

RESEARCH ARTICLE

[View Article Online](#)
[View Journal](#) | [View Issue](#)



Cite this: *Inorg. Chem. Front.*, 2025, **12**, 5863

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

Hanns Micha Weinert,^a Pratima Dhawan,^a Timo Freese,^a Christoph Wölper^a and Stephan Schulz ^{a,b}

Received 7th March 2025,
Accepted 16th May 2025

DOI: 10.1039/d5qi00660k
rsc.li/frontiers-inorganic

The syntheses and structural characterization of monomeric group 13 diyls LM ($L = HC[C(Me)NAr]_2$; $Ar = 2,6-iPr_2C_6H_3$) stabilized by the sterically demanding, N,N -chelating β -diketiminato substituent ($L = HC[C(Me)NAr]_2$; $Ar = 2,6-iPr_2C_6H_3$) represent milestones in low-valent main group element chemistry. These monovalent carbonoidic 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.

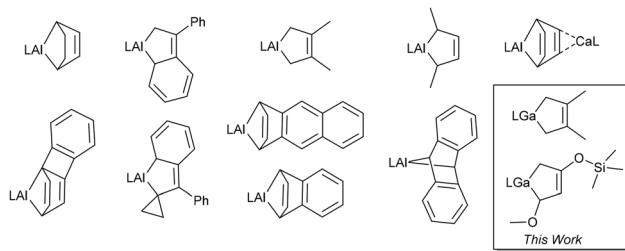
The transition metal-like behaviour of group 13 diyls results from the presence of an energetically high-lying donor orbital (HOMO) and a low lying acceptor orbital (LUMO).^{6–11,12} The HOMO–LUMO energy gap was found to increase with increasing atomic number of the group 13 element resulting from a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

The ability of both LAi and LGa to undergo oxidative addition reactions was demonstrated in several reactions with

Monovalent group 13 diyls of the type LM ($L = HC[C(Me)NAr]_2$; $Ar = 2,6-iPr_2C_6H_3$) are group 13 analogues of NHCs. While LAi 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 $LGa(C_6H_{10})$ (**1**) and $LGa(C_8H_{16}O_2Si)$ (**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 $L(Cl)M(C_4Cl_5)$ ($M = Ga$ **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 $[LGaCH_2Ph]^+$ (**10**), obtained by reaction of $L(Cl)GaBn$ with $AgOTf$ and $NaB(C_6F_5)_4$, reacted rapidly, but no defined reaction product was identified.

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 15¹⁸ and 16¹⁹ 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 $[L(X)M]_2Pn$ ^{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 -diketiminato $Ga(i)$ 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 LAi 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 alanediyi LAi with conjugated organic π -systems.

^aInstitute of Inorganic Chemistry, University of Duisburg-Essen, Universitätsstr.5-7, 45141 Essen, Germany

^bCenter for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Carl-Benz-Straße 199, 47057 Duisburg, Germany.

E-mail: stephan.schulz@uni-due.de

† Electronic supplementary information (ESI) available: 1H 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>



addition reactions with LGa and LIn were only reported for heteroatomic diene systems, *i.e.* α -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 diene²⁸) 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-cyclohexadiene, 1,3-cyclooctadiene, 1,3,5-cycloheptatriene, 1,3,5,7-cyclooctatetraene, failed. In marked contrast, the corresponding alanediyi 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 $[(dpp\text{-bian})\text{Ga}]^+$ (*dpp*-bian = *N*-protonated 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) and $[\text{Ga}(\text{PDI}^{\text{dipp}})]^-$ (*PDI* = 2,6-(2,6-*i*Pr₂C₆H₃NCMe)₂-C₅H₃N) also show different reactivities towards the diene. While the cycloaddition reaction with 2,3-dimethyl-1,3-butadiene and $[\text{Ga}(\text{PDI}^{\text{dipp}})]^-$, similar to that of LGa, required a reaction time of one day at 80 °C, the reaction with $[(dpp\text{-bian})\text{Ga}]^+$ 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.

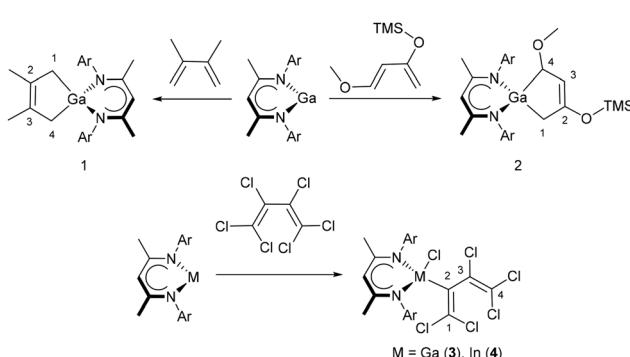
Neglecting the fact that the primary chlorine atoms are less sterically constrained, the insertion should statistically occur in a two-to-one ratio at the primary C centre. However, the chlorine atoms at the secondary carbon atom are of allylic nature, which weakens the Cl–C bond. Consequently, this 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†).

Compounds **1–4** show the expected resonances in their ¹H and ¹³C NMR spectra including the characteristic singlets for the γ -H proton (approx. 5 ppm) and the symmetrically equivalent Me groups of the β -diketiminato 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 ¹³C NMR spectra also clearly prove the formation of the cycloaddition products due to characteristic resonances for an unsaturated GaC₄ 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 ¹³C 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 ¹H and ¹³C NMR spectra (Table S1†). Due to the electropositive nature of the group 13 metal, the resonances of the metal-bound CH_x group

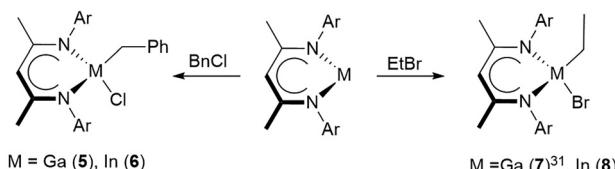


Scheme 2 Synthesis of compounds **1–4** by (1,4) cycloaddition and oxidative addition reactions of substituted butadienes with gallanediyl and indanediyl (TMS = SiMe₃).

Table 1 Selected ¹³C NMR chemical shifts δ [ppm] of the GaC₄ 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		

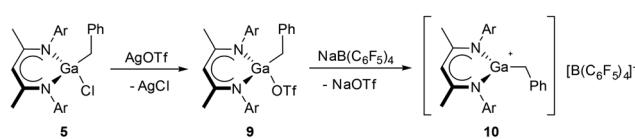




Scheme 3 C-X bond activation reactions of LM (M = Ga, In).

are found at a higher field (5δ 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-d₈ 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 $\text{NaB}(\text{C}_6\text{F}_5)_4$ failed, we reacted **7** with $\text{Ag}(\text{OTf})$ to give the triflate-substituted compound $\text{L}(\text{TfO})\text{GaCH}_2\text{Ph}$ (**9**), which then reacted with $\text{NaB}(\text{C}_6\text{F}_5)_4$ to $[\text{LGaCH}_2\text{Ph}]^+[\text{B}(\text{C}_6\text{F}_5)_4^-$ (**10**) containing the cation $[\text{LGaCH}_2\text{Ph}]^+$ (**10**⁺) as well as several by-products (Scheme 4). Salt **10** was difficult to isolate and only a very few

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

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.

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 (¹H, ¹³C) NMR spectroscopy, whereas **9** and **10** were only prepared in NMR-scale reactions and characterized by *in situ* ¹H NMR spectroscopy. Table S1† summarizes selected resonances of the ¹H and ¹³C NMR spectra of **1–10**. The ¹H 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 $\text{LGa}(\text{C}_6\text{H}_{10})$ (**1**) and $\text{LAi}(\text{C}_6\text{H}_{10})^{25f}$ crystallize in an isomorphous crystal structure with almost identical cell data. Selected molecular structures ($\text{LGa}(\text{C}_6\text{H}_{10})$ **1**, $\text{L}(\text{Cl})\text{Ga}(\text{CH}_2\text{C}_6\text{H}_5)$ **5**, $[\text{LGa}(\text{CH}_2\text{C}_6\text{H}_5)]^+$ **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**

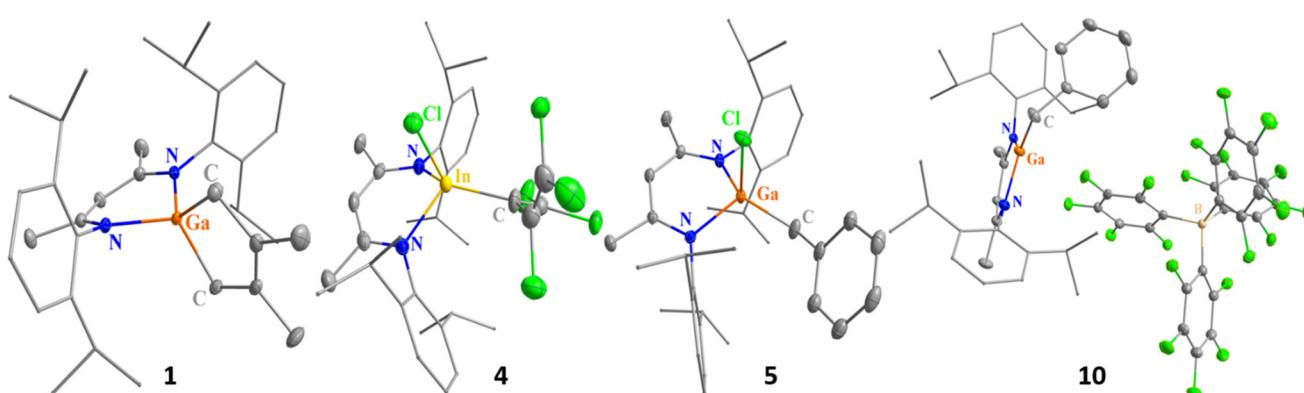


Fig. 1 Molecular structure of $\text{LGa}(\text{C}_6\text{H}_{10})$ (**1**), $\text{L}(\text{Cl})\text{In}(\text{C}_4\text{Cl}_5)$ (**4**), $\text{L}(\text{Cl})\text{Ga}(\text{CH}_2\text{C}_6\text{H}_5)$ (**5**) and $[\text{LGa}(\text{CH}_2\text{C}_6\text{H}_5)]^+$ (**10**) in the crystal. H atoms are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



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)
7³¹	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 ₆ F 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 perchlorated 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(C₆H₁₀) 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(^tBu)GaB(C₆F₅)₃, [LGaAd][An] (Ad = 1-adamantyl, An = [HB(C₆F₅)₃][–] or [B(C₆F₅)₄][–]) are the only reported complexes containing a tricoordinate Ga centre substituted by a β-diketiminato substituent and one additional organyl group. However in contrast to compound **10**, [LGaAd][B(C₆F₅)₄] was obtained directly from the salt metathesis reaction of L(Br)GaAd with NaB(C₆F₅)₄. Both complexes were used for the catalytic reduction of CO₂ with Et₃SiH, yielding H₂C(OSiEt₃)₂.³⁴

The Ga center in the cations of compound **10** and [LGaAd][B(C₆F₅)₄] are trigonal planar coordinated with the sum of bond angles of 359.87(9)^o and 359.70(6)^o (see Table 2). The Ga–C bond length (1.969(2) Å) of [LGaAd][B(C₆F₅)₄] is elongated and the N–Ga–N bond angle (99.76(8)^o) is slightly more acute compared to 1.9373(14) Å and 101.62(5)^o 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 cyclo-addition 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) cyclo-addition 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 com-

pounds **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, [LGaCH₂Ph][NaB(C₆F₅)₄] **10** containing the three-coordinate Ga cation [LGaCH₂Ph]⁺ (**10**⁺) was synthesized by reaction of L(TfO)GaCH₂Ph **9** with NaB(C₆F₅)₄ and structurally characterised.

Experimental section

General procedures

All manipulations were carried out using standard Schlenk and glovebox techniques under a dry and O₂-free argon atmosphere. Toluene, diethyl ether, *n*-pentane, *n*-hexane, and CH₂Cl₂ (DCM) were dried using an MBraun Solvent Purification System. Benzene and deuterated benzene were freshly distilled from Na/K alloy. DCM-d₂ was distilled from CaH₂ and activated Alox. All solvents were degassed and stored over activated molecular sieves. The starting reagents LGa,^{2,35} LIn (LIn was isolated),⁴ Na[B(C₆F₅)₄],³⁶ and L(Br)Ga(CH₂CH₃) (7)³¹ were prepared according to literature methods. ¹H (400 MHz, 600 MHz) and ¹³C{¹H} (100.7 MHz, 150.9 MHz), ¹⁹F (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 C₆D₅H (¹H: δ = 7.16), C₆D₆ (¹³C: δ = 128.06), or CDHCl₂ (¹H: δ = 5.32), CD₂Cl₂ (¹³C: δ = 54.00) and for ¹⁹F via the chi-values (χ). 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(C₆H₁₀) (**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-



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 μ mol, 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, 1059, 1020, 934, 867, 798, 759, 693, 643, 630, 531, 481 cm^{-1} . **1H NMR** (400 MHz, C_6D_6 , 25 $^{\circ}C$): δ 7.07 (s, 6 H, C_6H_3 -2,6*i*Pr₂), 4.74 (s, 1 H, γ -CH), 3.45 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 1.72 (s, 6 H, $Ga(CH_2CCH_3)_2$), 1.55 (s, 6 H, ArNCCH₃), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12 H $CH(CH_3)_2$), 1.12 (s, 4 H, $Ga(CH_2CCH_3)_2$). **^{13}C NMR** (100.6 MHz, C_6D_6 , 25 $^{\circ}C$): δ 168.8 (ArNCCH₃), 144.1, 141.6, 127.1, 124.4 (ArC), 132.7 ($Ga(CH_2CCH_3)_2$), 95.8 (γ -CH), 28.5 ($CH(CH_3)_2$), 25.1, 24.8 ($CH(CH_3)_2$), 23.5 (ArNCCH₃), 21.5 ($Ga(CH_2CCH_3)_2$), 20.5 ($Ga(CH_2CCH_3)_2$).

Synthesis of LGa($C_8H_{16}O_2Si$) (2)

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

Anal. calcd for $C_{37}H_{57}GaN_2O_2Si$: 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} . **1H NMR** (400 MHz, C_6D_6 , 25 $^{\circ}C$): δ 7.23-7.01 (m, 6 H, C_6H_3 -2,6*i*Pr₂), 5.57 (m, 1 H, $Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$), 4.74 (s, 1 H, γ -CH), 4.07 (m, 1 H, $Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$), 3.62 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, $CH(CH_3)_2$), 3.53 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, $CH(CH_3)_2$), 3.36 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, $CH(CH_3)_2$), 3.31 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, $CH(CH_3)_2$), 3.15 (s, 3 H, $Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$), 1.55 (s, 3 H, ArNCCH₃), 1.52 (s, 3 H, ArNCCH₃), 1.50 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.37 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CH(CH_3)_2$), 1.33 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.16 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CH(CH_3)_2$), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.37 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CH(CH_3)_2$), 1.27, 1.22, 1.11, 1.07 (m, 2 H, $Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$), 0.07 (s, 9 H, $Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$). **^{13}C NMR** (100.6 MHz, C_6D_6 , 25 $^{\circ}C$): δ 169.4, 168.8 (ArNCCH₃), 158.5 ($Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$), 145.3, 144.1, 143.9, 143.9, 142.0, 141.2, 127.3, 127.2, 124.7, 124.6, 124.4, 124.1 (ArC), 112.8 ($Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$), 96.3 (γ -CH), 80.0 ($Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$), 57.9 ($Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$), 28.5, 28.5, 28.5, 28.4 ($CH(CH_3)_2$), 25.6, 25.5, 25.4, 25.2, 25.0, 24.9, 24.8, 24.8 ($CH(CH_3)_2$), 23.9, 23.4 (ArNCCH₃), 15.6 ($Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$), 0.8 ($Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$). **^{29}Si NMR** (79.5 MHz, C_6D_6 , 25 $^{\circ}C$): δ 0.8 ($Ga(CH_2)(COSiCH_3)_3(CH)(CHOCH_3)$).

Synthesis of L(Cl)Ga(C_4Cl_5) (3)

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

Anal. calcd for $C_{33}H_{41}Cl_6GaN_2$: 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} . **1H NMR** (400 MHz, C_6D_6 , 25 $^{\circ}C$): δ 7.15-7.05 (m, 5 H, C_6H_3 -2,6*i*Pr₂), 7.00 (m, 1 H, C_6H_3 -2,6*i*Pr₂), 4.76 (s, 1 H, γ -CH), 3.51 (sept, $^3J_{HH}$ = 6.6 Hz, 1 H, $CH(CH_3)_2$), 3.40 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, $CH(CH_3)_2$), 3.33 (m, $^3J_{HH}$ = 6.6 Hz, 2 H, $CH(CH_3)_2$), 1.56 (s, 3 H, ArNCCH₃), 1.54 (s, 3 H, ArNCCH₃), 1.52 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CH(CH_3)_2$), 1.50 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, $CH(CH_3)_2$), 1.48 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.44 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CH(CH_3)_2$), 1.18 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CH(CH_3)_2$), 1.14 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CH(CH_3)_2$), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.03 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, $CH(CH_3)_2$). **^{13}C NMR** (100.6 MHz, C_6D_6 , 25 $^{\circ}C$): δ 170.8, 170.6 (ArNCCH₃), 145.2, 144.8, 144.6, 140.3, 140.1, 128.2, 128.2, 124.8, 124.7, 124.6, 124.5 (ArC), 132.6, 120.1, not all quaternary signal could be detected (GaC_4Cl_5), 97.2 (γ -CH), 29.6, 29.4, 28.4, 28.3 ($CH(CH_3)_2$), 25.6, 25.6, 25.4, 25.0, 24.7, 24.6, 24.1 ($CH(CH_3)_2$), 24.5, 24.4 (ArNCCH₃).

Synthesis of L(Cl)In(C_4Cl_5) (4)

To a suspension of 100 mg LiIn (188 μ mol) in 10 ml of *n*-pentane, 35.2 μ l of hexachloro-1,3-butadiene (58.8 mg, 225 μ mol) was added under light exclusion. After 16 h, the slightly cloudy solution was filtered, and concentrated. Storage at -30 $^{\circ}C$ afforded **4** as a crystalline solid (suitable for sc-XRD). **Yield:** 60 mg (76 μ mol, 40%).

Anal. calcd for $C_{33}H_{41}Cl_6InN_2$: 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} . **1H NMR** (600 MHz, C_6D_6 , 25 $^{\circ}C$): δ 7.12-7.05 (m, 4 H, C_6H_3 -2,6*i*Pr₂), 7.04 (t, $^3J_{HH}$ = 4.6 Hz, 1 H, C_6H_3 -2,6*i*Pr₂), 7.00 (m, 1 H, C_6H_3 -2,6*i*Pr₂), 4.72 (s, 1 H, γ -CH), 3.61 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, $CH(CH_3)_2$), 3.43 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, $CH(CH_3)_2$), 3.36 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, $CH(CH_3)_2$), 3.26 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, $CH(CH_3)_2$), 1.57 (s, 3 H, ArNCCH₃), 1.55 (s, 3 H, ArNCCH₃), 1.52 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.47 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CH(CH_3)_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.16 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CH(CH_3)_2$), 1.14 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, $CH(CH_3)_2$), 1.10 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CH(CH_3)_2$). **^{13}C NMR** (150.9 MHz, C_6D_6 , 25 $^{\circ}C$): δ 171.5, 171.5 (ArNCCH₃), 144.4, 144.1, 143.3, 143.0, 142.1, 141.8, 127.7, 127.7, 125.0, 124.8, 124.5, 124.3 (ArC), 130.2, 127.8, 119.9 (InC_4Cl_5), 96.6 (γ -CH), 29.1, 28.9,



28.8, 28.6 ($\text{CH}(\text{CH}_3)_2$), 25.1, 25.0, 24.9, 24.9, 24.8, 24.8, 24.8, 24.6, 24.6 ($\text{CH}(\text{CH}_3)_2$ and ArNCCH_3).

Synthesis of $\text{L(Cl)Ga(CH}_2\text{C}_6\text{H}_5)$ (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 $\text{C}_{36}\text{H}_{48}\text{ClGaN}_2$: C, 70.43, H, 7.88; N, 4.56 wt%. Found: C, 71.0, H, 7.91; N, 5.04 wt%. **ATR-IR:** ν 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} . **$^1\text{H NMR}$** (400 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ 7.21–7.07 (m, 6 H, $\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 6.92–6.84 (m, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.85–6.79 (m, 1 H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.44–6.39 (m, 1 H, $\text{CH}_2\text{C}_6\text{H}_5$), 4.87 (s, 1 H, $\gamma\text{-CH}$), 3.73 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 3.25 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 1.94 (s, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 1.56 (s, 6 H, ArNCCH_3), 1.33 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.18 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.16 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.15 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$). **$^1\text{H NMR}$** (400 MHz, DCM-d₂, 25 $^\circ\text{C}$): δ 7.34 (t, $^3J_{\text{HH}} = 7.6$ Hz, 2 H, $\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 7.28–7.23 (m, 4 H, $\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 6.79–6.72 (m, 3 H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.13–6.05 (m, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 5.29 (s, 1 H, $\gamma\text{-CH}$), 3.40 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 3.18 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 1.87 (s, 6 H, ArNCCH_3), 1.70 (s, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 1.41 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.20 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.15 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 0.90 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$). **$^{13}\text{C NMR}$** (100.6 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ 169.6 (ArNCCH_3), 146.3, 142.8, 140.7, 127.7, 125.8, 123.9 ($\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 140.7, 128.2, 127.9, 123.3 ($\text{CH}_2\text{C}_6\text{H}_5$), 97.6 ($\gamma\text{-CH}$), 29.3, 28.0 ($\text{CH}(\text{CH}_3)_2$), 26.5, 25.0, 24.5, 24.0 ($\text{CH}(\text{CH}_3)_2$), 23.4 (ArNCCH_3), 19.2 ($\text{CH}_2\text{C}_6\text{H}_5$). **$^{13}\text{C NMR}$** (100.6 MHz, DCM-d₂, 25 $^\circ\text{C}$): δ 170.3 (ArNCCH_3), 146.3, 143.3, 141.2, 140.6, 128.2, 128.0, 127.8, 125.8, 124.3, 123.2 (ArC), 97.6 ($\gamma\text{-CH}$), 29.6, 28.1 ($\text{CH}(\text{CH}_3)_2$), 26.4, 25.2, 24.7, 24.2 ($\text{CH}(\text{CH}_3)_2$), 23.9 (ArNCCH_3), 19.2 ($\text{CH}_2\text{C}_6\text{H}_5$).

Synthesis of $\text{L(Cl)In(CH}_2\text{C}_6\text{H}_5)$ (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 $\text{C}_{36}\text{H}_{48}\text{ClInN}_2$: C, 65.61, H, 7.34; N, 4.25 wt%. Found: C, 65.3, H, 7.25; N, 4.63 wt%. **ATR-IR:** ν 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} . **$^1\text{H NMR}$** (400 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ 7.15–7.04 (m, 6 H, $\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 6.88–6.82 (m, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.80–6.75 (m, 1 H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.47–6.37 (m, 1 H, $\text{CH}_2\text{C}_6\text{H}_5$), 4.77 (s, 1 H, $\gamma\text{-CH}$), 3.73 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 3.23 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 2 H,

$\text{CH}(\text{CH}_3)_2$), 2.15 (s, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 1.56 (s, 6 H, ArNCCH_3), 1.27 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.22 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.18 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$). **$^{13}\text{C NMR}$** (100.6 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ 170.3 (ArNCCH_3), 145.0, 142.7, 142.0, 127.2, 125.5, 123.9 ($\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 140.7, 128.6, 127.6, 123.5 ($\text{CH}_2\text{C}_6\text{H}_5$), 96.9 ($\gamma\text{-CH}$), 29.1, 27.9 ($\text{CH}(\text{CH}_3)_2$), 26.5, 24.7, 24.4, 24.2 ($\text{CH}(\text{CH}_3)_2$), 24.0 (ArNCCH_3), 19.9 (only observed in HSQC, $\text{CH}_2\text{C}_6\text{H}_5$).

Synthesis of $\text{L(Br)In(CH}_2\text{CH}_3)$ (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 $\text{C}_{31}\text{H}_{46}\text{BrInN}_2$: C, 58.05, H, 7.23; N, 4.37 wt%. Found: C, 57.9, H, 7.32; N, 4.12 wt%. **ATR-IR:** ν 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} . **$^1\text{H NMR}$** (400 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ 7.14–7.03 (m, 4 H, $\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 7.03 (dd, $^3J_{\text{HH}} = 7.4$ Hz, 1.9 Hz, 2 H, $\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 4.83 (s, 1 H, $\gamma\text{-CH}$), 3.89 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 3.21 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 1.58 (s, 6 H, ArNCCH_3), 1.47 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.24 (dd, $^3J_{\text{HH}} = 6.8$, 5.3 Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.08 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 0.86 (t, $^3J_{\text{HH}} = 7.9$ Hz, 3 H, InCH_2CH_3), 0.73–0.62 (m, 2 H, InCH_2CH_3). **$^{13}\text{C NMR}$** (100.6 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ 169.7 (ArNCCH_3), 144.6, 142.4, 141.9, 126.8, 125.0, 123.4 ($\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 96.8 ($\gamma\text{-CH}$), 28.7, 27.6 ($\text{CH}(\text{CH}_3)_2$), 27.3, 24.4, 23.9, 23.8 ($\text{CH}(\text{CH}_3)_2$), 23.7 (ArNCCH_3), 11.0 (InCH_2CH_3).

Synthesis of $\text{L(TfO)Ga(CH}_2\text{C}_6\text{H}_5)$ (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).

$^1\text{H NMR}$ (400 MHz, DCM-d₂, 25 $^\circ\text{C}$): δ 7.35 (t, $^3J_{\text{HH}} = 7.6$, 2 H, $\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 7.29 (dd, $J_{\text{HH}} = 7.8$; 1.8 Hz, 2 H, $\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 7.20 (dd, $J_{\text{HH}} = 7.6$; 1.9 Hz, 2 H, $\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 6.80–6.70 (m, 3 H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.14–6.08 (m, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 5.58 (s, 1 H, $\gamma\text{-CH}$), 3.50 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 2.79 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 1.95 (s, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 1.94 (s, 6 H, ArNCCH_3), 1.19 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.09 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.07 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.02 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$). **$^1\text{H NMR}$** (400 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ 7.19–7.09 (m, 6 H, $\text{C}_6\text{H}_3\text{-2,6}^{\text{i}}\text{Pr}_2$), 6.98 (dd, $J_{\text{HH}} = 6.4$; 2.9 Hz, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.78–6.73 (m, 3 H, $\text{CH}_2\text{C}_6\text{H}_5$), 5.15 (s, 1 H, $\gamma\text{-CH}$), 3.84 (sept, $^3J_{\text{HH}} = 6.7$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 2.74 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 2 H, $\text{CH}(\text{CH}_3)_2$), 1.99 (s, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 1.60 (s, 6 H, ArNCCH_3), 1.37 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 1.25 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 0.96 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$), 0.92 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$).



Synthesis of $[\text{LGaCH}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ (10)

11 mg of $\text{NaB}(\text{C}_6\text{F}_5)_4$ (14 μmol) was added to a solution of 10 mg (14 μmol) of $\text{L}(\text{TfO})\text{Ga}(\text{CH}_2\text{C}_6\text{H}_5)$ (9) in DCM-d_2 in a *J*-Young NMR tube. The formation of $[\text{LGaCH}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ (10) was confirmed by ^1H 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 globox freezer.

$^1\text{H NMR}$ (400 MHz, DCM-d_2 , 25 $^\circ\text{C}$): δ 7.59–7.51 (m, 2 H, $\text{C}_6\text{H}_3\text{-2,6-iPr}_2$), 7.38 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2 H, $\text{C}_6\text{H}_3\text{-2,6-iPr}_2$), 6.98–6.93 (m, 1 H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.89–6.84 (m, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.10 (s, 1 H, $\gamma\text{-CH}$), 6.11–6.07 (m, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 2.66 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$), 2.47 (s, 2 H, $\text{CH}_2\text{C}_6\text{H}_5$), 2.16 (s, 6 H, ArNCCH_3), 1.26 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.01 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$).

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 $\text{MoK}\alpha$ radiation, $\lambda = 0.71073$ \AA) and on a Bruker AXS D8 Venture diffractometer (2, 4, 6) with Photon II detector (monochromated $\text{CuK}\alpha$ radiation, $\lambda = 1.54178$ \AA , 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.

References

- 1 C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, Synthesis and Structure of a Monomeric Aluminum(I) Compound $[\{\text{HC}(\text{CMeNAr})_2\}\text{Al}](\text{Ar}=\text{2,6-i,Pr}_2\text{C}_6\text{H}_3)$: A Stable Aluminum Analogue of a Carbene, *Angew. Chem., Int. Ed.*, 2000, **39**, 4274.
- 2 M. Stender, B. E. Eichler, N. J. Hardman, P. P. Power, J. Prust, M. Noltemeyer and H. W. Roesky, Synthesis and Characterization of $\text{HC}(\text{C}(\text{Me})\text{N}(\text{C}_6\text{H}_3\text{-2,6-i-Pr}_2)_2)_2\text{MX}_2$ ($\text{M} = \text{Al}$, $\text{X} = \text{Cl}$; $\text{M} = \text{Ga}$, In , $\text{X} = \text{Me}$, Cl , I): Sterically Encumbered β -Diketiminato Group 13 Metal Derivatives, *Inorg. Chem.*, 2001, **40**, 2794.
- 3 N. J. Hardman, B. E. Eichler and P. P. Power, Synthesis and characterization of the monomer $\text{Ga}\{(\text{NDippCMe})_2\text{CH}\}$ (Dipp = $\text{C}_6\text{H}_3\text{Pr}_2\text{-2,6}$): a low valent gallium(i) carbene analogue, *Chem. Commun.*, 2000, 1991.
- 4 M. S. Hill and P. B. Hitchcock, A mononuclear indium(i) carbene analogue, *Chem. Commun.*, 2004, 1818.
- 5 M. S. Hill, P. B. Hitchcock and R. Pongtavornpinyo, Neutral carbene analogues of the heaviest Group 13 elements: Consideration of electronic and steric effects on structure and stability, *Dalton Trans.*, 2005, 273.
- 6 (a) M. Zhong, S. Sinhababu and H. W. Roesky, The unique β -diketiminato ligand in aluminum(i) and gallium(i) chemistry, *Dalton Trans.*, 2020, **49**, 1351; (b) T. Chu and G. I. Nikonov, Oxidative Addition and Reductive Elimination at Main-Group Element Centers, *Chem. Rev.*, 2018, **118**, 3608.
- 7 C. Weetman, H. Xu and S. Inoue, Recent Developments in Low-Valent Aluminum Chemistry, *Encycl. Inorg. Bioinorg. Chem.*, 2020, 1.
- 8 J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, The Aluminyl Anion: A New Generation of Aluminium Nucleophile, *Angew. Chem., Int. Ed.*, 2021, **60**, 1702.

9 K. Hobson, C. J. Carmalt and C. Bakewell, Recent advances in low oxidation state aluminium chemistry, *Chem. Sci.*, 2020, **11**, 6942.

10 J. Kretsch, A. Kreyenschmidt, T. Schillmöller, C. Sindlinger, R. Herbst-Irmer and D. Stalke, Mixed Low-Valent Alanes from the Bis(4-methyl-benzoxazol-2-yl)methanide Ligand, *Inorg. Chem.*, 2021, **60**, 7389.

11 Y. Liu, J. Li, X. Ma, Z. Yang and H. W. Roesky, The chemistry of aluminum(I) with β -diketiminate ligands and penta-methylcyclopentadienyl-substituents: Synthesis, reactivity and applicationsm, *Coord. Chem. Rev.*, 2018, **374**, 387.

12 (a) P. P. Power, Main-group elements as transition metals, *Nature*, 2010, **463**, 171; (b) C. Weetman and S. Inoue, The Road Travelled: After Main-Group Elements as Transition Metals, *ChemCatChem*, 2018, **10**, 4213; (c) M. Asay, C. Jones and M. Driess, *N*-Heterocyclic Carbene Analogues with Low-Valent Group 13 and Group 14 Elements: Syntheses, Structures, and Reactivities of a New Generation of Multitalented Ligands, *Chem. Rev.*, 2011, **111**, 354.

13 P. Vasko and C. W. Lau, Oxidative addition or Werner coordination complex? Reactivity of β -diketiminate supported main group and first-row transition metal complexes towards ammonia, *Dalton Trans.*, 2022, **51**, 13444.

14 T. Chu, I. Korobkov and G. I. Nikonov, Oxidative Addition of σ Bonds to an Al(I) Center, *J. Am. Chem. Soc.*, 2014, **136**, 9195.

15 (a) E. Herappe-Mejía, K. Trujillo-Hernández, J. Carlos Garduño-Jiménez, F. Cortés-Guzmán, D. Martínez-Otero and V. Jancik, Synthesis of substituted β -diketiminate gallium hydrides *via* oxidative addition of H–O bonds, *Dalton Trans.*, 2015, **44**, 16894; (b) A. Seifert, D. Scheid, G. Linti and T. Zessin, Oxidative Addition Reactions of Element–Hydrogen Bonds with Different Polarities to a Gallium(I) Compound, *Chem. – Eur. J.*, 2009, **15**, 12114; (c) S. Schneider and C. von Hänisch, Trapping reactions with highly unstable hydrides of antimony and bismuth, *Chem. Commun.*, 2022, **58**, 1522; (d) S. Schneider, S. Ivlev and C. von Hänisch, Stibine as a reagent in molecular chemistry - targeted synthesis of primary and secondary stibanyl-gallanes and their lighter homologues, *Chem. Commun.*, 2021, **57**, 3781.

16 (a) T. Chu, Y. Boyko, I. Korobkov and G. I. Nikonov, Transition Metal-like Oxidative Addition of C–F and C–O Bonds to an Aluminum(I) Center, *Organometallics*, 2015, **34**, 5363; (b) C. Bakewell, A. J. P. White and M. R. Crimmin, Reactions of Fluoroalkenes with an Aluminium(I) Complex, *Angew. Chem., Int. Ed.*, 2018, **57**, 6638; (c) M. R. Crimmin, M. J. Butler and A. J. P. White, Oxidative addition of carbon–fluorine and carbon–oxygen bonds to Al(I), *Chem. Commun.*, 2015, **51**, 15994.

17 O. Kysliak, H. Görls and R. Kretschmer, Cooperative Bond Activation by a Bimetallic Main-Group Complex, *J. Am. Chem. Soc.*, 2021, **143**, 142.

18 (a) G. PrabuSankar, A. Doddi, C. Gemel, M. Winter and R. A. Fischer, P–P Bond Activation of P_4 Tetrahedron by Group 13 Carbenoid and its Bis Molybdenum Pentacarbonyl Adduct, *Inorg. Chem.*, 2010, **49**, 7976; (b) C. Ganesamoorthy, J. Krüger, C. Wölper, A. S. Nizovtsev and S. Schulz, Reduction of $[\text{Cp}^*\text{Sb}]_4$ with Subvalent Main-Group Metal Reductants: Syntheses and Structures of $[(\text{L}^1\text{Mg})_4(\text{Sb}_4)]$ and $[(\text{L}^2\text{Ga})_2(\text{Sb}_4)]$ Containing Edge-Missing Sb_4 Units, *Chem. – Eur. J.*, 2017, **23**, 2461; (c) C. Ganesamoorthy, D. Bläser, C. Wölper and S. Schulz, Temperature-Dependent Electron Shuffle in Molecular Group 13/15 Intermetallic Complexes, *Angew. Chem., Int. Ed.*, 2014, **53**, 11587; (d) F. Hennersdorf, J. Frötschel and J. J. Weigand, Selective Derivatization of a Hexaphosphane from Functionalization of White Phosphorus, *J. Am. Chem. Soc.*, 2017, **139**, 14592.

19 N. J. Hardman and P. P. Power, Dimeric Gallium Oxide and Sulfide Species Stabilized by a Sterically Encumbered β -Diketiminate Ligand, *Inorg. Chem.*, 2001, **40**, 2474.

20 (a) C. Ganesamoorthy, C. Helling, C. Wölper, W. Frank, E. Bill, G. E. Cutsail and S. Schulz, From stable Sb- and Bi-centered radicals to a compound with a Ga=Sb double bond, *Nat. Commun.*, 2018, **9**, 87; (b) M. K. Sharma, H. M. Weinert, C. Wölper and S. Schulz, Gallaphosphene $\text{L}(\text{Cl})\text{GaPGaL}$: A novel phosphinidene transfer reagent, *Chem. – Eur. J.*, 2024, **30**, e202400110; (c) M. K. Sharma, C. Wölper, G. Haberhauer and S. Schulz, Reversible and Irreversible $[2 + 2]$ Cycloaddition Reactions of Heteroallenes to a Gallaphosphene, *Angew. Chem., Int. Ed.*, 2021, **60**, 21784.

21 C. Helling, C. Wölper, Y. Schulte, G. E. Cutsail and S. Schulz, Synthesis of a Ga-Stabilized As-Centered Radical and a Gallastibene by Tailoring Group 15 Element–Carbon Bond Strengths, *Inorg. Chem.*, 2019, **58**, 10323.

22 (a) L. Tuscher, C. Ganesamoorthy, D. Bläser, C. Wölper and S. Schulz, A Gallium-Substituted Distibene and an Antimony-Analogue Bicyclo[1.1.0]butane: Synthesis and Solid-State Structures, *Angew. Chem., Int. Ed.*, 2015, **54**, 10657; (b) H. M. Weinert, C. Wölper and S. Schulz, Redox Potentials of Group 13 Metal-Substituted Dipnictenes: A Comparative Cyclic Voltammetry Study, *Organometallics*, 2021, **40**, 3486; (c) H. M. Weinert, C. Wölper, J. Haak, G. E. Cutsail and S. Schulz, Synthesis, structure and bonding nature of heavy dipnictene radical anions, *Chem. Sci.*, 2021, **12**, 14024; (d) H. M. Weinert, Y. Schulte, A. Gehlhaar, C. Wölper, G. Haberhauer and S. Schulz, Metal-coordinated distibene and dibismuthene dications – isoelectronic analogues of butadiene dications, *Chem. Commun.*, 2023, **59**, 7755; (e) M. K. Sharma, S. Chabbra, C. Wölper, H. M. Weinert, E. J. Reijerse, A. Schnegg and S. Schulz, Modulating the frontier orbitals of $\text{L}(\text{X})\text{GaP}_2$ ($\text{X} = \text{Cl}, \text{B}(\text{r})$) and their facile oxidation to radical cations, *Chem. Sci.*, 2022, **13**, 12643; (f) M. K. Sharma, H. M. Weinert, B. Li, C. Wölper, J. T. Henthorn, G. E. Cutsail, G. Haberhauer and S. Schulz, Syntheses and Structures of 5-Membered Heterocycles Featuring 1,2-Diphospha-1,3-Butadiene and Its Radical Anion, *Angew. Chem., Int. Ed.*, 2023, **62**, e202309466; (g) H. M. Weinert, C. Wölper, A. Radović, G. E. Cutsail, H. Siera, G. Haberhauer and S. Schulz, From Neutral



Diarsenes to Diarsene Radical Ions and Diarsene Dications, *Chem. – Eur. J.*, 2024, e202400204.

23 (a) C. Helling, G. E. Cutsail, H. Weinert, C. Wölper and S. Schulz, Ligand Effects on the Electronic Structure of Heteroleptic Antimony-Centered Radicals, *Angew. Chem., Int. Ed.*, 2020, **59**, 7561; (b) J. Krüger, C. Wölper and S. Schulz, Stepwise Bi–Bi Bond Formation: From a Bi-centered Radical to Bi_4 Butterfly and Bi_8 Cuneane-Type Cluster, *Inorg. Chem.*, 2020, **59**, 11142.

24 C. Helling, J. C. Farmer, C. Wölper, R. Kretschmer and S. Schulz, Bond Activation by a Bimetallic GaI Complex: Avenue to Intermetallic Compounds, *Organometallics*, 2023, **42**, 72.

25 (a) S. Brand, H. Elsen, J. Langer, W. A. Donaubauer, F. Hampel and S. Harder, Facile Benzene Reduction by a Ca^{2+} /AlI Lewis Acid/Base Combination, *Angew. Chem., Int. Ed.*, 2018, **57**, 14169; (b) R. Y. Kong and M. R. Crimmin, Chemoselective C–C σ -Bond Activation of the Most Stable Ring in Biphenylen, *Angew. Chem., Int. Ed.*, 2021, **60**, 2619; (c) R. Y. Kong and M. R. Crimmin, Reversible insertion of CO into an aluminium–carbon bond, *Chem. Commun.*, 2019, **55**, 6181; (d) A. Dmitrienko, M. Pilkington and G. I. Nikonov, Reactions of an aluminium(I) diketiminato compound with arenes, *Mendeleev Commun.*, 2022, **32**, 68; (e) R. Y. Kong and M. R. Crimmin, Activation and Functionalization of C–C σ Bonds of Alkylidene Cyclopropanes at Main Group Centers, *J. Am. Chem. Soc.*, 2020, **142**, 11967; (f) C. Bakewell, M. Garçon, R. Y. Kong, L. O'Hare, A. J. P. White and M. R. Crimmin, Reactions of an Aluminum(I) Reagent with 1,2-, 1,3-, and 1,5-Dienes: Dearomatization, Reversibility, and a Pericyclic Mechanism, *Inorg. Chem.*, 2020, **59**, 4608.

26 H. M. Weinert, C. Wölper and S. Schulz, Synthesis of 5-Metalla-Spiro[4.5]Heterodecenes by [1,4]-Cycloaddition Reaction of Group 13 Diyls with 1,2-Diketones, *Chemistry*, 2023, **5**, 948.

27 (a) A. Dmitrienko, J. F. Britten, D. Spasyuk and G. I. Nikonov, Adduct of NacNacAl with Benzophenone and its Coupling Chemistry, *Chem. – Eur. J.*, 2020, **26**, 206; (b) A. Dmitrienko, M. Pilkington and G. I. Nikonov, Selective Cross-Coupling of Unsaturated Substrates on AlI, *Chem. – Eur. J.*, 2020, **27**, 5730.

28 S. Danishefsky and T. Kitahara, Useful diene for the Diels–Alder reaction, *J. Am. Chem. Soc.*, 1974, **96**, 7807.

29 P. Pykkö and M. Atsumi, Molecular Single-Bond Covalent Radii for Elements 1–118, *Chem. – Eur. J.*, 2009, **15**, 186.

30 (a) P. Dabeinghaus, T. Heizmann and I. Krossing, Activation of the GaI Cation for Bond Activation: from Oxidative Additions into C–Cl and H–P Bonds to Reversible Insertion into P₄, *Chem. – Eur. J.*, 2023, **29**, e202302212; (b) V. A. Dodonov, O. A. Kushnerova, R. V. Rumyantsev, A. S. Novikov, V. K. Osmanov and I. L. Fedushkin, Cycloaddition of isoselenocyanates to sodium and magnesium metallacycles, *Dalton Trans.*, 2022, **51**, 4113.

31 B. Li, C. Wölper and S. Schulz, C–Br Bond Activation of Bromoalkanes with Gallanediyl LGa, *Z. Anorg. Allg. Chem.*, 2023, **649**, e202200293.

32 (a) C. Helling, C. Ganesamoorthy, C. Wölper and S. Schulz, Geminal C–Cl and Si–Cl bond activation of chloromethanes and chlorosilanes by gallanediyl LGa, *Dalton Trans.*, 2022, **61**, 2050; (b) A. Kempter, C. Gemel and R. A. Fischer, Oxidative Addition of Group 13 and 14 Metal Halides and Alkyls to Ga(DDP) (DDP = Bulky Bisimidinate), *Inorg. Chem.*, 2008, **47**, 7279.

33 M. S. Hill, P. B. Hitchcock and R. Pongtavornpinyo, Oxidative addition reactions of alkyl halides with the group 13 carbene analogue $[\text{In}\{\text{N}(\text{Dipp})\text{C}(\text{Me})\}_2\text{CH}]$ (Dipp=2,6-iPr₂C₆H₃), *Inorg. Chem.*, 2007, **46**, 3783.

34 (a) J. A. B. Abdalla, I. M. Riddlestone, R. Tirfoin and S. Aldridge, Cooperative Bond Activation and Catalytic Reduction of Carbon Dioxide at a Group 13 Metal Center, *Angew. Chem., Int. Ed.*, 2015, **54**, 5098; (b) A. Caise, J. Hicks, M.Á Fuentes, J. M. Goicoechea and S. Aldridg, Partnering a Three-Coordinate Gallium Cation with a Hydroborate Counter-Ion for the Catalytic Hydrosilylation of CO₂, *Chem. – Eur. J.*, 2021, **27**, 2138.

35 M. Stender, R. J. Wright, B. E. Eichler, J. Prust, M. M. Olmstead, H. W. Roesky and P. P. Power, The synthesis and structure of lithium derivatives of the sterically encumbered β -diketiminato ligand $[(2,6\text{-Pr}^i_2\text{H}_3\text{C}_6)\text{N}(\text{CH}_3)\text{C}_2\text{CH}]^-$, and a modified synthesis of the aminoimine precursor, *Dalton Trans.*, 2001, 3465.

36 F. Forster, T. T. Metsänen, E. Irran, P. Hrobárik and M. Oestreich, Cooperative Al–H Bond Activation in DIBAL–H: Catalytic Generation of an Alumium-Ion-Like Lewis Acid for Hydrodefluorinative Friedel–Crafts Alkylation, *J. Am. Chem. Soc.*, 2017, **139**, 16334.

37 G. M. Sheldrick, Phase annealing in SHELX-90: direct methods for larger structures, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467.

38 (a) G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3; (b) C. B. Hübschle, G. M. Sheldrick and B. Dittrich, ShelXle: a Qt graphical user interface for SHELXL, *J. Appl. Crystallogr.*, 2011, **44**, 1281.

