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Lewis acid–base adducts of group 13 elements: synthesis, structure and reactivity toward benzaldehyde†

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Lewis acid–base adducts [LGa-M(C_6F_5)$_3$] (M = B **1**, Al **2**, Ga **3**) were prepared by the reaction of gallanediyl LGa {L = HC[C(Me)N(2,6-i-$Pr_2C_6H_3$)]$_2$} with the Lewis acids M(C_6F_5)$_3$ (M = B, Al, Ga). Benzaldehyde reacts with [LGa-M(C_6F_5)$_3$] (M = B **1**, Al **2**) at room temperature with the insertion and formation of [LGa(C_6F_5){CH(Ph)(OB(C_6F_5)$_2$)}] (**4**) and the zwitterionic species [LGa(C_6F_5){CH(Ph)(OAl(C_6F_5)$_2$)}] (**5**), respectively, which was found to decompose at 80 °C with the formation of {(C_6F_5)$_2$Al(OCH_2Ph)}$_2$ (**6**). Any attempts to isolate the insertion complex of [LGa-Ga(C_6F_5)$_3$] with benzaldehyde failed and only {(C_6F_5)$_2$Ga(OCH_2Ph)}$_2$ (**7**) was isolated at elevated temperatures. **2–5** and **7** were structurally characterized by heteronuclear NMR spectroscopy and single crystal X-ray diffraction.

Introduction

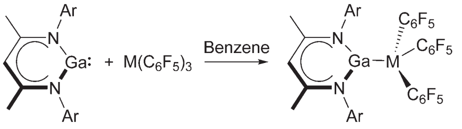
The activation of small molecules including the reversible splitting of H_2 by frustrated Lewis pairs (FLP) has received growing interest since the initial report of Stephan *et al.* in 2006.[1] Most FLPs contain the strong Lewis acid B(C_6F_5)$_3$ and Lewis basic phosphines PR_3, but other Lewis acids such Al(C_6F_5)$_3$ [2] and Lewis bases such as N-bases[3] and singlet carbenes CR_2 [4] have also been successfully applied for the synthesis of FLP. In addition, FLPs containing a constrained geometry with a rigid molecular backbone were initially prepared by Erker *et al.*,[5] while Uhl *et al.*, Stephan *et al.* and others expanded this class of compounds to Al/P FLPs.[6]

LGa ({L = HC[C(Me)N(2,6-i-$Pr_2C_6H_3$)]$_2$}), which is monomeric in the solid state and in solution,[7] may react as an electrophilic and a nucleophilic reagent due to the presence of an electron lone pair and an empty p-orbital. However, quantum chemical calculations proved that LGa is a good σ-donor but a poor π-acceptor.[8] The excellent σ-donor capacity of LGa was proven in reactions with Lewis acidic complexes such as B(C_6F_5)$_3$, yielding the Lewis acid–base adduct LGa-B(C_6F_5)$_3$,[9] and in reactions with a large variety of p- and d-block metal complexes.[10]

Due to our general interest in Lewis acid–base reactions,[11] we investigated the reactions of group 13 Lewis acid MR_3 (M = Al, Ga, In) and group 15 Lewis bases ER_3 (E = N, P, As, Sb, Bi)[12] and E_2R_4 (E = Sb, Bi).[13] In addition, these studies were expanded to group 13 diyl compounds Cp*M (M = Al, Ga, In), which also serve as Lewis bases due to the presence of an electron lone pair.[14] More recently, we started to investigate the reactions of LGa with different main group metal compounds including $InEt_3$,[15] $BiEt_3$,[16] Sb(NMe_2)$_3$,[17] E_2Et_4 (E = Sb, Bi)[18] as well as $TeEt_2$ and Te_2Et_2,[19] respectively, in detail. We herein expanded our investigations on the reactions of LGa with different group 13 Lewis acids M(C_6F_5)$_3$ (M = B, Al, Ga) and also report on their potential use for small molecule activation reactions such as benzaldehyde.

Results and discussion

LGa readily reacts at ambient temperature with M(C_6F_5)$_3$ (M = Al, Ga) to form the Lewis acid–base adducts [LGa-Al(C_6F_5)$_3$] **2** and [LGa-Ga(C_6F_5)$_3$] **3** in good yields as was previously reported for the reaction of LGa and B(C_6F_5)$_3$ (Scheme 1).[9] **2** and **3** are colourless solids, which are moderately stable toward air and can be stored at room temperature under an



M = B **1**; Al **2**; Ga **3**
Ar = 2,6-^{i}Pr_2-C_6H_3

Scheme 1 Synthesis of **1**, **2** and **3**.

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† Electronic supplementary information (ESI) available: Crystallographic data of 2–5, and 7 and ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectra and IR spectra of 2–7. CCDC 1477155–1477158. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt01688j

inert gas atmosphere for several months. ^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra of **1**, **2** and **3** are almost identical and show the characteristic resonances of the organic substituents. The formation of **2** and **3** was also confirmed by single crystal X-ray diffraction studies. A temperature dependent ^{1}H NMR spectroscopy study with compound **2** was performed (Fig. S26†), clearly demonstrating that the chemical shifts of the gallanediyl fragment LGa in **2** are shifted compared to those of pure LGa. According to these findings, we assume that **2** is only to a very less extent dissociated in solution at ambient temperature.

Fig. 1 and 2 show the molecular structures of **2** and **3**. **2** and **3** are isostructural and crystallize in the monoclinic crystal system in the space group $P2_1/n$. The Ga$^{\mathrm{I}}$ atom in **1–3** adopts trigonal planar geometries whereas the M$^{\mathrm{III}}$ atoms of the M(C$_6$F$_5$)$_3$ unit (M = B, Al, Ga) adopt distorted tetrahedral geometries. The average Ga–N bond lengths in **1** (1.942(6) Å), **2** (1.9265 Å) and **3** (1.9235 Å) are similar and considerably shorter than those observed in LGa (2.054(2) Å), which was previously explained by Power *et al.* by the conversion of the gallium electron lone pair into a gallium–boron donor–acceptor bond, and the concomitant development of positive and negative charges on the gallium and boron atoms.[9]

The Ga$^{\mathrm{I}}$–Al$^{\mathrm{III}}$ bond length of **2** (2.5482(4) Å) is in between those reported for Cp*Ga-AlR$_3$ {R = *t*-Bu (2.629(2) Å),[14] C$_6$F$_5$ (2.515(11) Å)},[20] while the Ga$^{\mathrm{I}}$–Ga$^{\mathrm{III}}$ bond length in **3** (2.4819(2) Å) is comparable to those observed in CpGa-GaCp$_2$I (2.4690(17) Å),[21] [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ga-GaI$_3$ (2.494(2) Å),[22] [HB(3,5-(*t*-Bu)$_2$Pz)$_3$]Ga-GaI$_3$ (2.506(3) Å).[23] In contrast, those reported for [Tm$^{t\text{-Bu}}$]Ga-GaI$_3$ (2.4138(4), 2.4254(3) Å); {Tm$^{t\text{-Bu}}$ = tris(2-mercapto-1-*tert*-butylimidazolyl)hydroborate},[24] Cp*Ga-Cp*GaX$_2$ {X = Cl, 2.4245(3); I, 2.437(2) Å},[25] [HB(3,5-(Me)$_2$Pz)$_3$]Ga-GaX$_3$ (X = Cl, 2.4155(7) Å; I, 2.4215(5) Å) and {[HB(3,5-(Me)$_2$Pz)$_3$]Ga}$_2$[Ga$_2$I$_4$] (2.4358(8) Å) are shorter.[26] In addition, the Ga$^{\mathrm{I}}$–M$^{\mathrm{III}}$ bond lengths in **2** (2.5482(4) Å) and **3** (2.4819(2) Å) slightly deviate from the sum of the covalent radii (single-bond covalent radii of Al 1.26 Å, Ga 1.24 Å).[27] However, one has to keep in mind that the covalent radii are not really helpful for the discussion of E–E distances due to a strong charge separation, in particular in the case of the organoaluminum compound. As a consequence, the intermetallic bond distances are strongly influenced by electrostatic repulsion between the metal atoms resulting from their relatively high partial positive charges.

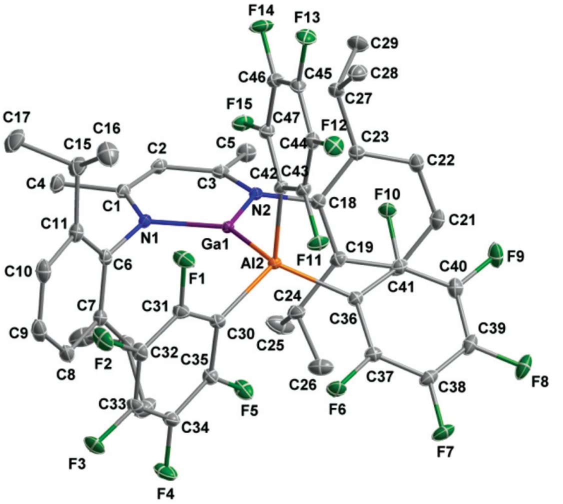


Fig. 1 Solid state structure of **2** (thermal ellipsoids are shown at 30% probability levels); H atoms are omitted for clarity. Selected bond lengths and angles in Å and °: Ga(1)–Al(2) 2.5482(4), Ga(1)–N(1) 1.9265(10), Ga(1)–N(2) 1.9261(9), Al(2)–C(30) 2.0007(12), Al(2)–C(36) 2.0082(12), Al(2)–C(42) 2.0114(11), N(2)–Ga(1)–N(1) 95.35(4), N(2)–Ga(1)–Al(2) 136.28(3), N(1)–Ga(1)–Al(2) 128.27(3), C(30)–Al(2)–Ga(1) 105.99(4), C(36)–Al(2)–Ga(1) 113.86(3), C(42)–Al(2)–Ga(1) 102.59(3), C(30)–Al(2)–C(36) 111.51(5), C(30)–Al(2)–C(42) 113.44(5), C(36)–Al(2)–C(42) 109.19(5).

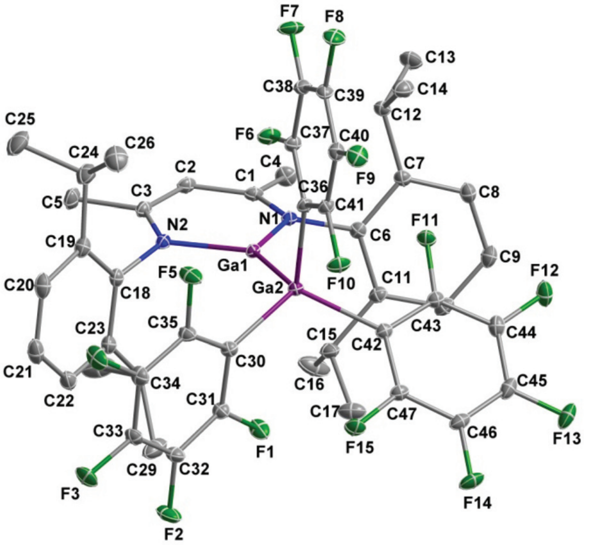
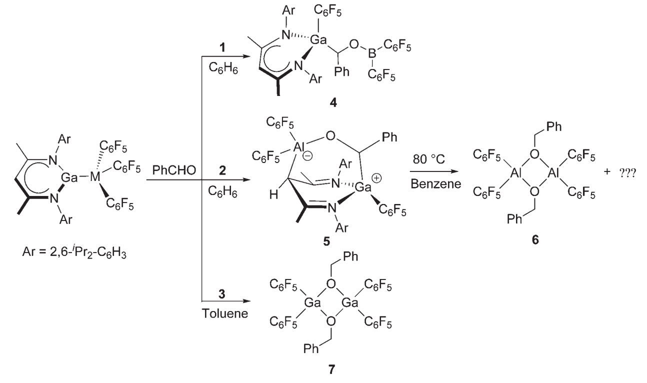


Fig. 2 Solid state structure of **3** (thermal ellipsoids are shown at 30% probability levels); H atoms are omitted for clarity. Selected bond lengths and angles in Å and °: Ga(1)–Ga(2) 2.4819(2), Ga(1)–N(1) 1.9233(9), Ga(1)–N(2) 1.9236(9), Ga(2)–C(30) 2.0053(11), Ga(2)–C(36) 2.0127(11), Ga(2)–C(42) 2.0154(11), N(1)–Ga(1)–N(2) 96.95(4), N(1)–Ga(1)–Ga(2) 136.39(3), N(2)–Ga(1)–Ga(2) 127.59(3), C(30)–Ga(2)–C(36) 112.89(4), C(30)–Ga(2)–C(42) 111.08(4), C(36)–Ga(2)–C(42) 108.04(4), C(30)–Ga(2)–Ga(1) 107.12(3), C(36)–Ga(2)–Ga(1) 102.94(3), C(42)–Ga(2)–Ga(1) 114.61(3).

In order to investigate the potential use of **1–3** for the activation of small molecules, we investigated exemplarily their reactions with benzaldehyde. The reaction of [LGa-B(C$_6$F$_5$)$_3$] **1** with an equimolar amount of benzaldehyde occurred with the insertion and subsequent migration of one C$_6$F$_5$ moiety, finally resulting in the formation of [LGa(C$_6$F$_5$){CH(Ph)(OB(C$_6$F$_5$)$_2$)}] **4** in high yield (Scheme 2).

The rather complex ^{1}H NMR spectrum shows four septets and eight doublets for the isopropyl substituents. In addition, four singlets for the γ-C*H* (5.00 ppm), the C*H*Ph (5.89 ppm) and the ArNCC*H*$_3$ protons (1.49, 1.33 ppm) result from the chirality of the CHPh carbon atom as well as the hindered rotation about the *N*-aryl bonds. The ^{13}C{^{1}H} NMR spectrum of **4** displays interestingly three (171.3, 171.3, 170.9 ppm) and two (100.0, 99.9 ppm) resonances for the ArN*C*CH$_3$ and γ-*C*H



Scheme 2 Reactivity studies of **1–3** with benzaldehyde.

carbon atoms, respectively. Nevertheless, $^{13}C\{^1H\}$ and ^{19}F NMR spectra are consistent with the formation of **4**. The molecular structure of **4** is further elucidated by single crystal X-ray diffraction studies.

Crystals of **4** suitable for a single crystal X-ray diffraction study were obtained from a saturated toluene solution at −30 °C after storage for 2 days. **4** crystallises in the monoclinic space group $P2_1/c$. The Ga atom adopts a distorted tetrahedral coordination geometry, whereas the B atom shows a trigonal planar coordination sphere and the sum of the bond angles is close to 360°. The six-membered C_3N_2Ga rings in LGa and LGa-B$(C_6F_5)_3$ **1** are essentially planar, whereas the Ga atom in **4** is out of plane (deviation from the best plane of the ligand backbone 0.721(4) Å). The bite angles of the chelating organic ligand L (96.1(1)° **1**, 95.4(1)° **2**, 96.0(1)° **3**, 96.0(1) **4**) are almost identical. The Ga–N bond lengths in **4** (1.951(3), 1.967(3) Å) are shorter than those in LGa as was observed for **2** and **3**.

The analogous reaction of **2** with benzaldehyde afforded the zwitterionic compound, [LGa(C_6F_5)\{CH(Ph)(OAl$(C_6F_5)_2$)\}] **5**. The formation of **5** most likely occurs with the initial formation of the insertion product as was observed for **4**, but we were not able to isolate this species. **5** is subsequently formed by the rearrangement of the two substituents \{C_6F_5, CH(Ph)(OAl$(C_6F_5)_2$)\} as shown in Scheme 3a.

This reaction also proves that β-diketiminate ligands should not be regarded as non-innocent ligands as was previously demonstrated in reactions of cationic β-diketiminate aluminium complexes of the type $[LAlR]^+B(C_6F_5)_4^-$ (R = Me, Et, ^{i}Bu), which were found to undergo cycloaddition reactions with alkenes and alkynes with the subsequent formation of similar β-diketimine complexes of the general type [κ3-*N*,*N*,C-\{HC(C(Me)N(2,6-i-$Pr_2C_6H_3$))$_2$(R′C═CR″)\}AlR]$^+$[B$(C_6F_5)_4$]$^-$ (R′ = R″ = Me; R′ = Ph, R″ = H) and [κ3-*N*,*N*,C-\{HC(C(Me)N(2,6-^{i}Pr$_2C_6H_3$))$_2$(R′CHCH$_2$)\}AlR]$^+$[B$(C_6F_5)_4$]$^-$ (R′ = H, ^{n}Bu).[28] In addition, we recently reported on the synthesis of the homoleptic thio-β-ketimine zinc complex [MesNC(Me)CH\{C(Me)NMes\}S]$_2$Zn by the reaction of elemental sulfur with [CH\{C(Me)NMes\}$_2$]ZnMe (Mes = 2,4,6-$Me_3C_6H_2$).[29]

The ^1H NMR spectrum of **5** shows four septets (3.26, 2.88, 2.57, 2.41 ppm), three distinct doublets (1.24, 0.98, 0.61 ppm) and two multiplets at 1.06 ppm (two overlapping doublets) and 0.44 ppm (three overlapping doublets) for the isopropyl substituents as well as the four expected singlets for the γ-C*H* (4.71 ppm), ArNCC*H*$_3$ (1.55, 1.53 ppm) and C*H*Ph (6.42 ppm)

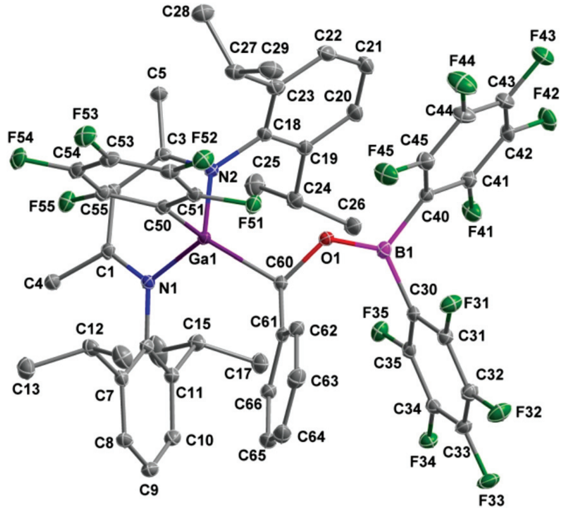


Fig. 3 Solid state structure of **4** (thermal ellipsoids are shown at 30% probability levels); H atoms are omitted for clarity. Selected bond lengths and angles in Å and °: Ga(1)–N(1) 1.951(3), Ga(1)–N(2) 1.967(3), Ga(1)–C(60) 2.010(3), Ga(1)–C(50) 2.034(3), B(1)–O(1) 1.332(4), B(1)–C(40) 1.583(5), B(1)–C(30) 1.589(5), O(1)–C(60) 1.470(4), C(60)–C(61) 1.510(4); N(1)–Ga(1)–N(2) 96.0(1), N(1)–Ga(1)–C(60) 109.9(1), N(2)–Ga(1)–C(60) 111.9(1), N(1)–Ga(1)–C(50) 110.2(1), N(2)–Ga(1)–C(50) 106.0(1), C(60)–Ga(1)–C(50) 120.2(2), O(1)–B(1)–C(40) 117.0(3), O(1)–B(1)–C(30) 125.1(3), C(40)–B(1)–C(30) 117.9(3), B(1)–O(1)–C(60) 125.0(2), O(1)–C(60)–Ga(1) 105.9(2), C(61)–C(60)–Ga(1) 117.4(2).

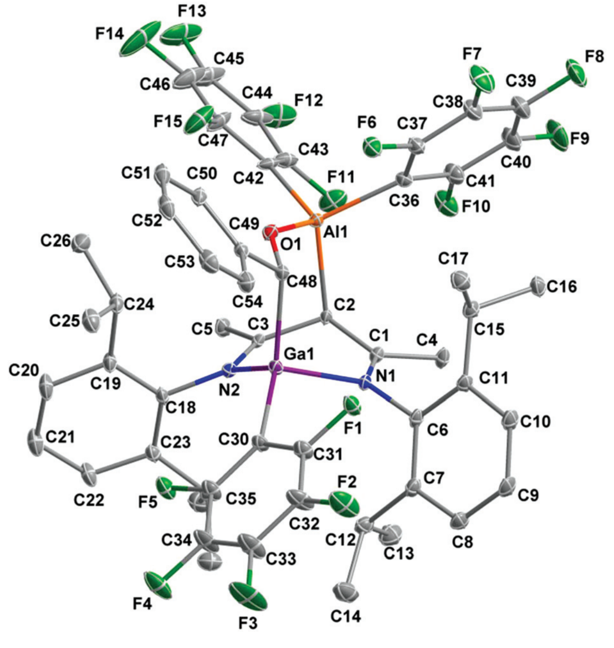
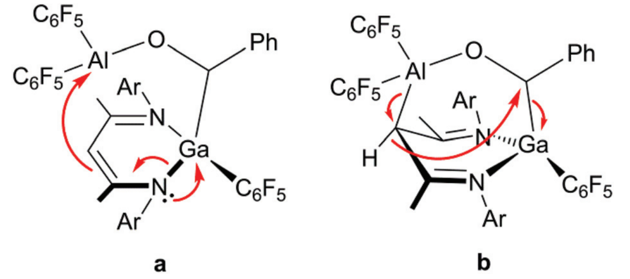


Fig. 4 Solid state structure of **5** (thermal ellipsoids are shown at 30% probability levels); H atoms and the lattice solvent are omitted for clarity.



Scheme 3 Proposed reaction mechanism for the formation of **5** and **6**.

groups. The γ-*C*H resonance of **5** (71.1 ppm) in the $^{13}C\{^1H\}$ NMR is shifted to a higher field compared to that observed for **2** (102.4 ppm) as was also observed for the imine carbon resonances (170.4 ppm **2**, 188.4, 186.6 ppm **5**). Such drastic chemical shifts were not observed in the $^{13}C\{^1H\}$ NMR spectrum of **4** in comparison to **1** and the findings are consistent with the conversion of the β-diketiminate ligand of **2** into a β-diketimine ligand in **5** (re-hybridization from sp^2 to sp^3). Any attempt to thermally convert **4** into a zwitterionic analogue of **5** failed since **4** was found to be thermally very stable and could be heated in benzene (80 °C) for several hours without any decomposition. In contrast, compound **5** is thermolabile and further decomposes above 40 °C with the subsequent formation of $\{(C_6F_5)_2Al(OCH_2Ph)\}_2$ **6** as well as so far unidentified products. A possible decomposition pathway is depicted in Scheme 3b.

An inspection of the reciprocal lattice of the crystals of **5** suggests a non-merohedral twinning with a pronounced overlap of the reflections. Even after re-collecting data with a reduced scan-width per frame and increased detector distance a separation was not possible. Consequently, the quality of the resulting structure model is limited but still good enough to confirm the connectivity of **5**.

4 and **5** are most likely formed in a two-step reaction process as was shown by *in situ* ^{1}H NMR spectroscopy studies on the stepwise reactions of benzaldehyde with $B(C_6F_5)_3$ and $Al(C_6F_5)_3$, which proceeded with the formation of the corresponding Lewis acid–base adducts, which then consequently reacted with LGa with the formation of **4** and **5**, respectively (Fig. S27 and S28†). The experiments clearly demonstrated that the simultaneous presence of both the Lewis acid and the Lewis base, which is the prerequisite for a concerted reaction mechanism as is typical for frustrated Lewis acid–base pairs, is not necessary.

Several attempts to synthesise the Ga–Ga analogues of **5** by the reaction of **3** and benzaldehyde failed and only the starting reagents were recovered. However, equimolar amounts of **3** and benzaldehyde reacted in toluene at 120 °C with the formation of $\{(C_6F_5)_2Ga(OCH_2Ph)\}_2$ **7** in 18% yield. **6** and **7** are moderately stable towards air. They dissolve well upon heating in benzene, toluene and chloroform but quickly precipitate at room temperature. The ^{1}H NMR spectra of **6** and **7** show singlets and multiplets for the –C*H*$_2$– (4.81 ppm for **6**, 4.74 ppm for **7**) and phenyl protons (6.99–6.66 ppm for **6** and **7**), while $^{13}C\{^1H\}$ NMR spectra could not be obtained due to their limited solubility.

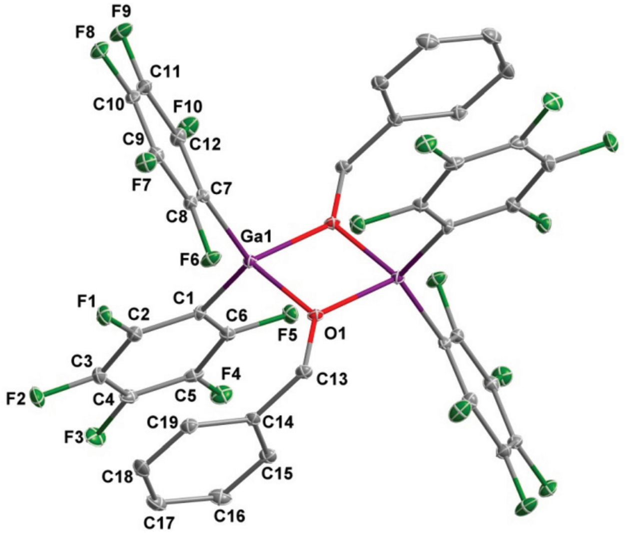


Fig. 5 Solid state structure of **7** (thermal ellipsoids are shown at 30% probability levels); H atoms are omitted for clarity. Selected bond lengths and angles in Å and °: Ga(1)–O(1) 1.913(2), Ga(1)–O(1)#1 1.915(2), Ga(1)–C(1) 1.963(3), Ga(1)–C(7) 1.972(3), Ga(1)–Ga(1)#1 2.9603(7), O(1)–C(13) 1.451(4), O(1)–Ga(1)#1 1.915(2), C(13)–C(14) 1.494(4), O(1)–Ga(1)–O(1)#1 78.7(2), O(1)–Ga(1)–C(1) 113.4(2), O(1)#1–Ga(1)–C(1) 112.9(1), O(1)–Ga(1)–C(7) 109.9(1), O(1)#1–Ga(1)–C(7) 114.1(1), C(1)–Ga(1)–C(7) 120.5(2), O(1)–Ga(1)–Ga(1)#1 39.4(1), O(1)#1–Ga(1)–Ga(1)#1 39.3(1), C(1)–Ga(1)–Ga(1)#1 120.5(1), C(7)–Ga(1)–Ga(1)#1 118.9(1), C(13)–O(1)–Ga(1) 130.4(2), C(13)–O(1)–Ga(1)#1 128.2(2), Ga(1)–O(1)–Ga(1)#1 101.3(1), O(1)–C(13)–C(14) 110.7(2).

The molecular structure of **7** was confirmed by single-crystal X-ray diffraction. Colourless crystals of **7** were obtained upon slow cooling of a warm benzene solution of **7** to room temperature. **7** crystallises in the triclinic space group $P\bar{1}$. The four-membered Ga_2O_2 ring possesses a planar structure with the distorted tetrahedral geometries for the Ga atoms. The CH_2Ph groups adopt a *trans*-orientation with an O1–C13–C14 angle of 110.7(2)°. The *endo*- and exocyclic bond angles within the Ga_2O_2 ring are 78.7(1)° (O1–Ga1–O1*) and 101.3(1)° (Ga1–O1–Ga1*), respectively. The Ga1–O1 (1.913(2) Å) and Ga1–O1* (1.915(2) Å) bond distances are almost identical (Fig. 5).

Conclusions

Benzaldehyde readily reacts with the Lewis acid–base adducts $[LGa\text{-}M(C_6F_5)_3]$ (M = B **1**, Al **2**), which were quantitatively formed in the reaction of LGa and $M(C_6F_5)_3$, with the formation of the insertion product **4** as well as the zwitterionic compound **5**. **5** is formed by the attack of the strongly Lewis-acidic aluminum atom on the γ-C atom of the β-diketiminate ligand. At elevated temperatures, **5** further reacts with subsequent activation of the γ-CH group and formation of **6** as well as so far unidentified compounds. A similar decomposition product **7** was obtained from the analogous reaction of [LGa-Ga(C_6F_5)$_3$] **3** and benzaldehyde, while the insertion analogue of **5** could not be isolated. The activation of other organic derivatives upon reaction with Lewis acid–base adducts derived from monovalent group 13 diyls is currently being investigated in our laboratory in order to obtain a deeper understanding of the mechanism of main-group element based homogeneous catalysis reactions.

Experimental

All manipulations were performed under an atmosphere of purified argon using standard Schlenk and glove-box techniques. Toluene and hexane were dried using a mBraun Solvent Purification System. Benzene was carefully dried over Na. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. The anhydrous nature of the solvents was verified by Karl Fischer titration. LGa {L = HC[C(Me)N(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$},[7] B(C_6F_5)$_3$,[30] Ga(C_6F_5)$_3$·OEt$_2$,[31] Al(C_6F_5)$_3$(toluene)$_{0.5}$,[32] and [LGa-B(C_6F_5)$_3$][9] were prepared according to literature methods and other chemicals were obtained from commercial sources and purified prior to use. The ^{1}H (300.1 MHz), ^{13}C{^{1}H} (75.5 MHz) and ^{19}F (282.4 MHz) NMR (δ in ppm) spectra were recorded using a Bruker Avance DPX-300 spectrometer and the spectra were referenced to internal C_6D_5H (^{1}H: δ = 7.154; ^{13}C: δ = 128.39). The microanalyses were performed at the elemental analysis laboratory of the University of Duisburg-Essen. IR spectra were recorded with an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The IR spectrometer was placed in a glovebox to guarantee measurements under inert gas conditions. The melting points were measured using a Thermo Scientific 9300 apparatus.

Synthesis of 2

A mixture of LGa (200 mg, 0.410 mmol) and Al(C_6F_5)$_3$($C_6H_5CH_3$)$_{0.5}$ (236 mg, 0.410 mmol) in 5 mL of benzene was stirred at room temperature for 4 h. The solution was concentrated to 2 mL and kept at room temperature for 1 day to afford colorless crystals of **2**. Yield: 315 mg (0.310 mmol, 76%). M.pt: 219 °C. Anal. calcd for $C_{47}H_{41}N_2AlF_{15}Ga$: C, 55.59; H, 4.07; N, 2.76. Found: C, 56.00; H, 4.09; N, 2.89%. IR (neat): ν 2965, 2931, 2871, 1638, 1540, 1506, 1439, 1377, 1361, 1316, 1261, 1178, 1106, 1065, 1054, 1024, 952, 869, 800, 760, 743, 719, 646, 606, 581, 528, 498, 448, 388 cm^{-1}. ^{1}H NMR (C_6D_6, 300.1 MHz): δ 7.01 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, C_6H_3(^{i}Pr)$_2$), 6.79 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, C_6H_3(^{i}Pr)$_2$), 5.07 (s, 1 H, γ-C*H*–), 2.75 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, –C*H*(CH$_3$)$_2$), 1.46 (s, 6 H, ArNCC*H*$_3$), 1.01 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, –CH(C*H*$_3$)$_2$), 0.90 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, –CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 170.38 (ArN*C*CH$_3$), 151.78 (*C*$_6$F$_5$), 148.71 (*C*$_6$F$_5$), 142.97 (NC of *C*$_6$H$_3$), 139.82 (*o*-C of *C*$_6$H$_3$), 138.87 (*C*$_6$F$_5$), 135.57 (*C*$_6$F$_5$), 129.03 (*m*-C of *C*$_6$H$_3$), 124.92 (*p*-C of *C*$_6$H$_3$), 102.37 (γ-*C*H–), 29.71 (–*C*H(CH$_3$)$_2$), 24.74 (ArNC*C*H$_3$), 24.11 (–CH(*C*H$_3$)$_2$), 23.91 (–CH(*C*H$_3$)$_2$). ^{19}F NMR (C_6D_6, 282.4 MHz): δ −118.95 (m), −154.39 (t, $^3J_{FF}$ = 20 Hz), −161.43 (m).

Synthesis of 3

3 was synthesized by following the procedure of **2** using LGa (400 mg, 0.821 mmol) and Ga(C_6F_5)$_3$·OEt$_2$ (529 mg, 0.821 mmol). Yield: 770 mg (0.727 mmol, 89%). M.pt: 220 °C. Anal. calcd for $C_{47}H_{41}N_2F_{15}Ga_2$: C, 53.34; H, 3.91; N, 2.65. Found: C, 53.80; H, 3.92; N, 2.64%. IR (neat): ν 2965, 2931, 2871, 1638, 1541, 1505, 1457, 1440, 1362, 1316, 1260, 1178, 1062, 1053, 1025, 953, 870, 800, 788, 760, 717, 645, 606, 528, 488, 445, 385 cm^{-1}. ^{1}H NMR (C_6D_6, 300.1 MHz): δ 7.00 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, C_6H_3(^{i}Pr)$_2$), 6.78 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, C_6H_3(^{i}Pr)$_2$), 5.05 (s, 1 H, γ-C*H*–), 2.75 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, –C*H*(CH$_3$)$_2$), 1.46 (s, 6 H, ArNCC*H*$_3$), 1.01 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, –CH(C*H*$_3$)$_2$), 0.90 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, *J* = 6.6 Hz, –CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 170.78 (ArN*C*CH$_3$), 150.87 (*C*$_6$F$_5$), 147.74 (*C*$_6$F$_5$), 142.97 (NC of *C*$_6$H$_3$), 139.63 (*o*-C of *C*$_6$H$_3$), 139.03 (*C*$_6$F$_5$), 135.55 (*C*$_6$F$_5$), 129.08 (*m*-C of *C*$_6$H$_3$), 124.95 (*p*-C of *C*$_6$H$_3$), 102.34 (γ-*C*H–), 29.80 (–*C*H(CH$_3$)$_2$), 24.76 (ArNC*C*H$_3$), 24.01 (–CH(*C*H$_3$)$_2$), 23.94 (–CH(*C*H$_3$)$_2$). ^{19}F NMR (C_6D_6, 282.4 MHz): δ −119.61 (m), −155.85 (t, $^3J_{FF}$ = 20 Hz), −161.63 (m).

Synthesis of 4

[LGa-B(C_6F_5)$_3$] (**1**) (410 mg, 0.410 mmol) was dissolved in 4 mL of toluene. Benzaldehyde (43.5 mg, 42 μL, 0.410 mmol) was added to the above solution and the reaction mixture was stirred at room temperature for 2 h. The solution was concentrated to 2 mL, layered with 1 mL of hexane and stored at −30 °C for 2 days to afford colorless microcrystals of **4**. Yield: 356 mg (0.322 mmol, 78%). M.pt: 200 °C. Anal. calcd for $C_{54}H_{47}N_2BF_{15}GaO$: C, 58.67; H, 4.29; N, 2.53. Found: C, 58.80; H, 4.30; N, 2.56%. IR (neat): ν 2968, 2930, 2871, 1651, 1520, 1481, 1455, 1439, 1385, 1312, 1258, 1174, 1145, 1093, 1073, 1054, 1017, 974, 961, 936, 916, 866, 842, 801, 776, 760, 740, 707, 626, 594, 578, 552, 531, 515, 501, 485, 441 cm^{-1}. ^{1}H NMR (C_6D_6, 300.1 MHz): δ 7.13–6.39 (m, 11 H, C_6H_3(^{i}Pr)$_2$, C_6H_5), 5.89 (s, 1 H, –C*H*-Ph), 5.00 (s, 1 H, γ-C*H*–), 3.47 (two sept, $^3J_{HH}$ = 6.9 Hz, 2 H, –C*H*(CH$_3$)$_2$), 2.71 (sept, $^3J_{HH}$ = 6.6 Hz, 1 H, –C*H*(CH$_3$)$_2$), 2.47 (sept, $^3J_{HH}$ = 6.6 Hz, 1 H, –C*H*(CH$_3$)$_2$), 1.63 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, –CH(C*H*$_3$)$_2$), 1.49 (s, 3 H, ArNCC*H*$_3$), 1.43 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, –CH(C*H*$_3$)$_2$), 1.33 (s, 3 H, ArNCC*H*$_3$), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, –CH(C*H*$_3$)$_2$), 1.03 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, –CH(C*H*$_3$)$_2$), 0.98 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, –CH(C*H*$_3$)$_2$), 0.83 (two overlapping d, $^3J_{HH}$ = 6.6 Hz, 6 H, –CH(C*H*$_3$)$_2$), −0.34 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, –CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 171.32 (ArN*C*CH$_3$), 171.27 (ArN*C*CH$_3$), 170.92 (ArN*C*CH$_3$), 148.58 (*C*$_6$F$_5$), 145.73 (*C*$_6$H$_3$), 145.34 (*C*$_6$F$_5$), 144.82 (*C*$_6$H$_3$), 144.23 (*C*$_6$H$_3$), 142.89 (*C*$_6$H$_3$), 142.71 (*C*$_6$H$_3$), 142.65 (*C*$_6$H$_3$), 142.12 (*C*$_6$H$_3$), 140.94 (*C*$_6$F$_5$), 139.97 (*C*$_6$F$_5$), 139.20 (*C*$_6$F$_5$), 135.87 (*C*$_6$F$_5$), 128.26 (*C*$_6$H$_3$), 126.65 (*C*$_6$H$_3$), 126.03 (*C*$_6$H$_3$), 125.80 (*C*$_6$H$_3$), 125.34 (*C*$_6$H$_3$), 125.21 (*C*$_6$H$_3$), 124.78 (*C*$_6$H$_3$), 123.47 (*C*$_6$H$_3$), 100.03 (γ-*C*H–), 99.93 (γ-*C*H–), 82.34 (–*C*H-Ph), 29.96 (–*C*H(CH$_3$)$_2$), 29.15 (–*C*H(CH$_3$)$_2$), 28.46 (–*C*H(CH$_3$)$_2$), 27.73 (–*C*H(CH$_3$)$_2$), 27.68 (ArNC*C*H$_3$), 25.58 (ArNC*C*H$_3$), 25.31

$(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 25.16 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 25.03 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 24.68 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 24.50 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 24.30 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 24.16 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 22.43 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$. ^{19}F NMR ($C_6D_6$, 282.4 MHz): δ −110.58 (m), −115.42 (m), −131.06 (m), −152.11 (t, $^3J_{\mathrm{FF}}$ = 20 Hz), −153.73 (t, $^3J_{\mathrm{FF}}$ = 20 Hz), −160.97 (m), −161.80 (m), −162.57 (m).

Synthesis of 5

[LGa-Al(C_6F_5)$_3$] (**2**) (100 mg, 0.098 mmol) was dissolved in 0.5 mL of benzene and benzaldehyde (10.4 mg, 10 μL, 0.098 mmol) was added. The solution was stirred at room temperature for 30 minutes and stored at 9 °C for 1 day to afford colorless crystals of **5**. Yield: 77 mg (0.069 mmol, 70%). Anal. calcd for $C_{54}H_{47}N_2AlF_{15}GaO$: C, 57.82; H, 4.22; N, 2.50. Found: C, 58.80; H, 4.30; N, 2.56%. IR (neat): ν 2968, 2932, 2872, 1638, 1595, 1582, 1531, 1509, 1443, 1387, 1366, 1317, 1272, 1225, 1178, 1165, 1068, 1025, 958, 865, 843, 798, 753, 721, 700, 652, 615, 582, 517, 497, 445, 404 cm^{-1}. ^{1}H NMR (C_6D_6, 300.1 MHz): δ 7.79–6.69 (m, 11 H, $\mathrm{C}_6H_3(^i\mathrm{Pr})_2$, C_6H_5), 6.42 (s, 1 H, $-\mathrm{C}H$-Ph), 4.71 (s, 1 H, γ-CH–), 3.26 (sept, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 1 H, $-\mathrm{C}H(\mathrm{CH}_3)_2$), 2.88 (sept, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 1 H, $-\mathrm{C}H(\mathrm{CH}_3)_2$), 2.57 (sept, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 1 H, $-\mathrm{C}H(\mathrm{CH}_3)_2$), 2.41 (sept, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 1 H, $-\mathrm{C}H(\mathrm{CH}_3)_2$), 1.55 (s, 3 H, ArNCC$H_3$), 1.53 (s, 3 H, ArNCC$H_3$), 1.24 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 3 H, $-\mathrm{CH}(\mathrm{C}H_3)_2$), 1.06 (two overlapping d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 6 H, $-\mathrm{CH}(\mathrm{C}H_3)_2$), 0.98 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3 H, $-\mathrm{CH}(\mathrm{C}H_3)_2$), 0.61 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 3 H, $-\mathrm{CH}(\mathrm{C}H_3)_2$), 0.44 (three overlapping d, 9 H, $-\mathrm{CH}(\mathrm{C}H_3)_2$). ^{13}C NMR ($C_6D_6$, 75.5 MHz): δ 188.56 (ArNCCH$_3$), 186.86 (ArNCCH$_3$), 152.11 (C_6F$_5$), 150.39 (C_6F$_5$), 149.00 (C_6F$_5$), 148.42 (C_6H$_3$), 147.15 (C_6F$_5$), 144.41 (C_6H$_3$), 143.98 (C_6F$_5$), 143.37 (C_6H$_3$), 141.36 (C_6H$_3$), 141.28 (C_6H$_3$), 140.67 (C_6F$_5$), 139.86 (C_6H$_3$), 139.25 (C_6H$_3$), 136.16 (C_6F$_5$), 129.19 (C_6H$_3$), 129.09 (C_6H$_3$), 128.91 (C_6H$_3$), 126.80 (C_6H$_3$), 126.36 (C_6H$_3$), 125.43 (C_6H$_3$), 125.16 (C_6H$_3$), 124.19 (C_6H$_3$), 123.81 (C_6H$_3$), 73.25 ($-C\mathrm{H}$-Ph), 71.10 (γ-CH–), 30.05 $(-C\mathrm{H}(\mathrm{CH}_3)_2)$, 29.47 $(-C\mathrm{H}(\mathrm{CH}_3)_2)$, 29.28 $(-C\mathrm{H}(\mathrm{CH}_3)_2)$, 28.21 $(-C\mathrm{H}(\mathrm{CH}_3)_2)$, 26.76 (ArNC$CH_3$), 26.34 (ArNC$CH_3$), 25.50 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 25.47 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 25.24 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 24.88 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 24.84 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 24.32 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 23.62 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$, 21.93 $(-\mathrm{CH}(C\mathrm{H}_3)_2)$. ^{19}F NMR ($C_6D_6$, 282.4 MHz): δ −115.76 (m), −119.01 (m), −120.62 (m), −150.84 (t, $^3J_{\mathrm{FF}}$ = 20 Hz), −152.44 (m), −160.37 (m), −160.85 (m).

Synthesis of 6

A solution of **5** (100 mg, 0.089 mmol) in 0.5 mL of C_6D_6 was heated at 80 °C for 4 h in a J-Young NMR tube. The reaction mixture was kept at room temperature for 2 days to afford **6** as a colorless microcrystalline solid. Yield: 37 mg (0.039 mmol, 88%). M.pt: >300 °C. Anal. calcd for $C_{38}H_{14}Al_2F_{20}O_2$: C, 48.74; H, 1.51. Found: C, 48.50; H, 1.69%. IR (neat): ν 1643, 1512, 1449, 1381, 1364, 1279, 1216, 1069, 956, 919, 828, 755, 701, 664, 611, 575, 543, 511, 464, 425 cm^{-1}. ^{1}H NMR (C_6D_6, 300.1 MHz): δ 6.97 (m, 2 H, C_6H_5), 6.71 (m, 3 H, C_6H_5), 4.81 (s, 2 H, –OCH_2–). ^{19}F NMR (C_6D_6, 282.4 MHz): δ −122.03 (m), −149.33 (t, $^3J_{\mathrm{FF}}$ = 20 Hz), −160.01 (m).

Synthesis of 7

A solution of [LGa-Ga(C_6F_5)$_3$] (**3**) (208 mg, 0.196 mmol) and benzaldehyde (20.8 mg, 20 μL, 0.196 mmol) in 1 mL of toluene was heated at 120 °C for 2 days. The reaction mixture was brought to room temperature and stored at 7 °C for 1 day to give colorless crystals of **7**. The crystals were washed twice with benzene (2 × 1 mL). Yield: 18 mg (0.0176 mmol, 18%). M.pt: 247 °C. Anal. calcd for $C_{38}H_{14}Ga_2F_{20}O_2$: C, 44.66; H, 1.38. Found: C, 44.52; H, 1.44%. IR (neat): ν 1640, 1511, 1464, 1451, 1372, 1280, 1214, 1067, 1017, 959, 919, 825, 810, 753, 720, 700, 632, 608, 524, 495, 408 cm^{-1}. ^{1}H NMR (C_6D_6, 300.1 MHz): δ 6.98 (m, 2 H, C_6H_5), 6.73 (m, 3 H, C_6H_5), 4.74 (s, 2 H, –OCH_2–). ^{19}F NMR (C_6D_6, 282.4 MHz): δ −123.68 (m), −149.50 (t, $^3J_{\mathrm{FF}}$ = 20 Hz), −159.81 (m).

Single crystal X-ray diffraction

Crystallographic data of **2–4** and **7**,‡ which were collected on a Bruker D8 Kappa APEX2 diffractometer (MoK$_\alpha$ radiation, λ = 0.71073 Å) at 100(1) K, are summarized in Table S1.† The solid-state structures of **2–4** and **7** are shown in Fig. 1–4. The structures were solved by direct methods (SHELXS-97)[33] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2014).[34] Absorption corrections were performed semi-empirically from equivalent reflections on the basis of multi-scans (Bruker AXS APEX2, TWINABS for **7**). Hydrogen atoms were refined using a riding model or rigid methyl groups. The crystal of **7** was a non-merohedral twin and the structure model was refined against HKLF5 data. Details on the best model available for **5** are given in the ESI.†

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‡ The crystallographic data of **2**, **3**, **4**, and **7** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1477155(**2**), 1477157(**3**), 1477158(**4**) and 1477156(**7**).

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