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Trans-Metal-Trapping Meets Frustrated-Lewis-Pair Chemistry: Ga(CH₂SiMe₃)₃-Induced C–H Functionalizations

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**ABSTRACT:** Merging two topical themes in main-group chemistry, namely, cooperative bimetals and frustrated-Lewis-pair (FLP) activity, this Forum Article focuses on the cooperativity-induced outcomes observed when the tris(alkyl)gallium compound GaR₃ (R = CH₂SiMe₃) is paired with the lithium amide LiTMP (TMP = 2,2,6,6-tetramethylpiperidide) or the sterically hindered N-heterocyclic carbene (NHC) 1,3-bis(tert-butyl)imidazol-2-ylidene (T'Bu). When some previously published work are drawn together with new results, unique tandem reactivities are presented that are driven by the steric mismatch between the individual reagents of these multicomponent reagents. Thus, the LiTMP/GaR₃ combination, which on its own fails to form a cocomplex, functions as a highly regioselective base (LiTMP)/trap (GaR₃) partnership for the metalation of N-heterocycles such as diazines, 1,3-benzoazoles, and 2-picolines in a trans-metal-trapping (TMT) process that stabilizes the emerging sensitive carbanions. Taking advantage of related steric incompatibility, a novel monometallic FLP system pairing GaR₃ with T'Bu has been developed for the activation of carbonyl compounds (via C=O insertion) and other molecules with acidic hydrogen atoms such as phenol and phenylacetylene. Shedding new light on how these non-cocomplexing partnerships operate and showcasing the potential of gallium reagents to engage in metalation reactions or FLP activations, areas where the use of this group 13 metal is scant, this Forum Article aims to stimulate more interest and activity toward the advancement of organogallium chemistry.

**INTRODUCTION**

Deprotonative metalation is one of the most useful and widely used synthetic tools to functionalize organic molecules by transforming a relatively inert C–H bond into a more polar (and therefore reactive) metal–C bond.¹ Lithium alkyls, in the company of sterically demanding lithium amides (such as LiTMP, where TMP = 2,2,6,6-tetramethylpiperidide), commonly perform these reactions, although they can suffer from low functional-group tolerance and limited selectivity, imposing in many cases the use of extremely low temperatures to minimize possible side reactions or decomposition of the generated lithiated intermediates.² Overcoming some of these limitations, alternative multicomponent metalating reagents have been developed that in many cases pair metals of different polarities within the same molecule. Lochman–Schlosser superbases³ were the prototype of these bimetallic reagents, while Uchiyama’s and Mongin’s TMP/zincate complexes⁴,⁵ as well as LiCl₂-activated Knochel’s turbo-Grignard reagents such as TMPMgCl⁶ represent more recent examples. Mulvey’s structural and reactivity studies using amidodialkyl bimetallic combinations established the concept of alkali-metal-mediated metalation, where combining an alkali metal with a less electronegative metal such as magnesium, zinc, manganese(II), or iron(II) can promote unprecedented regioselective magnesiation, zincation, manganation, or ferration of aromatic molecules usually inert toward single-metal magnesium,⁷ zinc,⁸ manganese(II),⁹ or iron(II)¹⁰ reagents. This usually occurs by the formation of “ate” complexes, resulting from cocomplexation of two distinct organometallic compounds, e.g., alkali metal and a second less electronegative metallic center (such as zinc or magnesium) with a variety of anionic ligands (e.g., alkyl, amido, or alkox groups) to give a single bimetallic entity (Figure 1a), where the metal with stronger Lewis acidity can accept more (Lewis) basic ligands. Such mixing of the metals and ligands, where the anionic charge is localized on the part of the molecule containing the more electronegative metal, can have cooperative consequences, in transferring the high reactivity of the alkali-metal component to the less polar metal while retaining its greater selectivity and functional group compatibility, enabling direct metal–H exchange at room temperature (contrasting with the low-temperature protocols required with RLi reagents).

Furthermore, in some cases, unique synergic regioselectivities are achievable, promoting the polymetalation of substrates at remote positions, again attributed to the synchronized cooperation of metals within the bimetallic reagent. Recent...
examples include regioselective dimagnesiation of N,N-dimethylaniline and the N-heterocyclic carbene (NHC) 1,3-bis(2,6-disopropylphenyl)imidazol-2-ylidene (IPr), where the supramolecular structure of the mixed sodium/magnesium base templates the regioselectivity of the deprotonation reaction. While most of such studies have focused on divalent metals, work on trivalent group 13 metals aluminum and gallium has evidenced that cooperative effects can also result from multicomponent solutions containing two separate metal species, which fail to form an ate (co)complex (Figure 1b). In these cases, a bimetallic cooperativity operates in tandem, with one metal (e.g., lithium, the base) performing metalation while another (e.g., aluminum, the trap) drives the equilibrium toward the target product, transforming low-yielding lithiations into quantitative reactions. For example, collaborating with Mulvey, we recently showed that the LiTMP-induced ortho metalation of anisole can be dramatically increased from 5% of lithiated anisole to 99% of aluminated product by adding Al(TMP)Bu, as a metal trap, in a process driven by the strong carbophilicity and bulk of the aluminum reagent via a transmetal-trapping (TMT) procedure (Scheme 1).

This stepwise cooperativity of the LiTMP/Al(TMP)Bu partnership relies primarily on the lack of cocomplexation between the two homometallic reagents as a result of their steric incompatibility. This bimetallic system has been successfully employed to execute metalations under mild conditions of a variety of molecules including 1,3-dimethoxybenzene, N,N-diisopropylbenzamide, ferrocene, or tetrahydrofuran (THF).

This TMT concept of steric mismatch between the single components of a mixed-metal system, which leads to a remarkable amplified metalation of a substrate, bears a similarity with frustrated-Lewis-pair (FLP) chemistry. Being a powerful methodology for small-molecule activation that has already found numerous applications in catalysis, FLP chemistry is based on the steric incompatibility of a Lewis acid (LA) and a Lewis base (LB) to form a stable donor/acceptor complex, enabling cooperative behaviors with added substrates through unique reaction pathways. Some key landmarks in this young but rapidly evolving field include dihydrogen activation and hydrogenation catalysis, as well as CO/CO2 reductions, the capture of greenhouse gases, and C–H activation processes (Scheme 2).

![Scheme 1. TMT Procedure for Ortho Metalation of the Benchmark Substrate Anisole](image1.png)

![Scheme 2. Selected Examples of FLPs Employed for Heterolytic Cleavage of Hydrogen and C–H Bond Activation](image2.png)
potential to sedate and stabilize unstable incipient carbanions arising from the deprotonation of N-heterocyclic molecules. NMR studies assessing cocomplexation between LiTMP, with the tris(alkyl)gallium complex GaR₃ (R = CH₃SiMe₃) containing bulky and thermally stable monosilyl groups, revealed that they fail to form a bimetallic complex. TMT was then successfully used for regioselective metalation of challenging sensitive, unactivated diazines in hydrocarbon solutions as well as the N=S heterocycle benzothiazole. Metallated intermediates of all of these reactions were isolated and structurally defined, showing remarkable stability. Remarkably, we can carry out these reactions under mild reaction conditions, using stoichiometric amounts of metalating reagents, and at room temperature, contrasting with previous reports that require large excesses of LiTMP (up to 4 equiv) as well as strict temperature control (−78 °C) to avoid decomposition of the lithio intermediates, and even under these restrictive conditions, yields tend to be moderate.

Scheme 3 summarizes some of our investigations of the metalation of pyrazine. Reacting 1 equiv of a GaR₃/LiTMP mixture using hexane as the solvent and the tridentate donor PMDETA (as a crystallization aid) afforded the 2-monogallated complex [1-(PMDETA)Li-3-(GaR)C₆H₄N₂] (1; Scheme 3). Furthermore, to show stoichiometric control, two hydrogen atoms can be removed from the 2 and 5 positions of pyrazine when the base/trap/substrate ratio was doubled to 2:2:1 (2 in Scheme 3). Contrastingly, when pyrazine was tackled by the related homoalkyllithium gallate [LiGaR₃], metation was inhibited, promoting instead the regioselective addition of an alkyl group to one α-carbon of the heterocycle (3 in Scheme 3). When the inherent instability of α-metalated pyrazines is pondered, the isolation of compounds 1 and 2 as stable crystalline solids at room temperature may seem surprising; however, their molecular structures provide important clues that help us to understand their stability. Figure 2 shows that two well-defined bonding modes are established for each metal, minimizing repulsions between the electron clouds of the nitrogen lone pair (tied up in forming dative bonds with lithium) and the negative charge of the carbanion, which is further stabilized by forming a more covalent and less polarized Ga−C bond, being also protected by the steric shelter of the bulky monosilyl groups.

Extension of the TMT approach to pyridazine, pyrimidine, and benzothiazole led to the isolation of complexes 4−6, respectively (Figure 3). Interestingly, for pyridazine, it was found that introducing the gallium trap to the heterocycle prior to the addition of LiTMP led to noticeably better regioselective control, driving the reaction toward the formation of C3-metalated product 4. In addition, while ring-closed 2-lithiated benzothiazole derivatives coexist in solution at room temperature with ring-opened forms, 6 is stable in solution and no equilibration with its metallo(2-isocyano)thiophenolate isomer could be detected.

Extending the scope of TMT to other N-heterocyclic molecules containing less acidic protons, here we report our findings on the exploration of deprotonation of N-methylbenzimidazole (BIm) and 2-picoline. When the same conditions as those for the metalation of diazines were applied, LiTMP and GaR₃ were added to a solution of the relevant substrate in hexane at room temperature. The addition of PMDETA produced [2-(GaR₃)-3-{Li(PMDETA)}-C₆H₄NCNMe] (7) and [(PMDETA)Li(2-CH₂-pyridine)-GaR₃] (8) as colorless crystals in high (isolated) yields of 81% and 79%, respectively (Scheme 4).

X-ray crystallography confirmed gallation of these heterocyclic substrates, with BIm metalated at its C2 position (Figure 4), whereas 2-picoline undergoes lateral deprotonation (Figure 5). Within contact-ion-pair structures, both lithium and gallium centers in 7 and 8 display tetrahedral geometries, with lithium attached to four nitrogen atoms (three from PMDETA and one
from the metalated heterocycle), whereas the GaR₃ fragment coordinates to the carbon atom that has experienced deprotonation, showing the same distinct Li–N/Ga–C bonding preferences previously discussed for 2. The Ga–sp² C(Blm) bond distance of 2.054(3) Å is in excellent agreement with the similar Ga–sp² C(btz) bond of 2.062(3) Å previously found in 6.³¹ While 2-picolyl anions can exhibit different coordination modes to metals depending on the degree of delocalization of the negative charge into the ring,³² the geometrical parameters of 8 suggest that this fragment is best described as a carbanionic ligand, forming a Ga–CH₂ bond [Ga–C(Blm) bond distance 2.099(4) Å in Figure 5] that is comparable to the remaining Ga–Calkyl bonds in 8 (mean 2.027 Å). This particular bonding mode is further supported by the Li–N bond distance [Li–N1 2.055(8) Å in Figure 5], which is noticeably longer than the corresponding bond found in the enamido complex [(2-CH₂-pyridine)Li(PMDETA)] [Li–N 2.002(4) Å]³³e and is similar to that found in 7 [Li–N2 2.063(6) Å].³³f

Solubility in deuterated THF enabled 7 and 8 to be characterized using ¹H and ¹³C NMR spectroscopy (see the Experimental Section and Supporting Information). For 7, the most diagnostic resonance in the ¹³C NMR spectrum appears at 188.8 ppm for the benzimidazole C2 ring carbon that was metalated and is now attached to gallium, which is significantly downfield compared to the C2 resonance observed in free Blm (142.7 ppm).³⁵ Contrasting with Boche’s previous NMR studies,³³g which revealed that at room temperature 2-lithio-N-methylbenzimidazole undergoes partial ring opening in deuterated THF, the ¹H and ¹³C NMR spectra of 7 displayed well-resolved signals with no detectable resonances that could be assigned to a ring-opened α-isocyanomethyleneilide species. Lateral metalation of 2-picoline in 8 was confirmed by the presence of four multiplets in the aromatic region of the ¹H NMR spectrum (from 6.5 to 8.1 ppm) along with a singlet at 1.79 ppm for the CH₂–Ga moiety, whereas the ¹³C NMR spectrum displayed an informative signal at 30.8 ppm attributed to the CH₃–Ga fragment.

Multicomponent bimetallic reagents have also shown great promise in deprotonating NHCS. Some of our recent work has shown that sodium magnesiates¹² and zinicates⁵⁷ can promote direct mangesiation (or zincation) at the imidazole backbone of unsaturated carbene such as IPr. In contrast, LiGaR₃ does not promote metalation of this carbene, but the coordination adduct [IPr-LiGaR₃] (9; Scheme 5).³⁸ However, the TMT approach led to the isolation of heteroleptic lithium gallate (THF)₂Li:Li:[C([N(2,6-Pr₂C₆H₄)]CHCGaR₃)] (10), where the metals connect via an anionic NHC that coordinates via its normal C2 position to lithium and its abnormal C4 position to gallium.³⁹ Electrophilic interception studies of 10 using methanol,³⁰ methyl triflate,³⁸ or Me₂SiCl⁴⁰ afforded allPr-GaR₃ (11), [CH₃C([N(2,6-Pr₂C₆H₄)]CHCGa(CH₂SiMe₃)₃] (12), and [Me₃SiC{[N-
It is rare to
Encouraged by these initial
Re
Within iron
10.1021/acs.inorgchem.7b00549
Scheme 7
These
accessible, steric incompatibility prevents GaR
°
ligand. Thus, whereas both
obtained in 77% yield by heating a THF solution of
hexane at room temperature furnished the normal isomer IPr
11
These studies revealed that the abnormal isomer
11
was evident from its
H NMR spectrum in THF-
H with sterically demanding I
Bu, we have recently reported the
reduction of aldehydes, by insertion into the C═O
functionality at the C2 carbene position, affording
zwitterionic compounds such as
BuCH(p-Br-C6H4)OGaR
16
(Scheme 7i).23d Reflecting the cooperativity of the
Bu/GaR
pair,

Scheme 7. Contrasting Reactivities of
Bu/GaR Mixtures with Various Carbonyl Compounds23d

Neither component is able to activate aldehydes on their own.
Interestingly, solution studies, supported by theoretical
calculations, reveal that 16 is the kinetic product of the
addition across the C═O functionality and over time (24 h,
room temperature) evolves into its thermodynamic product 17
(Scheme 7ii), resulting from formal insertion into the C═O
group at the C4 carbene position (Scheme 7iii).23d These
findings showed that
Bu can effectively act as a LB via both its
normal (C2) and its abnormal (C4) positions. The reactivity of
the NHC/Ga pair was further tested against ketones, and it was
found that reduction of the carbonyl moiety takes place only in
the case of electrophilic α,α,α-trifluorocetonophene furnishing
BuC(Ph)(CF3)OGaR
18
, while less electrophilic benzo-
phenone remains intact and the deactivation complex
Bu/GaR
15
is detected instead.23d Interestingly, with enolizable
ketones such as 2,4,6-trimethylacetophenone, a different FLP
reactivity pattern was revealed, affording mixed imidazolium
gallate salts [{[I
BuH]+}{(Ar)C(≡CH2)OGaR3}–] (19; Ar =
Me6C6H4) as a result of a C═H activation process (Scheme 7iv).
This reactivity was also seen for other unsaturated organic
substrates bearing α-acidic hydrogen atoms such as
diphenylacetonitrile affording [{[I
BuH]+}{Ph3C═C≡NGaR3}–] (20).23d

Here we extend the reactivity of this NHC/Ga FLP to other
molecules containing protic hydrogen atoms, susceptible to
undergoing C═H and X═H (X = O, N) activation. We start with
phenol whose deprotonation can be achieved by either of
the two components on their own (i.e.,
Bu or GaR3), as
evidenced by the mixture of products obtained upon the
addition of phenol to a hexane suspension of the
Bu/GaR3 pair. However, if phenol was added to the hexane suspension
of
Bu, followed by the addition of GaR3, a more controlled O═H
bond cleavage occurred, affording [{[I
BuH]+}{GaR2OPH}–] (21) in a 76% yield (Scheme 8). Selective formation of 21
was evident from its
H NMR spectrum in THF-d8, which
unambiguously revealed a 1:3 ratio of phenoxy (6.16, 6.52, and

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Scheme 5. Synthesis of Homoleptic Tetraalkyl Gallate 9,
Heteroleptic Gallate 10, and Abnormal Adduct 11

Scheme 6. Synthesis of Normal Adduct 14 and Its Thermal
Isomerization into the Abnormal Isomer 11

(2,6−′Pr2C6H3)3CHCGa(CH2SiMe3)2} (13), respectively.
Their structures were elucidated by X−ray crystallography,
revealing the preference of the anionic NHC ligand in
10 to react with electrophiles at its C2 position, leaving its C4
position intact; thus, all of these reactions introduce a new
method to access abnormal NHC/Ga complexes.

While using this bimetallic metalation/electrophilic quenching
approach allowed isolation of 11, treating IPr with GaR3 in
hexane at room temperature furnished the normal isomer IPr-
GaR3 (14; Scheme 6).38 It is rare to find examples where both

normal and abnormal metal NHC complexes have been
isolated or structurally characterized.38,41,42 Within iron
chemistry, Layfield has elegantly demonstrated thermal isomer-
ization of IPr−Fe(HMDS)2 to dIPrFe(HMDS)2 (3 h, 110 °C,
toluene), suggesting that formation of the abnormal NHC
complex is thermodynamically driven by the relief of steric
hindrance around the metal center.37 Motivated by this work,
we assessed the thermal stability of 14 towards isomerization.
These studies revealed that the abnormal isomer 11 can be
obtained in 77% yield by heating a THF solution of 14 at 100
°C for 1 h.38

Combining NMR spectroscopic and kinetic studies with DFT
calculations intimates that the isomerization occurred via
dissociative mechanism, akin to mechanisms proposed in
NHC/borane FLP systems,19a,43 evidencing the importance of
the substituent steric bulk on the nitrogen atoms of the NHC
ligand. Thus, whereas both 11 and 14 are stable and easily
accessible, steric incompatibility prevents GaR3 and
Bu from forming a stable normal adduct, rendering instead
dBu−GaR3 (15) at room temperature.38 Encouraged by these
initial findings hinting at the potential FLP reactivity that this
NHC/Ga system may exhibit, we have probed the reactivity of some
Very recently, Uhl and co-workers demonstrated the experimental section that the Ga–O bond length of 2.0150(17) Å in 22 is only slightly shorter than the Ga–N distance reported for the lithium gallate incorporating the [(Ph9Ga(μ-NMe2)-GaPh9)]− anion [Ga–N 2.051(1) Å], consistent with the terminal versus bridging mode of the amido ligand. The Ga–C bond in 23 of 2.031(3) Å is only slightly elongated in comparison with the Ga–C bond distance in anionic [(Ga(CCSiMe3)2(2,6-Pr2C6H5N(SiMe3)))]− (average Ga–C = 1.969 Å).47a

The formation of 23, where the LB 1Bu deprotonates phenylacetylene while the three monosilyl groups attached to gallium remain intact, contrasts with the results observed when IPr-GaR3 (14), containing a less sterically demanding NHC, is reacted with phenylacetylene. Here one R group on gallium acts as a base, to give IPr-GaR3(C≡CPh) (24), with IPr behaving as an ancillary ligand. This reactivity is similar to that described previously by Mitzel and co-workers for the reaction of GaMe3 and 4-ethyl-2,6-lutidine, where the metatation of terminal alkynyl by GaMe3 occurs with concomitant release of methane.48 Very recently, Uhl and co-workers demonstrated that gallium hydrazides can act as active Lewis pairs for the cooperative C–H bond activation of phenylacetylene49 where the steric bulk of the tris(alkyl)gallium reagent dictates the extent of metatation.50 Complexes 23 and 24 illustrate how the reactivity of these new NHC/Ga FLP systems can be finely tuned by small modifications on the steric bulk of the components, in this case the LB (Scheme 9).

Isolated in a 55% yield, the NHC complex was crystallographically characterized. The molecular structure of 24 is comparable to that of 14, where a Lewis adduct is formed by alkoxy ligands.45b The Ga–N bond length of 2.0150(17) Å in 22 is only slightly shorter than the Ga–N distance reported for the lithium gallate incorporating the [(Ph9Ga(μ-NMe2)-GaPh9)]− anion [Ga–N 2.051(1) Å], consistent with the terminal versus bridging mode of the amido ligand. The Ga–C bond in 23 of 2.031(3) Å is only slightly elongated in comparison with the Ga–C bond distance in anionic [(Ga(CCSiMe3)2(2,6-Pr2C6H5N(SiMe3)))]− (average Ga–C = 1.969 Å).47a

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Isolated in a 55% yield, the NHC complex was crystallographically characterized. The molecular structure of 24 is comparable to that of 14, where a Lewis adduct is formed by...
the coordination of a neutral gallium fragment to the normal (C2) position of a neutral IPr carbene. As previously seen in 14, the gallium center adopts a distorted tetrahedral geometry; however, the distortion is less pronounced, as evidenced by the C–Ga–C bond angles ranging from 100.09(14) to 116.63(14)°. This is most probably due to the relief of steric crowding by the replacement of one CH$_2$SiMe$_3$ group with the C=CPh group, causing a shortening of the Ga–C$_\text{NHC}$ bond [Ga–C$_9$ 2.104(4) Å in Figure 8 vs 2.1960(16) Å in 14]. The Ga–C$_\text{alkynyl}$ (Ga–C$_1$ in Figure 8) distance of 1.954(4) Å is slightly more contracted than that observed in 23 [2.031(3) Å], consistent with the neutral constitution of the former versus the gallate of the latter. Regarding its NMR characterization, while 23 is very insoluble in C$_6$D$_6$, 24 displayed an excellent solubility in this low-coordinating solvent. The most informative resonances in the $^{13}$C NMR spectrum are C$_\text{NHC}$–Ga at 179.4 ppm, which is upfield-shifted compared to the free carbene, and the two alkyne resonances at 106.9 ppm (Ga–C=CPh) and 112.5 ppm (GaC=CPh) (see the Experimental section and Supporting Information for details).

**CONCLUSION AND OUTLOOK**

Advancing the applications of organogallium complexes for the functionalization of organic substrates, this Forum Article discusses cooperative behaviors observed when pairing tris(alkyl) gallium GaR$_3$ (R = CH$_2$SiMe$_3$) with the utility lithium amide LiTMP or the sterically hindered NHC fBu. When two topical areas of main-group chemistry, namely, cooperative...
bimetals and FLP activity, are merged, the reactivity of these systems is controlled by the steric mismatches between their individual components.

Thus, when stepwise metal compound/metal compound cooperation was exploited, sterically hindered LiTMP and GaR₂ were found not to undergo cocompaction to form a weakly basic, coordinatively saturated gallate. Instead, operating in a tandem manner, this bimetallic mixture can be used to effect room temperature deprotonation of sensitive heterocycles, revealing new regioselectivities and reactivity patterns that cannot be accomplished by the monometallic reagents alone. We describe this stepwise cooperative as TMT approaches, which exploit both the strong basicity of LiTMP (which carries out deprotonation of the substrate) and the pronounced carbophilicity of GaR₂ (which traps and stabilizes the incipient anion generated via metatation), facilitating challenging functionalizations to be accomplished with high selectivity under mild conditions at room temperature in a hydrocarbon solvent. We have also introduced two new examples of gallium TMT chemistry by structurally defining compounds 7 and 8 resulting from the regioselective deprotonation of BIm and 2-picoline, respectively.

When such steric incompatibility is present in the domain of monometallic chemistry, a novel FLP system pairing the same organogallium reagent with the bulky NHC has been developed for small-molecule activation. When GaR₂ as a LA was effectively combined with the LB I₈Bu, X—H (X = O, N, C) activation of molecules bearing acidic hydrogen atoms such as phenol or phenylacetylene was achieved, in a controlled manner and under mild reaction conditions to yield novel mixed-imidazolium gallate complexes 21 and 23, respectively. The subtle steric effects operating in these processes have been demonstrated by switching from I₈Bu to the related NHC I₇Pr, which suppresses the FLP reactivity in contact with phenylacetylene, denoting the NHC from acting as a base to becoming a spectator ligand, affording NHC complex 24, where phenylacetylene has been metatalated by one R group on gallium.

The chemistry developed for the organogallium reagent, presented in this paper, highlights stepwise cooperative processes based either on two metal reagents or on a single-metal reagent combined with a special ligand. By shedding new light on how these noncompelexing partnerships operate and showcasing the potential of gallium reagents to engage in metatation reactions or FLP activations, areas where the use of this metal is scant, this Forum Article aims to stimulate more interest and activity toward the advancement in organogallium chemistry, bridging the gap in practical utility and knowledge between gallium and its neighbors aluminum and boron.

**EXPERIMENTAL SECTION**

All reactions were carried out using standard Schlenk and glovebox techniques under an inert atmosphere of argon. Solvents (THF, hexane, benzene, and toluene) were dried by heating to reflux over sodium benzenophenone ketyl and distilled under nitrogen prior to use. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ¹H and 100.62 MHz for ¹³C[¹H]. 1-Methylbenzimidazolium, phenylacetylene, phenol, and diphenylamine were purchased from Sigma-Aldrich Chemicals or Alfa Aesar and used as received. 2-Picoline was dried by heating to reflux over calcium hydride, distilled under nitrogen, and stored over activated 4 Å molecular sieves prior to use. [Ga(CH₅SiMe₃)]⁺ I₈Bu⁻ and LiTMP³ were prepared according to literature methods and stored and handled under an inert atmosphere because of their air sensitivity (I₈Bu and pyrophoricity (Ga(CH₅SiMe₃) and LiTMP).

**Synthesis of [3-(PMDETA)Li-2-(GaR₃)C₆H₅N] (7).** At a suspension of LiTMP (0.074 g, 0.5 mmol) and Ga(CH₅SiMe₃) (0.165 g, 0.5 mmol) in hexane (10 mL) was added via solid addition tube at room temperature 1 equiv of 1-methylbenzimidazolide (66 mg, 0.5 mmol). A very fine white suspension was obtained and stirred for 2 h at room temperature, after which PMDETA was added (0.11 mL, 0.5 mmol), inducing a stronger precipitation. Gentle heating afforded a solution that, upon slow cooling, deposited X-ray suitable crystals (0.26 g, 81%). Anal. Calcd for C₅₀H₅₆Li⁺Ga₂N₃O: C, 73.88; H, 5.48; N, 8.29; Ga, 16.35. Found: C, 73.79; H, 5.10; N, 8.42; Ga, 16.25.

**Synthesis of [1-(PMDETA)Li-2-(GaR₃)C₆H₅N] (8).** To a suspension of LiTMP (0.074 mmol, 0.5 mmol) and Ga(CH₅SiMe₃) (0.165 g, 0.5 mmol) in hexane (10 mL) was added via syringe at room temperature 1 equiv of 2-picoline (46 mg, 0.5 µmol). A very fine orange suspension was obtained and stirred for 1 h at room temperature, after which PMDETA was added (0.11 mL, 0.5 mmol), inducing the formation of red oil separating from a yellow solution. The mixture was placed at ~20°C, affording X-ray suitable crystals (0.24 g, 79.3%). Anal. Calcd for C₃₂H₃₄Li⁺Ga₂N₃O: C, 73.71; H, 10.35; N, 9.28. Found: C, 52.60; H, 9.81; N, 9.78. ¹H NMR (298 K, CD₂Cl₂): δ −0.44 (6H, s, CH₂SiMe₂), 0.45 (27H, s, Si(CH₃)₃), 1.54–1.66 (8H, br mult, NCH₃C₆H₅), 1.72 (12H, s, NCH₃), 2.07 (3H, s, NCH₃), 2.12 (2H, s, ArCH₂), 6.35 (1H, t, ArCH), 7.09 (1H, t, ArCH), 7.23 (1H, d, ArCH), 7.35 (1H, d, ArCH). ¹³C[¹H] NMR (298 K, CD₂Cl₂): δ −0.5 (CH₂SiMe₂), 3.9 (Si(CH₃)₃), 38.9 (ArCH₃Ga), 45.2, 45.5, 53.1, 56.7 PMDETA, 113.9 (CH₃), 122.7 (CH₃), 135.4 (CH₃), 145.1 (CH₃), 174.1 (Car). Li NMR (298 K, CD₂Cl₂, reference LiCl in D,O at 0.00 ppm): δ 0.75. ¹H NMR (298 K, THF-d₈): δ −1.14 (2H, s, CH₂SiMe₂), −1.02 (4H, s, CH₂SiMe₂), −0.19 (9H, s, Si(CH₃)₃), −0.10 (18H, s, Si(CH₃)₃), 1.79 (2H, s, ArCH₂), 2.18 (12H, s, NCH₃), 2.24 (3H, s, NCH₃), 2.35 (4H, mult, NCH₃C₆H₅), 2.45 (4H, mult, NCH₃C₆H₅), 6.59 (1H, CH₃), 6.77 (1H, d, ArCH), 7.30 (1H, t, ArCH), 8.03 (1H, d, ArCH). ¹³C[¹H] NMR (298 K, THF-d₈): δ −0.4 (CH₂SiMe₂), 3.1 (Si(CH₃)₃), 3.7 (CH₃Ga), 4.1 (Si(CH₃)₃), 30.9 (ArCH₃Ga), 43.6, 66.1, 56.7, 56.8 (PMDETA), 114.8 (CH₃), 122.7 (CH₅Ga), 135.9 (CH₃), 147.0 (CH₃), 173.6 (Car). Li NMR (298 K, THF-d₈, reference LiCl in D,O at 0.00 ppm): δ 0.4. ¹H NMR (298 K, THF-d₈): δ −0.14 (2H, s, CH₂SiMe₂), −0.07 (27H, s, Si(CH₃)₃), 1.63 (18H, s, C(CH₃)₃), 6.16 (1H, t, p-ArCH), 6.52 (2H, d, p-ArCH), 6.79 (2H, t, m-ArCH), 7.75 (2H, s, imidazole backbone CH), 8.82 (1H, s, C2H), 13.1 (THF), 2.7 (CH₂SiMe₂), 3.5 (Si(CH₃)₃), 29.8 (C(CH₃)₃), 61.2 (C(CH₃)₃), 112.4 (p-ArCH), 121.0 (p-ArCH), 121.7 (imidazole backbone CH), 132.2 (NCH₃), 128.6 (m-ArCH), 168.7 (ArCO).
Synthesis of [IPr-GaR(PhCCGaR)]₃ (23). To a cooled solution of Ga(CH₃SiMe₃)₃ (0.165 g, 0.5 mmol) and IPr (0.2 g, 0.5 mmol) were added phenylacetylene (51 mg, 0.55 mmol), followed by BF₃ (0.09 g, 0.5 mmol). The obtained white, thick suspension was stirred for 2 h at 0 °C, after which the solvent was exchanged in vacuo for benzene (5 mL). Gentle heating afforded a solution that, upon cooling, affords X-ray-quality crystals (189 mg, 55%). Anal. Calcd for C₃H₆GaN₂Si₃: C, 60.66; H, 9.69; N, 4.56. Found: C, 60.43; H, 9.73; N, 4.84.

Crystallographic details and copies of NMR spectra for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

ASSOCIATED CONTENT

Supporting Information

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CCDC 1545610–1545615 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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