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Forum Article

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Trans-Metal-Trapping Meets Frustrated-Lewis-Pair Chemistry: $Ga(CH_2SiMe_3)_3$-Induced C−H Functionalizations

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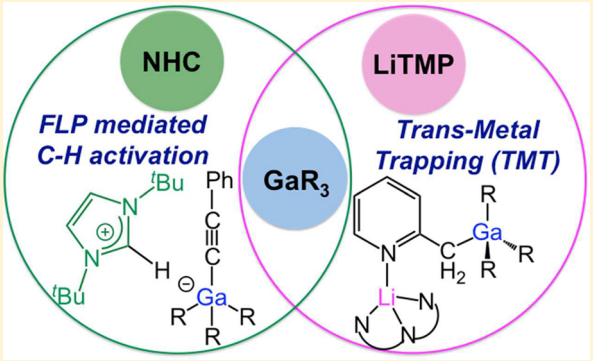
Supporting Information

ABSTRACT: Merging two topical themes in main-group chemistry, namely, cooperative bimetallics and frustrated-Lewis-pair (FLP) activity, this Forum Article focuses on the cooperativity-induced outcomes observed when the tris(alkyl)gallium compound GaR_3 (R = CH_2SiMe_3) 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 (I^tBu). 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/GaR_3 combination, which on its own fails to form a cocomplex, functions as a highly regioselective base (LiTMP)/trap (GaR_3) 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 GaR_3 with I^tBu 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 superbases[3] were the prototype of these bimetallic reagents, while Uchiyama's and Mongin's TMP/zincate complexes[4,5] as well as LiCl-powered Knochel's turbo-Grignard reagents such as TMPMgCl·LiCl[6] represent more recent examples.

Mulvey's structural and reactivity studies using amidoalkyl bimetallic combinations established the concept of alkali-metal-mediated metalation, where combining an alkali metal with a less electropositive 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 electropositive metallic center (such as zinc or magnesium) with a variety of anionic ligands (e.g., alkyl, amido, or alkoxy 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

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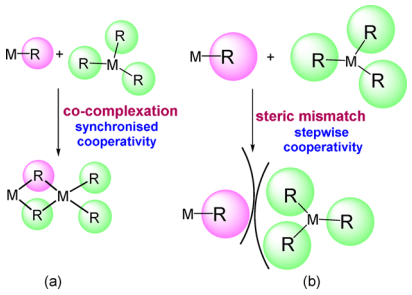
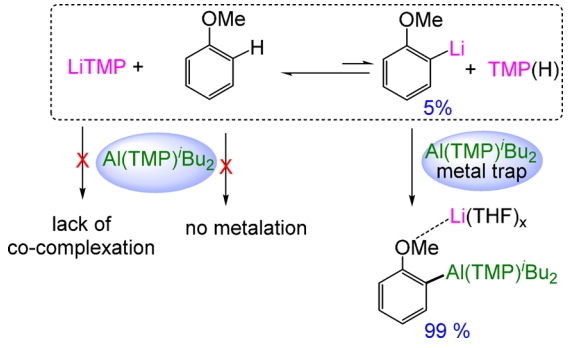


Figure 1. Contrast between synchronized (a) and stepwise (b) cooperativity.

examples include regioselective dimagnesiation of *N*,*N*-dimethylaniline[11] and the N-heterocyclic carbene (NHC) 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr),[12] where the supramolecular structure of the mixed sodium/magnesium base templates the regioselectivity of the deprotonation reaction.[13]

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)^{i}Bu$_2$ as a metal trap, in a process driven by the strong carbophilicity and bulk of the aluminum reagent via a trans-metal-trapping (TMT) procedure (Scheme 1).[14]

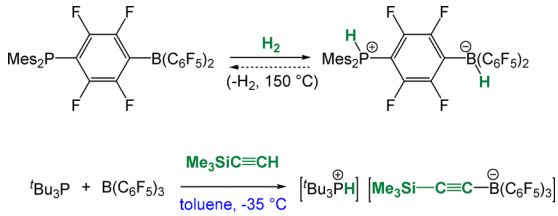
Scheme 1. TMT Procedure for Ortho Metalation of the Benchmark Substrate Anisole[14]



This stepwise cooperativity of the LiTMP/Al(TMP)^{i}Bu$_2$ 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,[15] *N*,*N*-diisopropylbenzamide,[15] ferrocene,[16] or tetrahydrofuran (THF).[17]

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.[18] Some key landmarks in this young but rapidly evolving field include dihydrogen activation[19] and hydrogenation catalysis,[20] as well as CO/CO$_2$ reductions,[21] the capture of greenhouse gases,[22] and C−H activation processes (Scheme 2).[23] Although the

Scheme 2. Selected Examples of FLPs Employed for Heterolytic Cleavage of Hydrogen[19a] and C−H Bond[23b] Activation



most powerful FLPs to date rely on the use of sterically hindered, electron-rich organophosphines as the LB component,[18,19a,20,24] NHCs, which have a myriad of applications in their own right,[25] are increasingly attracting attention in this field. While sharing many coordination features with phosphines, NHCs offer greater potential for subtle variations of their steric/electronic properties.[18d,25,26] In addition to their tuneability, the N-substituents are responsible for inducing "steric pressure" toward the LA component by being directed toward the carbene lone pair.[18d] Although most systems use a boron complex as the LA component,[18] the use of other group 13 elements, in particular aluminum,[27] is steadily growing in popularity with some other recent examples reported using gallium[28] and indium.[28e] Interestingly, although NHCs cannot activate hydrogen on their own, cyclic and acyclic (alkyl)(amino)carbenes can operate as single-site molecules for the activation of hydrogen under mild conditions.[29] Similarly, many of the heavier main-group multiple-bonded and open-shell species can be described as unimolecular FLPs (although typically not referred as such) because they contain donor and acceptor sites capable of activating small molecules.[30]

Building on recent advances from our group, this Forum Article brings together for the first time cooperative bimetallics and FLP chemistry, reporting on noncomplexing metal compound/metal compound and metal compound/ligand partnerships. Using the tris(alkyl)gallium GaR$_3$ (R = CH$_2$SiMe$_3$) as a connecting thread between these two fundamentally important areas, herein we compare their applications for the functionalization of several organic substrates. By pairing GaR$_3$ with the sterically demanding lithium amide LiTMP or the NHC 1,3-bis(*tert*-butyl)imidazol-2-ylidene (I^{t}Bu), we utilize steric mismatches to promote unique tandem reactivities, which to date are unprecedented in organogallium chemistry.

TMT and Sequential Metalation. Building on our previous LiTMP/Al(TMP)^{i}Bu$_2$ work,[14−17] we extended TMT approaches to the heavier group 13 metal, gallium. Possessing a higher electronegativity than aluminum, with the ability of forming even less polarized metal−C bonds, this system has the

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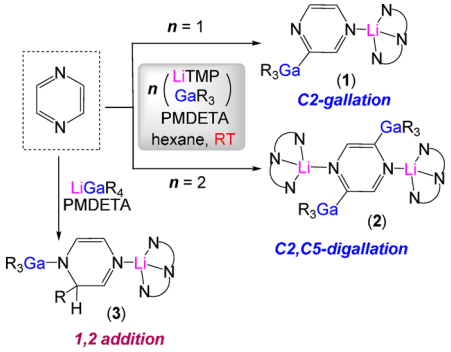
potential to sedate and stabilize unstable incipient carbanions arising from the deprotonation of N-heterocyclic molecules. NMR studies assessing cocomplexation between LiTMP, with the tris(alkyl)gallium complex GaR_3 (R = CH_2SiMe_3) containing bulky and thermally stable monosilyl groups, revealed that 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.[31] Metalated 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.[32] Scheme 3 summarizes some of our investigations of the

Scheme 3. Contrasting Approaches in the Synthesis of Mono- and Digallated Pyrazine and Addition Product[31]



metalation of pyrazine.[31] Reacting 1 equiv of a GaR_3/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_3)$C_4H_3N_2$] (**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 [$LiGaR_4$], metalation 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).[31]

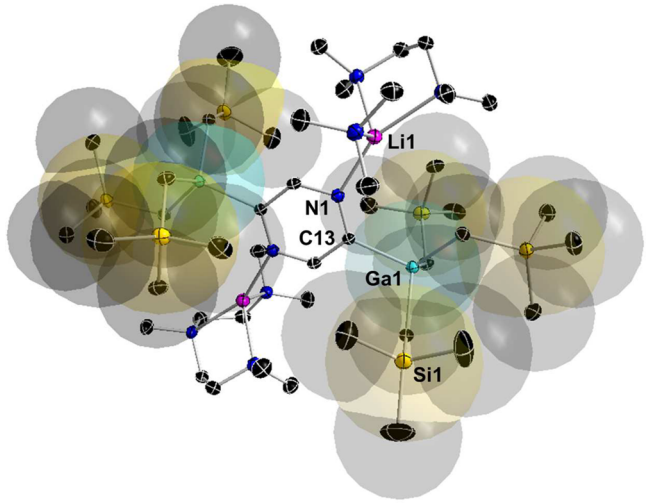


Figure 2. Molecular structure of **2** with 50% probability displacement ellipsoids and with superimposed translucent space-filling van der Waals surfaces for a probe of 1 Å radius for GaR_3 fragment. All hydrogen atoms have been omitted for clarity.

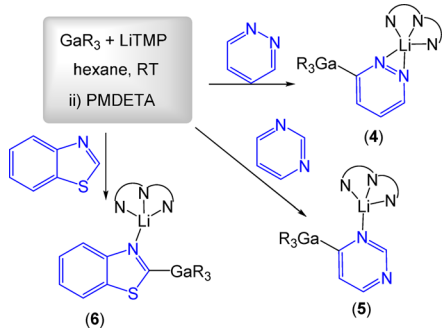


Figure 3. Products of TMT-executed metalations of pyridazine, pyrimidine, and benzothiazole.[31]

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,[33] **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 GaR_3 were added to a solution of the relevant substrate in hexane at room temperature. The addition of PMDETA produced [2-(GaR_3)-3-{Li(PMDETA)}-C_6H_4NCNMe] (**7**) and [(PMDETA)Li(2-CH_2-pyridine)-GaR_3] (**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

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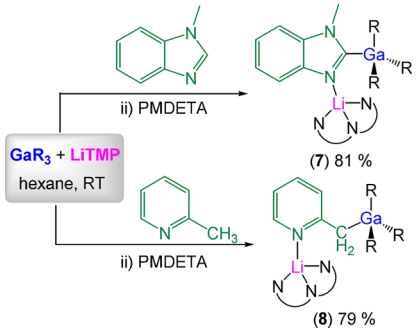
Scheme 4. Products of Lithium−Gallium TMT of BIm and 2-Picoline



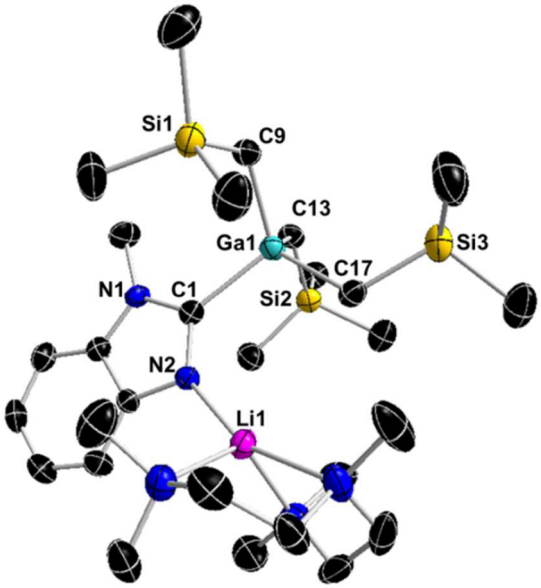


Figure 4. Molecular structure of **7** with 50% probability displacement ellipsoids. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ga1−C1 2.054(3), Ga1−C9 2.030(3), Ga1−C13 2.032(3), Ga1−C17 2.001(3), Li1−N2 2.063(6), Li1−N3 2.191(6), Li1−N4 2.302(6), Li1−N5 2.119(7); C1−Ga1−C13 104.24(13), C1−Ga1−C9 110.60(13), C1−Ga1−C17 108.78(12), C9−Ga1−C13 110.15(13), C17−Ga1−C13 112.64(14), C17−Ga1−C9 110.29(13), N2−Li1−N5 109.2(3), N2−Li1−N3 105.4(3), N5−Li1−N3 121.3(3), N2−Li1−N4 157.7(3), N5−Li1−N4 82.6(2), N3−Li1−N4 82.7(2).

from the metalated heterocycle), whereas the GaR_3 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−sp^2 C(BIm) bond distance of 2.054(3) Å is in excellent agreement with the similar Ga−sp^2 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,[34] the geometrical parameters of **8** suggest that this fragment is best described as a carbanionic ligand, forming a Ga−CH_2 bond [Ga−C13 2.099(4) Å in Figure 5] that is comparable to the remaining Ga−C_{alkyl} bonds in **8** (mean 2.027 Å). This particular bonding mode is further supported by the Li−N bond distance [Li1−N1 2.055(8) Å in Figure 5], which is noticeably longer than the corresponding bond found in the enamido complex

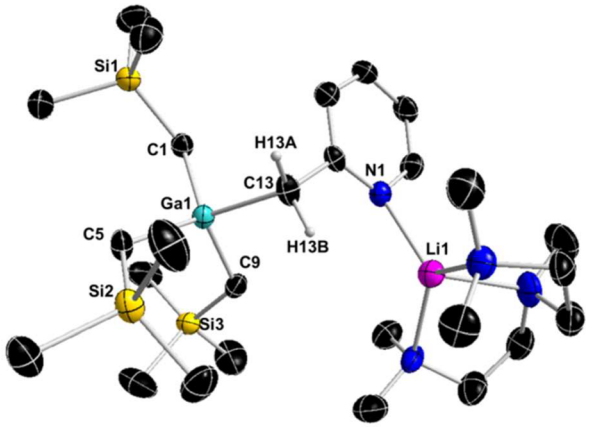


Figure 5. Molecular structure of **8** with 50% probability displacement ellipsoids. All hydrogen atoms and the minor disorder of the PMDETA ligand have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ga1−C1 2.025(4), Ga1−C5 2.030(4), Ga1−C9 2.025(4), Ga1−C13 2.099(4), Li1−N1 2.055(8), Li1−N2 2.178(8), Li1−N3 2.145(8), Li1−N4 2.11(2); C1−Ga1−C13 108.29(18), C1−Ga1−C9 111.06(18), C1−Ga1−C5 112.49(18), C9−Ga1−C13 102.59(19), C5−Ga1−C13 108.95(18), C5−Ga1−C9 112.88(19), N1−Li1−N4 108.6(5), N1−Li1−N3 121.8(4), N4−Li1−N3 125.5(5), N1−Li1−N2 123.4(4), N4−Li1−N2 84.6(4), N3−Li1−N2 84.4(3).

[(2-CH_2-pyridine)Li(PMDETA)] [Li−N 2.002(4) Å][34e] and is similar to that found in **7** [Li1−N2 2.063(6) Å].[35]

Solubility in deuterated THF enabled **7** and **8** to be characterized using ^{1}H and ^{13}C NMR spectroscopy (see the Experimental Section and Supporting Information). For **7**, the most diagnostic resonance in the ^{13}C 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 BIm (142.7 ppm).[36] Contrasting with Boche's previous NMR studies,[33] which revealed that at room temperature 2-lithio-*N*-methylbenzimidazole undergoes partial ring opening in deuterated THF, the ^{1}H and ^{13}C NMR spectra of **7** displayed well-resolved signals with no detectable resonances that could be assigned to a ring-opened α-isocyanomethylanilide species. Lateral metalation of 2-picoline in **8** was confirmed by the presence of four multiplets in the aromatic region of the ^{1}H NMR spectrum (from 6.5 to 8.1 ppm) along with a singlet at 1.79 ppm for the CH_2−Ga moiety, whereas the ^{13}C NMR spectrum displayed an informative signal at 30.8 ppm attributed to the CH_2−Ga fragment.

Multicomponent bimetallic reagents have also shown great promise in deprotonating NHCs. Some of our recent work has shown that sodium magnesiates[12] and zincates[37] can promote direct mangesiation (or zincation) at the imidazole backbone of unsaturated carbenes such as IPr. In contrast, $LiGaR_4$ does not promote metalation of this carbene, but the coordination adduct [IPr·$LiGaR_4$] (**9**; Scheme 5).[38] However, the TMT approach led to the isolation of heteroleptic lithium gallate $(THF)_2Li[:C\{[N(2,6\text{-}^iPr_2C_6H_3)]_2CHGaR_3\}]$ (**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,[38] methyl triflate,[38] or Me_3SiCl[40] afforded *a*IPr·GaR_3 (**11**), $[CH_3C\{[N(2,6\text{-}^iPr_2C_6H_3)]_2CHCGa(CH_2SiMe_3)_3\}]$ (**12**), and $[Me_3SiC\{[N$-

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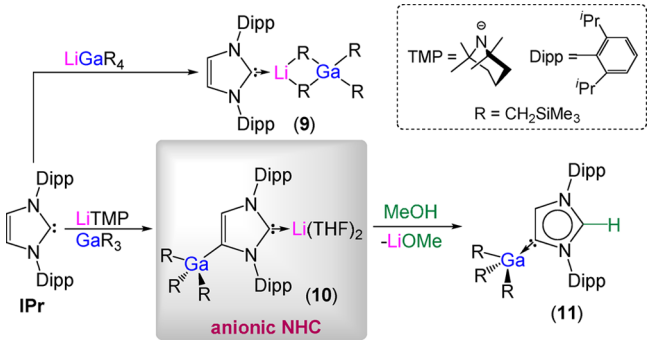
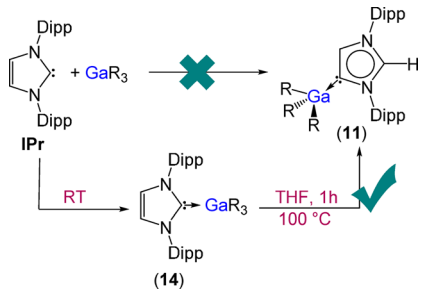
Scheme 5. Synthesis of Homoleptic Tetraalkyl Gallate 9, Heteroleptic Gallate 10, and Abnormal Adduct 11



$(2,6\text{-}^{i}Pr_2C_6H_3)]_2CHCGa(CH_2SiMe_3)_3\}]$ (**13**), respectively. Their structures were elucidated by X-ray crystallography, revealing the preference of the anionic NHC ligand present 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 GaR_3 in hexane at room temperature furnished the normal isomer IPr·GaR_3 (**14**; Scheme 6).[38] It is rare to find examples where both

Scheme 6. Synthesis of Normal Adduct 14 and Its Thermal Isomerization into the Abnormal Isomer 11[38]

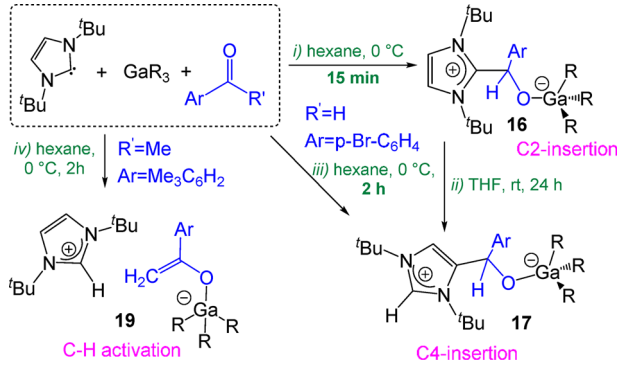


normal and abnormal metal NHC complexes have been isolated or structurally characterized.[38,41,42] Within iron chemistry, Layfield has elegantly demonstrated thermal isomerization of IPr·$Fe(HMDS)_2$ to *a*IPrFe$(HMDS)_2$ (3 h, 110 °C, toluene), suggesting that formation of the abnormal NHC complex is thermodynamically driven by the relief of steric hindrance around the metal center.[42] 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 intimated that the isomerization occurred via a 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 GaR_3 and I^{t}Bu from forming a stable normal adduct, rendering instead *a*I^{t}Bu·GaR_3 (**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 single-metal non-cocomplexing partnerships to promote C−H and C═O bond activation of a range of organic molecules.[28d]

FLP Activation of Organic Molecules by NHC/GaR_3 Pairings. Demonstrating that GaR_3 is a viable effective LA for promoting small-molecule-activation processes when paired with sterically demanding I^{t}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 I^{t}BuCH(*p*-Br-C_6H_4)OGaR_3 (**16**; Scheme 7i).[28d] Reflecting the cooperativity of the I^{t}Bu/GaR_3 pair,

Scheme 7. Contrasting Reactivities of I^{t}Bu/GaR_3 Mixtures with Various Carbonyl Compounds[28d]



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).[28d] These findings showed that I^{t}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*-trifluoroacetophenone furnishing *a*I^{t}BuC(Ph)(CF_3)OGaR_3 (**18**), while less electrophilic benzophenone remains intact and the deactivation complex *a*I^{t}Bu·GaR_3 (**15**) is detected instead.[28d] Interestingly, with enolizable ketones such as 2,4,6-trimethylacetophenone, a different FLP reactivity pattern was revealed, affording mixed imidazolium gallate salts $[\{I^tBuH\}^+\{(Ar)C(=CH_2)OGaR_3\}^-]$ (**19**; Ar = $Me_3C_6H_2$) 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 $[\{I^tBuH\}^+\{Ph_2C{=}C{=}NGaR_3\}^-]$ (**20**).[28d]

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., I^{t}Bu or GaR_3), as evidenced by the mixture of products obtained upon the addition of phenol to a hexane suspension of the I^{t}Bu/GaR_3 pair. However, if phenol was added to the hexane suspension of I^{t}Bu, followed by the addition of GaR_3, a more controlled O−H bond cleavage occurred, affording $[\{I^tBuH\}^+\{GaR_3OPh\}^-]$ (**21**) in a 76% yield (Scheme 8). Selective formation of **21** was evident from its ^{1}H NMR spectrum in THF-d_8, which unambiguously revealed a 1:3 ratio of phenoxy (6.16, 6.52, and

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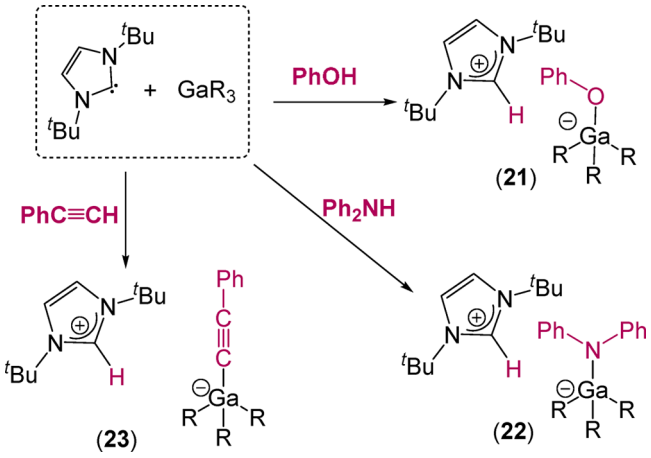
Scheme 8. FLP Activation of Phenol, Diphenylamine, and Phenylacetylene



6.79 ppm) to monosilyl (−0.78 and −0.07 ppm) anions, as well as three characteristic singlets for the imidazolium cation at 8.82, 7.75, and 1.3 ppm for the N_2CH, NCH and ^{t}Bu groups, respectively.

Encouraged by these results, we next took on more challenging substrates, probing the reactivity of the I^{t}Bu/GaR_3 pair toward diphenylaniline (Ph_2NH) and phenylacetylene (PhC≡CH). Following the same order of addition as that for **21**, N−H and C−H activations of diphenylaniline and phenylacetylene were accomplished, affording [{I^{t}BuH}$^+${GaR_3NPh_2}$^-$] (**22**) and [{I^{t}BuH}$^+${GaR_3CCPh}$^-$] (**23**) in 38% and 78% yields, respectively (Scheme 8). The modest isolated yield of **22** prompted us to inspect the filtrate more closely; thus, ^{1}H NMR spectra revealed unreacted diphenylamine and the formation of **15**. This finding suggests that, even at 0 °C, the competing NHC rearrangement process that deactivates the NHC/Ga pair can still take place. It should also be noted that secondary amines have previously been successfully employed as LBs in FLPs for hydrogen activation.[44] Thus, Rieger and co-workers paired $B(C_6F_5)_3$ with TMPH (TMPH = 2,2,6,6-tetramethylpiperidine) or ^{i}Pr$_2$NH,[44a] whereas Pápai and co-workers showed that, in certain cases (depending on the steric hindrance), a borane/imine combination after cleaving hydrogen and affording borane/amine adduct can react further with more hydrogen to afford ammonium hydroborate salt.[44b]

Compounds **21**−**23** could all be isolated as crystals and their structures elucidated by X-ray crystallography (Figures 6 and 7). These displayed similar general structural features of a salt-like ion-pair structure comprising a protonated imidazolium cation charge-balanced by a heteroleptic gallate anion. The gallate anion contains three monosilyl groups and the relevant anionic fragment stemming from X−H activation (X = O, N, C) of the substrate, that is, aryloxo PhO^- (**21**), amido Ph_2N^- (**22**), or alkynyl $PhC{\equiv}C^-$ (**23**) ligands.

All three structures show a distorted tetrahedral gallium geometry, as evidenced by C−Ga−X bond angles (X = C, O, N) ranging from 95.4(2)° to 115.6(2)° [mean angle 108.87° in **21**, 109.33° in **22**, and 109.36° in **23**]. The Ga−C_{alkyl} distances (Table S3) show little variation [mean 2.016 Å in **21**, 2.023 Å in **22**, and 2.022 Å in **23**] and agree well with the values of other tetracoordinated gallium species.[38,45] The Ga−O bond distance in **21** [1.981(4) Å] shows good agreement with literature values for gallium complexes containing terminal

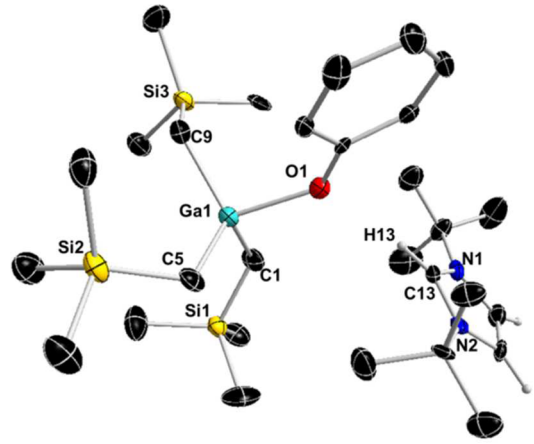


Figure 6. Molecular structure of **21** with 50% probability displacement ellipsoids. All hydrogen atoms except those on the imidazole ring have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ga1−O1 1.981(4), Ga1−C1 2.000(6), Ga1−C5 2.029(6), Ga1−C9 2.020(5); C1−Ga1−O1 95.4(2), O1−Ga1−C9 102.7(2), C1−Ga1−C9 117.8(3), C5−Ga1−O1 107.3(2), C5−Ga1−C1 115.6(2), C5−Ga1−C9 114.4(2), N1−C13−N2 109.2(5).

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 [{$Ph_3Ga(\mu$-NMe_2)-$GaPh_3$}$^-$] anion [Ga−N 2.051(1) Å],[46] consistent with the terminal versus bridging mode of the amido ligand. The Ga−C1 bond in **23** of 2.031(3) Å is only slightly elongated in comparison with the Ga−C bond distance in anionic [{$Ga(CCSiMe_3)_3$(2,6-^{i}Pr$_2$C$_6$H$_3$N(SiMe$_3$)}$^-$] (average Ga−C = 1.969 Å).[47a]

Multinuclear NMR analysis confirmed that the solid structures exhibited by **21**−**23** are preserved in THF-d_8 solutions (see the Experimental Section and Supporting Information). Two informative singles in a 2:1 ratio at 7.86 and 8.80 ppm for the C*H*N and NC*H*N protons, respectively, evidenced the presence of the imidazolium cation. The ^{13}C NMR spectrum of **23** displayed two resonances at 104.7 and 105.4 ppm, which can be assigned to the Cα and Cβ positions, respectively, of the alkynyl fragment.[47]

The formation of **23**, where the LB I^{t}Bu deprotonates phenylacetylene while the three monosilyl groups attached to gallium remain intact, contrasts with the results observed when IPr·GaR_3 (**14**), containing a less sterically demanding NHC, is reacted with phenylacetylene. Here one R group on gallium acts as a base, to give IPr·GaR_2(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 $GaMe_3$ and 4-ethynyl-2,6-lutidine, where the metalation of terminal alkyne by $GaMe_3$ 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 phenylacetylene[49] where the steric bulk of the tris(alkyl)gallium reagent dictates the extent of metalation.[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

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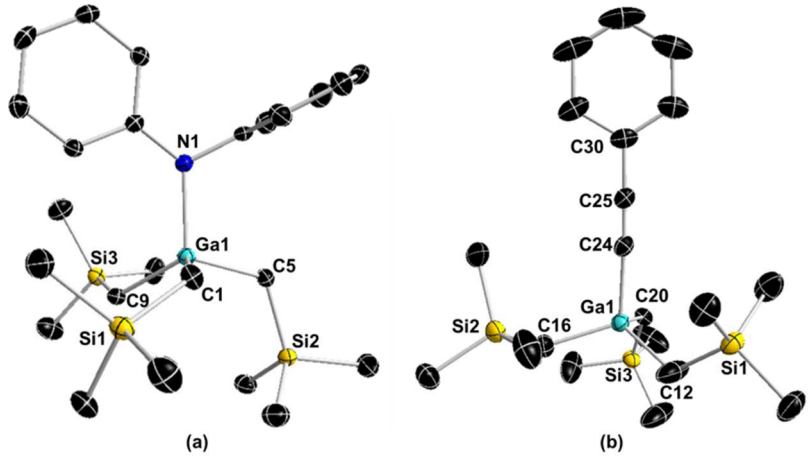
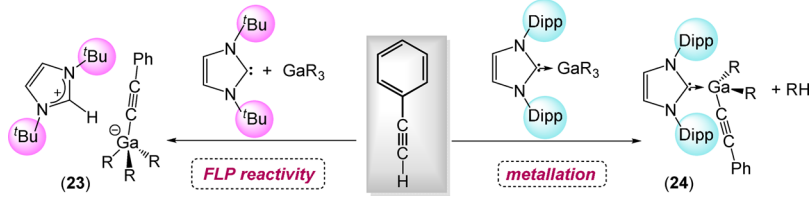


Figure 7. (a) Anionic moiety of the molecular structure of **22** with 50% probability displacement ellipsoids. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ga1−N1 2.0150(17), Ga1−C1 2.031(2), Ga1−C5 2.022(2), Ga1−C9 2.015(2); C1−Ga1−N1 103.88(8), N1−Ga1−C9 113.35(8), C1−Ga1−C9 113.31(9), C5−Ga1−N1 103.26(8), C5−Ga1−C1 109.25(9), C5−Ga1−C9 112.95(9). (b) Anionic moiety of molecular structure of **23** with 50% probability displacement ellipsoids. All hydrogen atoms and disorder components in two CH_2SiMe_3 groups have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ga1−C12 2.011(3), Ga1−C16 2.038(4), Ga1−C20 2.018(4), Ga1−C24 2.031(3), C24−C25 1.205(4); C12−Ga1−C20 107.74(18), C12−Ga1−C24 110.84(13), C20−Ga1−C24 103.46(13), C12−Ga1−C16 115.44(18), C20−Ga1−C16 110.07(16), C24−Ga1−C16 108.62(14).

Scheme 9. Contrasting Reactivities of Different NHC/GaR_3 Mixtures with Phenylacetylene: FLP-Induced Deprotonation versus Direct Gallation



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_2SiMe_3 group with the C≡CPh group, causing a shortening of the Ga−C_{NHC} bond [Ga−C9 2.104(4) Å in Figure 8 vs 2.1960(16) Å in **14**]. The Ga−$C_{alkynyl}$ (Ga−C1 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_6D_6, **24** displayed an excellent solubility in this low-coordinating solvent. The most informative resonances in the ^{13}C NMR spectrum are C_{NHC}−Ga at 179.4 ppm, which is upfield-shifted compared to the free carbene, and the two alkynyl resonances at 106.9 ppm (Ga—*C*≡CPh) and 112.5 ppm (GaC≡*C*Ph) (see the Experimental section and Supporting Information for details).

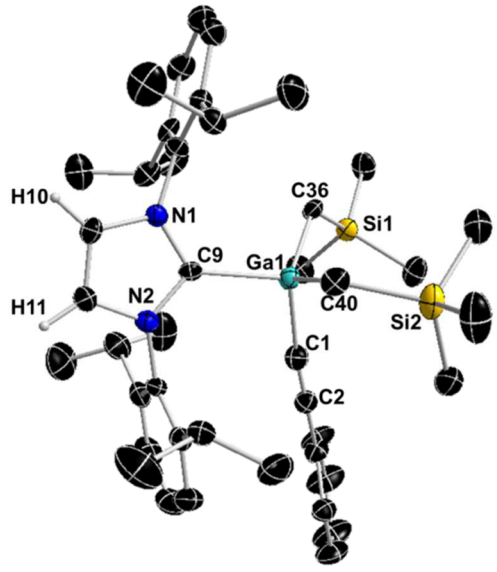


Figure 8. Molecular structure of **24** with 50% probability displacement ellipsoids. All hydrogen atoms except those on the imidazole ring and the minor disorder in the alkyne ligand have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ga1−C1 1.954(4), Ga1−C9 2.104(4), Ga1−C36 1.997(3), Ga1−C40 1.997(3), C1−C2 1.203(5); C1−Ga1−C40 110.43(15), C1−Ga1−C36 111.94(15), C40−Ga1−C36 116.63(14), C1−Ga1−C9 105.44(14), C40−Ga1−C9 100.09(14), C36−Ga1−C9 111.16(13), N1−C9−N2 103.7(3), Ga1−C1−C2 174.6(4).

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_2SiMe_3) with the utility lithium amide LiTMP or the sterically hindered NHC I^{t}Bu. When two topical areas of main-group chemistry, namely, cooperative

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bimetallics 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 cooperativity was exploited, sterically hindered LiTMP and GaR_3 were found not to undergo cocomplexation 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 cooperativity as TMT approaches, which exploit both the strong basicity of LiTMP (which carries out deprotonation of the substrate) and the pronounced carbophilicity of GaR_3 (which traps and stabilizes the incipient anion generated via metalation), 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 galium 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 exported 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 GaR_3 as a LA was effectively combined with the LB I^{t}Bu, 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 I^{t}Bu to the related NHC IPr, which suppresses the FLP reactivity in contact with phenylacetylene, demoting the NHC from acting as a base to becoming a spectator ligand, affording NHC complex **24**, where phenylacetylene has been metalated 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 noncocomplexing partnerships operate and showcasing the potential of gallium reagents to engage in metalation 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 benzophenone 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 ^{1}H and 100.62 MHz for ^{13}C{^{1}H}. 1-Methylbenzimidazole, 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. [$Ga(CH_2SiMe_3)_3$],[51] I^{t}Bu,[52] and LiTMP[53] were prepared according to literature methods and stored and handled under an inert atmosphere because of their air sensitivity (I^{t}Bu) and pyrophoricity ($Ga(CH_2SiMe_3)_3$ and LiTMP).

Synthesis of [3-(PMDETA)Li-2-(GaR_3)$C_8H_7N_2$] (7). To a suspension of LiTMP (0.074 g, 0.5 mmol) and $Ga(CH_2SiMe_3)_3$ (0.165 g, 0.5 mmol) in hexane (10 mL) was added via solid addition tube at room temperature 1 equiv of 1-methylbenzimidazole (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 $C_{29}H_{63}GaLiN_5Si_3$: C, 54.19; H, 9.88; N, 10.90. Found: C, 54.32; H, 10.06; N, 11.09. ^{1}H NMR (298 K, THF-d_8) δ −0.77 (6H, s, CH_2SiMe_3), −0.15 (27H, s, $Si(CH_3)_3$), 2.15 (12H, s, $N(CH_3)_2$), 2.21 (3H, s, NCH_3), 2.32 (4H, mult, NCH_2CH_2N), 2.43 (4H, mult, NCH_2CH_2N), 3.84 (3H, s, $ArNCH_3$), 7.03 (2H, mult, ArCH), 7.31 (1H, mult, ArCH), 7.37 (1H, mult, ArCH). ^{13}C{^{1}H} NMR (298 K, THF-d_8): δ −0.5 (CH_2SiMe_3), 3.1 ($Si(CH_3)_3$), 33.0 (NCH_3), 43.4, 46.2, 57.3, 58.8 (PMDETA), 109.5 (CHAr), 116.3 (CHAr), 120.9 (CHAr), 137.6 (CAr), 145.4 (CAr), 188.8 (CGa). ^{7}Li NMR (298 K, THF-d_8, reference LiCl in D_2O at 0.00 ppm): δ 3.24.

Synthesis of [1-(PMDETA)Li-2-CH_2(GaR_3)C_5H_4N] (8). To a suspension of LiTMP (0.074 g, 0.5 mmol) and $Ga(CH_2SiMe_3)_3$ (0.165 g, 0.5 mmol) in hexane (10 mL) was added via syringe at room temperature 1 equiv of 2-picoline (46 mg, 49 μL, 0.5 mmol). 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, 79.5%). Anal. Calcd for $C_{27}H_{62}GaLiN_4Si_3$: C, 53.71; H, 10.35; N, 9.28. Found: C, 52.60; H, 9.81; N, 9.78. ^{1}H NMR (298 K, C_6D_6): δ −0.44 (6H, s, CH_2SiMe_3), 0.45 (27H, s, $Si(CH_3)_3$), 1.54−1.66 (8H, br mult, NCH_2CH_2N), 1.77 (12H, s, NCH_3), 2.07 (3H, s, NCH_3), 2.12 (2H, s, $ArCH_2$), 6.35 (1H, t, ArCH), 7.09 (1H, t, ArCH), 7.23 (1H, d, ArCH), 7.35 (1H, d, ArCH). ^{13}C{^{1}H} NMR (298 K, C_6D_6): δ 0.7 (CH_2SiMe_3), 3.9 ($Si(CH_3)_3$), 38.9 ($ArCH_2Ga$), 45.2, 45.5, 53.1, 56.7 PMDETA, 113.9 (CHAr), 122.7 (CHAr), 135.4 (CHAr), 145.1 (CHAr), 174.1 (CAr). ^{7}Li NMR (298 K, C_6D_6, reference LiCl in D_2O at 0.00 ppm): δ 0.75. ^{1}H NMR (298 K, THF-d_8): δ −1.14 (2H, s, CH_2SiMe_3), −1.02 (4H, s, CH_2SiMe_3), −0.19 (9H, s, $Si(CH_3)_3$), −0.10 (18H, s, $Si(CH_3)_3$), 1.79 (2H, s, $ArCH_2$), 2.18 (12H, s, NCH_3), 2.24 (3H, s, NCH_3), 2.35 (4H, mult, NCH_2CH_2N), 2.45 (4H, mult, NCH_2CH_2N), 6.59 (1H, t, ArCH), 6.77 (1H, d, ArCH), 7.30 (1H, t, ArCH), 8.03 (1H, d, ArCH). ^{13}C{^{1}H} NMR (298 K, THF-d_8): δ 0.4 (CH_2SiMe_3), 3.1 ($Si(CH_3)_3$), 3.7 (CH_2SiMe_3), 4.1 ($Si(CH_3)_3$), 30.9 ($ArCH_2Ga$), 43.6, 46.1, 56.7, 56.8 (PMDETA), 114.8 (CHAr), 122.7 (CHAr), 135.9 (CHAr), 147.0 (CHAr), 173.8 (CAr). ^{7}Li NMR (298 K, THF-d_8, reference LiCl in D_2O at 0.00 ppm): δ 0.14−1.15 (br).

Synthesis of [{I^{t}BuH}$^+${($PhOGaR_3$}$^-$] (21). To a cooled solution of $Ga(CH_2SiMe_3)_3$ (0.165 g, 0.5 mmol in 10 mL of hexane) was added phenol (47 mg, 0.5 mmol), followed by I^{t}Bu (0.09 g, 0.5 mmol), and the obtained white suspension was stirred for 2 h at 0 °C. The suspension was concentrated to approximately 5 mL in volume, and 2 mL of toluene was added. Gentle heating afforded a solution that, upon cooling, deposited colorless X-ray-quality crystals (230 mg, 76%), which were isolated by filtration. Anal. Calcd for $C_{29}H_{59}N_2OSi_3Ga$: C, 57.50; H, 9.82; N, 4.62. Found: C, 57.85; H, 9.46; N, 5.33. ^{1}H NMR (298 K, THF-d_8): δ −0.78 (6H, s, CH_2SiMe_3), −0.07 (27H, s, $Si(CH_3)_3$), 1.63 (18H, s, $C(CH_3)_3$), 6.16 (1H, t, *p*-ArCH), 6.52 (2H, d, *o*-ArCH), 6.79 (2H, t, *m*-ArCH), 7.75 (2H, s, imidazole backbone CH), 8.82 (1H, s, C2H). ^{13}C{^{1}H} NMR (298 K, THF-d_8): δ 2.7 (CH_2SiMe_3), 3.5 ($Si(CH_3)_3$), 29.8 ($C(CH_3)_3$), 61.2 ($C(CH_3)_3$), 112.4 (*p*-ArCH), 121.0 (*o*-ArCH), 121.7 (imidazole backbone CH), 132.2 (NCHN), 128.6 (*m*-ArCH), 168.7 (ArC_{ipso}).

Synthesis of [{I^{t}BuH}$^+${Ph_2NGaR_3}$^-$] (22). To a cooled solution of $Ga(CH_2SiMe_3)_3$ (0.165 g, 0.5 mmol in 10 mL of hexane) was added diphenylamine (85 mg, 0.5 mmol), followed by I^{t}Bu (0.09 g, 0.5 mmol), and the obtained white suspension was stirred for 2 h at 0 °C. The suspension was concentrated to approximately 5 mL in volume, and 2 mL of toluene was added. Gentle heating afforded a solution that, upon cooling, deposited colorless X-ray-quality crystals (130 mg,

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38%). Anal. Calcd for $C_{35}H_{64}N_3Si_3Ga$: C, 61.74; H, 9.47; N, 6.17. Found: C, 58.18; H, 9.58; N, 5.22. Elemental and NMR spectroscopic analyses are consistent with the sample containing impurities such as unreacted diphenylamine. While ^{1}H monitoring of this reaction in THF-d_8 showed the formation of **22** as a pure compound (72% conversion; see Figures S13 and S14 in the Supporting Information), NMR analyses of crystalline samples consistently showed the presence of variable amounts of $NHPh_2$ and another unknown gallium species containing R groups.

^{1}H NMR (298 K, THF-d_8): δ −0.80 (6H, s, CH_2SiMe_3), −0.09 (27H, s, $Si(CH_3)_3$), 1.57 (18H, s, $C(CH_3)_3$), 6.39 (t, 2H, *p*-ArCH), 6.75 (d, 4H, *o*-ArCH), 6.89 (t, 4H, *m*-ArCH), 7.55 (2H, s, imidazole backbone), 8.32 (1H, s, C2*H*). ^{13}C{^{1}H} NMR (298 K, THF-d_8): δ 2.8 (CH_2SiMe_3), 3.8 ($Si(CH_3)_3$), 29.9 ($C(CH_3)_3$), 60.9 ($C(CH_3)_3$), 115.6 (*p*-ArCH), 123.9 (*o*-ArCH), 121.1 (imidazole backbone *C*H), 128.3 (*m*ArCH), 136.1 (NCHN), 157.2 (ArC_{ipso}).

Synthesis of [{I^{t}BuH}$^+${PhCCGaR$_3$}$^-$] (23). To a cooled solution of $Ga(CH_2SiMe_3)_3$ (0.165 g, 0.5 mmol in 10 mL of hexane) was added phenylacetylene (51 mg, 55 μL, 0.5 mmol), followed by I^{t}Bu (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, afforded X-ray-quality crystals (240 mg, 78%). Anal. Calcd for $C_{31}H_{60}GaN_2Si_3$: C, 60.66; H, 9.69; N, 4.56. Found: C, 60.43; H, 9.73; N, 4.84. ^{1}H NMR (298 K, THF-d_8): δ −1.01 (6H, s, CH_2SiMe_3), −0.02 (27H, s, $Si(CH_3)_3$), 1.66 (18H, s, $C(CH_3)_3$), 6.94 (1H, t, *p*-ArC*H*), 7.04 (2H, t, *m*-ArC*H*), 7.21 (2H, d, *o*-ArCH), 7.86 (2H, s, imidazole backbone *CH*), 8.81 (1H, s, C2*H*). ^{13}C{^{1}H} NMR (298 K, THF-d_8): δ 1.1 (CH_2SiMe_3), 3.5 ($Si(CH_3)_3$), 29.8 ($C(CH_3)_3$), 61.3 ($C(CH_3)_3$), 104.7 (PhC≡CGa), 105.4 (PhC≡CGa), 121.6 (imidazole backbone *C*H), 124.7 (*p*-ArCH), 128.1 (*m*-ArCH), 130.6 (ArC_{ipso}), 131.7 (*o*-ArCH), 132.3 (NCHN).

Synthesis of [IPr·GaR$_2$(CCPh)] (24). Equimolar amounts of $Ga(CH_2SiMe_3)_3$ (0.165 g, 0.5 mmol) and IPr (0.2 g, 0.5 mmol) were suspended in 10 mL of hexane and stirred for 30 min at room temperature. An equivalent of phenylacetylene (51 mg, 55 μL, 0.5 mmol) was added, and the obtained orange suspension was refluxed for 6 h. Slow cooling of the obtained orange solution afforded X-ray-quality crystals (189 mg, 55%). Anal. Calcd for $C_{43}H_{63}N_2Si_2Ga$: C, 70.38; H, 8.65; N, 3.82. Found: C, 69.32; H, 8.39; N, 3.59. ^{1}H NMR (298 K, C_6D_6): δ −1.04 (4H, mult, CH_2SiMe_3), 0.30 (18H, s, $Si(CH_3)_3$), 0.97 (12H, d, $CH(CH_3)_2$), 1.45 (12H, d, $CH(CH_3)_2$), 2.84 (4H, sept, $CH(CH_3)_2$), 6.40 (2H, s, imidazole backbone *CH*), 6.98 (1H, t, *p*-ArC*H*, alkyne ligand), 7.09 (6H, mult, ArC*H*, Dipp ligand), 7.19 (2H, t, *m*-ArC*H*, alkyne ligand), 7.46 (2H, d, *o*-Ar−C*H*, alkyne ligand). ^{13}C{^{1}H} NMR (298 K, C_6D_6): δ −1.7(CH_2SiMe_3), 2.9 ($Si(CH_3)_3$), 23.0 ($CH(CH_3)_2$), 25.9 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 106.9 (PhC≡CGa), 112.5 (PhC≡CGa), 124.2 (ArCH), 124.6 (imidazole backbone *C*H), 126.0 (ArCH), 130.9 (ArCH), 131.7 (ArCH), 135.4 (ArC), 145.8 (ArC), 179.4 (*C*Ga).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00549.

Crystallographic details and copies of NMR spectra for compounds **7**, **8**, and **21**−**24** (PDF)

Accession Codes

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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Notes

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