond III^{26,27}



Scheme 2. Synthesis of Compounds 1 – 4^a



^aIsolated crystalline yields are reported. *Quantitative yield by *in situ* ¹H NMR spectroscopy.

stored at room temperature under an argon atmosphere. THF-*d*₈ solutions of 4 do not display noticeable decomposition after several days at 80 °C, whereas slight decomposition of compounds 1 – 3 and IV was observed after 3 days in THF-*d*₈ at this temperature.

Compounds 1 and 2 crystallized from THF in the respective triclinic and orthorhombic space groups, *P* $\bar{1}$ and *Pccn* (Figure 1a, b). Each four-coordinate metal center adopts a distorted tetrahedral geometry, with a triflate moiety bound to each metal via Ga1–O1 (2.0637(13), 2.1066(13) Å) and Zn1–O4 (1.9966(13), 2.0413(16) Å) bonds. The triflate moieties adopt a *cisoid* conformation in the solid-state (O1–Ga1–Zn1–O4 = 3.98(8)° (1), 7.20(8)° (2)). Compound 3 crystallized from diethyl ether in the orthorhombic space group, *Pnma* (Figure 1c) and is structurally similar to IV.²⁵ A terminal chloride is bound to each metal in a *transoid* arrangement (Cl–Ga–Zn–Cl = 180°) with both metal centers, chloride ligands, and C3 residing on crystallographically special positions, such that the asymmetric unit contains half a molecule bisected by a mirror-plane coincident with these atoms.

Consistent with stronger σ -donating properties of TMEDA relative to THF, the Ga1–Zn1 bonds (Table 1) of 2 and 3 (2.4113(3); 2.4167(6) Å, respectively) are elongated by approximately 0.05 Å compared to 1 and IV (2.3686(3); 2.3920(6) Å, respectively). These distances are typical compared to previously reported covalent Ga–Zn bonds.^{25,27,30–34} Consistent with an intermediate oxidation level, the Ga–N distances (1.9372(15) – 1.9806(18) Å) of 1 – 3, IV are shorter compared to gallium(I) complex I

(2.0528(14), 2.0560(13) Å)¹⁸ and longer than the gallium(III) dichloride complex [(BDI)GaCl₂] (I–Cl₂; 1.926(3), 1.906(3) Å),³⁵ while the Ga1–Cl1 (2.3002(9) Å) and Zn1–Cl2 (2.2561(10) Å) bonds in 3 are elongated compared to gallium(III) and zinc(II) species I–Cl₂ (2.228(1), 2.218(1) Å)³⁵ and [(tmeda)ZnCl₂] (2.21 – 2.22 Å).^{36–39}

Compound 4 crystallized from diethyl ether with two crystallographically independent borate anions and gallium–zinc cations in the asymmetric unit (Figure 1d; space group *P* $\bar{1}$). In each cation, the gallium center adopts a near-planar trigonal geometry, while a distorted tetrahedral geometry is observed for zinc. Additionally, significant residual electron density was found approximately 2.5 Å from the gallium center in both cases and was modeled as a partial-occupancy chloride (occupancy of Cl1B = 0.05 in Ga1, Zn1 containing cation; occupancy of Cl2B = 0.15 in Ga2, Zn2-containing cation). Thus, according to this interpretation of the diffraction data, the cationic part of 4 predominantly exists as a donor–acceptor complex [(BDI)Ga·Zn(Cl)(tmeda)]⁺ containing a formally dative gallium–zinc bond between {(BDI)Ga} and {(tmeda)ZnCl}⁺ fragments, while the alternative Ga–Cl isomer may be energetically accessible and present as minor a cocrystalline component. Similar cocrystallization of isomers [(BDI)Ga·Zn(H)(tmeda)][BAr^F₄][−] and [(BDI)Ga(H)–Zn(tmeda)][BAr^F₄][−] was previously observed for compound III.²⁷ While this disorder precludes detailed structural discussion, it is notable that the Ga1–Zn1 distance (2.4306(6) Å) in 4 is significantly longer than compounds

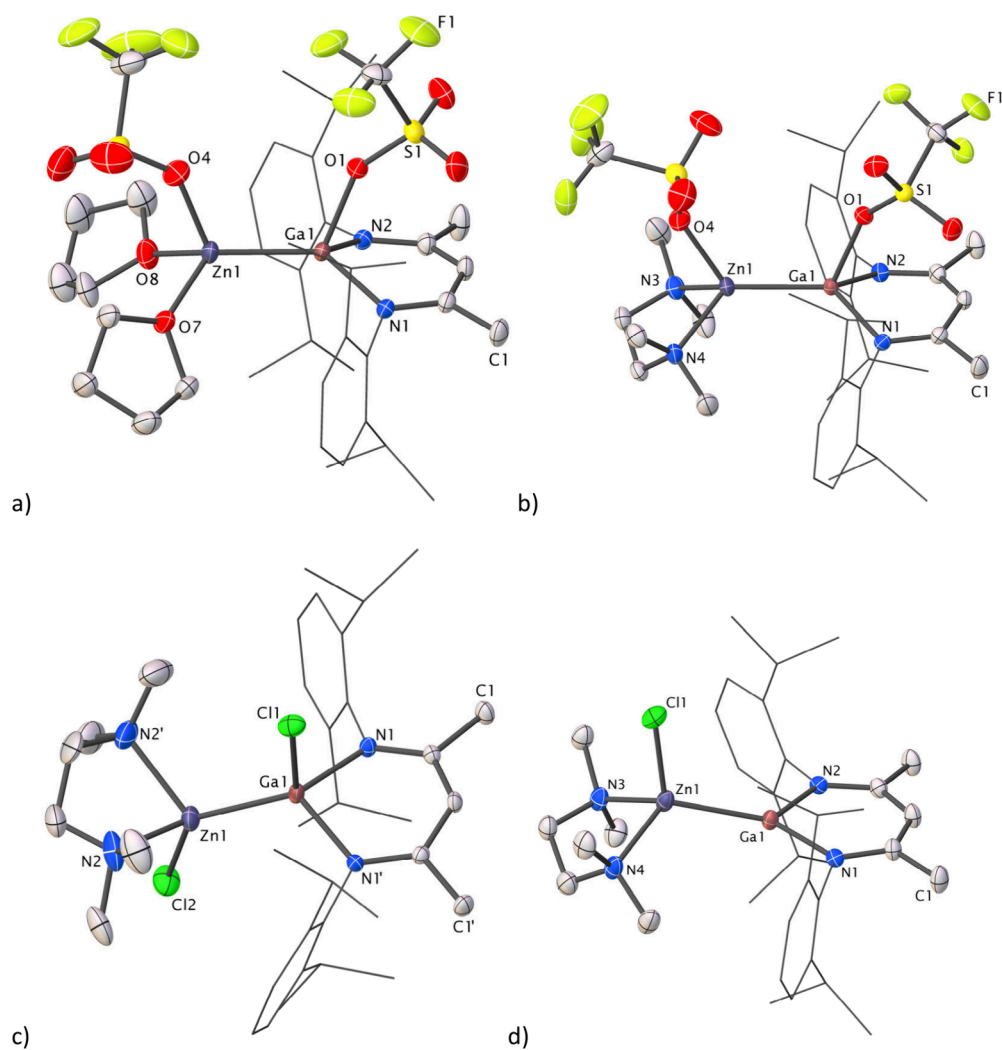


Figure 1. Displacement ellipsoid plots (30% level) of a) **1**, b) **2**, c) **3**, and d) the Ga1-containing cation in **4**. Dipp groups are shown in wireframe view, and hydrogen atoms are omitted for clarity. Only the major component of disordered residues is shown. Symmetry operation to generate primed atoms $+X, 3/2 - Y, +Z$.

Table 1. Selected Distances (Å), Angles (°), and Torsion Angles (°) for **IV**, **1** – **4**^a

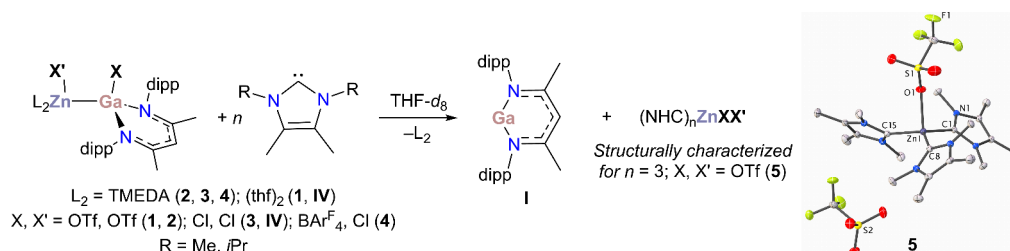
	Ga–Zn	Ga–N1	Ga–N2	Ga–X	Zn–L	Zn–L	Zn–X	N–Ga1–N	L–Zn–L	X–Ga–Zn–X
1	2.3686(3)	1.9379(14)	1.9372(15)	2.0637(13)	2.0154(13)	2.0467(15)	1.9933(16)	96.82(6)	94.06(6)	3.98(8)
2	2.4113(3)	1.9471(16)	1.9490(16)	2.1066(14)	2.1182(18)	2.1185(17)	2.0413(16)	95.21(7)	87.21(7)	7.20(8)
IV	2.3920(6)	1.965(2)	-	2.282(1)	2.098(2)	-	2.2016(14)	94.18(12) ^b	87.28(15) ^b	180.00(8)
3	2.4167(6)	1.9806(18)	-	2.3002(9)	2.150(3)	-	2.2561(10)	94.81(11) ^c	85.18(17) ^c	180.00(5)
4	2.4306(6)	1.919(3)	1.926(3)	-	2.112(3)	2.113(3)	2.2216(12)	95.69(11)	87.11(13)	-

^aValues for compound **IV** were published by Kempter et al.²⁵ X = Cl, compounds **IV**, **3**, **4**; X = OTf, compounds **1** and **2**; L = O^{THF}, compounds **IV** and **1**; L = N, compounds **2**, **3**, **4**. For compound **4**, values are shown for Ga1-containing molecule, only. ^bSymmetry operation to generate primed atoms $+X, 1/2 - Y, +Z$ ^cSymmetry operation to generate primed atoms $+X, 3/2 - Y, +Z$.

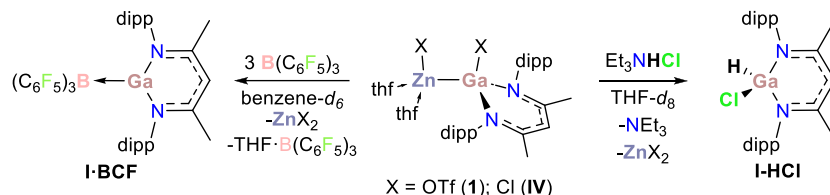
IV, **1** – **3**, consistent with a dative Ga→Zn interaction in the former case (Table 1).

Although NMR data for **IV** was reported in chloroform-*d*, we found that dissolution of compounds **IV** and **1** – **3** in this solvent resulted in quantitative formation of I–Cl₂³⁵ within minutes (**IV**, **3**) or hours (**1**, **2**). The subsequently obtained ¹H NMR spectra were, however, also identical to that previously reported for **IV**.²⁵ Thus, we suggest that Fischer and co-workers erroneously characterized I–Cl₂ as a result of reaction of **IV** with the NMR solvent.²⁵ While we forego any speculation as to the mechanism by which these complexes

react with chloroform, these observations and poor solubility in hydrocarbon solvents prompted NMR spectroscopic characterization in THF-*d*₈. The ¹H NMR spectrum of **IV** in this solvent shows well-defined resonances at the expected chemical shift for dissociated THF, due to exchange of coordinated THF with the solvent. While the methine and methyl protons of the BDI ligand backbone provide sharply defined singlets, the isopropyl groups give rise to broad, unresolved signals, indicating a dynamic system with a rapidly exchanging time-averaged C_{2v} symmetric structure in solution. By contrast, **3** displays four well-resolved doublets and two

Scheme 3. Reaction of Compounds 1 – 4, IV with IME_4^a 

^aDisplacement ellipsoid plot (30%) of compound 5 with hydrogen atoms omitted.

Scheme 4. Reaction of Compounds 1 and IV with Et_3NHCl and with $\text{B}(\text{C}_6\text{F}_5)_3$ 

heptets for the isopropyl groups, consistent with C_s symmetry on the NMR time scale. Additionally, the resonances corresponding to the TMEDA ligand are split into four broad resonances (integral ratio 2:2:6:6), consistent with retention of the solid-state structure in solution. The ^1H NMR spectra of compounds 1 and 2 show a single broad resonance (4H) for the isopropyl methine and two doublets (12H each) for the isopropyl methyl protons, indicating time-averaged C_{2v} symmetry in solution at room temperature, perhaps due to lability of the triflate groups, which were indistinguishable by ^{13}C and ^{19}F NMR spectroscopy. The NMR spectrum of compound 4 is consistent with the major component of the crystal structure, with a single freely rotating C_{2v} -symmetric {BDIGa} unit and zinc-bound chloride indicated by a single heptet for the isopropyl methine protons. The resonances corresponding to the BDI ligand environments are upfield-shifted compared to I, consistent with donation of electron density from gallium to zinc.

Unlike Okuda's cationic hydride derivative III,²⁷ attempts to react THF- d_8 solutions of 1 or 4 with H_2 (1 bar, 80 °C) were futile, and the *in situ* NMR spectra remained unchanged after 1 week. Noting the relatively elongated metal–metal bonds for TMEDA-derivatives 2 and 3 compared to 1 and IV, we speculated that stronger σ -donor ligands such as NHC may result in a weakened and more reactive Ga–Zn bond. In fact, the addition of IME_2iPr_2 ($:\text{C}\{\text{N}(i\text{Pr})\text{C}(\text{CH}_3)\}_2$) to 4 resulted in the immediate displacement of I from the zinc center according to *in situ* NMR spectroscopy, and the formation of unidentified zinc-containing products (Scheme 3). The addition of two equiv IME_4 ($:\text{C}\{\text{N}(\text{CH}_3)\text{C}(\text{CH}_3)\}_2$) to a THF- d_8 solution of 1 resulted in the immediate precipitation of colorless needle-like single crystals, while the solution changed from colorless to pale-yellow. Analysis by *in situ* ^1H NMR spectroscopy showed a mixture of three BDI-containing species, which were identified as unreacted I, I, and a third species tentatively assigned as $[(\text{BDI})\text{Ga}(\text{OTf})\text{Zn}(\text{OTf})(\text{IME}_4)_x(\text{thf})_y]$. The reaction mixture remained apparently unchanged after 4 days at 70 °C, but addition of a third equiv of IME_4 resulted in the immediate precipitation of a further crop of crystalline needles with full consumption of 1 to provide I as the only soluble product in the ^1H NMR spectrum

(Scheme 3). X-ray diffraction analysis of the crystals deposited from the reaction mixture revealed the structure of the insoluble product as the ionized tris(NHC) zinc triflate derivative $[(\text{IME}_4)_3\text{Zn}(\text{OTf})][\text{OTf}]$ (5), which was separately synthesized and fully characterized (see Supporting Information for details). Compound 2 similarly reacts with three equiv IME_4 to provide I and 5 under elimination of TMEDA. Likewise, addition of two equiv IME_4 to compounds 3 and IV also leads to the selective extrusion of I and a species tentatively assigned as $(\text{IME}_4)_2\text{ZnCl}_2$, by comparison to the *in situ* reaction of two equiv IME_4 with ZnCl_2 . A brief assessment of the potential generality of this process indicated that the strong donor strength of IME_4 is crucial. Adding 4-dimethylaminopyridine (DMAP, 2.5 equiv) or acetonitrile (>60 equiv) to THF- d_8 solutions of 1 and IV did not result in well-defined dismutation. No change was observed upon addition of acetonitrile besides probable substitution of coordinated THF, while DMAP provided intractable mixtures in which (in the case of IV) traces of I were identified alongside several other species.

Alumanyl zinc and cadmium complexes of the general formula $[\text{LX}_2\text{Al}-\text{MX}']$ ($\text{M} = \text{Zn, Cd}$) display group 12-centered nucleophilicity or alternatively act as a 'masked' alumanylene $\{\text{LXAl}\}$.^{40–42} To probe reactivity of comparatively less-polarized Ga–Zn bonds, THF- d_8 solutions of 1 and IV were combined with the weak Brønsted acid, Et_3NHCl (Scheme 4). Compound IV selectively yielded gallium(III) hydride chloride $[(\text{BDI})\text{Ga}(\text{H})\text{Cl}]$ (I–HCl),⁴³ which could be consistent with addition of an HCl equivalent across either the Ga–Zn bond, or Ga(I) center of a 'masked' equivalent of gallylene I. The similar formation of I–HCl from 1, however, is indicative of the latter mode of reactivity. Similarly, 4 and I also react with Et_3NHCl to provide I–HCl. As a further example of masked gallylene reactivity, compounds 1 and IV both react with three equiv of the Lewis acid, $\text{B}(\text{C}_6\text{F}_5)_3$, in benzene- d_6 to yield the donor–acceptor complex, $[(\text{BDI})\text{Ga}-\text{B}(\text{C}_6\text{F}_5)_3]$ (I–BCF),⁴⁴ along with precipitation of an insoluble colorless solid, presumed to be the corresponding zinc(II) salt (Scheme 4).

Synonymous disproportionation and dismutation and the reverse comproportionation refer to homoelemental redox

reactions.⁴⁵ Neither the formation of heterometallic compounds **1**–**3**, **IV**,²⁵ and **II**²⁶ from Ga^I (**I**) and Zn^{II} or Al^{III} species [(L)_nMX₂]⁽⁺⁾ nor the reverse formation of **I** and [(L)_nMX₂]⁽⁺⁾ or **I**·BCF and ZnX₂ via Ga–M cleavage strictly involve a change in the metals' formal oxidation states (gallium is more electronegative than zinc and aluminum).^{46,47} The oxidation state formalism does not, however, describe the electron-transfer processes occurring in the formation and cleavage of covalent heteronuclear metal–metal bonds such as these, and these reactions can otherwise be regarded as redox processes. Thus, 'dismutation' of covalent Ga–Zn bonds can be induced by IMe₄ as a strong Lewis base that traps the zinc(II) di(pseudo)halide, or by B(C₆F₅)₃ a strong Lewis acid that traps the 'masked' gallylene **I**. Besides demonstrating the important role of ancillary ligands on the stability and reactivity of heterometallic complexes, these observations can also be thought of in terms of gallium-centered 'oxidative addition' and 'reductive elimination' of Zn–X bonds. The ability to trigger reductive elimination through the action of a Lewis acid or base may prove a useful strategy in mediating main group redox catalysis. We continue to explore similar heterometallic complexes as reactive reagents in main group-mediated redox chemistry.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.6c00068>.

Experimental procedures and characterization data (PDF)

Accession Codes

Deposition Numbers 2532008–2532012 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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