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# (1,4)-Cycloaddition and C–X bond activation reactions of monovalent group 13 diyls†

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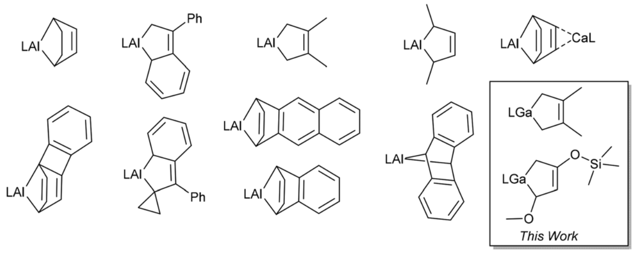
Monovalent group 13 diyls of the type LM (L = HC[C(Me)NAr]$_2$; Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$) are group 13 analogues of NHCs. While LAl is known to undergo (1,4)-cycloaddition with a variety of dienes including arenes, LGa only reacted with acyclic dienes, *i.e.*, butadiene and Danishefsky's diene, *via* (1,4)-cycloaddition to give LGa(C$_6$H$_{10}$) (**1**) and LGa(C$_8$H$_{16}$O$_2$Si) (**2**), whereas LIn completely failed to react with these substrates. However, LGa and LIn both reacted with the electron-poor hexachlorobutadiene with oxidative addition of the allyl C–Cl bond to give L(Cl)M(C$_4$Cl$_5$) (M = Ga **3**; In **4**). Similarly, L(X)MR (X = Cl, R = Bn, M = Ga **5**, In **6**; X = Br; R = Et, M = Ga **7**, In **8**) were obtained from oxidative addition with alkyl halides. Compounds **3–8** did not react with benzaldehyde, whereas the cation [LGaCH$_2$Ph]$^+$ (**10**), obtained by reaction of L(Cl)GaBn with AgOTf and NaB(C$_6$F$_5$)$_4$, reacted rapidly, but no defined reaction product was identified.

The syntheses and structural characterization of monomeric group 13 diyls LM (Al,[1] Ga,[2,3] In,[4] Tl[5]) stabilized by the sterically demanding, *N*,*N*‘-chelating β-diketiminate substituent (L = HC[C(Me)NAr]$_2$; Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$) represent milestones in low-valent main group element chemistry. These monovalent carbenoidic compounds, in which the metal centers adopt the oxidation state +1, are highly reactive toward a wide range of substrates.[6–11] In particular, their potential to activate small molecules in oxidative addition reactions has raised tremendous interest since such reactions are typically a domain of transition metal complexes.

The transition metal-like behaviour of group 13 diyls results from the presence of an energetically high-lying donor orbital (HOMO) and a low lying acceptor orbital (LUMO).[6–11,12] The HOMO–LUMO energy gap was found to increase with increasing atomic number of the group 13 element resulting from a more stabilised HOMO (lower in energy) and a destabilized LUMO (higher in energy).[13] As a consequence, both alanediyl LAl and gallanediyl LGa are far more reactive than indanediyl LIn.

The ability of both LAl and LGa to undergo oxidative addition reactions was demonstrated in several reactions with compounds containing E–H bonds (Al: E = H, Si, B, Al, C, N, P, O;[14] Ga: H, Sn, O, N, P, Sb, Bi[15]) and C–F bonds (Al,[16] Ga[17]), respectively. Moreover, insertion reactions of LM (M = Al, Ga, In) into E–E bonds of group 15[18] and 16[19] elements, which represent oxidative addition reactions to the group 13 diyl, and the synthesis of metallapnictenes LMPnM(X)L with M–Pn double bonds,[20,21] dipnictenes [L(X)MPn]$_2$ with Pn–Pn double bonds,[22] and pnictogen-centered radicals [L(X)M]$_2$Pn$^{\bullet}$[21,23] (M = Al, Ga, In; Pn = P, As, Sb, Bi) by reactions of LM with PnX$_3$ (Pn = halide, NR$_2$, OR) have been reported. Interestingly, the activity of a homobimetallic β-diketiminate Ga(I) compound for bond activation reactions was found to be even larger compared to that of monometallic LGa, indicating a beneficial cooperative effect of the two Ga(I) centers.[17,24]

While bond activation reactions have been reported, (1,4)-cycloaddition reactions of neutral group 13 diyls are rather unexplored and to the best of our knowledge limited to reactions of LAl with conjugated C–C double bond systems including (substituted) butadienes (Scheme 1),[25] whereas (1,4)-cyclo-



Scheme 1 Structurally characterized (1,4)-cycloaddition products of alanediyl LAl with conjugated organic π-systems.

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† Electronic supplementary information (ESI) available: $^1$H and $^{13}$C NMR as well as IR spectra and crystallographic details. CCDC 2387776–2387779, 2387895, 2387899 and 2387923. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d5qi00660k

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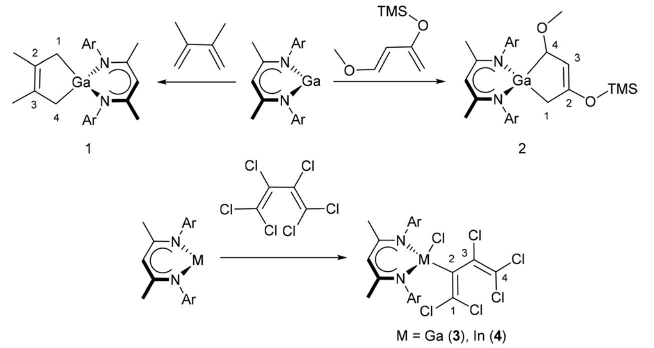
addition reactions with LGa and LIn were only reported for heteroatomic diene systems, *i.e.* $\alpha$-diketones.[26] (1,4)-cycloaddition reactions of LAl were also observed with benzaldehyde derivatives, and as-formed products were used in cross-coupling reactions with unsaturated substrates.[27]

We herein report on systematic reactivity studies of group 13 diyls with different dienes as well as on oxidative addition reactions with alkyl and aryl halides.

## Results and discussion

LGa reacted with both 2,3-dimethylbutadiene and (*E*)-1-methoxy-3-trimethylsilyloxy-1,3-butadien (Danishefsky's diene[28]) at elevated temperature (80–90 °C) in good yields to compounds **1** (64%) and **2** (54%) (Scheme 2), whereas any attempts to react these diyls with cyclic dienes, *i.e.* 1,3-cylohexadiene, 1,3-cyclooctadiene, 1,3,5-cycloheptatriene, 1,3,5,7-cyclooctatetraene, failed. In marked contrast, the corresponding alanediyl LAl was found to react also with aromatic dienes at ambient temperature,[25c,d] whereas LIn did not react with any of these dienes. Since Ga and Al have almost identical covalent radii,[29] steric effects cannot be responsible for the lower reactivity of LGa compared to LAl but rather their different frontier orbital energies. Interestingly, neutral LGa as well as the charged gallanediyl species [(dpp-bian)Ga]$^+$ (dpp-bian = *N*-protonated 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) and [Ga(PDI$^{dipp}$)]$^-$ (PDI = 2,6-(2,6-$^i$Pr$_2$C$_6$H$_3$NCMe)$_2$-C$_5$H$_3$N) also show different reactivities towards the diene. While the cycloaddition reaction with 2,3-dimethyl-1,3-butadiene and [Ga(PDIdipp)]$^-$, similar to that of LGa, required a reaction time of one day at 80 °C, the reaction with [(dpp-bian)Ga]$^+$ was almost instantaneous at ambient temperature.[30]

As the cationic Ga(I) species reacts rapidly with electron-rich dienes in contrast to the neutral and anionic species, we became interested to investigate how the latter react with electron-poor dienes. However, both LGa and LIn both reacted with the electron-poor hexachlorobutadiene at room temperature selectively with oxidative addition of the secondary C–Cl bond to give compounds **3** (51%) and **4** (40%), respectively. Neglecting the fact that the primary chlorine atoms are less sterically constrained, the insertion should statistically occur in a two-to-one ratio at the primary C centre. However, the chlorine atoms at the secondary carbon atom are of allylic nature, which weakens the Cl–C bond. Consequently, this stabilizes both ionic and radical intermediate and transition states, thereby activating the bond for the oxidative addition with group 13 diene. The selectivity toward the formation of compound **3** is likely higher than the isolated yield suggest, and hence no other reaction products were isolated (see Fig. S30†).



**Scheme 2** Synthesis of compounds **1–4** by (1,4) cycloaddition and oxidative addition reactions of substituted butadienes with gallanediyl and indanediyl (TMS = SiMe$_3$).

Compounds **1–4** show the expected resonances in their $^1$H and $^{13}$C NMR spectra including the characteristic singlets for the $\gamma$-H proton (approx. 5 ppm) and the symmetrically equivalent Me groups of the $\beta$-diketiminate ligand (1.5–2 ppm) as well as sets of doublets (0.5–2 ppm) and septets (2.5–4.5 ppm) for the $^i$Pr groups of the aryl groups (Table S1†). The $^{13}$C NMR spectra also clearly prove the formation of the cycloaddition products due to characteristic resonances for an unsaturated GaC$_4$ heterocycle (Table 1), with the deshielded C centers at the double bond and the shielded C centers proximal to the heteroatom. Unfortunately, due to the absence of protium in **3** and **4**, the detection and assignment of the diene by $^{13}$C NMR spectroscopy was difficult, and the proximal carbon atom for **3** and **4** could not be observed.

Oxidative addition reactions of C–X bonds to group 13 diyls have been frequently reported for LGa, which was shown to react with several chloromethanes and -silanes as well as bromoalkanes.[31,32] In contrast, LIn is less reactive, and so far only C–Br and C–I bond activation reactions with bromo- and iodoalkyls were reported, respectively.[33] We therefore became interested in expanding our studies to reactions of LM with alkyl/aryl halides.

LGa and LIn reacted with benzylchloride (BnCl) and EtBr with C–X bond activation (X = Cl, Br) and formation of L(X)MR (M = Ga, In; X = Cl, Br; R = Et, Bn, **5–8**, Scheme 3) in good yields (**5** 91%, **6** 61%, **7** 90%,[31] **8** 85%). Unlike the cycloaddition reactions **1** and **2**, which required elevated temperatures or did not react at all in the case of LIn, this oxidative addition proceeds readily at ambient temperature. Hence, the cycloaddition reaction of LGa with hexachlorobutadiene seems to be thermodynamically and kinetically favored.

Compounds **5–8** show the expected resonances of the L ligand and the alkyl/aryl groups in the $^1$H and $^{13}$C NMR spectra (Table S1†). Due to the electropositive nature of the group 13 metal, the resonances of the metal-bound CH$_x$ group

**Table 1** Selected $^{13}$C NMR chemical shifts $\delta$ [ppm] of the GaC$_4$ ring (Scheme 2) of **3–6**

| Scheme 2 | C$^1$ | C$^2$ | C$^3$ | C$^4$ |
|---|---|---|---|---|
| **1** | 20.5 | 132.7 | 132.7 | 20.5 |
| **2** | 15.6 | 158.5 | 112.8 | 80.0 |
| **3** | Not obs. | 115–135 ppm | | |
| **4** | Not obs. | 115–135 ppm | | |

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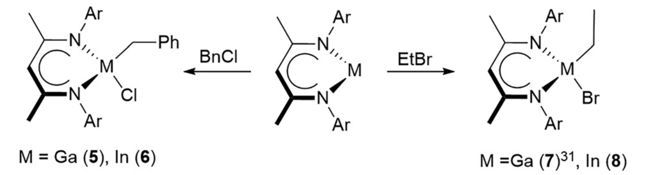
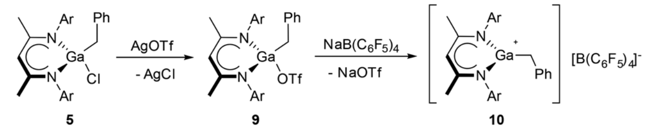


**Scheme 3** C–X bond activation reactions of LM (M = Ga, In).

are found at a higher field (**5** $\delta$ 1.94 (19.2), **6** 2.15 (19.9), **7** 0.47 (3.5), **8** 0.67 (5.7) ppm, C in parenthesis) compared to the starting substrate.

Due to the diagonal relationship of Ga and Mg and the use of benzyl Grignard reagents as benzyl transfer reagents in organic synthesis, we became furthermore interested in reactions of **5** and **6** with benzaldehyde. Unfortunately, no reaction was observed even under drastic reaction conditions. For instance, **5** did not react even at high temperatures of up to 115 °C in toluene-d$_8$ solution within 4 h and **6** failed to react at 60 °C over a period of one day. These findings point to either a less nucleophilic benzyl group in **5** and **6** or indicate a larger steric hindrance of **5** and **6** compared to benzyl Grignard reagents. We therefore became interested in the synthesis of the corresponding tricoordinate LGaR$^+$ cation, which was expected to show a higher reactivity compared to the neutral counterpart. Since the Cl-abstraction reaction of **5** with NaB(C$_6$F$_5$)$_4$ failed, we reacted **7** with Ag(OTf) to give the triflate-substituted compound L(TfO)GaCH$_2$Ph (**9**), which then reacted with NaB(C$_6$F$_5$)$_4$ to [LGaCH$_2$Ph][B(C$_6$F$_5$)$_4$] (**10**) containing the cation [LGaCH$_2$Ph]$^+$ (**10**$^+$) as well as several by-products (Scheme 4). Salt **10** was difficult to isolate and only a very few crystals were hand-picked for sc-XRD analysis. The addition of benzaldehyde to *in situ* formed **10** resulted in a colour change of the solution from colourless to yellow indicating a fast reaction. However, we were not able to isolate any product from this reaction mixture.



**Scheme 4** Synthesis of compounds **9** and **10**.

Compounds **1–8** are stable in the solid-state and benzene solutions at ambient temperature under an inert gas atmosphere. They were characterized by IR and heteronuclear ($^1$H, $^{13}$C) NMR spectroscopy, whereas **9** and **10** were only prepared in NMR-scale reactions and characterized by *in situ* $^1$H NMR spectroscopy. Table S1† summarizes selected resonances of the $^1$H and $^{13}$C NMR spectra of **1–10**. The $^1$H NMR resonances of the β-diketiminate ligand of the products **1–10** are shielded compared to the parent group 13 diyls.

## Structural characterisation

Suitable single crystals of compounds **1–6** and **10** were formed upon recrystallization from the solvent in which the reaction was performed or from either *n*-hexane or *n*-pentane (see experimental details), respectively. Compounds **1**, **5**, **6**, and **10** crystallize in triclinic space groups, compound **4** in a monoclinic space group, and compounds **2** and **3** in orthorhombic space groups (Table S2†). The structure of compound **7** has been reported previously.[31] Owing to very similar bond radii of Ga and Al,[29] LGa(C$_6$H$_{10}$) (**1**) and LAl(C$_6$H$_{10}$)[25f] crystallize in an isomorphic crystal structure with almost identical cell data. Selected molecular structures (LGa(C$_6$H$_{10}$) **1**, L(Cl)Ga(CH$_2$C$_6$H$_5$) **5**, [LGa(CH$_2$C$_6$H$_5$)]$^+$ **10**$^+$) are shown in Fig. 1 and those of all other compounds in Fig. S31–S37.† Table 2 summarizes selected bond lengths and angles.

The β-diketiminate N–M bond lengths are inverse to the positive charge at the group 13 center. The M–N bond lengths of all compounds are much shorter compared to the starting diyls LM, whereas the M–N bond length observed in cation **10**$^+$ is even shorter compared to neutral tetra-coordinated compounds. The differences are less pronounced for compounds **1–7**, but the shortest M–N bond was found for compounds **3**

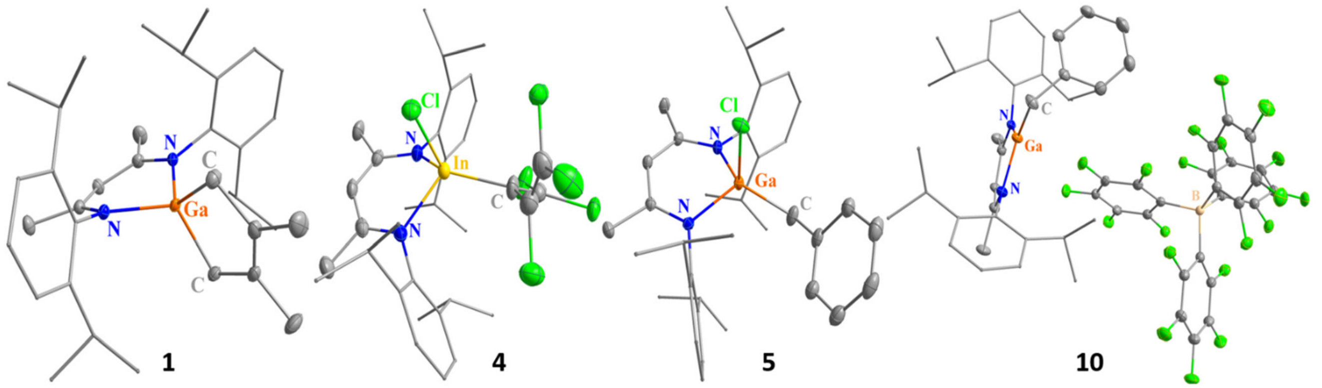


**Fig. 1** Molecular structure of LGa(C$_6$H$_{10}$) (**1**), L(Cl)In(C$_4$Cl$_5$) (**4**), L(Cl)Ga(CH$_2$C$_6$H$_5$) (**5**) and [LGa(CH$_2$C$_6$H$_5$)]$^+$ (**10**) in the crystal. H atoms are omitted for clarity and displacement ellipsoids are drawn at the 50% probability level. The 2,6-diisopropylphenyl groups are displayed as a wireframe.

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**Table 2** Selection of bond length [Å] and angles [°] of **1–7** and **10**

| | M–C/X | C–M–C/X | M–N | N–M–N |
|---|---|---|---|---|
| LGa[3] | | | 2.0560(14), 2.0528(15) | 87.53(5) |
| LIn[4] | | | 2.2682(9), 2.276(3) | 81.12(10) |
| **1** | 1.9845(8), 1.9732(8) | 94.26(3) | 1.9572(6), 1.9782(6) | 95.17(3) |
| **2** | 1.993(2), 2.0189(19) | 96.40(7) | 1.9673(17), 1.9674(18) | 93.61(8) |
| **3** | 1.9842(19), 2.1823(5) | 103.31(5) | 1.9231(10), 1.9232(10) | 99.76(6) |
| **4** | 2.169(4), 2.3828(8) | 110.60(12) | 2.117(3), 2.144(4) | 90.03(11) |
| **5** | 1.9643(9), 2.2154(3) | 114.71(3) | 1.9447(7), 1.9330(7) | 96.58(3) |
| **6** | 2.1542(15), 2.3887(4) | 118.41(5) | 2.1372(11), 2.1338(12) | 89.73(5) |
| **7**[31] | 1.9655(16), 2.3805(2) | 113.99(5) | 1.9339(12), 1.9477(12) | 96.21(5) |
| **10** | 1.9373(14) | 359.70(6)[a] | 1.8622(11), 1.8755(11) | 101.62(5) |
| [LGaAd], [B($C_6F_5$)$_4$][34b] | 1.969(2) | 359.70(9)[a] | 1.8812(19), 1.8842(19) | 99.76(8) |

[a] Σ of bond angles.

and **4** containing the perchlorinated organic ligand. Similarly, the Ga–C bond length in the cation **10**$^+$ (1.9373(14) Å) is also shortened compared to the neutral compound **5** (1.9643(9) Å). Compared to **1**, LAl($C_6H_{10}$) has shorter M–N bonds (1.9053(16), 1.9234(15) Å) and slightly shorter M–C bonds (1.975(2), 1.9640(16) Å).[25f] This is inconsistent with the smaller sum of covalent single bond radii of Ga–N (1.95 Å) compared to Al–N (1.97 Å).[29] However, the Al–N bond lengths are also significantly shorter than the sum of the covalent radii due to an additional ionic contribution resulting from its electropositive nature (bond polarity).

Apart from the zwitterion L($^t$Bu)GaB($C_6F_5$)$_3$, [LGaAd][An] (Ad = 1-adamantyl, An = [HB($C_6F_5$)$_3$]$^-$ or [B($C_6F_5$)$_4$]$^-$) are the only reported complexes containing a tricoordinate Ga centre substituted by a β-diketiminate substituent and one additional organyl group. However in contrast to compound **10**, [LGaAd][B($C_6F_5$)$_4$] was obtained directly from the salt metathesis reaction of L(Br)GaAd with NaB($C_6F_5$)$_4$. Both complexes were used for the catalytic reduction of $CO_2$ with $Et_3SiH$, yielding $H_2C(OSiEt_3)_2$.[34]

The Ga center in the cations of compound **10** and [LGaAd][B($C_6F_5$)$_4$] are trigonal planar coordinated with the sum of bond angles of 359.87(9)° and 359.70(6)° (see Table 2). The Ga–C bond length (1.969(2) Å) of [LGaAd][B($C_6F_5$)$_4$] is elongated and the N–Ga–N bond angle (99.76(8)°) is slightly more acute compared to 1.9373(14) Å and 101.62(5)° for **10**. However, both differences are probably just a reflection of the higher steric demand of the adamantyl group compared to a benzyl group.

## Conclusions

We investigated the ability of group 13 diyls to undergo cycloaddition reaction with conjugated C=C double bond systems. In contrast to LAl, which is known to react with a variety of different dienes, we found that only LGa reacted in (1,4) cycloaddition reactions with acyclic dienes to give spiro compounds **1** and **2**, whereas LIn failed to react. However, both LGa and LIn reacted with electron poor hexachlorobutadiene selectively with oxidative addition of the allyl C–Cl bond to give compounds **3** and **4**, respectively. Oxidative addition was also observed in reactions of both group 13 diyls with BnCl and EtBr to give compounds **5–8**. Finally, [LGaCH$_2$Ph][NaB($C_6F_5$)$_4$] **10** containing the three-coordinate Ga cation [LGaCH$_2$Ph]$^+$ (**10**$^+$) was synthesized by reaction of L(TfO)GaCH$_2$Ph **9** with NaB($C_6F_5$)$_4$ and structurally characterised.

## Experimental section

### General procedures

All manipulations were carried out using standard Schlenk and glovebox techniques under a dry and $O_2$-free argon atmosphere. Toluene, diethyl ether, *n*-pentane, *n*-hexane, and $CH_2Cl_2$ (DCM) were dried using an MBraun Solvent Purification System. Benzene and deuterated benzene were freshly distilled from Na/K alloy. DCM-d$_2$ was distilled from $CaH_2$ and activated Alox. All solvents were degassed and stored over activated molecular sieves. The starting reagents LGa,[2,35] LIn (LK was isolated),[4] Na[B($C_6F_5$)$_4$],[36] and L(Br)Ga($CH_2CH_3$) (7)[31] were prepared according to literature methods. $^1$H (400 MHz, 600 MHz) and $^{13}$C{$^1$H} (100.7 MHz, 150.9 MHz), $^{19}$F (376.4 MHz, 564.6 MHz) NMR spectra were recorded using a Bruker Avance Neo 400 MHz or a Bruker Avance III HD 600 spectrometer and referenced to internal $C_6D_5H$ ($^1$H: $\delta$ = 7.16), $C_6D_6$ ($^{13}$C: $\delta$ = 128.06), or $CDHCl_2$ ($^1$H: $\delta$ = 5.32), $CD_2Cl_2$ ($^{13}$C: $\delta$ = 54.00) and for $^{19}$F *via* the chi-values ($\chi$). Heteronuclear NMR experiments were proton decoupled by default. The assignment was assisted by 2D-NMR experiments. IR spectra were recorded in a glovebox using a Bruker Alpha FT-IR spectrometer equipped with a single reflection ATR sampling module. Microanalyses were performed at the Elemental Analysis Laboratory of the University of Duisburg-Essen.

### Synthesis of LGa($C_6H_{10}$) (1)

2,3-Dimethylbutadiene (40.5 mg, 492 μmol) was added to a solution of LGa (200 mg, 410 μmol) in 5 ml of benzene. The resulting clear yellow solution was stirred at 80 °C for 1 h during which the colour faded. The solution was concentrated to 1 ml and layered with *n*-hexane. Small amounts of a colourless solid were removed by filtration and the filtrate was con-

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centrated to incipient crystallization (approx. 0.5 ml). Storage at ambient temperature yielded 150 mg of **1** as a colourless crystalline solid suitable for sc-XRD. **Yield**: 150 mg (263 µmol, 64%).

**Anal. calcd** for C$_{35}$H$_{51}$GaN$_2$: C, 73.81, H, 9.03; N, 4.92 wt%. Found: C, 73.0, H, 8.85; N, 4.76 wt%. **ATR-IR**: *ν* 2962, 2868, 1555, 1524, 1460, 1438, 1392, 1386, 1316, 1260, 1177, 1136, 1100, 1082, 1059, 1020, 934, 867, 798, 759, 693, 643, 630, 531, 481 cm$^{-1}$. **$^1$H NMR** (400 MHz, C$_6$D$_6$, 25 °C): *δ* 7.07 (s, 6 H, C$_6$*H*$_3$-2,6$^i$Pr$_2$), 4.74 (s, 1 H, γ-C*H*), 3.45 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 1.72 (s, 6 H, Ga(CH$_2$CC*H*$_3$)$_2$), 1.55 (s, 6 H, ArNCC*H*$_3$), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12 H CH(C*H*$_3$)$_2$), 1.12 (s, 4 H, Ga(C*H*$_2$CCH$_3$)$_2$). **$^{13}$C NMR** (100.6 MHz, C$_6$D$_6$, 25 °C): *δ* 168.8 (ArN*C*CH$_3$), 144.1, 141.6, 127.1, 124.4 (Ar*C*), 132.7 (Ga(CH$_2$*C*CH$_3$)$_2$), 95.8 (γ-*C*H), 28.5 (*C*H(CH$_3$)$_2$), 25.1, 24.8 (CH(*C*H$_3$)$_2$), 23.5 (ArNC*C*H$_3$), 21.5 (Ga(CH$_2$C*C*H$_3$)$_2$), 20.5 (Ga(*C*H$_2$CCH$_3$)$_2$).

### Synthesis of LGa(C$_8$H$_{16}$O$_2$Si) (2)

To a solution of 100 mg LGa (205 µmol) in 2 ml of toluene, 53.0 mg of Danishefsky's diene (308 µmol) was added. The clear yellow solution was stirred at 90 °C for 1 h during which the yellow colour faded. The almost colourless solution was then concentrated to incipient crystallization and stored at −6 °C overnight. **2** was obtained as a colourless crystalline solid by filtration suitable for sc-XRD. **Yield**: 73 mg (111 µmol, 54%).

**Anal. calcd** for C$_{37}$H$_{57}$GaN$_2$O$_2$Si: C, 67.37, H, 8.71; N, 4.25 wt%. Found: C, 67.3, H, 8.63; N, 4.25 wt%. **ATR-IR**: *ν* 2964, 2928, 2868, 2790, 1616, 1551, 1516, 1460, 1438, 1388, 1316, 1282, 1251, 1165, 1086, 1018, 936, 910, 840, 796, 759, 642, 529, 487 cm$^{-1}$. **$^1$H NMR** (400 MHz, C$_6$D$_6$, 25 °C): *δ* 7.23–7.01 (m, 6 H, C$_6$*H*$_3$-2,6$^i$Pr$_2$), 5.57 (m, 1 H, Ga(CH$_2$)(COSiCH$_3$)$_3$(C*H*)(CHOCH$_3$)), 4.74 (s, 1 H, γ-C*H*), 4.07 (m, 1 H, Ga(CH$_2$)(COSiCH$_3$)$_3$(CH)(C*H*OCH$_3$)), 3.62 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.53 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.36 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.31 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.15 (s, 3 H, Ga(CH$_2$)(COSiCH$_3$)$_3$(CH)(CHOC*H*$_3$)), 1.55 (s, 3 H, ArNCC*H*$_3$), 1.52 (s, 3 H, ArNCC*H*$_3$), 1.50 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.37 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.33 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.16 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.37 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.27, 1.22, 1.11, 1.07 (m, 2 H, Ga(C*H*$_2$)(COSiCH$_3$)$_3$(CH)(CHOCH$_3$)), 0.07 (s, 9 H, Ga(CH$_2$)(COSiC*H*$_3$)$_3$(CH)(CHOCH$_3$)). **$^{13}$C NMR** (100.6 MHz, C$_6$D$_6$, 25 °C): *δ* 169.4, 168.8 (ArN*C*CH$_3$), 158.5 (Ga(CH$_2$)(*C*OSiCH$_3$)$_3$(CH)(CHOCH$_3$)), 145.3, 144.1, 143.9, 143.9, 142.0, 141.2, 127.3, 127.2, 124.7, 124.6, 124.4, 124.1 (Ar*C*), 112.8 (Ga(CH$_2$)(COSiCH$_3$)$_3$(*C*H)(CHOCH$_3$)), 96.3 (γ-*C*H), 80.0 (Ga(CH$_2$)(COSiCH$_3$)$_3$(CH)(*C*HOCH$_3$)), 57.9 (Ga(CH$_2$)(COSiCH$_3$)$_3$(CH)(CHO*C*H$_3$)), 28.5, 28.5, 28.5, 28.4 (*C*H(CH$_3$)$_2$), 25.6, 25.5, 25.4, 25.2, 25.0, 24.9, 24.8, 24.8 (CH(*C*H$_3$)$_2$), 23.9, 23.4 (ArNC*C*H$_3$), 15.6 (Ga(*C*H$_2$)(COSiCH$_3$)$_3$(CH)(CHOCH$_3$)), 0.8 (Ga(CH$_2$)(COSi*C*H$_3$)$_3$(CH)(CHOCH$_3$)). **$^{29}$Si NMR** (79.5 MHz, C$_6$D$_6$, 25 °C): *δ* 0.8 (Ga(CH$_2$)(CO*Si*CH$_3$)$_3$(CH)(CHOCH$_3$)).

### Synthesis of L(Cl)Ga(C$_4$Cl$_5$) (3)

To a suspension of 250 mg LGa (513 µmol) in 25 ml of *n*-hexane stirred at −80 °C, 88.1 µl of hexachloro-1,3-butadiene (147 mg, 513 µmol) was added. The suspension was warmed to ambient temperature overnight and all solids were dissolved under mild heating. Storage at −30 °C afforded 195 mg of **3** as a crystalline solid suitable for sc-XRD. **Yield**: 195 mg (261 µmol, 51%).

**Anal. calcd** for C$_{33}$H$_{41}$Cl$_6$GaN$_2$: C, 52.98, H, 5.52; N, 3.74 wt%. Found: C, 53.2, H, 5.74; N, 3.93 wt%. **ATR-IR**: *ν* 3058, 2969, 2928, 2868, 1582, 1533, 1435, 1396, 1365, 1357, 1316, 1305, 1264, 1251, 1172, 1124, 1105, 1024, 947, 904, 811, 796, 757, 708, 619, 527, 438 cm$^{-1}$. **$^1$H NMR** (400 MHz, C$_6$D$_6$, 25 °C): *δ* 7.15–7.05 (m, 5 H, C$_6$*H*$_3$-2,6$^i$Pr$_2$), 7.00 (m, 1 H, C$_6$*H*$_3$-2,6$^i$Pr$_2$), 4.76 (s, 1 H, γ-C*H*), 3.51 (sept, $^3J_{HH}$ = 6.6 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.40 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.33 (m, $^3J_{HH}$ = 6.6 Hz, 2 H, C*H*(CH$_3$)$_2$), 1.56 (s, 3 H, ArNCC*H*$_3$), 1.54 (s, 3 H, ArNCC*H*$_3$), 1.52 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.50 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.48 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.44 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.18 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.14 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.03 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH(C*H*$_3$)$_2$). **$^{13}$C NMR** (100.6 MHz, C$_6$D$_6$, 25 °C): *δ* 170.8, 170.6 (ArN*C*CH$_3$), 145.2, 144.8, 144.6, 140.3, 140.1, 128.2, 128.2, 124.8, 124.7, 124.6, 124.5 (Ar*C*), 132.6, 120.1, not all quaternary signal could be detected (Ga*C*$_4$Cl$_5$), 97.2 (γ-*C*H), 29.6, 29.4, 28.4, 28.3 (*C*H(CH$_3$)$_2$), 25.6, 25.6, 25.4, 25.0, 24.7, 24.6, 24.1 (CH(*C*H$_3$)$_2$), 24.5, 24.4 (ArNC*C*H$_3$).

### Synthesis of L(Cl)In(C$_4$Cl$_5$) (4)

To a suspension of 100 mg LIn (188 µmol) in 10 ml of *n*-pentane, 35.2 µl of hexachloro-1,3-butadiene (58.8 mg, 225 µmol) was added under light exclusion. After 16 h, the slightly cloudy solution was filtered, and concentrated. Storage at −30 °C afforded **4** as a crystalline solid (suitable for sc-XRD). **Yield**: 60 mg (76 µmol, 40%).

**Anal. calcd** for C$_{33}$H$_{41}$Cl$_6$InN$_2$: C, 49.97, H, 5.21; N, 3.53 wt%. Found: C, 50.3, H, 5.42; N, 3.50 wt%. **ATR-IR**: *ν* 3061, 2928, 2868, 1594, 1543, 1518, 1462, 1456, 1435, 1384, 1361, 1318, 1264, 1178, 1118, 1102, 1023, 939, 891, 857, 809, 794, 772, 757, 730, 613, 562, 521, 448, 438 cm$^{-1}$. **$^1$H NMR** (600 MHz, C$_6$D$_6$, 25 °C): *δ* 7.12–7.05 (m, 4 H, C$_6$*H*$_3$-2,6$^i$Pr$_2$), 7.04 (t, $^3J_{HH}$ = 4.6 Hz, 1 H, C$_6$*H*$_3$-2,6$^i$Pr$_2$), 7.00 (m, 1 H, C$_6$*H*$_3$-2,6$^i$Pr$_2$), 4.72 (s, 1 H, γ-C*H*), 3.61 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.43 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.36 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$), 3.26 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 1.57 (s, 3 H, ArNCC*H*$_3$), 1.55 (s, 3 H, ArNCC*H*$_3$), 1.52 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.47 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.16 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.14 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.10 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$). **$^{13}$C NMR** (150.9 MHz, C$_6$D$_6$, 25 °C): *δ* 171.5, 171.5 (ArN*C*CH$_3$), 144.4, 144.1, 143.3, 143.0, 142.1, 141.8, 127.7, 127.7, 125.0, 124.8, 124.5, 124.3 (Ar*C*), 130.2, 127.8, 119.9 (In*C*$_4$Cl$_5$), 96.6 (γ-*C*H), 29.1, 28.9,

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28.8, 28.6 (*C*H(CH$_3$)$_2$), 25.1, 25.0, 24.9, 24.9, 24.8, 24.8, 24.8, 24.6, 24.6 (CH(*C*H$_3$)$_2$ and ArNC*C*H$_3$).

### Synthesis of L(Cl)Ga(CH$_2$C$_6$H$_5$) (5)

To a suspension of 300 mg LGa (616 μmol) in 5 ml of *n*-hexane, 106.2 μl of benzyl chloride (116.8 mg, 225 μmol) was added. LGa slowly dissolved while a colourless precipitate formed. The mixture was stored at −6 °C for 12 h and filtered. Storage of a saturated *n*-hexane solution at 8 °C gave crystals of **5** suitable for sc-XRD. **Yield**: 346 mg (564 μmol, 92%).

**Anal. calcd** for $C_{36}H_{48}ClGaN_2$: C, 70.43, H, 7.88; N, 4.56 wt%. Found: C, 71.0, H, 7.91; N, 5.04 wt%. **ATR-IR**: $\nu$ 3058, 3023, 2960, 2925, 2865, 1661, 1591, 1553, 1520, 1458, 1435, 1386, 1369, 1361, 1316, 1258, 1178, 1124, 1099,1054, 1019, 939, 870, 796, 769, 753, 695, 619, 549, 530, 460, 441, 403 cm$^{-1}$. **$^1$H NMR** (400 MHz, C$_6$D$_6$, 25 °C): $\delta$ 7.21–7.07 (m, 6 H, C$_6$*H*$_3$-2,6$^{\rm i}$Pr$_2$), 6.92–6.84 (m, 2 H, CH$_2$C$_6$*H*$_5$), 6.85–6.79 (m, 1 H, CH$_2$C$_6$*H*$_5$), 6.44–6.39 (m, 1 H, CH$_2$C$_6$*H*$_5$), 4.87 (s, 1 H, γ-C*H*), 3.73 (sept, $^3J_{\rm HH}$ = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 3.25 (sept, $^3J_{\rm HH}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 1.94 (s, 2 H, C*H*$_2$C$_6$H$_5$), 1.56 (s, 6 H, ArNCC*H*$_3$), 1.33 (d, $^3J_{\rm HH}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.18 (d, $^3J_{\rm HH}$ = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.16 (d, $^3J_{\rm HH}$ = 6.9 Hz, 6 H, CH (C*H*$_3$)$_2$), 1.15 (d, $^3J_{\rm HH}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$). **$^1$H NMR** (400 MHz, DCM-d$_2$, 25 °C): $\delta$ 7.34 (t, $^3J_{\rm HH}$ = 7.6 Hz, 2 H, C$_6$*H*$_3$-2,6$^{\rm i}$Pr$_2$), 7.28–7.23 (m, 4 H, C$_6$*H*$_3$-2,6$^{\rm i}$Pr$_2$), 6.79–6.72 (m, 3 H, CH$_2$C$_6$*H*$_5$), 6.13–6.05 (m, 2 H, CH$_2$C$_6$*H*$_5$), 5.29 (s, 1 H, γ-C*H*), 3.40 (sept, $^3J_{\rm HH}$ = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 3.18 (sept, $^3J_{\rm HH}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 1.87 (s, 6 H, ArNCC*H*$_3$), 1.70 (s, 2 H, C*H*$_2$C$_6$H$_5$), 1.41 (d, $^3J_{\rm HH}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.20 (d, $^3J_{\rm HH}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.15 (d, $^3J_{\rm HH}$ = 6.8 Hz, 6 H, CH (C*H*$_3$)$_2$), 0.90 (d, $^3J_{\rm HH}$ = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$). **$^{13}$C NMR** (100.6 MHz, C$_6$D$_6$, 25 °C): $\delta$ 169.6 (ArN*C*CH$_3$), 146.3, 142.8, 140.7, 127.7, 125.8, 123.9 (*C*$_6$H$_3$-2,6$^{\rm i}$Pr$_2$), 140.7, 128.2, 127.9, 123.3 (CH$_2$*C*$_6$H$_5$), 97.6 (γ-*C*H), 29.3, 28.0 (*C*H(CH$_3$)$_2$), 26.5, 25.0, 24.5, 24.0 (CH(*C*H$_3$)$_2$), 23.4 (ArNC*C*H$_3$), 19.2 (*C*H$_2$C$_6$H$_5$). **$^{13}$C NMR** (100.6 MHz, DCM-d$_2$, 25 °C): $\delta$ 170.3 (ArN*C*CH$_3$), 146.3, 143.3, 141.2, 140.6, 128.2, 128.0, 127.8, 125.8, 124.3, 123.2 (Ar*C*), 97.6 (γ-*C*H), 29.6, 28.1 (*C*H(CH$_3$)$_2$), 26.4, 25.2, 24.7, 24.2 (CH(*C*H$_3$)$_2$), 23.9 (ArNC*C*H$_3$), 19.2 (*C*H$_2$C$_6$H$_5$).

### Synthesis of L(Cl)In(CH$_2$C$_6$H$_5$) (6)

To a suspension of 100 mg LIn (188 μmol) in 3 ml of *n*-hexane, 32.4 μl of benzyl chloride (35.6 mg, 282 μmol) was added. All LIn dissolved slowly and the resulting solution was stirred for 12 h. The solution was concentrated and stored at −30 °C to give **6** as a yellow crystalline solid. **Yield**: 76 mg (115 μmol, 61%).

**Anal. calcd** for $C_{36}H_{48}ClInN_2$: C, 65.61, H, 7.34; N, 4.25 wt%. Found: C, 65.3, H, 7.25; N, 4.63 wt%. **ATR-IR**: $\nu$ 3055, 3020, 2966, 2925, 2868, 1597, 1550, 1516, 1458, 1435, 1386, 1367, 1342, 1316, 1264, 1207, 1175, 1102, 1086, 1016, 934, 861, 794, 751, 695, 543, 524, 445 cm$^{-1}$. **$^1$H NMR** (400 MHz, C$_6$D$_6$, 25 °C): $\delta$ 7.15–7.04 (m, 6 H, C$_6$*H*$_3$-2,6$^{\rm i}$Pr$_2$), 6.88–6.82 (m, 2 H, CH$_2$C$_6$*H*$_5$), 6.80–6.75 (m, 1 H, CH$_2$C$_6$*H*$_5$), 6.47–6.37 (m, 1 H, CH$_2$C$_6$*H*$_5$), 4.77 (s, 1 H, γ-C*H*), 3.73 (sept, $^3J_{\rm HH}$ = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 3.23 (sept, $^3J_{\rm HH}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 2.15 (s, 2 H, C*H*$_2$C$_6$H$_5$), 1.56 (s, 6 H, ArNCC*H*$_3$), 1.27 (d, $^3J_{\rm HH}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.22 (d, $^3J_{\rm HH}$ = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.18 (d, $^3J_{\rm HH}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.10 (d, $^3J_{\rm HH}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$). **$^{13}$C NMR** (100.6 MHz, C$_6$D$_6$, 25 °C): $\delta$ 170.3 (ArN*C*CH$_3$), 145.0, 142.7, 142.0, 127.2, 125.5, 123.9 (*C*$_6$H$_3$-2,6$^{\rm i}$Pr$_2$), 140.7, 128.6, 127.6, 123.5 (CH$_2$*C*$_6$H$_5$), 96.9 (γ-*C*H), 29.1, 27.9 (*C*H(CH$_3$)$_2$), 26.5, 24.7, 24.4, 24.2 (CH(*C*H$_3$)$_2$), 24.0 (ArNC*C*H$_3$), 19.9 (only observed in HSQC, *C*H$_2$C$_6$H$_5$).

### Synthesis of L(Br)In(CH$_2$CH$_3$) (8)

To a suspension of 50 mg LIn (94 μmol) in 3 ml of *n*-hexane, 10 μl of bromoethane (15.3 mg, 140 μmol) was added. All LIn dissolved and the solution was stirred for 12 h. The solution was concentrated and stored at −30 °C to yield **8** as a pale yellow crystalline solid. **Yield**: 51 mg (79.5 μmol, 85%).

**Anal. calcd** for $C_{31}H_{46}BrInN_2$: C, 58.05, H, 7.23; N, 4.37 wt%. Found: C, 57.9, H, 7.32; N, 4.12 wt%. **ATR-IR**: $\nu$ 3062, 2966, 2923, 2865, 1562, 1529, 1465, 1440, 1397, 1364, 1319, 1273, 1258, 1235, 1179, 1114, 1063, 1025, 942, 858, 797, 780, 764, 729, 709, 645, 628, 602, 529, 494, 443 cm$^{-1}$. **$^1$H NMR** (400 MHz, C$_6$D$_6$, 25 °C): $\delta$ 7.14–7.03 (m, 4 H, C$_6$*H*$_3$-2,6$^{\rm i}$Pr$_2$), 7.03 (dd, $^3J_{\rm HH}$ = 7.4 Hz, 1.9 Hz, 2 H, C$_6$*H*$_3$-2,6$^{\rm i}$Pr$_2$), 4.83 (s, 1 H, γ-C*H*), 3.89 (sept, $^3J_{\rm HH}$ = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 3.21 (sept, $^3J_{\rm HH}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 1.58 (s, 6 H, ArNCC*H*$_3$), 1.47 (d, $^3J_{\rm HH}$ = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.24 (dd, $^3J_{\rm HH}$ = 6.8, 5.3 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.08 (d, $^3J_{\rm HH}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.86 (t, $^3J_{\rm HH}$ = 7.9 Hz, 3 H, InCH$_2$C*H*$_3$), 0.73–0.62 (m, 2 H, InC*H*$_2$CH$_3$). **$^{13}$C NMR** (100.6 MHz, C$_6$D$_6$, 25 °C): $\delta$ 169.7 (ArN*C*CH$_3$), 144.6, 142.4, 141.9, 126.8, 125.0, 123.4 (*C*$_6$H$_3$-2,6$^{\rm i}$Pr$_2$), 96.8 (γ-*C*H), 28.7, 27.6 (*C*H(CH$_3$)$_2$), 27.3, 24.4, 23.9, 23.8 (CH(*C*H$_3$)$_2$), 23.7 (ArNC*C*H$_3$), 11.0 (InCH$_2$*C*H$_3$).

### Synthesis of L(TfO)Ga(CH$_2$C$_6$H$_5$) (9)

Equimolar amounts of **5** (75 mg, 122 μmol) and AgOTf (32 mg, 123 μmol) were dissolved in 5 mL of DCM. After stirring for 30 min all volatiles were removed *in vacuo* and the residue was extracted with toluene, yielding almost pure **9**. Further purification and growing of crystals for sc-XRD failed. **Yield**: 76 mg (104 μmol, 85% disregarding the impurities).

**$^1$H NMR** (400 MHz, DCM-d$_2$, 25 °C): $\delta$ 7.35 (t, $^3J_{\rm HH}$ = 7.6, 2 H, C$_6$*H*$_3$-2,6$^{\rm i}$Pr$_2$), 7.29 (dd, $J_{\rm HH}$ = 7.8; 1.8 Hz, 2 H, C$_6$*H*$_3$-2,6$^{\rm i}$Pr$_2$), 7.20 (dd, $J_{\rm HH}$ = 7.6; 1.9 Hz, 2 H, C$_6$*H*$_3$-2,6$^{\rm i}$Pr$_2$), 6.80–6.70 (m, 3 H, CH$_2$C$_6$*H*$_5$), 6.14–6.08 (m, 2 H, CH$_2$C$_6$*H*$_5$), 5.58 (s, 1 H, γ-C*H*), 3.50 (sept, $^3J_{\rm HH}$ = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 2.79 (sept, $^3J_{\rm HH}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 1.95 (s, 2 H, C*H*$_2$C$_6$H$_5$), 1.94 (s, 6 H, ArNCC*H*$_3$), 1.19 (d, $^3J_{\rm HH}$ = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.09 (d, $^3J_{\rm HH}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.07 (d, $^3J_{\rm HH}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.02 (d, $^3J_{\rm HH}$ = 6.7 Hz, 6 H, CH (C*H*$_3$)$_2$). **$^1$H NMR** (400 MHz, C$_6$D$_6$, 25 °C): $\delta$ 7.19–7.09 (m, 6 H, C$_6$*H*$_3$-2,6$^{\rm i}$Pr$_2$), 6.98 (dd, $J_{\rm HH}$ = 6.4; 2.9 Hz, 2 H, CH$_2$C$_6$*H*$_5$), 6.78–6.73 (m, 3 H, CH$_2$C$_6$*H*$_5$), 5.15 (s, 1 H, γ-C*H*), 3.84 (sept, $^3J_{\rm HH}$ = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 2.74 (sept, $^3J_{\rm HH}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 1.99 (s, 2 H, C*H*$_2$C$_6$H$_5$), 1.60 (s, 6 H, ArNCC*H*$_3$), 1.37 (d, $^3J_{\rm HH}$ = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.25 (d, $^3J_{\rm HH}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.96 (d, $^3J_{\rm HH}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.92 (d, $^3J_{\rm HH}$ = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$).

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### Synthesis of [LGaCH$_2$Ph][B(C$_6$F$_5$)$_4$] (10)

11 mg of NaB(C$_6$F$_5$)$_4$ (14 μmol) was added to a solution of 10 mg (14 μmol) of L(TfO)Ga(CH$_2$C$_6$H$_5$) (**9**) in DCM-d$_2$ in a *J*-Young NMR tube. The formation of [LGaCH$_2$Ph][B(C$_6$F$_5$)$_4$] (**10**) was confirmed by $^1$H NMR spectroscopy. Single crystals suitable for sc-XRD were grown by layering the DCM solution with toluene in an NMR tube and storage at −30 °C in the glovebox freezer.

**$^1$H NMR** (400 MHz, DCM-d$_2$, 25 °C): $\delta$ 7.59–7.51 (m, 2 H, C$_6$*H*$_3$-2,6$^i$Pr$_2$), 7.38 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, C$_6$*H*$_3$-2,6$^i$Pr$_2$), 6.98–6.93 (m, 1 H, CH$_2$C$_6$*H*$_5$), 6.89–6.84 (m, 2 H, CH$_2$C$_6$*H*$_5$), 6.10 (s, 1 H, γ-C*H*), 6.11–6.07 (m, 2 H, CH$_2$C$_6$*H*$_5$), 2.66 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 2.47 (s, 2 H, C*H*$_2$C$_6$H$_5$), 2.16 (s, 6 H, ArNCC*H*$_3$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.01 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$).

### Crystallographic details

Crystals were mounted on nylon loops in inert oil. Data of were collected on a Bruker AXS D8 Kappa diffractometer (**1**, **3**, **5**, **10**) with APEX2 detector (monochromated Mo$_{K\alpha}$ radiation, $\lambda$ = 0.71073 Å) and on a Bruker AXS D8 Venture diffractometer (**2**, **4**, **6**) with Photon II detector (monochromated Cu$_{K\alpha}$ radiation, $\lambda$ = 1.54178 Å, microfocus source) at 100(2) K. The structures were solved by Direct Methods (SHELXS-97)[37] and refined anisotropically by full-matrix least-squares on $F^2$ (SHELXL-2017).[38] Absorption corrections were performed semi-empirically from equivalent reflections based on multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. In all cases, hydrogen atoms were treated with the riding model on idealized geometries with the 1.2-fold isotropic displacement parameters of the equivalent $U_{ij}$ of the corresponding carbon atom. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5-fold isotropic displacement parameters of the equivalent $U_{ij}$ of the corresponding carbon atom. Compound **2** was twinned by inversion and refined accordingly. The chlorinated ligand of compound **3** is disordered over a mirror plane. The local symmetry was ignored in the refinement (negative PART). The chlorinated ligand of compound **4** is disordered over two positions. RIGU restraints were applied to its atoms' displacement parameters and atoms in close proximity were refined with common displacement parameters (EADP). In compound **5**, the highest electron residue might be an alternate position of the Cl1 atom with very low occupancy. However, the occupancy is too low to verify this by identifying other atoms of the disorder. The dichloromethane molecule in the crystal of **10** is only occupied by approximately 14.5%. Its bond lengths were restrained to be equal and RIGU restraints were applied to its displacement parameters.

## Author contributions

M. W. designed the experiments and performed the experimental work together with P. D. and T. F. The single crystal X-ray diffraction measurements and analyses were performed by C. W. assisted by P. D. and T. F., and the overall work was supervised by S. S. The manuscript was written with contributions from all authors. All authors approved the final version of the manuscript.

## Data availability

The data supporting this article have been included as part of the ESI.† CCDC 2387776 (**1**), 2387777 (**2**), 2387778 (**3**), 2387779 (**4**), 2387895 (**5**), 2387899 (**6**), and 2387923 (**10**) contain the supplementary crystallographic data for this paper.†

## Conflicts of interest

There are no conflicts to declare.

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