Understanding the Subtleties of Frustrated Lewis Pair Activation of Carbonyl Compounds by N-Heterocyclic Carbene/Alkyl Gallium Pairings

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Abstract: This study reports the use of the trisalkylgallium GaR₃ (R = CH₂SiMe₃), containing sterically demanding monosilyl groups, as an effective Lewis acid component for Frustrated Lewis Pair activation of carbonyl compounds, when combined with the bulky N-heterocyclic carbene 1,3-bis(*tert*-butyl)imidazol-2-ylidene (I^tBu) or 1,3-bis(*tert*-butyl)imidazolin-2-ylidene (SI^tBu). The reduction of aldehydes can be achieved by insertion into the C=O functionality *via* the C2 (so-called normal) position of the carbene affording zwitterionic products [I^tBuCH₂OGaR₃] (1) or [I^tBuCH(p-Br-C₆H₄)OGaR₃] (2) or alternatively *via* its abnormal (C4) site yielding [aI^tBuCH(p-Br-C₆H₄)OGaR₃] (3). Proving the cooperative behaviour of both components, I^tBu and GaR₃, when separated neither of them are able to activate any of these substrates. NMR spectroscopic studies of the new compounds point to complex equilibria involving the formation of kinetic and thermodynamic species as implicated through the aid of DFT calculations. Extension to ketones proved to be successful for electrophilic α,α,α-trifluoroacetophenone yielding [aI^tBuC(Ph)(CF₃)OGaR₃] (7); however in the case of ketones and nitriles bearing acidic hydrogen atoms, C-H bond activation takes place preferentially, affording novel imidazolium gallate salts such as [(I^tBuH)⁺[(p-I-C₆H₄)C(CH₂)OGaR₃]⁻] (8) or [(I^tBuH)⁺{Ph₂C=C=NGaR₃}⁻] (12).

Introduction

The chemistry of sterically mismatched Lewis acid-base pairs capable of unusual reactivities, today commonly referred as “frustrated Lewis pairs (FLPs)”, has been brought to the forefront of main group chemistry by the seminal work of Stephan and co-workers.^[1,2] Since then, the field of FLP chemistry has snowballed due in part to the ever-growing scope of small molecules that can be activated (e.g., H₂ and greenhouse gasses), and also because of its progression from stoichiometric to catalytic processes.^[2e,f] Although the most powerful FLPs to date rely on the use of sterically hindered, electron-rich organophosphines as the Lewis base (LB) component,^[1-3] N-heterocyclic carbenes (NHCs) are increasingly gaining attention due to their related coordination chemistry, tuneability and excellent potential for subtle variations of their steric/electronic properties.^[4-6] The Lewis acidic component of these pairs is still heavily dominated by boron

complexes, with aluminium species showing slow but steady growth in popularity.^[7-9] By comparison, the use of heavier gallium Lewis acids (LA) has barely started. In this context, studies on the reaction of 4-ethynyl-2,6-lutidine with a range of group 13 compounds have revealed that while using B(C₆F₅)₃ leads to FLP activation processes, alkyl complexes of the heavier Al, Ga and In display a common but distinct reactivity, promoting metalation of the ethynyl group with concomitant elimination of the relevant alkane.^[10] Breaking new ground in the field, Aldridge has reported an ambiphilic gallium system, containing an activated β-diketiminato ligand, capable of cooperative activation of protic, hydridic and apolar H-X bonds.^[11] Furthermore, the enhanced Lewis acidity of Ga alkyl fragments has proved to be key for promoting direct Ge-H exchange of phenylacetylene using mixed Ga/Ge complexes.^[12a] Interesting recent work by Schultz has also uncovered the double agent role of Ga systems as they can reverse their role in FLP chemistry, acting instead as a LB, being part of a gallanediyl framework, which facilitates insertion of benzaldehyde when combined with [M(C₆F₅)₃] (M= B or Al) LAs.^[13]

Advancing rational design of elusive main group abnormal NHC (aNHC) complexes, our first look at NHC-Ga alkyl complexes shed light on normal-to-abnormal NHC rearrangement mechanisms,^[14] which bears resemblance to mechanisms proposed in NHC/borane FLP systems.^[4] In particular, it was found that steric incompatibility prevented trimethylsilylmethylgallium(III) (GaR₃) and 1,3-bis(*tert*-butyl)imidazol-2-ylidene (I^tBu) from forming a stable normal adduct.^[14] Encouraged by these initial findings, here we present a systematic study probing the reactivity of these NHC/Ga combinations towards carbonyl compounds, an area where other, mostly, but not limited to, PR₃/B based FLP systems have shown considerable promise in synthesis and catalysis.^[13,15-17] Combining X-ray crystallographic with spectroscopic and theoretical investigations, new insights are provided into the intriguing chemoselectivities and mechanisms of these processes, which intensifies the potential of gallium tris(alkyl) complexes for FLP activation.

Results and Discussion

Reactions with aldehydes

We started by reacting GaR₃/I^tBu with the simplest and most reactive aldehyde, namely paraformaldehyde, in hexane suspension at 0 °C. Mixing all three components immediately produced a white precipitate which could be solubilised by addition of toluene to obtain X-ray amenable crystals of zwitterion [I^tBuCH₂OGaR₃] 1 in a 66% yield (Scheme 1a).

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Scheme 1. FLP-induced synthesis of zwitterionic compounds **1** and **2**.

A single crystal X-ray diffraction analysis (Fig 1) revealed addition of the $\text{t}^{\text{Bu}}\text{GaR}_3$ pair across the $\text{C}=\text{O}$ functionality to construct a new, single carbon-carbon bond [i.e., $\text{C1}-\text{C24}$, 1.505(3) Å] and an oxygen-gallium bond. The C_3O -tetra-coordinated gallium atom adopts a distorted tetrahedral geometry [bond angles ranging from 102.90(9)° to 116.28(11)°: mean value, 109.16°]. $\text{Ga}-\text{C}_{\text{alkyl}}$ and $\text{Ga}-\text{O}$ bond distances [mean $\text{Ga}-\text{C}$, 2.012 Å; $\text{Ga1}-\text{O1}$, 1.9317(15) Å] are in good agreement with literature values of other tetracoordinated gallium species.^[14,18]

Figure 1. Molecular structure of **1** with 50% probability displacement ellipsoids. All H atoms except those in the starting carbonyl group have been omitted for clarity. Selected bond distances (Å) and bond angles (°): $\text{Ga}(1)-\text{O}(1)$ 1.9317(15), $\text{Ga}(1)-\text{C}(12)$ 2.012(3), $\text{Ga}(1)-\text{C}(16)$ 2.012(2), $\text{Ga}(1)-\text{C}(20)$ 2.011(3), $\text{O}(1)-\text{C}(24)$ 1.384(3), $\text{C}(1)-\text{C}(24)$ 1.505(3), $\text{O}(1)-\text{Ga}(1)-\text{C}(20)$ 103.41(9), $\text{O}(1)-\text{Ga}(1)-\text{C}(12)$ 105.21(9), $\text{C}(20)-\text{Ga}(1)-\text{C}(12)$ 110.86(13), $\text{O}(1)-\text{Ga}(1)-\text{C}(16)$ 102.90(9), $\text{C}(20)-\text{Ga}(1)-\text{C}(16)$ 116.27(11), $\text{C}(12)-\text{Ga}(1)-\text{C}(16)$ 116.28(11), $\text{N}(1)-\text{C}(1)-\text{N}(2)$ 107.50(19).

The most informative resonance in the ^1H NMR spectrum in d_8 -THF is a singlet at 5.05 ppm for formerly aldehydic protons (i.e. H24A in Fig. 1), which displays a significant upfield shift (vs. 9.58 ppm in free formaldehyde). Similarly, in the ^{13}C NMR spectrum, the resonances of former carbenic and $\text{C}=\text{O}$ fragments are observed at 153.2 ppm and 58.6 ppm, respectively (vs. 213.2 ppm and 195.2 ppm in the free reagents).

Applying the same protocol to the aromatic aldehyde 4-bromobenzaldehyde, afforded [$\text{t}^{\text{Bu}}\text{CH}(\text{p}-\text{Br}-\text{C}_6\text{H}_4)\text{OGaR}_3$] (**2**) in 42% crystalline yield (Scheme 1b). As evidenced by X-ray crystallographic studies, **2** (Fig. 2) has the same molecular structure as **1** and displays similar gross structural features.

Figure 2. Molecular structure of **2** with 50% probability displacement ellipsoids. All H atoms except that on the former carbonyl group have been omitted for clarity. Selected bond distances (Å) and bond angles (°): $\text{Ga}(1)-\text{O}(1)$ 1.9522(16), $\text{Ga}(1)-\text{C}(19)$ 2.021(2), $\text{Ga}(1)-\text{C}(23)$ 2.005(2), $\text{Ga}(1)-\text{C}(27)$ 2.027(2), $\text{O}(1)-\text{C}(12)$ 1.372(3), $\text{C}(1)-\text{C}(12)$ 1.525(3), $\text{O}(1)-\text{Ga}(1)-\text{C}(23)$ 105.42(9), $\text{O}(1)-\text{Ga}(1)-\text{C}(19)$ 103.48(9), $\text{C}(23)-\text{Ga}(1)-\text{C}(19)$ 114.57(10), $\text{O}(1)-\text{Ga}(1)-\text{C}(27)$ 102.42(8), $\text{C}(23)-\text{Ga}(1)-\text{C}(27)$ 111.41(11), $\text{C}(19)-\text{Ga}(1)-\text{C}(27)$ 117.58(10), $\text{N}(1)-\text{C}(1)-\text{N}(2)$ 107.8(2).

Although in the solid state **2** is molecularly isostructural with **1**, NMR spectroscopic analyses revealed a much more complex scenario in solution. As **2** exhibited poor solubility in arene solvents such as C_6D_6 , its solution studies were conducted in d_8 -THF where two different species containing reduced carbonyl group were observed together with the free starting materials.^[19] One species can be confidently assigned to complex **2**, displaying informative resonances in the ^{13}C NMR spectrum at 72.3 and 154.2 ppm for the $\text{OCH}(\text{Ar})$ and NCN fragments respectively. Interestingly, over the course of 24 hours,^[20] **2** evolved completely into the new complex (Fig S32 in SI), which could be isolated and structurally defined as [$\text{t}^{\text{Bu}}\text{CH}(\text{p}-\text{Br}-\text{C}_6\text{H}_4)\text{OGaR}_3$] (**3**) (Fig. 3).

Figure 3. Molecular structure of **3** with 50% probability displacement ellipsoids. All H atoms except those of the imidazole ring and the former carbonyl group have been omitted for clarity. Selected bond distances (Å) and bond angles (°): $\text{Ga}(1)-\text{O}(1)$ 1.943(5), $\text{Ga}(1)-\text{C}(19)$ 2.019(8), $\text{Ga}(1)-\text{C}(23)$ 2.020(7), $\text{Ga}(1)-\text{C}(27)$ 2.012(8), $\text{O}(1)-\text{C}(12)$ 1.335(9), $\text{C}(2)-\text{C}(12)$ 1.541(10), $\text{O}(1)-\text{Ga}(1)-\text{C}(27)$ 109.6(3), $\text{O}(1)-\text{Ga}(1)-\text{C}(19)$ 102.0(3), $\text{C}(27)-\text{Ga}(1)-\text{C}(19)$ 114.4(3), $\text{O}(1)-\text{Ga}(1)-$

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C(23) 102.8(3), C(27)-Ga(1)-C(23) 113.3(3), C(19)-Ga(1)-C(23) 113.3(3), N(1)-C(1)-N(2) 109.9(7).

Being constitutionally isomeric with **2**, complex **3** also contains an OCHAr fragment coordinated to Ga, resulting from the addition of the carbene across the C=O bond of the aldehyde. However in this case, this has occurred *via* one of the C atoms located at the backbone of the imidazole ring (so called abnormal^[21a,22] or C4-position) [C2 in Fig. 3], whereas the former carbenic C in I'Bu [C1 in Fig. 3] is now protonated. Consistent with the lack of symmetry in the imidazole ring, ¹H NMR spectrum of **3** in *d*₈-THF showed two singlets for the non-equivalent protons of the imidazole ring at 8.45 and 7.84 ppm. Furthermore, the ¹³C NMR spectrum displays a resonance at 72.7 ppm which can be assigned to the reduced C=O functionality (i.e., C12 in Fig. 3), whereas the formally C2 and C4 carbons of I'Bu (i.e., C1 and C2 in Fig. 3) resonate at 131.8 and 149.0 ppm respectively.

Complexes **2** and **3** can be described as kinetic and thermodynamic products of the activation of 4-bromobenzaldehyde by GaR₃/I'Bu combinations. Supporting this interpretation, monitoring the reaction over a range of temperatures revealed, that at 230K, by mixing GaR₃ and the aldehyde, an adduct must be formed (as all resonances are slightly upfield when compared to those of the free starting materials). Under these conditions, addition of I'Bu led to the almost instantaneous formation of **2**. Interestingly, by increasing the temperature to 323K we observed full conversion of **2** into **3** over just 15 minutes (see Fig S15-17 in SI). During these solution studies, the persistent presence of small amounts of the three components of these complexes, I'Bu, GaR₃ and ArCHO, suggested that all these species co-exist in equilibrium. Further support was found by dissolving isolated crystals of **3** in *d*₈-THF the resulting ¹H NMR spectrum of which showed, once again, the presence of resonances for the three starting materials. These findings are consistent with the reversible cleavage in solution of the newly formed C-C and Ga-O bond in both adducts **2** and **3**. It should be noted that a similar equilibrium has been reported previously by Erker for the reactions of geminal P/B FLP systems with benzaldehyde and *trans*-cinammic aldehyde.^[15]

By irrefutably establishing interconversion of **2** into **3**, it was possible to prepare **3** rationally from starting materials in hexane at 0 °C simply by extending the reaction time from 15 minutes to two hours (Scheme 2).

Scheme 2. FLP-induced synthesis of compounds **3**, **4**, **5** and **6**.

Furthermore, this approach to access C4-substituted abnormal adducts can be successfully extended to other aldehydes, including benzaldehyde, 4-anisaldehyde and ferrocenecarboxaldehyde affording alkoxo derivatives [al'BuCH(C₆H₅)OGaR₃] (**4**), [al'BuCH(p-OMe-C₆H₄)OGaR₃] (**5**) and [al'BuCH(FeCp₂)OGaR₃] (**6**) in a 62, 56 and 48% isolated crystalline yield respectively (Scheme 2).

Multinuclear NMR spectroscopic studies confirmed that in all cases the insertion of the substrate has taken place *via* the I'Bu C4-position (see SI for details). Mimicking the situation with **3**, activation products **4-6** are in equilibrium with their free components when dissolved in *d*₈-THF. Interestingly, the position of this dissociative equilibrium seems to correlate with the electronic nature of the Ar group substituents of the aldehyde. Thus, by replacing the electron-withdrawing bromide with H (in **4**) or electron-donating OMe (in **5**) leads to higher ratios of free I'Bu, GaR₃ and the relevant aldehyde. On the other hand, with **6**, which contains a ferrocenyl substituent, no measurable sign of dissociation is observed. An interesting solvent effect was also evident in these processes. Contrasting with the studies using *d*₈-THF, when C₆D₆ was employed compound **4** (which is the only one partially soluble in this arene solvent), showed no evidence of being in equilibrium with its free components, suggesting that donor solvents such as THF favour cleavage of the complex.

Mechanistic implications and DFT calculations

Previous studies using NHC-based FLP systems containing B^[4e, 23] and Al^[7a, 9a] LAs have shown their ability to reduce CO₂ and other carbonyl compounds using either the C2 or C4 position of their NHC component. However, as far as we are aware, this is the first time that both possible constitutional isomers (i.e., **2** and **3**) have been isolated and structurally defined. Furthermore, our investigations also indicate that the formation of the C4-inserted products is thermodynamically controlled. It should also be stressed that I'Bu is not capable of activating any of the studied substrates on its own. Also despite the fact that our solution studies evidence the presence of variable amounts of free I'Bu and GaR₃, the abnormal complex [(al'Bu)GaR₃] (which is observed as the only product when both reagents are mixed in the absence of the aldehyde)^[14] has not been detected.

Intrigued by these findings we have carried DFT calculations^[24] employing the B3LYP method^[25] and the 6-311G(d,p) basis set^[26] to optimise structures and cast light on the thermodynamics involved in these processes. Geometrical parameters of optimised structures [I'BuCH(p-Br-C₆H₄)OGaR₃] (**II_{Ar}**) and [al'BuCH(p-Br-C₆H₄)OGaR₃] (**III_{Ar}**) are in excellent agreement with those obtained experimentally by X-ray analysis of **2** and **3**, respectively (Table S3), with only a slight underestimation of the strength of the Ga-O interaction ($\Delta[d(\text{Ga-O})_{\text{calc}}-d(\text{Ga-O})_{\text{exp}}] = 0.063$ and 0.057 Å for **II_{Ar}** and **III_{Ar}** respectively). Interestingly, consistent with experimental observations, model **III_{Ar}** was computed to be more stable than **II_{Ar}**, although only by a modest margin of 3.9 kcal mol⁻¹ (Fig. 4).

Figure 4. Modelled structures and relative energies of FLP adducts **II_{Ar}** and **III_{Ar}**.

NMR studies (*vide supra*) suggest that formation of **2** takes place via initial coordination of 4-bromobenzaldehyde to Lewis acidic GaR₃, which increases the polarity of the C=O bond and facilitates its nucleophilic attack by ^tBu. Supporting this interpretation, both steps were found to be exothermic, with an overall energy gain of 13.1 kcal mol⁻¹ [Scheme 3(i)]. Contrastingly, illustrating the relevance of GaR₃, the reaction of ^tBu with 4-bromobenzaldehyde was found to be endothermic by 12.4 kcal mol⁻¹, which is consistent with lack of reactivity witnessed experimentally. The activation of the aldehyde by forming a donor-acceptor intermediate is reminiscent to that proposed by Tamm for the fixation of CO₂ and N₂O by NHC/B(C₆F₅)₃ FLP combinations.^[23]

Scheme 3. Proposed scenarios for the reaction of 4-bromobenzaldehyde with GaR₃/^tBu combinations.

Formation of C4-substituted **3** could happen via a similar pathway, although in this case, abnormal ^a^tBu should act as the LB in the activation process [Scheme 3(ii)]. Having just one N-atom adjacent to their carbenic position, abnormal NHCs are significantly less stabilised than their normal isomers as well as being significantly better donors.^[21] Although usually considered as transient species, Bertrand has succeeded in the isolation of a stable free aNHC derived from a 1,2,3,4-tetraarylated imidazolium salt.^[21a] The computed energy difference between free ^a^tBu and ^tBu is +17.2 kcal mol⁻¹.^[27] Assuming a fast ^tBu/^a^tBu isomerisation equilibrium,^[28] as soon as more nucleophilic ^a^tBu is formed in solution (even as a minor product in comparison to ^tBu), it can

react with the aldehyde-GaR₃ donor-acceptor complex furnishing **3** [Scheme 3(ii)]. This C4-insertion is found to be significantly more energetically favoured (by 10.3 kcal mol⁻¹) than the competitive formation of abnormal complex [(^a^tBu)GaR₃], resulting from substitution of 4-bromobenzaldehyde as a donor to the GaR₃ fragment [Scheme 3 (iii)]. Nevertheless, a plausible alternative reaction pathway for the formation of **3** could be the insertion of 4-bromobenzaldehyde into this aNHC Ga complex. This possibility was investigated experimentally by dissolving isolated crystals of [(^a^tBu)GaR₃] and the aldehyde ArCHO in d₈-THF. ¹H NMR monitoring of the reaction mixture showed that at room temperature, after 2 days no reaction was observed between the reagents, which suggests that [(^a^tBu)GaR₃] is actually a deactivation product and once it is formed, any possible FLP reactivity with unsaturated substrates is inhibited. This is in line with previous studies in other related FLP systems containing B or Al LAs for which it has been reported that the relevant abnormal NHC complexes fail to exhibit FLP reactivity.^[4, 9a]

The lability of complex **2**, which is in dynamic equilibrium with its free components, is also key in promoting the formation of **3**, as it enables over time the ^tBu/^a^tBu isomerisation. Thus complex **1**, resulting from the formal C2-insertion of formaldehyde, displays no signs of dissociation in solutions over prolonged period of time and does not seem to readily form the relevant C4-insertion isomer. Offering further support to these experimental findings, DFT calculations on the optimised structures [^tBuCH₂OGaR₃] (**II_H**) and [^a^tBuCH₂OGaR₃] (**III_H**), showed that in this case there is not a clear thermodynamic drive for the C2/C4 isomerization (see SI for details). Both models have almost identical energies (**III_H** being just 0.2 kcal mol⁻¹ more stable than **II_H**). The small size of the reduced aldehyde in **1** may also contribute to the lack of lability observed for this complex. In this regard, dissociation energy of model **II_H** into ^tBu, GaR₃ and CH₂O was found to be +31.7 kcal mol⁻¹ (18.6 kcal mol⁻¹ greater than for **II_{Ar}**).

Reactions with ketones: C4 insertion vs C-H activation

We next turned our attention to the reactivity of these NHC/Ga combinations towards ketones (Scheme 4).

Scheme 4. Contrasting reactivities of ^tBu/GaR₃ mixtures with ketones.

Initial studies using benzophenone led to the formation of the deactivation complex [(^a^tBu)GaR₃]. Trying to circumvent this

problem, we next probed the same reaction using the saturated version of *l*Bu, namely bis(*tert*-butyl)imidazolin-2-ylidene (*Sl*Bu). However even under forcing reaction conditions (60°C, 12h), formation of an insertion product could not be detected (see SI). Moving to the more electrophilic α,α,α -trifluoroacetophenone, containing the strong electron withdrawing CF_3 group, furnished [*al*BuC(Ph)(CF_3)OGaR₃] (**7**) in a 63% isolated crystalline yield (Scheme 4). Established by X-ray crystallographic studies, the molecular structure of **7** is reminiscent to that of **3** (Fig. 5), revealing that the *l*Bu has added across the C=O group of the ketone by its abnormal C4-position [i.e., C2 in Fig. 5]. Multinuclear NMR studies are consistent with the retention of the solid-state structure of **7** in *d*₈-THF solution. As observed for compounds **3-6**, two singlets show up in the ¹H NMR spectrum at 8.67 and 7.21 ppm for the imidazole hydrogen atoms, which is consistent with the lack of symmetry in the heterocyclic ring. ¹³C NMR spectrum showed an informative resonance at 81.7 ppm belonging to the reduced C=O group (which resonates at 191.2 ppm in the starting material).

Figure 5. Molecular structure of **7** with 50% probability displacement ellipsoids. All hydrogen atoms except those on the imidazole ring are omitted for clarity. Selected bond distances (Å) and bond angles (°): Ga(1)–O(1) 1.9692(14), Ga(1)–C(12) 2.022(2), Ga(1)–C(16) 2.012(2), Ga(1)–C(20) 2.010(2), O(1)–C(24) 1.361(2), C(2)–C(24) 1.544(3), O(1)–Ga(1)–C(20) 107.81(9), O(1)–Ga(1)–C(12) 104.63(8), C(20)–Ga(1)–C(12) 116.46(9), O(1)–Ga(1)–C(16) 96.37(8), C(20)–Ga(1)–C(16) 115.00(10), C(12)–Ga(1)–C(16) 113.70(10), N(1)–C(1)–N(2) 110.93(18).

Contrasting with the reactivity studies on aldehydes, ¹H NMR monitoring of the reaction of *l*Bu, GaR₃ and PhC(O)CF₃ did not detect the initial formation of a C2 insertion isomer or an equilibrium between the starting materials and adduct **7**. A plausible explanation may lie in the large steric hindrance of electron withdrawing CF₃, which has been described as intermediate in size between ⁱPr and ^tBu substituents,^[29] which may make difficult the approach of normal *l*Bu to the electrophilic C=O group of the substrate. The reduced steric congestion on *al*Bu, having just one N^tBu-fragment adjacent to its carbenic position, seems to be sufficient to promote instead formation of C4-insertion adduct **7**. Further support was found by DFT calculations, where the reaction of *l*Bu, GaR₃ and PhC(O)CF₃ to give [*al*BuC(Ph)(CF₃)OGaR₃] (**III**_{CF₃}) was calculated to be exergonic by 14.5 kcal mol^{–1}. Geometrical parameters of the optimised structure **III**_{CF₃} (Fig. 6) are in excellent agreement with those found experimentally by X-ray analysis of **7** (see Table S4,

SI). Contrastingly, attempts to optimise the structure of the C2-insertion product analogous to **II**_A and **II**_H, led consistently to a structure where the normal carbenic carbon of the NHC is located 5.708 Å from the C=O group of the ketone, evidencing the steric incompatibility of the reagents to promote a C2 addition process (**II**_{CF₃} in Fig. 6). It should be noted that this model was found to be 12.4 kcal mol^{–1} less stable than **III**_{CF₃}.

Figure 6. Modelled structures and relative energies of FLP adducts **II**_{CF₃} and **III**_{CF₃}.

Interestingly, the reactions of GaR₃/*l*Bu with enolizable ketones 4-iodoacetophenone or 2,4,6-trimethylacetophenone revealed a different FLP reactivity pattern, promoting in this case the C–H activation processes to yield mixed imidazolium gallate salts [(*l*BuH)⁺{(p-I-C₆H₄)C(CH₂)OGaR₃}[–]] (**8**) and [(*l*BuH)⁺{(Me₃C₆H₂)C(CH₂)OGaR₃}[–]] (**9**) (Scheme 4). Analogous reactivity was observed when using *Sl*Bu, leading to the chemoselective formation of [(*Sl*BuH)⁺{(p-I-C₆H₄)C(CH₂)OGaR₃}[–]] (**10**) and [(*Sl*BuH)⁺{(Me₃C₆H₂)C(CH₂)OGaR₃}[–]] (**11**) (isolated yields ranging from 60 to 84%, see SI for details). The low solubility of these compounds in hexane precluded their isolation as single crystals. NMR spectroscopic studies confirmed the presence of an imidazolium cation [singlets at 8.72 and 7.78 ppm for the imidazole protons integrating one and two protons respectively in the ¹H NMR spectrum] as well as the formation of an enolate anion [olefinic Hs resonate at 3.86 and 4.12 ppm whilst the C=CH₂ fragment gives rise to two resonances at 163.3 and 79.9 ppm in the ¹³C NMR spectrum].

The isolation of **8-10** uncovers the ability of these NHC/Ga systems for the activation of acidic C–H bonds. Evidencing their cooperative behaviour, neither the carbenes employed nor GaR₃ can deprotonate these substrates on their own. This approach can be extended to other unsaturated organic substrates containing α -acidic protons.

Thus *l*Bu/GaR₃ readily activates diphenylacetonitrile, affording novel [(*l*BuH)⁺{Ph₂C=C=NGaR₃}[–]] (**12**) in 64% yield (Scheme 5), with *l*Bu abstracting the α -proton of the substrate while the alkyl groups on Ga are mere spectators in the reaction.^[30] This

reactivity contrasts with that observed by Mitzel for the reaction of 4-ethynyl-2,6-lutidine with GaEt_3 , where metallation of the ethynyl group is observed along with elimination of ethane.^[10] Replacing tBu by Si^tBu furnished the analogous compound $[\text{Si}^t\text{BuH}]^+\{\text{Ph}_2\text{C}=\text{C}=\text{NGaR}_3\}^-$ (**13**).

Scheme 5. Synthesis of compound **12** by C-H activation of diphenylacetonitrile employing a GaR_3/tBu combinations.

Elucidated by a single crystal X-ray diffraction analysis, the molecular structure of **12** shows a salt-like ion-pair structure comprised of a protonated imidazolium cation charge-balanced by a heteroleptic gallate anion containing a 3:1 ratio of monosilyl groups to keteniminate ligands (Fig. 7).

Figure 7. Molecular structure of **12** with 50% probability displacement ellipsoids. All H atoms except those on the imidazole ring and minor disorder in one of the two tBu substituents are omitted for clarity. Selected bond distances (Å) and bond angles ($^\circ$): Ga(1)-N(3) 2.0726(19), Ga(1)-C(12) 2.000(2), Ga(1)-C(16) 1.988(2), Ga(1)-C(20) 1.999(3), N(3)-C(24) 1.171(3), C(24)-C(25) 1.378(3), N(3)-Ga(1)-C(20) 101.08(9), N(3)-Ga(1)-C(12) 100.57(9), C(20)-Ga(1)-C(12) 113.75(11), N(3)-Ga(1)-C(16) 103.06(9), C(20)-Ga(1)-C(16) 117.63(10), C(12)-Ga(1)-C(16) 116.82(10), N(1)-C(1)-N(2) 109.7(2).

The heteroallene nature of the keteniminate ligand is evident from the shortening of the C24-C25 bond (1.378 Å) and elongation of the N3-C24 bond (1.171 Å) compared to the bonds in the free nitrile Ph_2CHCN (1.470 (2) Å and 1.147(2) Å, respectively).^[31] These bond distances as well as the near linearity of the C25-C24-N3 angle (175.26 $^\circ$) are in close agreement with other structurally characterised metal-keteniminate complexes.^[31,32] As far as we can ascertain, this is the first example of a structurally characterised Ga-keteniminate complex. Its ^1H NMR spectrum in d_8 -THF displays three singlets for the imidazolium cation at 8.68, 7.59 and 1.56 ppm for the N_2CH , NCH and tBu groups respectively. In agreement with previous literature values, the

newly formed ketenimine ligand gives rise to two low intensity resonances in the ^{13}C NMR spectrum, at 55.7 and 143.4 ppm for the Ph_2C and $\text{C}=\text{N}$ groups respectively. The $\nu(\text{C}=\text{C}=\text{N})$ stretch, which is the most characteristic vibrational mode in the IR spectrum for the ketenimine ligand, is visible at 2073.5 cm^{-1} .^[32]

Conclusions

The bulky trisalkylgallium, $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$, has been found to be a viable, effective Lewis acid for promoting small molecule activation when combined with a strong base such as 1,3-bis(*tert*-butyl)imidazol-2-ylidene (tBu) thus further expanding the versatility of Frustrated Lewis pair chemistry. The activation of carbonyl compounds can be achieved either by reduction of the $\text{C}=\text{O}$ functionality affording zwitterionic compounds such as $[\text{tBuCH}_2\text{OGaR}_3]$ (**1**) by forming a new C-C bond, or by C-H bond activation yielding $[\text{tBuH}]^+\{(\text{Me}_3\text{C}_6\text{H}_2)\text{C}(\text{CH}_2)\text{OGaR}_3\}^-$ (**9**), for instance. The unprecedented isolation of conformational isomers $[\text{tBuCH}(p\text{-Br-C}_6\text{H}_4)\text{OGaR}_3]$ (**2**) and $[\text{atBuCH}(p\text{-Br-C}_6\text{H}_4)\text{OGaR}_3]$ (**3**), resulting from the activation of 4-bromobenzaldehyde by this novel FLP system has revealed that tBu can effectively act as a Lewis base not only via its *normal* C2 position (kinetic product) but also via its C4 (*abnormal*) site (thermodynamic product). Evidencing the synergistic behaviour of these NHC/ GaR_3 pairings, when separated none of the components is able to activate these carbonyl compounds.

Experimental Section

Full experimental and computational details and characterization of compounds **1-13** are included in the Supporting Information. CCDC 1492929-1492933 contain the supplementary crystallographic data of this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[\text{tBuCH}_2\text{OGaR}_3]$ (1**)** A solution of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) was cooled on an ice bath. Paraformaldehyde (0.015 g, 0.5 mmol) was then added, followed by the addition of bis(*tert*-butyl)imidazol-2-ylidene (tBu) (0.09 g, 0.5 mmol). Obtained white suspension was stirred for 2 h at 0 $^\circ\text{C}$. Toluene was added (1 mL) and the mixture was gently heated until all of the visible solid had dissolved. Slow cooling of the resulting solution afforded a crop of colourless crystals (0.18 g, 66%). Anal. Calcd for $\text{C}_{24}\text{H}_{55}\text{N}_2\text{OSi}_3\text{Ga}$: C, 53.21; H, 10.23; N, 5.17. Found: C, 53.11; H, 10.31; N, 5.39. ^1H NMR (298 K, d_8 -THF) δ (ppm) -0.82 (6H, s, CH_2SiMe_3), -0.06 (27H, s, $\text{Si}(\text{CH}_3)_3$), 1.81 (18H, s, $\text{C}(\text{CH}_3)_3$), 5.05 (2H, s, OCH_2), 7.50 (2H, s, imidazole backbone CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, d_8 -THF) δ (ppm) 1.3 (CH_2SiMe_3), 3.5 ($\text{Si}(\text{CH}_3)_3$), 31.0 ($\text{C}(\text{CH}_3)_3$), 58.6 (CH_2O), 63.1 ($\text{C}(\text{CH}_3)_3$), 118.6 (imidazole backbone CH), 153.2 ($\text{C}_{\text{imidazole-CH}_2\text{O}}$).

Synthesis of $[\text{tBuCH}(p\text{-Br-C}_6\text{H}_4)\text{OGaR}_3]$ (2**)** To a cooled solution of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) 4-bromobenzaldehyde (92 mg, 0.5 mmol) was added forming a bright yellow solution. Bis(*tert*-butyl)imidazol-2-ylidene (tBu) (0.09 g, 0.5 mmol) was then added and the obtained white suspension was stirred for **15 min at 0 $^\circ\text{C}$** . The solvent was exchanged *in vacuo* for 5 mL of hexane and 5 mL of toluene and the resulting solution was placed at -33 $^\circ\text{C}$ yielding a crop of colourless crystals (0.145 g, 42%). Anal. Calcd for $\text{C}_{30}\text{H}_{58}\text{N}_2\text{OSi}_3\text{GaBr}$:

C, 51.72; H, 8.39; N, 4.02. Found: C, 52.33; H, 8.84; N, 4.01. **¹H NMR (298 K, d₈-THF)** δ(ppm) -0.81 (6H, mult, CH₂SiMe₃), -0.06 (27H, s, Si(CH₃)₃), 1.62 (9H, s, C(CH₃)₃), 1.74 (9H, s, C(CH₃)₃), 6.79 (1H, s, CHO), 7.29 (4H, mult, Ar-CH), 7.76 (2H, s, imidazole backbone CH), **¹³C{¹H} NMR (298 K, d₈-THF)** δ(ppm) 2.9 (CH₂SiMe₃), 3.5 (Si(CH₃)₃), 31.7 (C(CH₃)₃), 31.9 (C(CH₃)₃), 64.1 (C(CH₃)₃), 66.3 (C(CH₃)₃), 72.3 (CHO), 119.0 (imidazole backbone CH), 121.8 (C-Br), 131.7 (Ar-CH), 133.2 (Ar-CH), 148.5 (Ar-C_{ipso}), 154.2 (C_{imidazole}-CHO).

Synthesis of [al¹BuCH(p-Br-C₆H₄)OGaR₃] (3) To a cooled solution of Ga(CH₂SiMe₃)₃ (0.165 g, 0.5 mmol in 10 mL hexane) 4-bromobenzaldehyde (92 mg, 0.5 mmol) was added forming a bright yellow solution. Bis(*tert*-butyl)imidazol-2-ylidene (I¹Bu) (0.09 g, 0.5 mmol) was then added and the obtained white suspension was stirred for **2 h at 0 °C** and concentrated in *vacuo* to approximately 5 mL hexane. Toluene was added (3 mL) and the mixture was gently heated until all of the visible solid had dissolved. Slow cooling of the resulting solution afforded a crop of colourless crystals (0.20 g, 57%). Anal. Calcd for C₃₀H₅₈N₂O_{Si}₃GaBr: C, 51.72; H, 8.39; N, 4.02. Found: C, 51.20; H, 8.41; N, 4.23. **¹H NMR (298 K, d₈-THF)** δ(ppm) -0.92 (6H, mult, CH₂SiMe₃), -0.10 (27H, s, Si(CH₃)₃), 1.59 (9H, s, C(CH₃)₃), 1.69 (9H, s, C(CH₃)₃), 6.14 (1H, s, CHO), 7.32 (4H, mult, Ar-CH), 7.84 (1H, s, imidazole backbone, CH), 8.45 (1H, s, C₂-H). **¹³C{¹H} NMR (298 K, d₈-THF)** δ(ppm) 1.9 (CH₂SiMe₃), 3.5 (Si(CH₃)₃), 29.7 (C(CH₃)₃), 30.9 (C(CH₃)₃), 60.2 (C(CH₃)₃), 63.3 (C(CH₃)₃), 72.7 (CHO), 120.2 (C-Br), 121.8 (imidazole backbone CH), 129.9 (Ar-CH), 131.2 (Ar-CH), 131.8 (NCHN), 146.3 (Ar-C_{ipso}) 149.0 (C_{imidazole}-CHO).

Synthesis of [al¹BuC(Ph)(CF₃)OGaR₃] (7) A solution of Ga(CH₂SiMe₃)₃ (0.165 g, 0.5 mmol in 10 mL hexane) was cooled on an ice bath. α,α,α-trifluoroacetophenone (70 μL, 0.5 mmol) was then added, followed by the addition of bis(*tert*-butyl)imidazol-2-ylidene (I¹Bu) (0.09 g, 0.5 mmol). Obtained white suspension was stirred for 2 h at 0 °C. Toluene was added (2 mL) and the mixture was gently heated until all of the visible solid had dissolved. Slow cooling of the resulting solution afforded oil which upon cooling at -33 °C afforded a crop of colourless crystals (0.215 g, 63%). Anal. Calcd for C₃₁H₅₈F₃N₂O_{Si}₃Ga: C, 54.29; H, 8.52; N, 4.08. Found: C, 54.11; H, 7.97; N, 4.56. **¹H NMR (298 K, d₈-THF)** δ(ppm) -0.83 (6H, s, CH₂SiMe₃), -0.05 (27H, s, Si(CH₃)₃), 1.51 (9H, s, C(CH₃)₃), 1.72 (9H, s, C(CH₃)₃), 7.21 (3H, mult, imidazole backbone CH + o-CH), 7.53 (3H, mult, m-CH + p-CH), 8.67 (1H, s, C₂-H). **¹³C{¹H} NMR (298 K, d₈-THF)** δ(ppm) 3.2 (CH₂SiMe₃), 3.5 (Si(CH₃)₃), 29.4 (C(CH₃)₃), 32.1 (C(CH₃)₃), 60.6 (C(CH₃)₃), 66.6 (C(CH₃)₃), 81.7 (q, OC(Ph)CF₃), 119.1 (imidazole backbone CH), 127.6 (Ar-CH), 128.1 (Ar-CH), 129.4 (Ar-CH), 134.1 (NCHN), 141.5 (Ar-C_{ipso}), 145.8 (C_{imidazole}-OC(Ph)CF₃). CF₃ could not be confidentially assigned due to the low intensity of its resonances and noise in the baseline. **¹⁹F NMR (298 K, d₈-THF)** δ(ppm) -69.92 br s (additional resonances arising from the decomposition of this sensitive substrate are observed in the ¹⁹F NMR spectrum of both product and starting material).

Synthesis of [(I¹BuH)⁺{Ph₂C=C=NGaR₃}⁻] (12) To a cooled solution of Ga(CH₂SiMe₃)₃ (0.165 g, 0.5 mmol in 10 mL hexane) diphenylacetonitrile (97 mg, 0.5 mmol) was added followed by bis(*tert*-butyl)imidazol-2-ylidene (I¹Bu) (0.09 g, 0.5 mmol) and the obtained yellow suspension was stirred for 2 h at 0 °C. Toluene was added (3 mL) and the mixture was gently heated until all of the visible solid had dissolved. Slow cooling of the resulting solution afforded yellow oil which upon standing provided X-ray quality crystals (0.225 g, 64%). Anal. Calcd for C₃₇H₆₄GaN₃Si₃: C, 63.04; H, 9.15; N, 5.96. Found: C, 61.12; H, 8.51; N, 6.04. The sample consistently shows low values for carbon content. Small amounts of unreacted diphenylacetonitrile are observed in NMR spectra. **¹H NMR (298 K, d₈-THF)** δ(ppm) -0.69 (6H, s, CH₂SiMe₃), -0.02 (27H, s, Si(CH₃)₃), 1.56 (18H, s, C(CH₃)₃), 6.46 (2H, mult, p-CH), 6.92 (4H, t, m-CH), 7.28 (4H, t, o-CH), 7.59 (2H, s, imidazole backbone CH), 8.68 (1H, s, C₂-H). **¹³C{¹H} NMR (298 K, d₈-THF)** δ(ppm) 2.7 (CH₂SiMe₃), 3.1 (Si(CH₃)₃), 29.7

(C(CH₃)₃), 55.7 (Ph₂C=C=N), 61.1 (C(CH₃)₃), 117.9 (Ar-CH), 121.4 (imidazole backbone CH), 123.1 (Ar-CH), 128.4 (Ar-CH), 131.9 (NCHN), 143.4 (Ph₂C=C=N), 144.2 (Ar-C_{ipso}).

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Keywords: cooperative chemistry • FLP • small molecule activation • gallium • carbene ligands

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By pairing a Ga tris(alkyl) complex with N-heterocyclic carbene $t^i\text{Bu}$, three different types of FLP activation processes for carbonyl compounds have been uncovered, namely (i) reduction of C=O (via nucleophilic addition of the NHC using either its C2 or C4 position) and (ii) C-H activation.

M. Uzelac, D. R. Armstrong, A. R. Kennedy and E. Hevia*

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Understanding the Subtleties of Frustrated Lewis Pair Activation of Carbonyl Compounds by N-Heterocyclic Carbene/Alkyl Gallium Pairings

Marina Uzelac, David R. Armstrong, Alan R. Kennedy, and Eva Hevia^{*[a]}

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Experimental details

General

All reactions were carried out using standard Schlenk and glove box 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 ¹H, and 100.62 MHz for ¹³C{¹H}. Elemental analyses were obtained using a Perkin Elmer 2400 elemental analyser. Infrared spectra were obtained as Nujol mulls on NaCl plates and recorded on a Nicolet 360 FTIR spectrometer spanning range 4000 - 400 cm⁻¹. Benzaldehyde, 4-bromobenzaldehyde, paraformaldehyde, ferrocenecarboxaldehyde, p-anisaldehyde, trifluoroacetophenone, 4'-iodoacetophenone, 2',4',6'-trimethylacetophenone, benzophenone, benzonitrile, diphenylacetonitrile were purchased from Sigma Aldrich Chemicals and Alfa Aesar and used as received. All liquid reagents were dried and stored over 4 Å molecular sieves prior to use. [Ga(CH₂SiMe₃)₃],¹ I^tBu² and SI^tBu³ were prepared according to literature methods.

X-Ray Crystallography

Crystallographic data were measured at 123(2) K for compounds **2**, **3**, **7**, and **12** and at 150(2) K for compound **1** with Oxford Diffraction Gemini S or Xcalibur E instruments and with graphite-monochromated Mo (λ=0.71073 Å) or Cu (λ=1.54180 Å) radiation. All structures were refined to convergence on *F*² using all unique reflections and programs from the

¹ L. M. Dennis, W. Patnode, *J. Am. Chem. Soc.* **1932**, 54, 182.

² E. C. Hurst, K. Wilson, I. J. Fairlamb, V. Chechik, *New J. Chem.* **2009**, 33, 1837.

³ (a) K. Arentsen, S. Caddick, F. G. Cloke, *Tetrahedron*, 2005, **61**, 9710; (b) M. K. Denk, A. Thadani, K. Hatano, A. J. Lough *Angew. Chem. Int. Ed.* 1997, **36**, 2607.

SHELX family.⁴ The final model for structure **12** included constraints and restraints on bond lengths and displacement parameters that were required to model disorder for one *tert*-butyl group. For **3**, the Flack parameter refined to -0.002(18). Selected crystallographic data are presented in Table S1 and S2 and full details in cif format can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1: Selected crystallographic and refinement parameters for compounds **1-3**.

compound	1	2	3
Empirical formula	C ₂₄ H ₅₅ GaN ₂ OSi ₃	C ₃₀ H ₅₈ BrGaN ₂ OSi ₃	C ₃₀ H ₅₈ BrGaN ₂ OSi ₃
Formula weight	541.69	696.68	696.68
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P -1	P 2 ₁ /c	P 1
χ (Å)	0.71073	0.71073	1.5418
<i>a</i> (Å)	10.9666(6)	9.7662(4)	10.2429(6)
<i>b</i> (Å)	12.2423(7)	20.9419(9)	10.3065(6)
<i>c</i> (Å)	13.4006(9)	18.5239(8)	10.3660(6)
α (°)	99.013(5)	90	109.759(5)
β (°)	101.912(5)	100.234(5)	110.805(6)
γ (°)	105.054(5)	90	97.572(5)
<i>V</i> (Å ³)	1657.33(18)	3728.3(3)	922.44(10)
<i>Z</i>	2	4	1
μ (mm ⁻¹)	0.955	1.929	3.392
2 θ max (°)	59.98	55.00	138.43
Measured reflections	25467	33294	11818
Unique reflections	8904	8504	6187
Observed reflections	6483	6527	5348
<i>R</i> _{int}	0.0400	0.0449	0.0468
<i>R</i> [on <i>F</i> , obs refln only]	0.0485	0.0378	0.0454
w <i>R</i> [on <i>F</i> ² , all data]	0.1205	0.0822	0.1086
GoF	1.035	1.036	1.038
Largest diff peak/hole (e Å ⁻³)	1.665/-0.714	0.731/-0.380	0.610/-0.402

Table S2: Selected crystallographic and refinement parameters for compounds **7** and **12**.

compound	7	12
Empirical formula	C ₃₁ H ₅₈ F ₃ GaN ₂ OSi ₃	C ₃₇ H ₆₄ GaN ₃ Si ₃
Formula weight	685.78	704.90
Crystal system	Monoclinic	Monoclinic
Space group	P 2 ₁ /n	P 2 ₁ /c
χ (Å)	0.71073	0.71073
<i>a</i> (Å)	9.7056(4)	14.1628(6)
<i>b</i> (Å)	16.5713(7)	18.0691(8)
<i>c</i> (Å)	23.9252(10)	16.5681(8)
α (°)	90	90
β (°)	96.071(4)	99.490(4)
γ (°)	90	90

⁴ G. M. Sheldrick, Acta Crystallogr., **2008**, A64, 112.

$V (\text{\AA}^3)$	3826.4(3)	4181.9(3)
Z	4	4
$\mu (\text{mm}^{-1})$	0.852	0.770
$2\theta_{\text{max}} (^{\circ})$	59.99	59.99
Measured reflections	113826	20370
Unique reflections	10865	10853
Observed reflections	7577	7212
R_{int}	0.0925	0.0453
$R [\text{on } F, \text{ obs refln only}]$	0.0438	0.0526
$wR [\text{on } F^2, \text{ all data}]$	0.0990	0.1021
GoF	1.021	0.993
Largest diff peak/hole ($\text{e } \text{\AA}^{-3}$)	0.587/-0.379	0.617/-0.544

Synthesis of products

1. Synthesis of $[\text{I}^t\text{BuCH}_2\text{OGaR}_3]$ (**1**)

A solution of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) was cooled on an ice bath. Paraformaldehyde (0.015 g, 0.5 mmol) was then added, followed by the addition of bis(*tert*-butyl)imidazol-2-ylidene (I^tBu) (0.09 g, 0.5 mmol). Obtained white suspension was stirred for 2 h at 0 °C. Toluene was added (1 mL) and the mixture was gently heated until all of the visible solid had dissolved. Slow cooling of the resulting solution afforded a crop of colourless crystals (0.18 g, 66%). Anal. Calcd for $\text{C}_{24}\text{H}_{55}\text{N}_2\text{OSi}_3\text{Ga}$: C, 53.21; H, 10.23; N, 5.17. Found: C, 53.11; H, 10.31; N, 5.39.

^1H NMR (298 K, d_8 -THF) δ (ppm) -0.82 (6H, s, CH_2SiMe_3), -0.06 (27H, s, $\text{Si}(\text{CH}_3)_3$), 1.81 (18H, s, $\text{C}(\text{CH}_3)_3$), 5.05 (2H, s, OCH_2), 7.50 (2H, s, imidazole backbone CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, d_8 -THF) δ (ppm) 1.3 (CH_2SiMe_3), 3.5 ($\text{Si}(\text{CH}_3)_3$), 31.0 ($\text{C}(\text{CH}_3)_3$), 58.6 (CH_2O), 63.1($\text{C}(\text{CH}_3)_3$), 118.6 (imidazole backbone CH), 153.2 ($\text{C}_{\text{imidazole}}\text{-CH}_2\text{O}$).

2. Synthesis of $[\text{I}^t\text{BuCH}(p\text{-Br-C}_6\text{H}_4)\text{OGaR}_3]$ (**2**)

To a cooled solution of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) 4-bromobenzaldehyde (92 mg, 0.5 mmol) was added forming a bright yellow solution. Bis(*tert*-butyl)imidazol-2-ylidene (I^tBu) (0.09 g, 0.5 mmol) was then added and the obtained white suspension was stirred for **15 min at 0 °C**. The solvent was exchanged *in vacuo* for 5 mL of hexane and 5 mL of toluene and the resulting solution was placed at -33 °C yielding a crop of colourless crystals (0.145 g, 42%). Anal. Calcd for $\text{C}_{30}\text{H}_{58}\text{N}_2\text{OSi}_3\text{GaBr}$: C, 51.72; H, 8.39; N, 4.02. Found: C, 52.33; H, 8.84; N, 4.01.

¹H NMR (298 K, d₈-THF) δ(ppm) -0.81 (6H, mult, CH₂SiMe₃), -0.06 (27H, s, Si(CH₃)₃), 1.62 (9H, s, C(CH₃)₃), 1.74 (9H, s, C(CH₃)₃), 6.79 (1H, s, CHO), 7.29 (4H, mult, Ar-CH), 7.76 (2H, s, imidazole backbone CH). **¹³C{¹H} NMR (298 K, d₈-THF)** δ(ppm) 2.9 (CH₂SiMe₃), 3.5 (Si(CH₃)₃), 31.7 (C(CH₃)₃), 31.9 (C(CH₃)₃), 64.1 (C(CH₃)₃), 66.3 (C(CH₃)₃), 72.3 (CHO), 119.0 (imidazole backbone CH), 121.8 (C-Br), 131.7 (Ar-CH), 133.2 (Ar-CH), 148.5 (Ar-C_{ipso}), 154.2 (C_{imidazole}-CHO).

3. Synthesis of [a^tBuCH(*p*-Br-C₆H₄)OGaR₃] (**3**)

To a cooled solution of Ga(CH₂SiMe₃)₃ (0.165 g, 0.5 mmol in 10 mL hexane) 4-bromobenzaldehyde (92 mg, 0.5 mmol) was added forming a bright yellow solution. Bis(*tert*-butyl)imidazol-2-ylidene (I^tBu) (0.09 g, 0.5 mmol) was then added and the obtained white suspension was stirred for **2 h at 0 °C** and concentrated in *vacuo* to approximately 5 mL hexane. Toluene was added (3 mL) and the mixture was gently heated until all of the visible solid had dissolved. Slow cooling of the resulting solution afforded a crop of colourless crystals (0.20 g, 57%). Anal. Calcd for C₃₀H₅₈N₂OSi₃GaBr: C, 51.72; H, 8.39; N, 4.02. Found: C, 51.20; H, 8.41; N, 4.23.

¹H NMR (298 K, d₈-THF) δ(ppm) -0.92 (6H, mult, CH₂SiMe₃), -0.10 (27H, s, Si(CH₃)₃), 1.59 (9H, s, C(CH₃)₃), 1.69 (9H, s, C(CH₃)₃), 6.14 (1H, s, CHO), 7.32 (4H, mult, Ar-CH), 7.84 (1H, s, imidazole backbone, CH), 8.45 (1H, s, C2-H). **¹³C{¹H} NMR (298 K, d₈-THF)** δ(ppm) 1.9 (CH₂SiMe₃), 3.5 (Si(CH₃)₃), 29.7 (C(CH₃)₃), 30.9 (C(CH₃)₃), 60.2 (C(CH₃)₃), 63.3 (C(CH₃)₃), 72.7 (CHO), 120.2 (C-Br), 121.8 (imidazole backbone CH), 129.9 (Ar-CH), 131.2 (Ar-CH), 131.8 (NCHN), 146.3 (Ar-C_{ipso}) 149.0 (C_{imidazole}-CHO).

4. Synthesis of [a^tBuCH(C₆H₅)OGaR₃] (**4**)

A solution of Ga(CH₂SiMe₃)₃ (0.165 g, 0.5 mmol in 10 mL hexane) was cooled on an ice bath. Benzaldehyde (51 μL, 0.5 mmol) was then added, followed by the addition of bis(*tert*-butyl)imidazol-2-ylidene (I^tBu) (0.09 g, 0.5 mmol). Obtained light yellow suspension was stirred for 2 h at 0 °C. Toluene was added (2 mL) and the mixture was gently heated until all of the visible solid had dissolved. Cooling of the resulting solution at -33 °C afforded a colourless microcrystalline solid (0.19 g, 62 %). Anal. Calcd for: C₃₀H₅₉N₂GaOSi₃: C, 58.32; H, 9.63; N, 4.53. Found: C, 57.89; H, 9.39; N, 4.24.

¹H NMR (298 K, C₆D₆) δ(ppm) -0.32 (6H, mult, CH₂SiMe₃), 0.46 (27H, s, Si(CH₃)₃), 0.78 (9H, s, C(CH₃)₃), 1.06 (9H, s, C(CH₃)₃), 6.38 (2H, s, CHO), 6.93 (1H, s, imidazole backbone CH), 7.09 (1H, t, *p*-CH), 7.28 (2H, t, *m*-CH), 7.39 (1H, s, C2-*H*), 7.55 (2H, d, *o*-CH).

¹H NMR (298 K, *d*₈-THF) δ(ppm) -0.92 (6H, mult, CH₂SiMe₃), -0.09 (27H, s, Si(CH₃)₃), 1.56 (9H, s, C(CH₃)₃), 1.69 (9H, s, C(CH₃)₃), 6.17 (1H, s, OCH), 7.07 (1H, t, *p*-CH), 7.16 (2H, t, *m*-CH), 7.34 (2H, d, *o*-CH), 7.85 (1H, s, imidazole backbone CH), 8.43 (1H, s, C2-*H*).

¹³C{¹H} NMR (298 K, *d*₈-THF) δ(ppm) 1.9 (CH₂SiMe₃), 3.5 (Si(CH₃)₃), 29.7 (C(CH₃)₃), 30.8 (C(CH₃)₃), 60.1 (C(CH₃)₃), 63.1 (C(CH₃)₃), 73.3 (OCH), 121.8 (imidazole backbone CH), 126.5 (Ar-CH), 128.0 (Ar-CH), 128.1 (Ar-CH), 131.4 (NCHN), 147.2 (Ar-*C*_{ipso}) 149.3 (C_{imidazole}-OCH).

5. Synthesis of [*a*I^{*t*}BuCH(*p*-OMe-C₆H₄)OGaR₃] (5)

To a cooled solution of Ga(CH₂SiMe₃)₃ (0.165 g, 0.5 mmol in 10 mL hexane) *p*-anisaldehyde (61 μL, 0.5 mmol) was added followed by bis(*tert*-butyl)imidazol-2-ylidene (I^{*t*}Bu) (0.09 g, 0.5 mmol) and the obtained white suspension was stirred for 2 h at 0 °C. Toluene was added (3 mL) and the mixture was gently heated until all of the visible solid had dissolved. Slow cooling of the resulting solution afforded colourless microcrystalline solid (0.183g, 56%). Anal. Calcd for C₃₁H₆₁GaN₂O₂Si₃: C, 57.48; H, 9.49; N, 4.32. Found: C, 57.65; H, 8.69; N, 4.39.

¹H NMR (298 K, *d*₈-THF) δ(ppm) -0.93 (6H, mult, CH₂SiMe₃), -0.10 (27H, s, Si(CH₃)₃), 1.68 (9H, s, C(CH₃)₃), 1.69 (9H, s, C(CH₃)₃), 3.70 (1H, s, OCH₃), 6.12 (1H, s, CHO), 6.72 (2H, d, Ar-CH), 7.22 (2H, d, Ar-CH), 7.83 (1H, s, imidazole backbone CH), 8.41 (1H, s, C2-*H*), **¹³C{¹H} NMR (298 K, *d*₈-THF)** δ(ppm) 1.9 (CH₂SiMe₃), 3.6 (Si(CH₃)₃), 29.7 (C(CH₃)₃), 30.8 (C(CH₃)₃), 55.2 (OCH₃), 60.0 (C(CH₃)₃), 63.0 (C(CH₃)₃), 72.9 (OCH), 113.6 (Ar-CH), 121.7 (imidazole backbone CH), 129.0 (Ar-CH), 131.3 (NCHN), 141.3 (Ar-*C*_{ipso}) 147.7(C_{imidazole}-OCH), 159.1 (C-OMe).

6. Synthesis of [*a*I^{*t*}BuCH(FeCp₂)OGaR₃] (6)

To a cooled solution of Ga(CH₂SiMe₃)₃ (0.165 g, 0.5 mmol in 10 mL hexane) ferrocenecarboxaldehyde (0.107 g, 0.5 mmol) was added forming a bright red solution. Bis(*tert*-butyl)imidazol-2-ylidene (I^{*t*}Bu) (0.09 g, 0.5 mmol) was then added and the obtained orange suspension was stirred for 2 h at 0 °C. Toluene was added (3 mL) and the mixture was gently heated until all of the visible solid had dissolved. Slow cooling of the resulting

solution afforded a crop of orange crystals (0.173g, 48%). Anal. Calcd for $C_{34}H_{63}FeGaN_2O_2Si_3$: C, 56.27; H, 8.75; N, 3.86. Found: C, 53.75; H, 8.42; N, 3.99. Sample consistently shows low value of the carbon content.

1H NMR (298 K, d_8 -THF) δ (ppm) -0.86 (6H, mult, CH_2SiMe_3), -0.03 (27H, s, $Si(CH_3)_3$), 1.65 (9H, s, $C(CH_3)_3$), 1.69 (9H, s, $C(CH_3)_3$), 3.75 (1H, s, $FeCp_2$), 3.89 (1H, s, $FeCp_2$), 3.94 (1H, s, $FeCp_2$), 4.14 (5H, s, $FeCp_2$), 4.42 (1H, s, $FeCp_2$), 6.24 (1H, s, OCH), 7.67 (1H, s, imidazole backbone CH), 8.36 (1H, s, $C2-H$). **$^{13}C\{^1H\}$ NMR (298 K, d_8 -THF)** δ (ppm) 2.0 (CH_2SiMe_3), 3.6 ($Si(CH_3)_3$), 29.7 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$), 60.0 ($C(CH_3)_3$), 63.4 ($C(CH_3)_3$), 66.7 ($FeCp_2-C$), 67.4 ($FeCp_2-C$), 67.5 ($FeCp_2-C$), 69.4 ($FeCp_2-C$), 69.5 ($FeCp_2-C$), 70.3 ($FeCp_2-C$), 100.7 (CHO), 120.2 (imidazole backbone CH), 130.6 (NCHN) 148.0 ($C_{imidazole-CHO}$).

7. Synthesis of [$aI^tBuC(Ph)(CF_3)OGaR_3$] (**7**)

A solution of $Ga(CH_2SiMe_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) was cooled on an ice bath. α,α,α -trifluoroacetophenone (70 μ L, 0.5 mmol) was then added, followed by the addition of bis(*tert*-butyl)imidazol-2-ylidene (I^tBu) (0.09 g, 0.5 mmol). Obtained white suspension was stirred for 2 h at 0 °C. Toluene was added (2 mL) and the mixture was gently heated until all of the visible solid had dissolved. Slow cooling of the resulting solution afforded oil which upon cooling at -33 °C afforded a crop of colourless crystals (0.215 g, 63%). Anal. Calcd for $C_{31}H_{58}F_3N_2OSi_3Ga$: C, 54.29; H, 8.52; N, 4.08. Found: C, 54.11; H, 7.97; N, 4.56.

1H NMR (298 K, d_8 -THF) δ (ppm) -0.83 (6H, s, CH_2SiMe_3), -0.05 (27H, s, $Si(CH_3)_3$), 1.51 (9H, s, $C(CH_3)_3$), 1.72 (9H, s, $C(CH_3)_3$), 7.21 (3H, mult, imidazole backbone CH + *o*- CH), 7.53 (3H, mult, *m*- CH + *p*- CH), 8.67 (1H, s, $C2-H$). **$^{13}C\{^1H\}$ NMR (298 K, d_8 -THF)** δ (ppm) 3.2 (CH_2SiMe_3), 3.5 ($Si(CH_3)_3$), 29.4 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 60.6 ($C(CH_3)_3$), 66.6 ($C(CH_3)_3$), 81.7 (q, $OC(Ph)CF_3$), 119.1 (imidazole backbone CH), 127.6 (Ar- CH), 128.1 (Ar- CH), 129.4 (Ar- CH), 134.1 (NCHN), 141.5 (Ar- C_{ipso}), 145.8 ($C_{imidazole-OC(Ph)CF_3}$). CF_3 could not be confidentially assigned due to the low intensity of its resonances and noise in the baseline. **^{19}F NMR (298 K, d_8 -THF)** δ (ppm) -69.92 br s (additional resonances arising from the decomposition of this sensitive substrate are observed in the ^{19}F NMR spectrum of both product and starting material).

8. Synthesis of [$\{I^tBuH\}^+\{(p-I-C_6H_4)C(CH_2)OGaR_3\}^-$] (**8**)

To a cooled solution of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) 4'-iodoacetophenone (0.123 g, 0.5 mmol) was added followed by bis(*tert*-butyl)imidazol-2-ylidene (I^tBu) (0.09 g, 0.5 mmol) and the obtained yellow suspension was stirred for 2 h at 0 °C and protected from light. Straw solid (282 mg, 74%) was isolated by filtration. Anal. Calcd for $\text{C}_{31}\text{H}_{60}\text{GaIN}_2\text{OSi}_3$: C, 49.14; H, 7.98; N, 3.70. Found: C, 49.07; H, 7.81; N, 3.40.

^1H NMR (298 K, d_8 -THF) δ (ppm) -0.74 (6H, s, CH_2SiMe_3), -0.06 (27H, s, $\text{Si}(\text{CH}_3)_3$), 1.62 (18H, s, $\text{C}(\text{CH}_3)_3$), 3.86 (s, 1H, CH_2), 4.12 (s, 1H, CH_2), 7.41 (2H, d, Ar-CH), 7.55 (2H, d, Ar-CH), 7.78 (2H, s, imidazole backbone CH), 8.72 (1H, s, C2-H). **$^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, d_8 -THF)** δ (ppm) 2.3 (CH_2SiMe_3), 3.5 ($\text{Si}(\text{CH}_3)_3$), 29.7 ($\text{C}(\text{CH}_3)_3$), 61.2 ($\text{C}(\text{CH}_3)_3$), 79.9 ($\text{CH}_2=\text{C}$), 90.8 (C-I), 121.5 (imidazole backbone CH), 129.2 (Ar-CH), 131.9 (NCHN), 136.3 (Ar-CH), 145.8 (Ar- C_{ipso}), 163.3 (C-O).

9. Synthesis of [$\{\text{I}^t\text{BuH}\}^+\{(\text{Me}_3\text{C}_6\text{H}_2)\text{C}(\text{CH}_2)\text{OGaR}_3\}^-$] (**9**)

To a cooled solution of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) 2',4',6'-trimethylacetophenone (0.081 g, 0.5 mmol) was added followed by bis(*tert*-butyl)imidazol-2-ylidene (I^tBu) (0.09 g, 0.5 mmol) and the obtained yellow suspension was stirred for 2 h at 0 °C. The off-white solid (203 mg, 60%) was isolated by filtration. Anal. Calcd for $\text{C}_{34}\text{H}_{67}\text{N}_2\text{OSi}_3\text{Ga}$: C, 60.60; H, 10.02; N, 4.16. Found: C, 58.15; H, 9.62 N, 3.88. The sample shows consistently low value for carbon content. Small amounts of unreacted ketone are observed in NMR spectra.

^1H NMR (298 K, d_8 -THF) δ (ppm) -0.72 (6H, s, CH_2SiMe_3), -0.08 (27H, s, $\text{Si}(\text{CH}_3)_3$), 1.63 (18H, s, $\text{C}(\text{CH}_3)_3$), 2.13 (3H, s, CH_3), 2.33 (6H, s, CH_3), 3.13 (s, 1H, CH_2), 3.85 (s, 1H, CH_2), 6.57 (2H, s, Ar-CH), 7.81 (2H, s, imidazole backbone CH), 8.75 (1H, s, C2-H). **$^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, d_8 -THF)** δ (ppm) 2.3 (CH_2SiMe_3), 3.5 ($\text{Si}(\text{CH}_3)_3$), 21.00 (Ar- CH_3), 21.3 (Ar- CH_3), 29.7 ($\text{C}(\text{CH}_3)_3$), 61.2 ($\text{C}(\text{CH}_3)_3$), 81.4 ($\text{CH}_2=\text{C}$), 121.6 (imidazole backbone CH), 127.6 (Ar-CH), 132.0 (NCHN), 133.3 (Ar-C), 135.8 (Ar-C), 145.1 (Ar- C_{ipso}), 165.7 (C-O).

10. Synthesis of [$\{\text{SI}^t\text{BuH}\}^+\{(\text{p-I-C}_6\text{H}_4)\text{C}(\text{CH}_2)\text{OGaR}_3\}^-$] (**10**)

To a cooled solution of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) 4'-iodoacetophenone (0.123 g, 0.5 mmol) was added followed by bis(*tert*-butyl)imidazolin-2-ylidene (SI^tBu) (0.09 g, 0.5 mmol) and the obtained of-white suspension was stirred for 2 h at 0 °C and protected from light. The peach-coloured solid (211 mg, 62%) was isolated by

filtration. Anal. Calcd for $C_{31}H_{62}N_2IOSi_3Ga$: C, 49.01; H, 8.23; N, 3.69. Found: C, 48.26; H, 7.69; N, 3.41.

1H NMR (298 K, d_8 -THF) δ (ppm) -0.74 (6H, s, CH_2SiMe_3), -0.05 (27H, s, $Si(CH_3)_3$), 1.37 (18H, s, $C(CH_3)_3$), 3.85 (s, 1H, CH_2), 3.92 (s, 4H, CH_2 backbone), 4.13 (s, 1H, CH_2), 7.43 (2H, d, Ar-CH), 7.56 (2H, d, Ar-CH), 7.88 (1H, s, C2-H). **$^{13}C\{^1H\}$ NMR (298 K, d_8 -THF)** δ (ppm) 2.3 (CH_2SiMe_3), 3.5 ($Si(CH_3)_3$), 27.9 ($C(CH_3)_3$), 46.2 (NCH_2CH_2N), 57.5 ($C(CH_3)_3$), 79.8 ($CH_2=C$), 90.9 (C-I), 129.1 (Ar-CH), 136.4 (Ar-CH), 145.8 (Ar- C_{ipso}), 152.9 (NCHN), 163.2 (C-O).

11. Synthesis of [$\{Si^tBuH\}^+\{(Me_3C_6H_2)C(CH_2)OGaR_3\}^-$] (11)

To a cooled solution of $Ga(CH_2SiMe_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) 2',4',6'-trimethylacetophenone (0.081 g, 0.5 mmol) was added followed by bis(tert-butyl)imidazolin-2-ylidene (Si^tBu) (0.09 g, 0.5 mmol) and the obtained white suspension was stirred for 2 h at 0 °C after which a white solid was isolated by filtration (272 mg, 80%). Anal. Calcd for $C_{34}H_{67}N_2OSi_3Ga$: C, 60.42; H, 10.29; N, 4.14. Found: C, 60.66; H, 10.16; N, 4.65.

1H NMR (298 K, d_8 -THF) δ (ppm) -0.72 (6H, s, CH_2SiMe_3), -0.06 (27H, s, $Si(CH_3)_3$), 1.37 (18H, s, $C(CH_3)_3$), 2.15 (3H, s, CH_3), 2.34 (6H, s, CH_3), 3.16 (s, 1H, CH_2), 3.85 (s, 4H, CH_2 backbone), 3.86 (s, 1H, CH_2), 6.60 (2H, s, Ar-CH), 7.87 (1H, s, C2-H). **$^{13}C\{^1H\}$ NMR (298 K, d_8 -THF)** δ (ppm) 2.3 (CH_2SiMe_3), 3.6 ($Si(CH_3)_3$), 21.0 (Ar- CH_3), 21.3 (Ar- CH_3), 28.0 ($C(CH_3)_3$), 46.2 (NCH_2CH_2N), 57.5 ($C(CH_3)_3$), 81.7 ($CH_2=C$), 127.16 (Ar-CH), 133.6 (Ar-C), 135.9 (Ar-C), 145.1 (Ar- C_{ipso}), 152.8 (NCHN), 165.6 (C-O).

12. Synthesis of [$\{I^tBuH\}^+\{Ph_2C=C=NGaR_3\}^-$] (12)

To a cooled solution of $Ga(CH_2SiMe_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) diphenylacetonitrile (97 mg, 0.5 mmol) was added followed by bis(tert-butyl)imidazol-2-ylidene (I^tBu) (0.09 g, 0.5 mmol) and the obtained yellow suspension was stirred for 2 h at 0 °C. Toluene was added (3 mL) and the mixture was gently heated until all of the visible solid had dissolved. Slow cooling of the resulting solution afforded yellow oil which upon standing provided X-ray quality crystals (0.225 g, 64%). Anal. Calcd for $C_{37}H_{64}GaN_3Si_3$: C, 63.04; H, 9.15; N, 5.96. Found: C, 61.12; H, 8.51; N, 6.04. The sample consistently shows low values for carbon content. Small amounts of unreacted diphenylacetonitrile are observed in NMR spectra.

^1H NMR (298 K, d_8 -THF) $\delta(\text{ppm})$ -0.69 (6H, s, CH_2SiMe_3), -0.02 (27H, s, $\text{Si}(\text{CH}_3)_3$), 1.56 (18H, s, $\text{C}(\text{CH}_3)_3$), 6.46 (2H, mult, p -CH), 6.92 (4H, t, m -CH), 7.28 (4H, t, o -CH), 7.59 (2H, s, imidazole backbone CH), 8.68 (1H, s, C2-H). **$^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, d_8 -THF)** $\delta(\text{ppm})$ 2.7 (CH_2SiMe_3), 3.1 ($\text{Si}(\text{CH}_3)_3$), 29.7 ($\text{C}(\text{CH}_3)_3$), 55.7 ($\text{Ph}_2\text{C}=\text{C}=\text{N}$), 61.1 ($\text{C}(\text{CH}_3)_3$), 117.9 (Ar-CH), 121.4 (imidazole backbone CH), 123.1 (Ar-CH), 128.4 (Ar-CH), 131.9 (NCHN), 143.4 ($\text{Ph}_2\text{C}=\text{C}=\text{N}$), 144.2 (Ar- C_{ipso}).

13. Synthesis of $[\{\text{SI}^t\text{BuH}\}^+\{\text{Ph}_2\text{C}=\text{C}=\text{NGaR}_3\}^-]$ (**13**)

To a cooled solution of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ (0.165 g, 0.5 mmol in 10 mL hexane) diphenylacetonitrile (96 mg, 0.5 mmol) was added followed by bis(*tert*-butyl)imidazolin-2-ylidene (SI^tBu) (0.09 g, 0.5 mmol) and the obtained yellow suspension was stirred for 2 h at 0 °C. The yellow solid was isolated by filtration (305 mg, 86%). Anal. Calcd for $\text{C}_{37}\text{H}_{66}\text{N}_3\text{Si}_3\text{Ga}$: C, 62.86; H, 9.41; N, 5.94. Found: C, 62.15; H, 9.06; N, 6.28.

^1H NMR (298 K, d_8 -THF) $\delta(\text{ppm})$ -0.68 (6H, s, CH_2SiMe_3), 0.00 (27H, s, $\text{Si}(\text{CH}_3)_3$), 1.28 (18H, s, $\text{C}(\text{CH}_3)_3$), 3.75 (s, 4H, CH_2), 6.48 (t, 2H, p -CH), 6.95 (t, 4H, m -CH), 7.30 (4H, d, o -CH), 7.78 (1H, s, C2-H). **$^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, d_8 -THF)** $\delta(\text{ppm})$ 2.8 (CH_2SiMe_3), 3.1 ($\text{Si}(\text{CH}_3)_3$), 27.9 ($\text{C}(\text{CH}_3)_3$), 46.0 ($\text{NCH}_2\text{CH}_2\text{N}$), 55.6 ($\text{Ph}_2\text{C}=\text{C}=\text{N}$), 57.5 ($\text{C}(\text{CH}_3)_3$), 118.0 (Ar-CH), 123.0 (Ar-CH), 128.4 (Ar-CH), 143.1 ($\text{Ph}_2\text{C}=\text{C}=\text{N}$), 144.0 (Ar- C_{ipso}), 152.6 (NCHN).

Control reactions

Several control reactions were conducted in sealed Young's tap NMR tubes to demonstrate that GaR_3 interacts, but does not activate aldehydes (**Fig S1**) or ketones (**Fig S2**) and that I^tBu does not interact or activate aldehydes (**Fig S3**) or ketones (**Fig S4**) in any way. Furthermore, isolated crystalline sample of pre-formed $\text{aI}^t\text{Bu}\cdot\text{GaR}_3$ has also been shown not to react with 4-bromobenzaldehyde (**Fig S5**). Also, the mixture of equimolar amounts of GaR_3 and SI^tBu (**Fig S6**) displays no signs of interaction between these two reagents even when heated over prolonged periods of time. Finally, ^1H and ^{13}C NMR spectra (**Fig S7** and **S8**) of the crude reaction mixture of $\text{I}^t\text{Bu}/\text{GaR}_3$ pair with benzophenone reveals the deactivation of the pair and no reaction with this ketone.

Figure S1: Comparison of ^1H NMR spectra in C_6D_6 of pure GaR_3 (bottom), pure 4-bromobenzaldehyde (middle) and a mixture of equimolar amounts of GaR_3 and 4-bromobenzaldehyde (top) revealing interaction between the two, but no reaction [$\text{R} = \text{CH}_2\text{SiMe}_3$].

Figure S2: Comparison of ^1H NMR spectra in C_6D_6 of pure GaR_3 (bottom) and a mixture of equimolar amounts of GaR_3 and 2,4,6-trimethylacetophenone (top) revealing interaction between the two, but no reaction [$\text{R} = \text{CH}_2\text{SiMe}_3$].

Figure S3: Comparison of ^1H NMR spectra in C_6D_6 of pure I'Bu (bottom) and a mixture of equimolar amounts of I'Bu and 4-anisaldehyde (top) revealing no interaction or any reaction between the two.

Figure S4: Comparison of ^1H NMR spectra in C_6D_6 of pure I'Bu (bottom) and a mixture of equimolar amounts of I'Bu and 2,4,6-trimethylacetophenone (top) revealing no interaction or any type of reaction between the two.

Figure S5: ^1H NMR spectrum of the mixture of $a^i\text{Bu-GaR}_3$ and 4-bromobenzaldehyde in $d_8\text{-THF}$ standing for 48 h in a sealed Young's tap NMR tube at room temperature revealing no reaction between the two.

Figure S6: ^1H NMR spectrum of an equimolar mixture of SI^iBu and GaR_3 after 9h heating in C_6D_6 at 90°C revealing no reaction between the two.

Figure S7: ¹H NMR spectrum of reaction mixture (benzophenone + GaR₃ + *i*Bu in hexane at 0 °C for 2 h) in C₆D₆ revealing the deactivation the FLP pair and no reactivity towards benzophenone.

Figure S8: ¹³C NMR spectrum of reaction mixture (benzophenone + GaR₃ + *i*Bu in hexane at 0 °C for 2 h) in C₆D₆ revealing the deactivation the FLP pair and no reactivity towards benzophenone.

Variable Temperature ^1H NMR studies

0.08g (0.25 mmol) of GaR_3 was dissolved in 0.4 mL of d_8 -THF in the glovebox, followed by addition of 40 mg (0.25 mmol) of 4-bromobenzaldehyde. The reaction mixture was kept in a sealed Young's tap NMR tube and ^1H and ^{13}C NMR spectra were recorded at room temperature before the addition of I^tBu (**Fig S9** and **S10**). 45 mg (0.25 mmol) of I^tBu was placed in the tube and as soon as all three components were mixed, the tube was placed into the NMR machine cooled to 230 K. The reaction was regularly monitored by ^1H NMR spectroscopy and the temperature was gradually increased. At 230 K, the presence of free starting materials and compound **2** is evident (**Fig S11** and **S12**), as it is at 303 K (**Fig S13**). At 323 K, species **3** is first observed (in addition to free components and compound **2**) as can be seen in **Fig S14**. After leaving the tube to stand at 323 K for 15 min another ^1H NMR spectrum was recorded which revealed that species **2** ceased to exist and only compound **3** is present together with some starting material (**Fig S15**). This observation was further confirmed by the ^{13}C NMR spectrum (**Fig S16**). The overview of this experiment is shown in **Fig S17**.

Figure S9: ^1H NMR spectrum of GaR_3 and 4-bromobenzaldehyde in d_8 -THF at 298 K.

Figure S10: ¹³C NMR spectrum of GaR₃ and 4-bromobenzaldehyde in d₈-THF at 298K.

Figure S11: ¹H NMR spectrum of the reaction mixture recorded at 230 K as soon as tBu was added.

Figure S12: ¹³C NMR spectrum of the reaction mixture recorded at 230 K as soon as ^tBu was added.

Figure S13: ¹H NMR spectrum of the reaction mixture recorded at 303 K.

Figure S14: ^1H NMR spectrum of the reaction mixture recorded at 323 K.

Figure S15: ^1H NMR spectrum of the reaction mixture recorded upon standing at 323 K for 15 min.

Figure S16: ¹³C NMR spectrum of the reaction mixture recorded upon standing at 323 K for 15 min.

Figure S17 : ¹H NMR spectra (high-field region) of the reaction mixture in the 230 – 323 K temperature range.

DFT calculations

Density Functional Theory (DFT) calculations⁵ were performed using the Gaussian computational package G03.⁶ In this series of calculations the geometries of the molecules and ions were optimised by employing the B3LYP density functionals^{7,8} and the 6-311G** basis set.^{9,10}

Table S3: Comparison of calculated and experimentally found structural parameters for compounds **2** and **3**.

Structural parameters	<i>t</i> BuCH(C ₆ H ₄ Br)OGaR ₃ (2)		<i>al</i> ^t BuCH(C ₆ H ₄ Br)OGaR ₃ (3)	
	calculated	experimental	calculated	experimental
C ^{NHC} -C ^{substrate} (Å)	1.547	1.525(3)	1.532	1.541(10)
Ga-O ^{substrate} (Å)	2.016	1.9522(16)	2.000	1.943(5)
N-C-N (°)	107.8	107.8(2)	110.4	109.9(7)

Table S4: Comparison of calculated and experimentally found structural parameters for compounds **1** and **7**.

Structural parameters	<i>t</i> BuCH ₂ OGaR ₃ (1)		<i>al</i> ^t BuC(CF ₃)(C ₆ H ₄)OGaR ₃ (7)	
	calculated	experimental	calculated	experimental
C ^{NHC} -C ^{substrate} (Å)	1.519	1.505(3)	1.552	1.544(3)
Ga-O ^{substrate} (Å)	2.010	1.9317(15)	2.061	1.9692(14)
N-C-N (°)	105.9	107.50(19)	110.7	110.93(18)

Table S5: Comparison of total and relative energies for different variations of components of activation of 4-bromobenzaldehyde, formaldehyde and α,α,α -trifluoroacetophenone.

	Total energies (a.u.)		Relative energies (kcal mol ⁻¹)	
	normal	abnormal	normal	abnormal
<i>t</i> Bu	-540.827324	-540.799845	0.0	17.2
<i>t</i> Bu·GaR ₃	-3811.699566	-3811.710306	6.6	0.0
<i>t</i> Bu· p -Br-C ₆ H ₄ ·GaR ₃	-6730.925145	-6730.931310	3.9	0.0
p -Br-C ₆ H ₄ ·GaR ₃	-6190.088449	-6190.087370	0.0	0.7
<i>t</i> Bu· p -Br-C ₆ H ₄	-3460.012109	-3460.012511	0.2	0.0
<i>t</i> Bu·CH ₂ O·GaR ₃	-3926.286551	-3926.286937	0.2	0.0

⁵ W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **1996**, 100, 12974.

⁶ Gaussian 03, Revision B.0.5, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

⁷ A.D. Becke, *Phys. Rev. A* **1988**, 38, 3098.

⁸ C.T. Lee, W.T. Yang and R.G. Parr, *Phys. Rev. B* **1998**, 37, 785.

⁹ A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **1980**, 72, 5639.

¹⁰ R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.* **1980**, 72, 650.

$I^tBu \cdot C(Ph)CF_3O \cdot GaR_3$	-4494.503483	-4494.517676	12.4	0.0
$C(Ph)CF_3O \cdot GaR_3$	-3953.673983	-3953.673983	0.0	0.0
$I^tBu \cdot C(Ph)CF_3O$	-1223.625316	-1223.614338	0.0	6.9

Table S6: Total energies of GaR_3 and substrates used in this study.

	Total energies (a.u.)
GaR_3	-3270.872410
p-Br- C_6H_4	-2919.204596
CH_2O	-114.536341
$CF_3C(Ph)O$	-682.794775

Optimised geometry and energy of $Ga(CH_2SiMe_3)_3$, I^tBu , aI^tBu , $I^tBu \cdot GaR_3$ and $aI^tBu \cdot GaR_3$ were obtained previously employing the same methods and basis set.¹¹

1. Optimized geometry of 4-bromobenzaldehyde

Principal bond lengths (Å)		Principal bond angles(°)		Principal bond indices	
C_1-C_2	1.393	$C_1-C_2-C_3$	118.7	C_1-C_2	1.41
C_2-C_3	1.391	$C_2-C_3-C_4$	120.6	C_2-C_3	1.43
C_3-C_4	1.397	$C_3-C_4-C_5$	119.6	C_3-C_4	1.38
C_4-C_5	1.400	$C_4-C_5-C_6$	120.4	C_4-C_5	1.35
C_5-C_6	1.387	$C_5-C_6-C_1$	119.0	C_5-C_6	1.46

¹¹ M. Uzelac, A. Hernán-Gómez, D. R. Armstrong, A. R. Kennedy, E. Hevia, *Chem. Sci.*, 2015, **6**, 5719.

C_6-C_1	1.396	$C_6-C_1-C_2$	121.6	C_6-C_1	1.39
C_1-Br	1.913	C_6-C_1-Br	119.2	C_1-Br	1.05
C_4-C_7	1.481	$C_3-C_4-C_7$	120.1	C_4-C_7	1.05
C_7-O	1.209	C_4-C_7-H	114.5	C_7-O	1.82
C_7-H	1.112	C_4-C_7-O	124.6	C_7-H	0.91

Figure S18: Representation of molecular orbitals HOMO-1, HOMO and LUMO of p-bromobenzaldehyde.

2. Optimized geometry of α,α,α -trifluoroacetophenone

Principal bond lengths (Å)		Principal bond angles(°)		Principal bond indices	
C_1-C_2	1.393	$C_1-C_2-C_3$	120.2	C_1-C_2	1.43
C_2-C_3	1.391	$C_2-C_3-C_4$	119.9	C_2-C_3	1.44
C_3-C_4	1.403	$C_3-C_4-C_5$	119.4	C_3-C_4	1.37
C_4-C_5	1.404	$C_4-C_5-C_6$	120.4	C_4-C_5	1.35
C_5-C_6	1.387	$C_5-C_6-C_1$	119.9	C_5-C_6	1.46
C_6-C_1	1.396	$C_6-C_1-C_2$	120.1	C_6-C_1	1.42

C_7-C_8	1.558	$C_4-C_7-C_8$	118.5	C_7-C_8	1.02
C_4-C_7	1.486	$C_3-C_4-C_7$	123.7	C_4-C_7	1.05
C_7-O	1.207	C_4-C_7-O	123.9	C_7-O	1.80
C_8-F	1.330; 1.352; 1.352	C_7-C_8-F	111.2; 110.9; 110.9	C_8-F	0.91; 0.87; 0.87

Figure S19: Representation of molecular orbitals HOMO-1, HOMO and LUMO of trifluoroacetophenone.

3. Optimised geometry of formaldehyde

Principal bond lengths (Å)		Principal bond angles(°)	
H-C	1.110	H-C-O	122.3
C-O	1.200	H-C-H	115.5

4. Optimised geometry of GaR₃ + 4-bromobenzaldehyde

Principal bond lengths (Å)		Principal bond angles(°)	
C₁-C₂	1.394	C₁-C₂-C₃	118.8
C₂-C₃	1.389	C₂-C₃-C₄	120.5
C₃-C₄	1.401	C₃-C₄-C₅	119.7
C₄-C₅	1.404	C₄-C₅-C₆	120.2
C₅-C₆	1.385	C₅-C₆-C₁	119.1
C₆-C₁	1.398	C₆-C₁-C₂	121.7
C₁-Br	1.907	C₆-C₁-Br	119.1
C₄-C₇	1.462	C₃-C₄-C₇	119.3
C₇-H	1.102	C₄-C₇-H	116.4
C₇-O	1.225	C₄-C₇-O	123.8
Ga-O	2.284	C₇-O-Ga	126.6
Ga-C₈	2.019	O-Ga-C₈	96.7
Ga-C₉	2.015	O-Ga-C₉	94.1
Ga-C₁₀	2.009	O-Ga-C₁₀	101.4
C₈-Si₁₁	1.883	Ga-C₈-Si₁₁	118.2
C₉-Si₁₂	1.878	Ga-C₉-Si₁₂	122.0
C₁₀-Si₁₃	1.881	Ga-C₁₀-Si₁₃	122.5
Si₁₁-C_{Me}	1.897; 1.894; 1.895	C₈-Si₁₁-C_{Me}	111.1; 110.1; 110.7
Si₁₂-C_{Me}	1.894; 1.895; 1.898	C₉-Si₁₂-C_{Me}	111.3; 110.3; 110.7
Si₁₃-C_{Me}	1.894; 1.896; 1.896	C₁₀-Si₁₃-C_{Me}	110.5; 108.7; 111.7

5. Optimized geometry $t\text{BuI} + 4\text{-bromobenzaldehyde}$

Principal bond lengths (Å)		Principal bond angles(°)	
C ₁ -C ₂	1.390	C ₁ -C ₂ -C ₃	118.9
C ₂ -C ₃	1.396	C ₂ -C ₃ -C ₄	121.2
C ₃ -C ₄	1.396	C ₃ -C ₄ -C ₅	118.6
C ₄ -C ₅	1.396	C ₄ -C ₅ -C ₆	121.2
C ₅ -C ₆	1.392	C ₅ -C ₆ -C ₁	119.0
C ₆ -C ₁	1.392	C ₆ -C ₁ -C ₂	121.2
C ₁ -Br	1.925	C ₆ -C ₁ -Br	119.5
C ₄ -C ₇	1.556	C ₃ -C ₄ -C ₇	124.9
C ₇ -H	1.110	C ₄ -C ₇ -H	100.8
C ₇ -O	1.329	C ₄ -C ₇ -O	117.1
C ₇ -C ₈	1.555	C ₇ -O-C ₈	112.8
C ₈ -N ₉	1.365	C ₇ -C ₈ -N ₉	127.5
N ₉ -C ₁₀	1.385	C ₈ -N ₉ -C ₁₀	108.5
C ₁₀ -C ₁₁	1.347	N ₉ -C ₁₀ -C ₁₁	108.3
C ₁₁ -N ₁₂	1.387	C ₁₀ -C ₁₁ -N ₁₂	107.4
N ₁₂ -C ₈	1.368	C ₁₁ -N ₁₂ -C ₈	108.9
N ₉ -C ₁₃	1.529	N ₁₂ -C ₈ -N ₉	106.9
C ₁₃ -C _{Me}	1.539; 1.528; 1.538	C ₁₀ -N ₉ -C ₁₃	120.0
C ₁₂ -C ₁₄	1.518	N ₉ -C ₁₃ -C _{Me}	106.3; 108.4; 112.0
C ₁₄ -C _{Me}	1.544; 1.539; 1.539	C ₁₁ -N ₁₂ -C ₁₄	123.0
		N ₁₂ -C ₁₄ -C _{Me}	109.1; 110.4; 109.1

6. Optimized geometry *al*^tBu + 4-bromobenzaldehyde

Principal bond lengths (Å)		Principal bond angles(°)	
C ₁ -C ₂	1.390	C ₁ -C ₂ -C ₃	118.8
C ₂ -C ₃	1.395	C ₂ -C ₃ -C ₄	121.3
C ₃ -C ₄	1.397	C ₃ -C ₄ -C ₅	118.4
C ₄ -C ₅	1.395	C ₄ -C ₅ -C ₆	121.3
C ₅ -C ₆	1.393	C ₅ -C ₆ -C ₁	118.9
C ₆ -C ₁	1.390	C ₆ -C ₁ -C ₂	121.2
C ₁ -Br	1.928	C ₆ -C ₁ -Br	119.6
C ₄ -C ₇	1.568	C ₃ -C ₄ -C ₇	125.2
C ₇ -H	1.128	C ₄ -C ₇ -H	102.5
C ₇ -O	1.321	C ₄ -C ₇ -O	114.6
C ₇ -C ₈	1.562	C ₄ -C ₇ -C ₈	109.7
C ₈ -N ₉	1.405	C ₇ -C ₈ -N ₉	129.1
N ₉ -C ₁₀	1.340	C ₈ -N ₉ -C ₁₀	108.4
C ₁₀ -N ₁₁	1.336	N ₉ -C ₁₀ -N ₁₁	110.1
N ₁₁ -C ₁₂	1.385	C ₁₀ -N ₁₁ -C ₁₂	107.0
C ₁₂ -C ₈	1.368	N ₁₁ -C ₁₂ -C ₈	109.2
N ₉ -C ₁₃	1.525	C ₁₂ -C ₈ -N ₉	105.2
C ₁₃ -C _{Me}	1.531; 1.537; 1.536	C ₁₀ -N ₉ -C ₁₃	122.2
N ₁₁ -C ₁₄	1.499	N ₉ -C ₁₃ -C _{Me}	109.1; 107.0; 109.0
C ₁₄ -C _{Me}	1.533; 1.537; 1.538	C ₁₀ -N ₁₁ -C ₁₄	127.4
		N ₁₁ -C ₁₄ -C _{Me}	108.1; 109.8; 108.1

7. Optimized geometry of II_{Ar}

Principal bond lengths (Å)		Principal bond angles(°)		Principal Bond Indices	
C₁-C₂	1.389	C₁-C₂-C₃	119.0	C₁-C₂	1.41
C₂-C₃	1.395	C₂-C₃-C₄	121.3	C₂-C₃	1.41
C₃-C₄	1.396	C₃-C₄-C₅	118.3	C₃-C₄	1.41
C₄-C₅	1.397	C₄-C₅-C₆	121.2	C₄-C₅	1.39
C₅-C₆	1.391	C₅-C₆-C₁	119.2	C₅-C₆	1.43
C₆-C₁	1.392	C₆-C₁-C₂	120.9	C₆-C₁	1.40
C₁-Br	1.919	C₆-C₁-Br	119.6	C₁-Br	1.04
C₄-C₇	1.547	C₃-C₄-C₇	124.6	C₄-C₇	0.96
C₇-H	1.098	C₄-C₇-H	104.6	C₇-H	0.87
C₇-O	1.369	C₄-C₇-O	113.2	C₇-O	1.02
C₇-C₈	1.547	C₄-C₇-C₈	111.9	C₇-C₈	0.96
C₈-N₉	1.362	C₇-C₈-N₉	127.4	C₈-N₉	1.30
N₉-C₁₀	1.382	C₈-N₉-C₁₀	108.2	N₉-C₁₀	1.15
C₁₀-C₁₁	1.348	N₉-C₁₀-C₁₁	108.2	C₁₀-C₁₁	1.63
C₁₁-N₁₂	1.383	C₁₀-C₁₁-N₁₂	107.6	C₁₁-N₁₂	1.14
N₁₂-C₈	1.366	C₁₁-N₁₂-C₈	108.4	N₁₂-C₈	1.28
N₉-C₁₃	1.540	N₁₂-C₈-N₉	107.8	N₉-C₁₃	0.84
N₁₂-C₁₄	1.532	C₁₀-N₉-C₁₃	121.1	N₁₂-C₁₄	0.85
C₁₃-C_{Me}	1.540; 1.529; 1.534	N₉-C₁₃-C_{Me}	107.5; 108.0; 111.3	C₁₃-C_{Me}	1.00; 1.00; 1.01
C₁₄-C_{Me}	1.539; 1.536; 1.536	C₁₁-N₁₂-C₁₄	122.0	C₁₄-C_{Me}	1.00; 1.00; 1.00
		N₁₂-C₁₄-C_{Me}	108.9; 110.1; 109.4		
O-Ga	2.016	C₇-O-Ga	120.2	O-Ga	0.33
Ga-C₁₅	2.027	O-Ga-C₁₅	105.4	Ga-C₁₅	0.56
Ga-C₁₆	2.058	O-Ga-C₁₆	103.5	Ga-C₁₆	0.59
Ga-C₁₇	2.046	O-Ga-C₁₇	102.4	Ga-C₁₇	0.57
C₁₅-Si₁₈	1.874	Ga-C₁₅-Si₁₈	121.9	C₁₅-Si₁₈	0.83
C₁₆-Si₁₉	1.875	Ga-C₁₆-Si₁₉	123.7	C₁₆-Si₁₉	0.83

$C_{17}-Si_{20}$	1.875	$Ga-C_{17}-Si_{20}$	118.9	$C_{17}-Si_{20}$	0.83
$Si_{18}-C_{Me}$	1.896; 1.902; 1.897	$C_{15}-Si_{18}-C_{Me}$	111.8; 111.2; 111.2	$Si_{18}-C_{Me}$	0.80; 0.81; 0.81
$Si_{19}-C_{Me}$	1.904; 1.895; 1.898	$C_{16}-Si_{19}-C_{Me}$	112.2; 114.1; 109.4	$Si_{19}-C_{Me}$	0.81; 0.81; 0.81
$Si_{20}-C_{Me}$	1.899; 1.901; 1.894	$C_{17}-Si_{20}-C_{Me}$	110.3; 111.5; 112.7	$Si_{20}-C_{Me}$	0.81; 0.81; 0.82

Figure S20: Representation of molecular orbitals HOMO-1, HOMO and LUMO of **II_{Ar}**.

8. Optimized geometry of **III_{Ar}**

Principal bond lengths (Å)		Principal bond angles(°)		Principal Bond Indices	
C_1-C_2	1.391	$C_1-C_2-C_3$	119.0	C_1-C_2	1.41
C_2-C_3	1.394	$C_2-C_3-C_4$	121.2	C_2-C_3	1.43
C_3-C_4	1.397	$C_3-C_4-C_5$	118.5	C_3-C_4	1.40
C_4-C_5	1.395	$C_4-C_5-C_6$	121.1	C_4-C_5	1.40
C_5-C_6	1.393	$C_5-C_6-C_1$	119.2	C_5-C_6	1.41
C_6-C_1	1.390	$C_6-C_1-C_2$	121.0	C_6-C_1	1.41
C_1-Br	1.921	C_6-C_1-Br	119.6	C_1-Br	1.03

C₄-C₇	1.545	C₃-C₄-C₇	122.6	C₄-C₇	0.96
C₇-H	1.105	C₄-C₇-H	104.1	C₇-H	0.87
C₇-O	1.370	C₄-C₇-O	114.1	C₇-O	1.02
C₇-C₈	1.532	C₄-C₇-C₈	112.6	C₇-C₈	0.97
C₈-N₉	1.405	C₇-C₈-N₉	130.6	C₈-N₉	1.12
N₉-C₁₀	1.341	C₈-N₉-C₁₀	107.7	N₉-C₁₀	1.32
C₁₀-N₁₁	1.334	N₉-C₁₀-N₁₁	110.4	C₁₀-N₁₁	1.31
N₁₁-C₁₂	1.309	C₁₀-N₁₁-C₁₂	107.1	N₁₁-C₁₂	1.13
C₁₂-C₈	1.365	N₁₁-C₁₂-C₈	109.1	N₁₂-C₈	1.59
N₉-C₁₃	1.529	N₁₂-C₈-N₉	105.7	N₉-C₁₃	0.85
C₁₂-C₁₄	1.504	C₁₀-N₉-C₁₃	121.6	N₁₁-C₁₄	0.87
C₁₃-C_{Me}	1.537; 1.530; 1.534	N₉-C₁₃-C_{Me}	108.7; 109.8; 107.5	C₁₃-C_{Me}	1.00; 1.00; 1.01
C₁₄-C_{Me}	1.533; 1.537; 1.537	C₁₀-N₁₁-C₁₄	127.5	C₁₄-C_{Me}	1.00; 1.00; 1.00
		N₁₁-C₁₄-C_{Me}	107.9; 107.9; 109.5		
O-Ga	2.000	C₇-O-Ga	124.0	O-Ga	0.36
Ga-C₁₅	2.048	O-Ga-C₁₅	103.8	Ga-C₁₅	0.60
Ga-C₁₆	2.039	O-Ga-C₁₆	103.9	Ga-C₁₆	0.60
Ga-C₁₇	2.056	O-Ga-C₁₇	105.8	Ga-C₁₇	0.59
C₁₅-Si₁₈	1.867	Ga-C₁₅-Si₁₈	123.9	C₁₅-Si₁₈	0.85
C₁₆-Si₁₉	1.873	Ga-C₁₆-Si₁₉	122.2	C₁₆-Si₁₉	0.84
C₁₇-Si₂₀	1.874	Ga-C₁₇-Si₂₀	124.0	C₁₇-Si₂₀	0.84
Si₁₈-C_{Me}	1.897; 1.904; 1.906	C₁₅-Si₁₈-C_{Me}	113.4; 111.4; 111.2	Si₁₈-C_{Me}	0.80; 0.80; 0.82
Si₁₉-C_{Me}	1.900; 1.902; 1.897	C₁₆-Si₁₉-C_{Me}	110.7; 111.3; 112.8	Si₁₉-C_{Me}	0.81; 0.81; 0.81
Si₂₀-C_{Me}	1.897; 1.905; 1.894	C₁₇-Si₂₀-C_{Me}	113.0; 110.9; 110.5	Si₂₀-C_{Me}	0.80; 0.81; 0.82

Figure S21: Representation of molecular orbitals HOMO-1, HOMO and LUMO of **III_{Ar}**.9. Optimized geometry of **II_H**

Principal bond lengths (Å)		Principal bond angles(°)	
C₁-C₂	1.519	C₁-C₂-N₃	126.2
C₂-N₃	1.359	C₂-N₃-C₄	108.8
N₃-C₄	1.382	N₃-C₄-C₅	107.2
C₄-C₅	1.351	C₄-C₅-N₆	110.1
C₅-N₆	1.387	C₅-N₆-C₂	108.0
N₆-C₂	1.359	N₆-C₂-N₃	105.9
N₃-C₇	1.524	C₂-N₃-C₇	125.4
N₆-C₈	1.526	N₃-C₇-C_{Me}	107.9; 108.0; 109.5
C₇-C_{Me}	1.537; 1.539; 1.535	C₂-N₆-C₈	129.1
C₈-C_{Me}	1.537; 1.539; 1.535	N₆-C₈-C_{Me}	108.6; 107.7; 109.5
C₁-O	1.375	C₂-C₁-O	111.8
C₁-H	1.100; 1.099	H-C₁-O	112.9; 113.9
O-Ga	2.010	H-C₁-H	105.1
Ga-C₉	2.045	C₁-O-Ga	143.3
Ga-C₁₀	2.054	O-Ga-C₉	101.3
Ga-C₁₁	2.028	O-Ga-C₁₀	102.4
C₉-Si₁₂	1.872	O-Ga-C₁₁	103.2
C₁₀-Si₁₃	1.873	Ga-C₉-Si₁₂	121.9
C₁₁-Si₁₄	1.871	Ga-C₁₀-Si₁₃	121.5
Si₁₃-C_{Me}	1.903; 1.898; 1.896	Ga-C₁₁-Si₁₄	121.5
Si₁₄-C_{Me}	1.895; 1.900; 1.903	C₉-Si₁₂-C_{Me}	111.3; 110.7; 111.8
Si₁₅-C_{Me}	1.903; 1.897; 1.898	C₁₀-Si₁₃-C_{Me}	112.6; 110.8; 110.8
		C₁₁-Si₁₄-C_{Me}	112.0; 108.5; 106.7

10. Optimized geometry of III_H

Principal bond lengths (Å)		Principal bond angles(°)	
C ₁ -C ₂	1.516	C ₁ -C ₂ -C ₃	126.2
C ₂ -C ₃	1.364	C ₂ -C ₃ -N ₄	108.8
C ₃ -N ₄	1.383	C ₃ -N ₄ -C ₅	107.2
N ₄ -C ₅	1.335	N ₄ -C ₅ -N ₆	110.1
C ₅ -N ₆	1.340	C ₅ -N ₆ -C ₂	108.0
N ₆ -C ₂	1.401	N ₆ -C ₂ -C ₃	105.9
N ₄ -C ₇	1.503	C ₃ -N ₃ -C ₇	125.4
N ₆ -C ₈	1.525	N ₄ -C ₇ -C _{Me}	107.9; 108.0; 109.5
C ₇ -C _{Me}	1.537; 1.537; 1.533	C ₂ -N ₆ -C ₈	129.1
C ₈ -C _{Me}	1.537; 1.533; 1.535	N ₆ -C ₈ -C _{Me}	108.6; 107.7; 109.5
C ₁ -O	1.374	C ₂ -C ₁ -O	111.8
C ₁ -H	1.106; 1.101	H-C ₁ -O	112.9; 113.9
O-Ga	1.979	H-C ₁ -H	105.1
Ga-C ₉	2.056	C ₁ -O-Ga	124.1
Ga-C ₁₀	2.046	O-Ga-C ₉	105.8
Ga-C ₁₁	2.041	O-Ga-C ₁₀	102.3
C ₉ -Si ₁₂	1.871	O-Ga-C ₁₁	105.4
C ₁₀ -Si ₁₃	1.866	Ga-C ₉ -Si ₁₂	123.3
C ₁₁ -Si ₁₄	1.869	Ga-C ₁₀ -Si ₁₃	123.0
Si ₁₂ -C _{Me}	1.901; 1.905; 1.895	Ga-C ₁₁ -Si ₁₄	122.0
Si ₁₃ -C _{Me}	1.904; 1.897; 1.906	C ₉ -Si ₁₂ -C _{Me}	113.1; 110.9; 110.9
Si ₁₄ -C _{Me}	1.904; 1.897; 1.899	C ₁₀ -Si ₁₃ -C _{Me}	112.6; 111.9; 111.4
		C ₁₁ -Si ₁₄ -C _{Me}	111.0; 112.2; 111.5

11. Optimized geometry of GaR₃ + α,α,α -trifluoroacetophenone

Principal bond lengths (Å)		Principal bond angles(°)	
C ₁ -C ₂	1.394	C ₁ -C ₂ -C ₃	120.2
C ₂ -C ₃	1.390	C ₂ -C ₃ -C ₄	119.9
C ₃ -C ₄	1.405	C ₃ -C ₄ -C ₅	119.5
C ₄ -C ₅	1.406	C ₄ -C ₅ -C ₆	120.3
C ₅ -C ₆	1.386	C ₅ -C ₆ -C ₁	119.9
C ₆ -C ₁	1.396	C ₆ -C ₁ -C ₂	120.2
C ₇ -C ₈	1.558	C ₄ -C ₇ -C ₈	118.9
C ₄ -C ₇	1.476	C ₃ -C ₄ -C ₇	123.3
C ₇ -O	1.214	C ₄ -C ₇ -O	123.3
C ₈ -F	1.349; 1.349; 1.332	C ₇ -C ₈ -F	110.8; 110.7; 111.2
Ga-O	2.557	C ₇ -O-Ga	151.2
Ga-C ₁₂	2.010	O-Ga-C ₁₂	92.3
Ga-C ₁₃	2.006	O-Ga-C ₁₃	99.1
Ga-C ₁₄	2.003	O-Ga-C ₁₄	89.7
C ₁₂ -Si ₁₅	1.883	Ga-C ₁₂ -Si ₁₅	120.0
C ₁₃ -Si ₁₆	1.881	Ga-C ₁₃ -Si ₁₆	123.2
C ₁₄ -Si ₁₇	1.883	Ga-C ₁₄ -Si ₁₇	119.5
Si ₁₅ -C _{Me}	1.896; 1.897; 1.893	C ₁₂ -Si ₁₅ -C _{Me}	110.4; 110.1; 111.6
Si ₁₆ -C _{Me}	1.896; 1.896; 1.894	C ₁₃ -Si ₁₆ -C _{Me}	111.8; 109.7; 111.0
Si ₁₇ -C _{Me}	1.894; 1.894; 1.896	C ₁₄ -Si ₁₇ -C _{Me}	110.1; 110.2; 111.2

12. Optimized geometry of I^tBu + trifluoroacetophenone

Principal bond lengths (Å)		Principal bond angles(°)	
C ₁ -C ₂	1.393	C ₁ -C ₂ -C ₃	120.2
C ₂ -C ₃	1.391	C ₂ -C ₃ -C ₄	120.0
C ₃ -C ₄	1.403	C ₃ -C ₄ -C ₅	119.4
C ₄ -C ₅	1.404	C ₄ -C ₅ -C ₆	120.4
C ₅ -C ₆	1.387	C ₅ -C ₆ -C ₁	119.9
C ₆ -C ₁	1.396	C ₆ -C ₁ -C ₂	120.1
C ₄ -C ₇	1.486	C ₃ -C ₄ -C ₇	123.7
C ₇ -C ₈	1.558	C ₄ -C ₇ -C ₈	118.5
C ₇ -O	1.207	C ₄ -C ₇ -O	123.8
C ₈ -F	1.355; 1.351; 1.329	C ₇ -C ₈ -F	110.2; 111.6; 111.5
C ₇C ₁₂	4.475	C ₄ -C ₇ -C ₁₂	119.6
C ₁₂ -N ₁₃	1.365	C ₇ -C ₁₂ -N ₁₃	137.7
N ₁₃ -C ₁₄	1.393	C ₁₂ -N ₁₃ -C ₁₄	112.1
C ₁₄ -C ₁₅	1.354	N ₁₃ -C ₁₄ -C ₁₅	106.3
C ₁₅ -N ₁₆	1.392	C ₁₄ -C ₁₅ -N ₁₆	106.4
C ₁₂ -N ₁₆	1.365	C ₁₅ -N ₁₆ -C ₁₂	112.0
N ₁₃ -C ₁₇	1.493	C ₁₆ -C ₁₂ -N ₁₃	103.2
N ₁₆ -C ₁₈	1.495	C ₁₂ -N ₁₃ -C ₁₇	121.8
		C ₁₂ -N ₁₆ -C ₁₈	121.7
C ₁₇ -C _{Me}	1.537; 1.538; 1.535	N ₁₃ -C ₁₇ -C _{Me}	108.5; 110.2; 108.3
C ₁₈ -C _{Me}	1.537; 1.538; 1.534	N ₁₆ -C ₁₈ -C _{Me}	108.3; 108.4; 110.1

13. Optimized geometry of *al*^tBu + trifluoroacetophenone

Principal bond lengths (Å)		Principal bond angles(°)	
C ₁ -C ₂	1.393	C ₁ -C ₂ -C ₃	120.1
C ₂ -C ₃	1.395	C ₂ -C ₃ -C ₄	120.7
C ₃ -C ₄	1.397	C ₃ -C ₄ -C ₅	118.7
C ₄ -C ₅	1.396	C ₄ -C ₅ -C ₆	120.8
C ₅ -C ₆	1.392	C ₅ -C ₆ -C ₁	120.2
C ₆ -C ₁	1.394	C ₆ -C ₁ -C ₂	119.4
C ₇ -C ₈	1.581	C ₄ -C ₇ -C ₈	106.2
C ₄ -C ₇	1.576	C ₃ -C ₄ -C ₇	125.6
C ₇ -O	1.316	C ₄ -C ₇ -O	114.0
C ₈ -F	1.384; 1.352; 1.336	C ₇ -C ₈ -F	115.1; 111.8; 110.6
C ₇ -C ₁₂	1.576	C ₄ -C ₇ -C ₁₂	108.8
C ₁₂ -C ₁₃	1.368	C ₇ -C ₁₂ -C ₁₃	128.3
C ₁₃ -N ₁₄	1.381	C ₁₂ -C ₁₃ -N ₁₄	109.2
N ₁₄ -C ₁₅	1.334	C ₁₃ -N ₁₄ -C ₁₅	107.1
C ₁₅ -N ₁₆	1.340	N ₁₄ -C ₁₅ -N ₁₆	110.3
C ₁₂ -N ₁₆	1.409	C ₁₅ -N ₁₆ -C ₁₂	108.1
N ₁₄ -C ₁₇	1.500	C ₁₆ -C ₁₂ -C ₁₃	105.2
N ₁₆ -C ₁₈	1.532	C ₁₃ -N ₁₄ -C ₁₇	125.2
		C ₁₂ -N ₁₆ -C ₁₈	130.7
C ₁₇ -C _{Me}	1.537; 1.537; 1.533	N ₁₄ -C ₁₇ -C _{Me}	108.1; 107.9; 109.7
C ₁₈ -C _{Me}	1.538; 1.536; 1.532	N ₁₆ -C ₁₈ -C _{Me}	109.3; 107.5; 108.9

14. Optimized geometry of II_{Cf3}

Principal bond lengths (Å)		Principal bond angles(°)		Principal Bond Indices	
C ₁ -C ₂	1.393	C ₁ -C ₂ -C ₃	120.2	C ₁ -C ₂	1.43
C ₂ -C ₃	1.390	C ₂ -C ₃ -C ₄	119.9	C ₂ -C ₃	1.45
C ₃ -C ₄	1.405	C ₃ -C ₄ -C ₅	119.5	C ₃ -C ₄	1.35
C ₄ -C ₅	1.406	C ₄ -C ₅ -C ₆	120.3	C ₄ -C ₅	1.34
C ₅ -C ₆	1.386	C ₅ -C ₆ -C ₁	119.9	C ₅ -C ₆	1.47
C ₆ -C ₁	1.396	C ₆ -C ₁ -C ₂	120.2	C ₆ -C ₁	1.41
C ₄ -C ₇	1.476	C ₃ -C ₄ -C ₇	123.3	C ₄ -C ₇	1.08
C ₇ -C ₈	1.559	C ₄ -C ₇ -C ₈	118.8	C ₇ -C ₈	0.91
C ₇ -O	1.214	C ₄ -C ₇ -O	123.3	C ₇ -O	1.22
C ₈ -F	1.350; 1.346; 1.334	C ₇ -C ₈ -F	110.6; 110.9; 111.2	C ₈ -F	0.87; 0.88; 0.90
C ₇C ₁₂	5.708	C ₁₂ -C ₁₃ -N ₁₄	112.2	C ₇C ₁₂	0.0001
C ₁₂ -N ₁₃	1.365	C ₁₃ -N ₁₄ -C ₁₅	106.4	C ₁₂ -N ₁₃	1.26
N ₁₃ -C ₁₄	1.394	N ₁₄ -C ₁₅ -N ₁₆	106.3	N ₁₃ -C ₁₄	1.10
C ₁₄ -C ₁₅	1.352	C ₁₅ -N ₁₆ -C ₁₂	112.2	C ₁₄ -C ₁₅	1.67
C ₁₅ -N ₁₆	1.394	N ₁₆ -C ₁₂ -N ₁₃	103.0	C ₁₅ -N ₁₆	1.10
N ₁₆ -C ₁₂	1.366	C ₁₂ -N ₁₃ -C ₁₇	124.6	N ₁₆ -C ₁₂	1.26
N ₁₃ -C ₁₇	1.489	C ₁₂ -N ₁₆ -C ₁₈	124.2	N ₁₃ -C ₁₇	0.90
N ₁₆ -C ₁₈	1.489	N ₁₃ -C ₁₇ -C _{Me}	108.7; 109.7; 108.7	N ₁₆ -C ₁₈	0.90
C ₁₇ -C _{Me}	1.533; 1.540; 1.540	N ₁₆ -C ₁₈ -C _{Me}	108.6; 109.5; 109.1	C ₁₇ -C _{Me}	0.99; 1.00; 0.99
C ₁₈ -C _{Me}	1.540; 1.539; 1.533	C ₇ -O-Ga	153.5	C ₁₈ -C _{Me}	1.00; 0.99; 0.99
O-Ga	2.562	O-Ga-C ₁₉	92.7	O-Ga	0.12
Ga-C ₁₉	2.008	O-Ga-C ₂₀	98.3	Ga-C ₁₉	0.61
Ga-C ₂₀	2.007	O-Ga-C ₂₁	90.1	Ga-C ₂₀	0.60
Ga-C ₂₁	2.003	Ga-C ₁₉ -Si ₂₂	120.2	Ga-C ₂₁	0.60
C ₁₉ -Si ₂₂	1.882	Ga-C ₂₀ -Si ₂₃	123.4	C ₁₉ -Si ₂₂	0.82
C ₂₀ -Si ₂₃	1.880	Ga-C ₂₁ -Si ₂₄	119.6	C ₂₀ -Si ₂₃	0.82
C ₂₁ -Si ₂₄	1.883	C ₁₉ -Si ₂₂ -C _{Me}	110.7; 111.6; 110.0	C ₂₁ -Si ₂₄	0.82

$\text{Si}_{22}\text{-C}_{\text{Me}}$	1.893; 1.897; 1.896	$\text{C}_{20}\text{-Si}_{23}\text{-C}_{\text{Me}}$	111.7; 109.7; 111.1	$\text{Si}_{22}\text{-C}_{\text{Me}}$	0.82; 0.82; 0.82
$\text{Si}_{23}\text{-C}_{\text{Me}}$	1.896; 1.896; 1.894	$\text{C}_{21}\text{-Si}_{24}\text{-C}_{\text{Me}}$	110.3; 110.1; 111.4	$\text{Si}_{23}\text{-C}_{\text{Me}}$	0.82; 0.82; 0.82
$\text{Si}_{24}\text{-C}_{\text{Me}}$	1.894; 1.894; 1.896			$\text{Si}_{24}\text{-C}_{\text{Me}}$	0.82; 0.82; 0.82

Figure S22: Representation of molecular orbitals HOMO-1, HOMO and LUMO of II_{CF_3} .

15. Optimized geometry of III_{CF_3}

Principal bond lengths (Å)		Principal bond angles(°)		Principal Bond Indices	
$\text{C}_1\text{-C}_2$	1.393	$\text{C}_1\text{-C}_2\text{-C}_3$	120.1	$\text{C}_1\text{-C}_2$	1.44
$\text{C}_2\text{-C}_3$	1.394	$\text{C}_2\text{-C}_3\text{-C}_4$	120.6	$\text{C}_2\text{-C}_3$	1.43
$\text{C}_3\text{-C}_4$	1.397	$\text{C}_3\text{-C}_4\text{-C}_5$	119.0	$\text{C}_3\text{-C}_4$	1.41
$\text{C}_4\text{-C}_5$	1.395	$\text{C}_4\text{-C}_5\text{-C}_6$	120.5	$\text{C}_4\text{-C}_5$	1.40
$\text{C}_5\text{-C}_6$	1.392	$\text{C}_5\text{-C}_6\text{-C}_1$	120.3	$\text{C}_5\text{-C}_6$	1.43
$\text{C}_6\text{-C}_1$	1.394	$\text{C}_6\text{-C}_1\text{-C}_2$	119.5	$\text{C}_6\text{-C}_1$	1.43
$\text{C}_4\text{-C}_7$	1.559	$\text{C}_3\text{-C}_4\text{-C}_7$	122.8	$\text{C}_4\text{-C}_7$	0.94
$\text{C}_7\text{-C}_8$	1.576	$\text{C}_4\text{-C}_7\text{-C}_8$	104.5	$\text{C}_7\text{-C}_8$	0.90
$\text{C}_7\text{-O}$	1.355	$\text{C}_4\text{-C}_7\text{-O}$	112.6	$\text{C}_7\text{-O}$	1.04

C₈-F	1.367; 1.353; 1.335	C₇-C₈-F	113.4; 112.5; 110.6	C₈-F	0.90; 0.86; 0.95
C₇-C₁₂	1.552	C₄-C₇-C₁₂	110.3	C₇-C₁₂	0.95
C₁₂-C₁₃	1.367	C₇-C₁₂-C₁₃	126.9	C₁₂-C₁₃	1.59
C₁₃-N₁₄	1.378	C₁₂-C₁₃-N₁₄	109.2	C₁₃-N₁₄	1.13
N₁₄-C₁₅	1.311	C₁₃-N₁₄-C₁₅	107.1	N₁₄-C₁₅	1.31
C₁₅-N₁₆	1.340	N₁₄-C₁₅-N₁₆	110.7	C₁₅-N₁₆	1.33
N₁₆-C₁₂	1.411	C₁₅-N₁₆-C₁₂	107.5	N₁₆-C₁₂	1.13
N₁₄-C₁₇	1.504	N₁₆-C₁₂-C₁₃	105.5	N₁₄-C₁₇	0.87
N₁₆-C₁₈	1.542	C₁₃-N₁₄-C₁₇	125.2	N₁₆-C₁₈	0.84
C₁₇-C_{Me}	1.532; 1.537; 1.537	C₁₂-N₁₆-C₁₈	133.8	C₁₇-C_{Me}	1.00; 1.00; 1.01
C₁₈-C_{Me}	1.541; 1.533; 1.527	N₁₄-C₁₇-C_{Me}	107.9; 107.8; 109.4	C₁₈-C_{Me}	1.00; 1.00; 1.01
		N₁₆-C₁₈-C_{Me}	108.0; 106.8; 111.9		
O-Ga	2.061	C₇-O-Ga	139.3	O-Ga	0.32
Ga-C₁₉	2.058	O-Ga-C₁₉	101.9	Ga-C₁₉	0.55
Ga-C₂₀	2.031	O-Ga-C₂₀	108.8	Ga-C₂₀	0.58
Ga-C₂₁	2.039	O-Ga-C₂₁	95.5	Ga-C₂₁	0.57
C₁₉-Si₂₂	1.873	Ga-C₁₉-Si₂₂	122.1	C₁₉-Si₂₂	0.84
C₂₀-Si₂₃	1.875	Ga-C₂₀-Si₂₃	124.2	C₂₀-Si₂₃	0.83
C₂₁-Si₂₄	1.874	Ga-C₂₁-Si₂₄	123.7	C₂₁-Si₂₄	0.84
Si₂₂-C_{Me}	1.895; 1.908; 1.895	C₁₉-Si₂₂-C_{Me}	111.8; 110.2; 112.5	Si₂₂-C_{Me}	0.79; 0.82; 0.81
Si₂₃-C_{Me}	1.901; 1.896; 1.898	C₂₀-Si₂₃-C_{Me}	111.2; 113.7; 110.0	Si₂₃-C_{Me}	0.81; 0.81; 0.81
Si₂₄-C_{Me}	1.903; 1.894; 1.901	C₂₁-Si₂₄-C_{Me}	111.7; 112.7; 110.4	Si₂₄-C_{Me}	0.80; 0.81; 0.82

Figure S23: Representation of molecular orbitals HOMO-1, HOMO and LUMO of **III_{CF3}**.

Figure S26: ¹H NMR spectrum of **2** in d₈-THF (presence of **3** and free components observed, see further spectra).

Figure S27: Aromatic region of ¹H NMR spectrum of **2** in d₈-THF.

Figure S28: High field region of ^1H NMR spectrum of **2** in $\text{d}_8\text{-THF}$.

Figure S29: High field region of ^1H NMR spectrum of **2** in $\text{d}_8\text{-THF}$.

Figure S30: ^{13}C NMR spectrum of **2** in $\text{d}_8\text{-THF}$.

Figure S31: High field region of ^{13}C NMR of **2** in $\text{d}_8\text{-THF}$.

Figure S32: ^1H NMR spectrum of **3** in $d_8\text{-THF}$.

Figure S33: Aromatic region of ^1H NMR spectrum of **3** in $d_8\text{-THF}$.

Figure S34: High field region of ^1H NMR spectrum of **3** in d_8 -THF (# = grease)

Figure S35: ^{13}C NMR spectrum of **3** in d_8 -THF (# = grease).

Figure S36: ¹H NMR spectrum of **4** in C₆D₆.

Figure S37: ¹H NMR spectrum of **4** in d₈-THF.

Figure S38: ¹³C NMR spectrum of **4** in d₈-THF. Figure S39: ¹H NMR spectrum of **5** in d₈-THF.

Figure S40: ¹³C NMR spectrum of **5** in d₈-THF.

Figure S41: ¹H NMR spectrum of **6** in d₈-THF.

Figure S42: ¹³C NMR spectrum of **6** in d₈-THF.

Figure S43: ¹H NMR spectrum of **7** in d₈-THF.

Figure S44: ¹³C NMR spectrum of **7** in d₈-THF.

Figure S45: ¹⁹F NMR spectrum of **7** in d₈-THF (# = impurity).

Figure S46: ¹H NMR spectrum of **8** in d₈-THF. Figure S47: ¹³C NMR spectrum of **8** in d₈-THF.

Figure S48: ¹H NMR spectrum of **9** in d₈-THF.

Figure S49: ¹³C NMR spectrum of **9** in d₈-THF.

Figure S50: ^1H NMR spectrum of **10** in $\text{d}_8\text{-THF}$.

Figure S51: ^{13}C NMR spectrum of **10** in $\text{d}_8\text{-THF}$.

Figure S52: ¹H NMR spectrum of **11** in d₈-THF

Figure S53: ¹³C NMR spectrum of **11** in d₈-THF

Figure S54: ¹H NMR spectrum of **12** in d₈-THF.

Figure S55: ¹³C NMR spectrum of **12** in d₈-THF.

Figure S56: Part of the ^{13}C NMR spectrum of **12** in $\text{d}_8\text{-THF}$.

Figure S57: Part of the ^{13}C NMR spectrum of **12** in $\text{d}_8\text{-THF}$.

Figure S58: ¹H NMR spectrum of **13** in d₈-THF Figure S59: ¹³C NMR spectrum of **13** in d₈-THF.

Figure S60: Part of the ^{13}C NMR spectrum of **13** in d_8 -THF.

IR spectra of products **12** and **13**

Figure S61: IR spectrum of **12**.

Figure S62: IR spectrum of **13**.

Cartesian coordinates**1. Model II_{Ar}**

Ga	-0.769709744	-1.5834316297	0.452434623
Br	4.6348981809	2.9897164869	-4.01971941
Si	-2.9880231785	-2.1989858598	3.0296015771
Si	2.1335331946	-3.4641637875	0.5074106799
Si	-2.4822139714	-2.9039568733	-2.2063337462
O	0.3688177787	0.0780865345	0.5387272417
N	0.166557355	2.662612761	2.0813609496
N	-1.4921955753	3.1292749601	0.7142150878
C	-0.3884361813	2.3416870829	0.8797721747
C	-0.6149900936	3.6375254626	2.6717190728
H	-0.3968836153	4.0531565538	3.6349372254
C	-1.6305830742	3.9285889103	1.8341765509
H	-2.4254239126	4.6364040814	1.9569148973
C	1.3500586749	2.0487694052	2.8522211408
C	2.5146832535	1.7135400285	1.9191610281
H	2.2439364021	0.9235551978	1.2252547111
H	3.3411294007	1.3526967822	2.5353164086
H	2.8597887076	2.5941345279	1.3738671163
C	0.829815886	0.7997776685	3.5751579945
H	0.4997685334	0.0593874034	2.850364111
H	0.0031549893	1.0504166412	4.2453020174
H	1.6363963513	0.3732706175	4.1764856449
C	1.8427736149	3.0861579888	3.8783973486
H	2.7546053612	2.692796085	4.3291501017
H	1.1370108416	3.2538342474	4.6944984305
H	2.0900490067	4.0423507835	3.4104608139
C	-2.5131458602	3.1533175301	-0.4275600833
C	-3.3308995147	1.8538872083	-0.3974421825
H	-2.7307022269	0.9640563369	-0.5724714401
H	-4.0971939363	1.899628671	-1.1747756985
H	-3.8284106472	1.7345476523	0.5667785926
C	-1.8146597118	3.3841644892	-1.7761680269
H	-1.2501921644	4.3190150416	-1.7687414564
H	-2.5806662161	3.4600008185	-2.5508629042
H	-1.1401538002	2.5809207732	-2.0600465461
C	-3.4768055643	4.3315994993	-0.2007627891
H	-4.0834336911	4.2090354597	0.6984572011
H	-4.1628417225	4.3623943209	-1.0479261362
H	-2.9574826121	5.2919823753	-0.1628339654
C	0.0743028921	1.2501484492	-0.1041796617
H	-0.784316155	1.1204291	-0.7769501087
C	1.2167938047	1.7467951697	-1.0210110236
C	1.8845831175	0.784712748	-1.7834102347
H	1.6131872346	-0.2557243813	-1.6640884569
C	2.8922274366	1.1427159039	-2.6736385458
H	3.4002177312	0.3862825271	-3.2576462387
C	3.2423348177	2.4837188697	-2.8001747864

C	2.5998086617	3.4622381022	-2.052595546
H	2.8840214117	4.5020631088	-2.1507857011
C	1.588072316	3.0840800459	-1.1695510446
H	1.1023487172	3.8596806974	-0.586880899
C	-2.3729494019	-1.0938910393	1.6459839495
H	-2.1305916346	-0.1237947094	2.1031527194
H	-3.2242583587	-0.9039645092	0.9794802392
C	-4.6045735599	-1.506655742	3.7596761366
H	-4.4593165156	-0.4960262908	4.1562989099
H	-4.9798111942	-2.1316936861	4.5771839559
H	-5.3908177933	-1.4510224057	2.999529382
C	-1.7392260155	-2.2958304433	4.455277599
H	-0.7955347939	-2.7445803424	4.1342632805
H	-2.1326274054	-2.9019799338	5.2779495189
H	-1.5163960148	-1.3020573534	4.8576838993
C	-3.3558841321	-3.9622067973	2.439667888
H	-4.0821235804	-3.9690206147	1.6209129195
H	-3.7721878039	-4.5668927832	3.2521213149
H	-2.4511815304	-4.4635132272	2.0847940885
C	0.4529263187	-3.0151012963	1.2045682541
H	0.6020549014	-2.7773407457	2.2664666064
H	-0.152190118	-3.933057109	1.1997276246
C	2.7740877839	-5.0568598413	1.325160134
H	2.8522945746	-4.9389028776	2.4109217567
H	3.7644886845	-5.3366829783	0.9499480641
H	2.0985594683	-5.8974635641	1.1359180822
C	3.4152952107	-2.1085983442	0.8473201387
H	3.1330597512	-1.1652052705	0.3743506823
H	4.4025178892	-2.3962083614	0.4708638196
H	3.5134541878	-1.9236087189	1.9221411781
C	2.0942755962	-3.7857974671	-1.3620743524
H	1.3691194901	-4.5653862465	-1.6143456899
H	3.0739688142	-4.1188721384	-1.7203595759
H	1.8206835656	-2.8903809404	-1.9270457783
C	-1.2280273266	-1.6799959747	-1.5390792041
H	-1.5584072073	-0.6845894155	-1.8728819013
H	-0.2845791175	-1.8651732485	-2.0684940555
C	-2.4992445296	-2.8697146202	-4.1071665483
H	-2.7406061379	-1.8700763393	-4.4835468489
H	-3.2378915055	-3.5663534772	-4.518137708
H	-1.5215822733	-3.145213338	-4.5156306239
C	-2.0940456617	-4.6808267575	-1.6768103561
H	-1.0948247377	-4.9813487969	-2.0065244609
H	-2.810352256	-5.3849971769	-2.1127234656
H	-2.1326316256	-4.800131155	-0.590535237
C	-4.2387996226	-2.4761573196	-1.6267940702
H	-4.3278454745	-2.5218826592	-0.5382394266
H	-4.9691491331	-3.173557449	-2.0499169998
H	-4.5294774957	-1.468182633	-1.9417930254

2. Model III_{Ar}

Ga	0.9472765579	1.5875573901	-1.1763465639
Br	-6.0904118933	-2.7712237557	-0.8471755938
Si	-1.3664490712	4.0464675979	-1.7526352244
Si	3.7844670333	2.478428543	0.5855040045
Si	1.5279433261	-0.7066477805	-3.7141296898
O	-0.1574393637	0.6234655328	0.1844299018
N	1.7617401582	-2.537492537	2.7716826123
N	0.2626749129	-0.9338171052	2.8540180692
C	1.1095899794	-1.6891386873	3.568373829
H	1.2493863055	-1.6189157563	4.6278776269
C	0.3837874577	-1.312153057	1.5064724535
C	1.3170137391	-2.3078184466	1.4844501707
H	1.7019636477	-2.8437033285	0.6357832127
C	-0.5227517163	0.2121912978	3.4923799086
C	-0.6570388781	-0.0600570557	4.9988324659
H	-1.2933735404	0.7179659123	5.4218218126
H	0.2967856675	-0.0055290854	5.5299803221
H	-1.1322722445	-1.0237205262	5.2014006122
C	0.2629681126	1.5058415085	3.2435570698
H	-0.2855642491	2.3464420719	3.6754623871
H	0.372387593	1.6661925873	2.1717508189
H	1.24996221	1.4654112774	3.7123532618
C	-1.9172696464	0.2956059131	2.8692904033
H	-2.4460357723	-0.6580170985	2.9270593293
H	-1.8564729259	0.6195970539	1.8340848899
H	-2.4942517929	1.0403838986	3.4218893003
C	2.8000684272	-3.5508790909	3.1672174647
C	3.0562230317	-3.4583949542	4.6753472707
H	3.4411720631	-2.4772295467	4.9631301357
H	3.8109522741	-4.1984630429	4.9450249513
H	2.1582982727	-3.6796966754	5.2577332101
C	4.0894965621	-3.2338825761	2.3934267947
H	3.9470507838	-3.3226237689	1.3150867149
H	4.8700181051	-3.9395688572	2.6855681472
H	4.4355623201	-2.2208627074	2.6068350752
C	2.2616464511	-4.9446588529	2.807074118
H	1.3339403742	-5.1576902519	3.3432143426
H	2.998546747	-5.7023853549	3.0811551144
H	2.0698942187	-5.0383369892	1.7365232226
C	-0.2754608916	-0.7399671276	0.2479058246
H	0.3040897233	-1.2345838541	-0.5528907389
C	-1.7166963886	-1.2574718989	0.0440406424
C	-2.0954479776	-2.5683860934	0.3446418755
H	-1.3826065127	-3.2561243769	0.7880479968
C	-3.3863774509	-3.0251150474	0.0860974312
H	-3.670314504	-4.0419402141	0.3257945935
C	-4.3064666297	-2.1553195404	-0.4888689576
C	-3.95310776	-0.8494864474	-0.8089215089

H	-4.6751002026	-0.1823862607	-1.2622128764
C	-2.6584996713	-0.4104144265	-0.5394692857
H	-2.3611648319	0.6032368197	-0.7743867361
C	-0.4311924611	2.5347222542	-2.3418407928
H	0.0938913037	2.8261644784	-3.2625422259
H	-1.1591968118	1.7736671297	-2.6534442175
C	-2.1262420146	3.8144261717	-0.0268485098
H	-2.8160097571	2.9650776561	-0.0017458384
H	-2.6884709009	4.7049202946	0.2742602454
H	-1.3543477865	3.6322475885	0.7258203416
C	-0.2408904723	5.5720084421	-1.6925957717
H	0.5579068731	5.4538087133	-0.9557134091
H	-0.8094707279	6.4700205549	-1.4288410415
H	0.2293213459	5.7532259239	-2.6646537206
C	-2.8009563335	4.4515441236	-2.9347362257
H	-2.4347915164	4.6285730819	-3.9511832796
H	-3.3492637528	5.3455116372	-2.6182087356
H	-3.5173697873	3.6248702876	-2.9863902061
C	2.0789107455	2.8793238657	-0.0598196182
H	2.1925281957	3.7749049332	-0.6863011903
H	1.4462049819	3.1985709486	0.778832176
C	5.0758591387	2.521044648	-0.8028810684
H	4.8761316476	1.7630620765	-1.5652761031
H	6.0836000011	2.3440193808	-0.4125673225
H	5.0821377919	3.4957017308	-1.3012868334
C	4.3351116326	3.7355229169	1.9046081464
H	4.3290577237	4.7527922435	1.500374145
H	5.347177213	3.5306752136	2.2708049101
H	3.6607485805	3.7266799307	2.7677824284
C	3.8967938117	0.7634468641	1.4101026048
H	3.1881996978	0.6773244765	2.2401658691
H	4.9034908344	0.5921882927	1.8071589954
H	3.6738704788	-0.029265412	0.6909599815
C	2.0540852524	0.1390599294	-2.1270978533
H	3.0016803864	0.6469328051	-2.3557613445
H	2.3256903572	-0.626727876	-1.3862319873
C	1.4611557343	0.5278392764	-5.148995746
H	0.7007233119	1.2943899917	-4.9792710377
H	1.2241476753	0.0237373787	-6.0916556842
H	2.4219965831	1.0364326488	-5.2784974647
C	2.7768696971	-2.0639853077	-4.1910486224
H	3.7819157487	-1.6487994184	-4.3185061263
H	2.5008902668	-2.5581745367	-5.1288990357
H	2.8391734194	-2.8379415059	-3.4178466298
C	-0.1652174112	-1.5517151196	-3.5760349563
H	-0.173584126	-2.3317023583	-2.8071538469
H	-0.4372022496	-2.0297901596	-4.5229800629
H	-0.9554208037	-0.8384324034	-3.3270478038

3. Model II_{CF3}

Ga	1.5378564177	1.9758338714	-0.2056220116
Si	1.9457843917	0.779283312	2.921862596
Si	4.6066372797	2.7536406628	-1.3319589057
Si	-0.4656087638	4.6406611592	-0.9831524847
F	-3.2533940514	0.4917065203	-1.2842364489
F	-2.3754753302	-1.3775669018	-0.5829001001
F	-1.7077622918	0.514345642	0.2399004106
O	0.0113869869	0.5922756561	-1.7284525053
C	1.8022208918	0.4516213509	1.0743508957
C	2.4332206572	-0.8139552456	3.8285649429
H	1.6857304815	-1.5975426076	3.669193246
H	2.5211133878	-0.650455842	4.9078355892
H	3.3949012293	-1.1961958526	3.4717417113
C	0.2915870414	1.3735529949	3.6255970105
H	-0.0084888886	2.335142868	3.2002549096
H	0.3506476663	1.4949655176	4.7121236852
H	-0.5069989053	0.6553020413	3.4152388697
C	3.2635256052	2.0904314941	3.2966533325
H	4.2483309602	1.7954207611	2.9213501408
H	3.3589676308	2.2486924646	4.3756875703
H	3.0136203425	3.0570617105	2.8476291203
C	2.8527855585	2.1770099468	-1.703268042
C	5.5502789096	1.4142972779	-0.3816562271
H	5.0725474378	1.1813710726	0.573970504
H	6.5758653109	1.7330822075	-0.1699964993
H	5.605936339	0.4854233951	-0.958258841
C	5.5381664605	3.0940772368	-2.9483214646
H	5.5768058971	2.200449313	-3.5793294033
H	6.5691539264	3.4094694274	-2.756909197
H	5.0515105865	3.8857058672	-3.5267782612
C	4.6076154532	4.3472559015	-0.30819639
H	4.0568513031	5.1457671756	-0.8141307977
H	5.628310947	4.7053918747	-0.13983525
H	4.148824386	4.1992166441	0.674414164
C	0.2355215895	3.4271870944	0.2702924055
C	-1.7169380843	5.7856748415	-0.1348054299
H	-2.5494740699	5.2167895447	0.2911581804
H	-2.1372653764	6.5128517263	-0.8373615587
H	-1.2505211579	6.3455833545	0.6819515122
C	-1.3641836134	3.7493562404	-2.3946005921
H	-0.6809396891	3.124801559	-2.9771996932
H	-1.8194318546	4.4707676909	-3.0805686057
H	-2.1667637636	3.108178964	-2.0167902224
C	0.9018021641	5.7189380168	-1.727302783
H	1.4560084825	6.2505249051	-0.9474917164
H	0.4823149012	6.4708011081	-2.4034025698
H	1.6212049917	5.1252247726	-2.2976555916
C	-1.0183214878	0.0051215563	-1.9913661552

C	-1.2898955471	-0.6078599999	-3.3066318953
C	-2.4645268415	-1.32160422	-3.5965229058
H	-3.2317222268	-1.455837563	-2.8474150967
C	-2.6485633123	-1.8686186898	-4.8608780945
H	-3.5550042778	-2.4200819304	-5.079399022
C	-1.671952655	-1.7101270365	-5.8419530906
H	-1.8215439968	-2.1382236488	-6.8266314007
C	-0.5016446139	-1.0019078212	-5.5614019831
H	0.2561548127	-0.8785105076	-6.3258693341
C	-0.3095790378	-0.4547429268	-4.3024969621
H	0.5901658792	0.0988323916	-4.0662081411
C	-2.1060242358	-0.092427455	-0.879344113
H	0.9416503204	-0.2150305689	0.936919198
H	2.6818476262	-0.110702366	0.7392014361
H	2.9299572479	1.1881919869	-2.1737615491
H	2.4178120877	2.8469694007	-2.4538656318
H	0.7556297386	4.0196856494	1.0384049684
H	-0.593574161	2.9399801048	0.7961423931
H	-4.7731968403	-4.60526413	4.0918043663
C	-4.5795670709	-3.5494579986	4.2950824145
C	-3.9286382583	-2.878706978	3.0716839792
H	-5.5296767581	-3.0629094064	4.5303806148
H	-3.9423551893	-3.4834729758	5.1804775866
N	-2.6508402374	-3.5796283907	2.7659396027
C	-4.8723097794	-2.9775228519	1.8679185382
C	-3.6225658151	-1.398922437	3.3663538887
C	-2.3822124079	-4.2235229548	1.5921768293
C	-1.5849405425	-3.6510652055	3.6607514807
H	-4.4310569368	-2.5169260242	0.9844113512
H	-5.8063935152	-2.4635378213	2.1123722647
H	-5.0893371663	-4.0165915796	1.6207835175
H	-2.9721320889	-1.2837425761	4.2368229618
H	-4.5493704692	-0.8559232338	3.5687234898
H	-3.1300195988	-0.9343185567	2.5094355404
N	-1.1123033898	-4.6894778127	1.7821914228
C	-0.6124339671	-4.3559883092	3.0397222958
H	-1.5897921588	-3.2063864343	4.6410405452
C	-0.3653549032	-5.5132520861	0.7922168148
H	0.3662657822	-4.6308356262	3.3933062856
C	1.0349779986	-4.9076062754	0.5877744664
C	-1.1179828982	-5.5161257628	-0.5434657919
C	-0.2559010773	-6.950921303	1.3326064616
H	0.9604280994	-3.8684528998	0.259150585
H	1.5756828059	-5.4725830778	-0.1756121888
H	1.632718723	-4.9335615573	1.501761333
H	-1.2244843167	-4.5028760576	-0.9333402932
H	-2.1199614965	-5.9277392379	-0.430896905
H	-0.5560508625	-6.1189198056	-1.2626513673
H	0.2838518663	-7.5845431024	0.6236906769
H	-1.2512239741	-7.3737990193	1.4867527151

H	0.2786363571	-6.9796829189	2.2856186789
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4. Model III_{CF3}

Ga	-0.0274884736	0.7386307566	-1.4096940253
Si	3.3032722503	0.07252289	-1.9602506793
Si	-1.3482342634	-0.4444408599	-4.3706561901
Si	-0.8768716902	4.0761211346	-1.6452799811
F	-0.2852728282	2.5509764344	1.8329193517
F	0.588333482	1.3803394388	3.4362889352
F	1.4669536369	1.3318050993	1.4546183107
O	-0.9619188371	0.2709203252	0.3664695375
N	1.5904723837	-2.5999443085	2.7452404612
N	-0.3427797489	-2.4480786642	1.7118639044
C	0.6150328442	-3.2789595735	2.1459027462
H	0.601803996	-4.3420471995	2.020019907
C	0.0529781762	-1.1347762608	2.0410542353
C	1.2490440689	-1.2662015184	2.6900803663
H	1.8786479015	-0.5052693793	3.1070492523
C	2.8537886982	-3.1472627938	3.351283103
C	4.041035365	-2.5672406304	2.5665369962
H	3.9858615138	-2.8432803727	1.5116109294
H	4.9747193275	-2.9568774602	2.977614322
H	4.0742768102	-1.4783851463	2.6313464819
C	2.8963389848	-2.7173284483	4.8259136538
H	2.9176571886	-1.6311671672	4.9302323074
H	3.7997574902	-3.1141816451	5.2934046274
H	2.0301741486	-3.0993062408	5.370954375
C	2.8479403526	-4.6763093122	3.2489362933
H	2.0072029441	-5.1188947138	3.7892916895
H	3.7651417852	-5.0571873221	3.6999621818
H	2.8295847061	-5.016486315	2.2108410212
C	-1.4971509436	-3.0374423684	0.8764956745
C	-0.9826140963	-3.1688970011	-0.5617384414
H	-1.7719057874	-3.589806585	-1.188577398
H	-0.1144594708	-3.8314285243	-0.6177779263
H	-0.7057686431	-2.1953925368	-0.9602121055
C	-1.8522549362	-4.4185353725	1.460511996
H	-2.7484827946	-4.7751997736	0.9513679405
H	-2.0771347692	-4.3572806402	2.5280894956
H	-1.0813211447	-5.175256405	1.2964541863
C	-2.7450074702	-2.15956672	0.9289493682
H	-2.5511675401	-1.1828072681	0.4932187322
H	-3.1170127664	-2.0437372448	1.9474993707
H	-3.5188079624	-2.6568924592	0.339353472
C	1.6215022124	-0.491028473	-1.3569590851
C	4.5471661678	-1.371990339	-1.8882202876
H	4.6690103515	-1.7396156546	-0.8630226775
H	5.5374493082	-1.0732409217	-2.248708008

H	4.212055175	-2.2143356246	-2.5024796757
C	4.010526412	1.4609988045	-0.8810038667
H	3.3913627375	2.3599054349	-0.9316724785
H	5.0224400558	1.7293180187	-1.2022512525
H	4.064090721	1.1610435878	0.1704596465
C	3.2676051112	0.6686644145	-3.7587656019
H	2.8806106731	-0.1042822071	-4.4300252433
H	4.2729565126	0.9315010838	-4.1039693133
H	2.6370064507	1.5543677856	-3.8764258117
C	-1.5681418628	0.1424288687	-2.6048665551
C	-0.3377384497	-2.0520393549	-4.457221627
H	0.6814305523	-1.9088540813	-4.08844399
H	-0.2701884828	-2.41250657	-5.4890380779
H	-0.7990458437	-2.847001803	-3.861853351
C	-3.0388028163	-0.8197103157	-5.158750161
H	-3.5767976732	-1.5896221778	-4.5956150766
H	-2.9360625959	-1.1731925519	-6.1904801701
H	-3.6711751416	0.0738107786	-5.176280977
C	-0.493779875	0.8418163317	-5.4672070938
H	-1.0727665902	1.7682291365	-5.5185268867
H	-0.379898255	0.4663149	-6.4896575255
H	0.5020855991	1.096735628	-5.0955347894
C	0.4019813374	2.7234612789	-1.4207118239
C	-0.144636934	5.7545106468	-1.1329110832
H	0.1453803968	5.7497705205	-0.0770831533
H	-0.8604252976	6.5709262166	-1.2775257381
H	0.7507895697	5.9890850597	-1.7175994696
C	-2.4492215981	3.8177668803	-0.6173590709
H	-2.9693882065	2.9022922477	-0.9147681491
H	-3.1425182439	4.6544424973	-0.7548959857
H	-2.2215867563	3.7427147305	0.4489171587
C	-1.4078419247	4.2218901185	-3.4612614543
H	-0.5483546772	4.3874670071	-4.118515744
H	-2.0969935329	5.0616988058	-3.5990513492
H	-1.9159016539	3.316865703	-3.8053179351
C	-0.6747339633	0.1903581535	1.688741104
C	-1.9351635009	0.3710503077	2.5882985592
C	-1.9941888174	-0.0819366732	3.9083447628
H	-1.1465097418	-0.5940243921	4.3491487966
C	-3.1393823959	0.1205182704	4.6770655345
H	-3.1727437023	-0.2405725208	5.6993004406
C	-4.2343491763	0.7898611668	4.1360466731
H	-5.1253825659	0.9497232049	4.7329434052
C	-4.1740663091	1.2563821099	2.8241013512
H	-5.0182901655	1.7850319457	2.3955558226
C	-3.0322382438	1.0475998374	2.0553721854
H	-2.9773983593	1.3915580662	1.0318215739
C	0.2806213931	1.3728431464	2.1042708025
H	1.7459669085	-0.7723499179	-0.3032443764
H	1.3658751158	-1.4163878877	-1.8883695379

H	-2.0931909233	-0.6536380375	-2.0611536699
H	-2.2712837888	0.9856716143	-2.6242177955
H	1.1304555691	2.8477406402	-2.2353637042
H	0.9618708732	2.9330547416	-0.5031688631

5. Model II_H

Ga	1.099209068	-0.1800694082	-0.4538073148
Si	2.870210793	-2.8194938931	0.8269318049
Si	1.8139805471	2.8830814825	0.8477612396
Si	1.989336639	-0.2483027978	-3.760433853
O	-0.6857620239	0.258662169	0.3595086873
N	-3.8711124008	0.8682979423	0.376331475
N	-3.3153758517	-0.3619363448	2.1037305646
C	-2.9797284356	-0.0544502255	0.823179362
C	-4.7700738713	1.1382995312	1.3911026222
H	-5.5754035695	1.8384278183	1.289112451
C	-4.4270744645	0.3801121894	2.4558073471
H	-4.8884222444	0.3210454841	3.4215648314
C	-2.6359483079	-1.3539329524	3.0431399787
C	-3.3345683502	-1.2944799714	4.4112515786
H	-3.2781662246	-0.3001746575	4.8591966916
H	-2.8113685419	-1.9805930863	5.0784958212
H	-4.3782923524	-1.6153136777	4.3654815058
C	-2.8090474124	-2.7763151089	2.4820533236
H	-3.8652814122	-2.9995504416	2.3106683842
H	-2.4252389016	-3.4925477611	3.2116102623
H	-2.2646251154	-2.9332720358	1.5528115629
C	-1.1647955424	-0.9570152688	3.2282663137
H	-0.623804039	-0.8657872097	2.2889061191
H	-0.6751481588	-1.7051443847	3.8558671797
H	-1.0968165653	0.0102484323	3.7316794272
C	-3.9373800552	1.5184097098	-1.0007333195
C	-5.0575555595	2.5710823478	-0.9956502574
H	-6.0473364235	2.1330472668	-0.8449371031
H	-5.0607245892	3.054750001	-1.9732685788
H	-4.8858596068	3.3486223362	-0.2483497159
C	-2.6074599657	2.2256105599	-1.2963240127
H	-2.4545642368	3.0474245896	-0.5931214302
H	-2.6478401671	2.6419100829	-2.3055284014
H	-1.7436311982	1.5698474904	-1.2188216718
C	-4.2936728558	0.4456424068	-2.0449583312
H	-3.5039466735	-0.291336007	-2.1790585877
H	-4.4567738986	0.9304164439	-3.0098474797
H	-5.2135065501	-0.0749388867	-1.76639277
C	1.316949418	-2.1704876285	0.0052134956
C	2.9369475247	-2.2932436855	2.6508664973
H	2.9448184322	-1.2051348668	2.7582033693
H	3.8358871399	-2.6822044844	3.1401842452

H	2.0714979443	-2.6751282329	3.20316125
C	2.9055917154	-4.7218709973	0.7990979301
H	2.0269050597	-5.1414215018	1.3004350914
H	3.7948692519	-5.1193256099	1.3002333
H	2.9075312502	-5.1014670511	-0.2279307924
C	4.4512543637	-2.2156574983	-0.0258249717
H	4.4715937555	-2.5019073654	-1.0820894829
H	5.3405858102	-2.6453286512	0.4470484881
H	4.5393116603	-1.126955955	0.0250125707
C	2.3537318808	1.13771196	0.4442461064
C	3.2772492626	3.9129947703	1.4947448447
H	3.7085786422	3.464723239	2.3958222718
H	2.9743836761	4.9357141438	1.7454479837
H	4.0761208579	3.977547953	0.7487335228
C	1.1437529186	3.7896797879	-0.6796015803
H	1.894763447	3.8305367355	-1.4750231077
H	0.865336717	4.820666527	-0.4360624294
H	0.2618676751	3.2886274849	-1.0866921754
C	0.4747162456	2.8926574164	2.1913156499
H	-0.3692787908	2.274405299	1.8755795832
H	0.1193300135	3.9077225228	2.3991525806
H	0.8624077866	2.479864345	3.1290037482
C	0.7253181094	0.1468434248	-2.4376703831
C	2.2827421292	-2.1178452575	-3.8988941736
H	2.6817432165	-2.5339439892	-2.9699733331
H	2.9944061612	-2.3467077846	-4.6989821255
H	1.3518755188	-2.6487708318	-4.1244522028
C	3.6503108794	0.601087831	-3.4240313683
H	3.525948263	1.6836489615	-3.3191050496
H	4.3562226896	0.4272758489	-4.2428925694
H	4.1125769035	0.2325921876	-2.50393037
C	1.388251018	0.3469246201	-5.4655299401
H	0.4365451343	-0.1233044696	-5.7349507584
H	2.1095065875	0.1111484862	-6.2555666882
H	1.2324421786	1.4308112652	-5.472245251
C	-1.7567448293	-0.5537815531	0.0723401784
H	0.4799767639	-2.457203927	0.6585692732
H	1.1621223179	-2.7265767334	-0.9282935518
H	3.2354536514	1.2060133139	-0.2076990862
H	2.7121185463	0.6822125591	1.3763538723
H	-0.188672628	-0.4094356819	-2.695200376
H	0.4700812934	1.2108938307	-2.5314565769
H	-2.0116127221	-0.5848879564	-0.9968141046
H	-1.6004474862	-1.6053038214	0.3518033406

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Ga	0.0182339213	1.4178525069	1.0592270698
Si	-0.0464987269	1.0864828149	4.4634237184

Si	3.0575394482	1.4766823783	-0.5477659616
Si	-2.5490292883	3.2358567408	-0.3734696769
O	-0.4238702794	-0.4771886346	0.6996203607
N	-0.3407101073	-2.8113176053	-3.1286310972
N	-0.2237449107	-3.0760483896	-0.9545115793
C	0.1030571202	-3.5977106878	-2.1450368605
H	0.6430480506	-4.5114397894	-2.2893628745
C	-0.9078269019	-1.8750972319	-1.1819765698
C	-0.9729563873	-1.7330436076	-2.5368451155
H	-1.4051507829	-0.9311066455	-3.1073775303
C	0.2265217922	-3.6911095599	0.3661376425
C	0.4962217848	-5.1877779954	0.1439397508
H	0.7367609835	-5.6328360489	1.1101697266
H	1.3544057056	-5.3731380429	-0.50733578
H	-0.3793975544	-5.708320441	-0.2538658766
C	1.5081403172	-2.9682668306	0.8043329595
H	1.8424074703	-3.3785603734	1.7603937693
H	1.302430861	-1.9043432252	0.9237670072
H	2.3078897433	-3.1120094051	0.072228856
C	-0.8817653374	-3.5258574501	1.4128265802
H	-1.8341081736	-3.9248549404	1.053859734
H	-0.9897773714	-2.4812343476	1.6980688698
H	-0.5949986276	-4.0874821487	2.3041412312
C	-0.1752267371	-3.0194249318	-4.6077017276
C	0.6152645144	-4.3084093123	-4.8585580246
H	1.6185408802	-4.2614781578	-4.4281953385
H	0.727070048	-4.4437361454	-5.9352519527
H	0.0973740443	-5.1891219014	-4.4702129
C	0.5915937328	-1.8125458099	-5.1713523239
H	0.0370545804	-0.8826863642	-5.0346192447
H	0.7522270653	-1.9518510029	-6.2424438658
H	1.5622209086	-1.7027133802	-4.683863716
C	-1.5760726141	-3.130088621	-5.2305804131
H	-2.1274457539	-3.9726509703	-4.8070484144
H	-1.4857666154	-3.2842822806	-6.3078066709
H	-2.1600748526	-2.2218535337	-5.0712343785
C	-1.4196415845	-0.8863409246	-0.1534340987
H	-1.8577591439	-0.0709990433	-0.7505575918
C	-0.7668149359	1.8170920503	2.9009142698
H	-0.7474893584	2.9104009861	3.0143825683
H	-1.8302786956	1.5453423297	2.8536505012
C	0.1221028295	-0.8025312207	4.3613093831
H	-0.8473577813	-1.2722996779	4.166832222
H	0.5129264769	-1.2161151328	5.2972040248
H	0.7965540285	-1.0921722684	3.5511168482
C	1.6657884671	1.8093407424	4.8444647333
H	2.3873864121	1.566534452	4.060092957
H	2.0555543583	1.4237288817	5.7925660983
H	1.6224432209	2.9004855889	4.9255144689
C	-1.1553563077	1.4582535446	5.9655761966

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H	-1.2729668931	2.5372213423	6.1099167997
H	-0.7404559757	1.042804247	6.8906156308
H	-2.1570338582	1.036207179	5.8321581183
C	2.0639774695	1.4010328073	1.0295594479
H	2.3859021281	2.2449846364	1.6555397267
H	2.3594535885	0.4995857205	1.5840295386
C	2.9415757417	3.1800157818	-1.3742110335
H	1.9197822679	3.4021603209	-1.6932414845
H	3.5890978481	3.238231815	-2.2556321789
H	3.2515220244	3.9723476721	-0.6851819406
C	4.9026571244	1.1368886331	-0.2238054438
H	5.3162838553	1.8681531234	0.478051758
H	5.4968937449	1.1863529878	-1.1430845282
H	5.0513310252	0.1450200923	0.2163368468
C	2.499063415	0.1805886695	-1.8280875201
H	2.576458388	-0.8311041109	-1.4172686562
H	3.1219599952	0.2294321427	-2.7282069437
H	1.4584891568	0.3444926301	-2.1208529663
C	-0.8346400587	2.4921854967	-0.4719261956
H	-0.1449371869	3.3339982233	-0.6246747843
H	-0.7502068466	1.8921948064	-1.3896177156
C	-2.6050222689	4.6399338724	0.8974815279
H	-2.409994972	4.2690720312	1.9070173914
H	-3.5841105519	5.1302561931	0.9033142745
H	-1.8536211126	5.4043072683	0.6743106434
C	-3.0708973131	3.9679978914	-2.0529678279
H	-2.3674011925	4.740207083	-2.380533667
H	-4.0663293301	4.4229728188	-2.0068500121
H	-3.0956713821	3.1976261002	-2.8316865796
C	-3.8848758833	1.9675798118	0.097785954
H	-3.9689148096	1.1668697106	-0.6447697911
H	-4.8665402657	2.4478562031	0.1690955647
H	-3.6715609185	1.503080711	1.0647746758
H	-2.2745909881	-1.3504323758	0.3729193518