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## Introduction

Compounds of low valent aluminium and gallium in the formal oxidation state of (II) date back to the pioneering discovery of gallium(II) dihalides by Worrall and co-workers in 1979.<sup>1</sup> This was achieved by the recrystallization of  $\text{Ga}_2\text{Cl}_4$  from dioxane at 0 °C to obtain  $\text{Ga}_2\text{Cl}_4$ (dioxane)<sub>2</sub>. In a similar manner,  $\text{Ga}_2\text{Br}_4$ (dioxane)<sub>2</sub> was also isolated and characterized.<sup>2</sup> In the regime of compounds with low valent aluminium, Uhl was the first to isolate and demonstrate the structure of a tetrakis[bis(trimethylsilyl)methyl]dialane in 1988 by a reaction of  $\text{AlCl}_3$  with  $\text{LiCH}(\text{SiMe}_3)_3$ .<sup>3</sup>

Since then a considerable number of Al(II) and Ga(II) atoms have been reported with a wide array of ligand environments (Chart 1). The bond distances vary from 2.5–2.75 Å among Al(II) atoms whereas they are 2.3–2.6 Å among gallium atoms. For example, the substitution of 2,4,6-(<sup>3</sup>Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>-(Trip) powder resulted in the isolation of the dialane  $\text{Trip}_2\text{Al-AlTrip}_2$  via the reduction of  $\text{Trip}_2\text{AlBr}$  with potassium.<sup>4</sup> In addition, the reduction of  $[\text{C}_6\text{H}_3\text{-}2,6-(\text{C}_6\text{H}_3\text{-}2,6-\text{I}^{\text{Pr}})_2]\text{AlI}_2$  with  $\text{KC}_8$  generates the aryl-based 1,2-diiodoalane.<sup>5</sup> Klimek *et al.* described the

## Synthesis and computational aspects of Al(II)–Al(II) and Ga(II)–Ga(II) dihalides based on an amidinate scaffold<sup>†</sup>

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Amidinate compounds with stabilized aluminium(II) and gallium(II) elements of composition  $\text{L}_2\text{M}_2\text{X}_2$  (**3** and **4**) have been prepared from their  $\text{LMX}_2$  (**1** and **2**) precursor, where  $\text{M} = \text{Al}$  (**1** and **4**) and  $\text{Ga}$  (**2** and **3**);  $\text{L} = \text{PhC}(\text{N}^{\text{i}}\text{Pr}_2\text{C}_6\text{H}_3)_2$  (**1** and **4**) and  $\text{PhC}(\text{N}^{\text{t}}\text{Bu})_2$  (**2** and **3**); and  $\text{X} = \text{I}$  (**1** and **4**) and  $\text{Cl}$  (**2** and **3**) and insights into their bonding are gained. The M–M bond lengths are reported along with the single-crystal X-ray structures of **1**–**4**.

preparation of compounds with Al–Al and Ga–Ga bonds as dihalide dimers containing the 1-azaallyl ligand  $[(\text{Me}_3\text{Si})_2\text{C}(\text{Ph})\text{C}(\text{Me}_3\text{Si})\text{N}]$ .<sup>6</sup> Arnold and coworkers synthesized and characterized dialane including hypercoordinated Al atoms with the  $\text{C}_5\text{Me}_5$  ( $\text{Cp}^*$ ) ring,  $[\text{Al}_2\text{I}_2(\eta^5\text{-Cp}^*)_2]$ .<sup>7</sup> This was followed by the synthesis of  $[\text{Al}_2\text{NBr}_2(\eta^5\text{-Cp}^*)_2]$  by Braunschweig and co-workers.<sup>8</sup>

Recently, Stalke and co-workers reported an Al(II) complex [<sup>4-Me</sup>Box<sub>2</sub>CH]HAl–AlH(DippNacNac)] based on the bis(4-methyl-benzoxazole-2-yl)methanide and  $\beta$ -diketiminate (NacNac) ligand.<sup>9</sup> To the best of our knowledge, the shortest distance among Al(II) atoms is reported by Andrade and co-

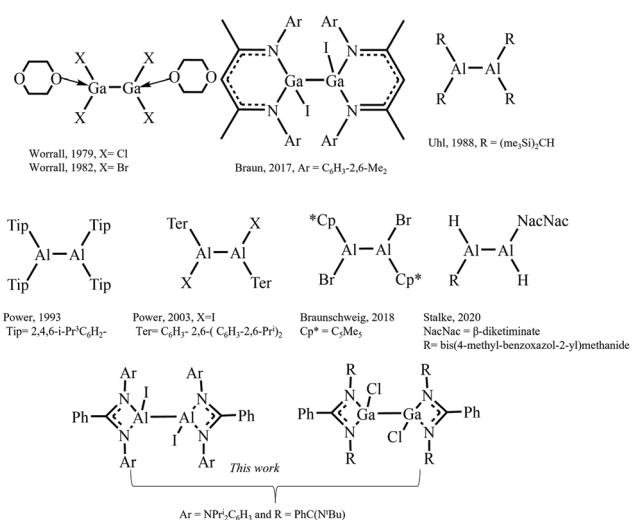


Chart 1 Selected examples of Al(II)–Al(II) and Ga(II)–Ga(II) compounds.

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<sup>†</sup>Electronic supplementary information (ESI) available: Experimental section, tables, crystallography details and additional figures. CCDC 2144443–2144447. For ESI and crystallographic data in CIF or other electronic format see DOI: [10.1039/d2dt00317a](https://doi.org/10.1039/d2dt00317a)



workers; they have reduced the dicarba-bridged dicyclopentadienylaluminium chloride dimer with 1,3- $\beta$ -diketiminate magnesium(i) to produce bis(dicarba[2]aluminocenophane) bearing an Al(ii)-Al(ii) distance of 2.5018(5) Å.<sup>10</sup> In contrast, the longest distance among Al(ii) centers is calculated as 2.751(2).<sup>11</sup> This was achieved by the reaction of aluminium trihalide with supersilyl-sodium to give  $[(R_2Al-Al(R_2)]$ , where R is the supersilyl, Si(*t*-Bu)<sub>3</sub>. Braun and coworkers utilized the sterically demanding  $\beta$ -diketiminate ligand Ldmp = [HC{(CMe)N(dmp)}<sub>2</sub>], where dmp = C<sub>6</sub>H<sub>3</sub>2,6-Me<sub>2</sub> and synthesized a gallium complex of composition [Ga<sub>2</sub>I<sub>2</sub>(Ldmp)<sub>2</sub>] in the oxidation state +II.<sup>12</sup> Fedushkin and coworkers reported a digallane of formula [Ga<sub>2</sub>(Ldmp)<sub>2</sub>] consisting of a redox active dpp-Bian ligand, where dpp-Bian is (1,2-bis [(2,6-diisopropyl phenyl)imino]acenaphthene).<sup>13</sup> So far, only three compounds with an Al=Al double bond have been reported. The first is a silyl-substituted dialumene by Inoue *et al.*<sup>14</sup> followed by an aryl analogue<sup>15</sup> and an amidophosphine-stabilized Al=Al double bond.<sup>16</sup>

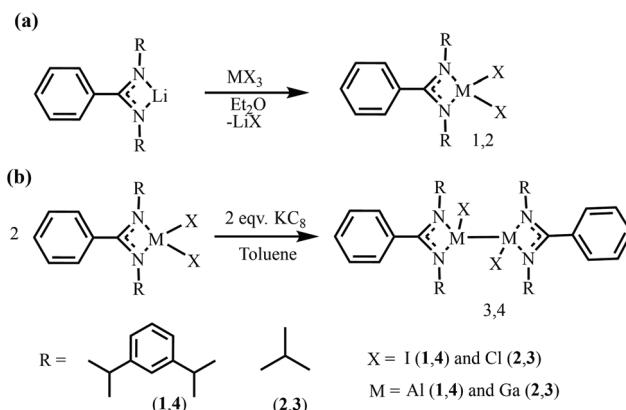
In spite of the several reports of compounds with Al-Al and Ga-Ga bonds, PhC(N<sup>t</sup>Bu)<sub>2</sub> (amidinate) stabilized double bonds are not known in the literature, although amidinates are widely used to stabilize compounds of low valent elements. It has been reported that an amidinate ligand stabilized the Si(i)-Si(i) bond.<sup>17</sup> In contrast, the 1,3- $\beta$ -diketiminate aluminium Al=Al has not been reported; therefore, we assumed that the amidinate might function as a better electron donor for the preparation of an Al=Al species. This unexplored synthetic route prompted the background of this work. Herein, we have synthesized amidinate-stabilized aluminium(ii) and gallium(ii) compounds of formula L<sub>2</sub>M<sub>2</sub>X<sub>2</sub> (**3** and **4**) from their LMX<sub>2</sub> (**1** and **2**) precursors, where M = Al (**1** and **4**) and Ga (**2** and **3**); L = PhC(N<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (**1** and **4**) and PhC(N<sup>t</sup>Bu)<sub>2</sub> (**2** and **3**); X is I (**1** and **4**) and Cl (**2** and **3**). However, we were not successful in isolating a crystalline [PhC(N<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (Al=Al) compound.<sup>18</sup>

## Results and discussion

Complex **1** was synthesized by treating one equivalent of AlI<sub>3</sub> with one equivalent of [PhC(N<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]Li in Et<sub>2</sub>O under a nitrogen atmosphere.<sup>19</sup> In a similar manner, complex **2** was prepared from GaCl<sub>3</sub> and [PhC(N<sup>t</sup>Bu)<sub>2</sub>]Li (Scheme 1(a)). Colourless crystals of **1** and **2** were isolated from the concentrated solution in Et<sub>2</sub>O at -4 °C. Compounds **3** and **4** were synthesized *via* the reduction of complexes **1** and **2** with 2 equivalents of KC<sub>8</sub> in toluene at room temperature for 24 hours (Scheme 1(b)). Colourless crystals of **3** and **4** were isolated from the concentrated solution in toluene at -30 °C. Compounds **3** and **4** remain stable for months under an inert atmosphere in toluene at room temperature and also in the solid state at room temperature.

As a side product from the synthesis of **2**, crystals of [PhC(HN<sup>t</sup>Bu)<sub>2</sub>][GaCl<sub>4</sub>] (**2a**) were isolated and were characterized by single-crystal X-ray diffraction (see the ES<sup>†</sup>).

Compound **1** crystallizes in the trigonal space group *P*3<sub>1</sub>21. The asymmetric unit contains half of the molecule (Fig. 1).



Scheme 1 Synthetic route for the synthesis of compounds **1**–**4**.

Crystals of **1** showed remarkable colour changes under polarized light from violet to yellow depending on the orientation of the crystals.

**1** is so far only the second crystallographically characterized benzamidinate aluminium diiodide complex apart from  $[(I_2Al)_2(\mu-\{Phamid_2\})]$  (Phamid<sub>2</sub> = 1,6- $\{2,6-iPrC_6H_3N\}_2C_6H_4$  reported by Jones *et al.*<sup>20</sup> The aluminium atom is coordinated by the amidinate chelate ligand and two iodine atoms in a distorted tetrahedral fashion. The Al-N distances (**1**: 1.890(2) Å) are slightly shorter than those in  $[(I_2Al)_2(\mu-\{Phamid_2\})]$  (1.901(5)–1.913(5) Å), whereas the mean Al-I distances are equal (**1**: 2.470(7) Å,  $[(I_2Al)_2(\mu-\{Phamid_2\})]$ : 2.471(5) Å).

Compound **2** crystallizes in the monoclinic space group *C*2/*c* with half a molecule in the asymmetric unit. The central gallium atom has a distorted tetrahedral coordination environ-

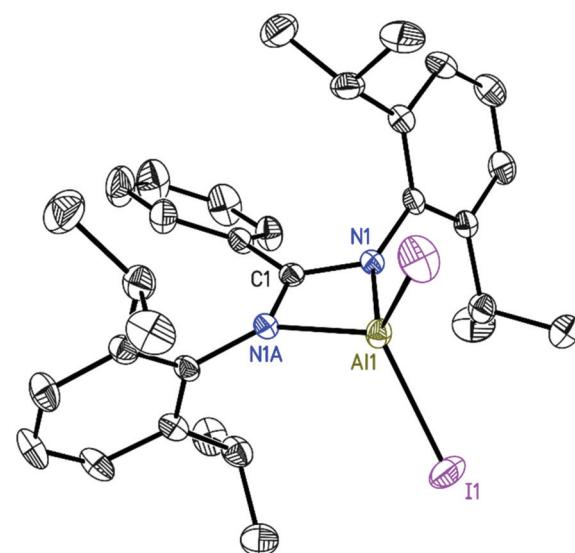
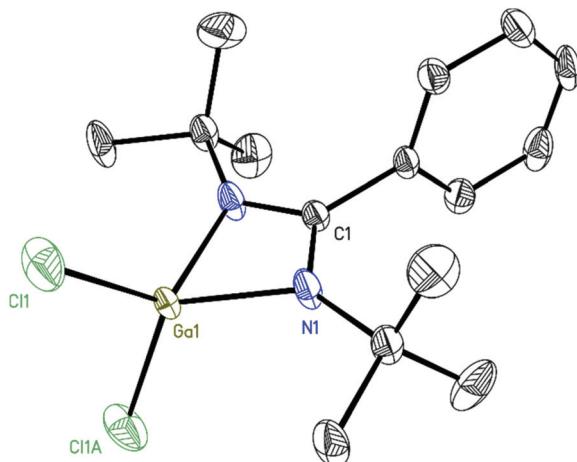


Fig. 1 Molecular unit of **1**. The anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–N1 1.341(3), Al1–N1 1.890(2), Al1–I1 2.4700(7), N1–Al1–N1A 70.86(12), N1–Al1–I1 117.49(6), and I1–Al1–I1A 113.96(4).



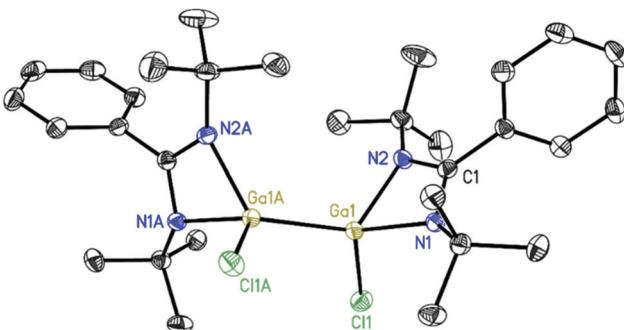


**Fig. 2** Molecular unit of **2**. The anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–N1 1.3288(16), Ga1–N1 1.9415(12), Ga1–Cl1 2.1424(5), N1–Ga1–N1A 68.10(7), N1–Ga1–Cl1 118.55(5), and Cl1–Ga1–Cl1A 109.10(3).

ment. The Ga–N (**2**: 1.9415(12) Å) and Ga–Cl bonds (**2**: 2.1424(5) Å) are slightly shorter than those in the related  $\text{PhC}(\text{N}^i\text{Pr})_2\text{GaCl}_2$  (1.950(3) Å and 2.1520(11) Å) (Fig. 2).<sup>21</sup>

Compound **3** crystallizes in the monoclinic space group  $C2/c$ . The asymmetric units contain half of a molecule. The overall coordination environment of the gallium center remains similar to the starting material **2**. However, the Ga–N distances (**3**: 1.9795(19) Å to 1.9807(19) Å and **2**: 1.9415(12) Å) and the Ga–Cl distance (**3**: 2.2126(8) Å and **2**: 2.1424(5) Å) are slightly elongated. The Ga–Ga distance (2.4053(6) Å) lies well within the range of the reported values for compounds with Ga–Ga single bonds (Fig. 3 and Fig. S1†).<sup>22</sup>

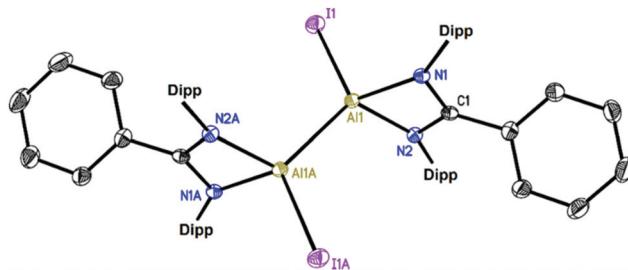
Compound **4** crystallizes in the monoclinic space group  $P2_1/c$ . The asymmetric unit contains half of a molecule. Compared to Al(III) precursor **1**, the Al–N distances in **4** are slightly elongated (**1**: 1.890(2) Å and **4**: 1.9145(14) Å to



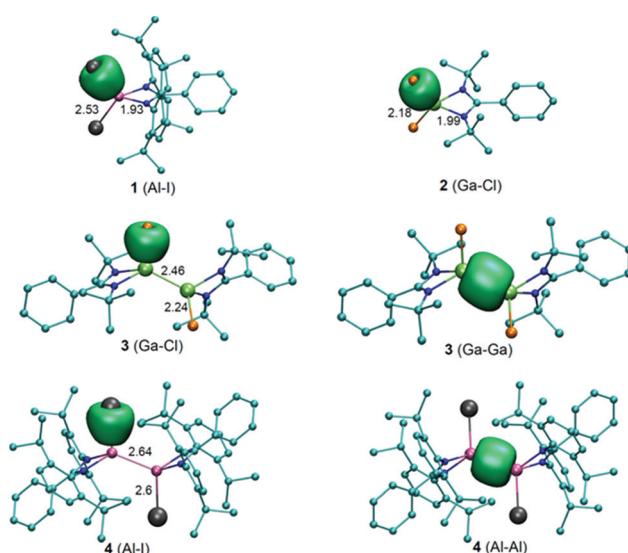
**Fig. 3** Molecular unit of **3**. The anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–N1 1.344(3), Ga1–N1 1.9807(19), Ga1–N2 1.9795(19), Ga1–Cl1 2.2126(8), Ga1–Ga1A 2.4053(6), N1–Ga1–N2 67.26(8), N1–Ga1–Cl1 111.23(6), N2–Ga1–Cl1 109.22(6), and Cl1–Ga1–Ga1A 116.01(3).

1.9466(14) Å). The same is true for the Al–I distance (**1**: 2.4700(7) Å and **4**: 2.5469(6) Å). The Al–Al distance (2.5803(10) Å) fits well to the already reported compounds with Al–Al single bonds (Fig. 4 and Fig. S10†).<sup>23</sup>

To understand the structure and bonding in the Al(II) and Ga(II) complexes, density functional theory (DFT) calculations were carried out for the systems **1**–**4** at the B3LYP/ECP(I),6-311++G\*\*<sup>24–27</sup> level of theory, where the effective core potential (ECP) with double- $\zeta$  LANL2DZ was used for iodine and the 6-311++G\*\* basis set was used for the other atoms. The optimized geometries of these molecules are shown in Fig. 5. The geometrical parameters (Table S8†) obtained from the calculations are in good agreement with that of the crystal structures. It can be seen that the metal–metal (M–M) bonds are formed in the dimers with bond lengths of 2.46 and 2.63 Å for Ga–Ga and Al–Al bonds, respectively. It should be noted that



**Fig. 4** Molecular unit of **4**. The anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–N1 1.341(2), Al1–N1 1.9466(14), Al1–N2 1.9145(14), Al1–I1 2.5469(6), Al1–Al1A 2.5803(10), N1–Al1–N2 69.39(6), N1–Al1–I1 109.92(4), N2–Al1–I1 113.53(4), and I1–Al1–Al1A 118.11(3).



**Fig. 5** The optimized geometries of **1**, **2**, **3**, and **4** were obtained at the B3LYP/ECP(I),6-311++G\*\* level of theory and the  $\sigma$ -type NBOs (isosurface = 0.06 a.u.) of the Ga–Cl, Al–I, Ga–Ga, and Al–Al bonds in these compounds. The hydrogen atoms are not shown for clarity. The important bond distances are indicated in Å units.



the formation of the M–M bonds is accompanied by the elongation ( $\sim 0.1$  Å) of the metal–halide (M–X) bonds.

The nature of bonding in these molecules was investigated by performing natural bond orbital (NBO) calculations<sup>28</sup> at the B3LYP/ECP(I),6-311++G\*\* level of theory for the optimized geometries obtained at the same level of theory. The resulting  $\sigma$ -type NBOs of the Ga–Cl, Al–I, Ga–Ga, and Al–Al bonds in 1, 2, 3, and 4 are shown in Fig. 5. The atomic orbital contribution and the NBO occupancies are given in Table S9.† It was found that the Al–I bonds in 1 and 4 and the Ga–Cl bonds in 2 and 3 are highly polarized towards the halogen atoms as seen from the orbital contribution of the bonds (I: 74.6% (1), Cl: 80.3% (2), Cl: 83.0% (3), and I: 83.0% (4)). The orbital occupancies of the M–X bonds are in the range 1.936–1.965  $e$ . The polarized nature of these bonds can also be seen from the natural population analysis (NPA) charges on the Al and Ga atoms (Al: +1.199/+1.084  $e$  in 1/4 and Ga: +1.394/+1.005  $e$  in 2/3, and Table S10†). The calculations also indicate that the M–X bonds (Al–X and Ga–X) in the monomers 1 and 2 are single bonds quantified by the Wiberg bond index (WBI) values (Al–I: 0.967 (1) and Ga–Cl: 0.780 (2)). The M–M bonds in 3 (Ga–Ga) and 4 (Al–Al) were also found to be single bonds with the WBI values of 0.851 and 0.819, respectively. The Ga–Ga bond in 3 was found to have a major contribution from the s (41.89%) and p (57.81%) orbitals of each Ga atom, while in 4, each Al atom contributed s (40.59%) and p (59.01%) orbitals to the Al–Al bond (Table S1†).

To further characterize the nature of the important bonds in 1, 2, 3, and 4, QTAIM calculations<sup>29</sup> were carried out at the B3LYP/ECP(I),6-311++G\*\* level of theory for the optimized geometries. The presence of (3, -1) bond critical points (BCPs) between the metal centers and the metal–halogen centers reiterate the existence of the M–M and M–X bonds (Table S11 and Fig. S13†). The electron densities at the BCPs for the Al–I bonds in 1 and 4 and the Ga–Cl bonds in 2 and 3 were in the range of 0.047–0.089  $e$  Å<sup>-3</sup>. In addition, the Laplacian ( $[\nabla^2\rho(r)]$ ) values at the BCPs for these bonds were found to be positive indicating that these bonds are highly polarized as seen in the NBOs.

## Conclusions

In summary, we present a successful use of an amidinate scaffold for the synthesis of novel amidinate-based aluminium(II) and gallium(II) dihalide dimers. X-ray crystal structures of compounds 3 and 4 fall into the examples of gallium(II) dichloride and aluminium(II) diiodide dimers. This indicates the ability of the amidinate ligand for stabilizing Al(II)–Al(II) and Ga(II)–Ga(II) bonds.

## Experimental section

### X-ray crystallography

Single crystals of compounds 1–4, suitable for X-ray analysis, were mounted in inert oil. The diffraction data were collected at 100(2) K on a Bruker D8 three-circle diffractometer equipped

with a SMART APEX II CCD detector and an INCOATEC Mo microsource with INCOATEC Quazar mirror optics ( $\lambda = 0.71073$ ).<sup>30</sup> The data were integrated with SAINT<sup>31</sup> and an empirical absorption correction with SADABS<sup>32</sup> was applied. For 2, TWINABS<sup>33</sup> was used. The structures were solved using SHELXT<sup>32</sup> and refined on  $F^2$  using SHELXL<sup>34</sup> in the graphical user interface ShelXle.<sup>35</sup> All non-hydrogen atoms were refined with anisotropic-displacement parameters.

Crystal data for 1 at 100(2) K:  $C_{31}H_{39}AlI_2N_2$ ,  $M_r = 720.42$  g mol<sup>-1</sup>,  $0.251 \times 0.213 \times 0.190$  mm, trigonal,  $P3_121$ ,  $a = 15.276(3)$  Å,  $c = 12.183(2)$  Å,  $V = 2462.1(10)$  Å<sup>3</sup>,  $Z = 3$ ,  $\mu(\text{Mo K}_\alpha) = 1.963$  mm<sup>-1</sup>,  $\theta_{\text{max}} = 26.425^\circ$ , 29 077 reflections measured, 3387 independent ( $R_{\text{int}} = 0.0273$ ),  $R_1 = 0.0157$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.0369$  (all data), res. density peaks: 0.389 to  $-0.220$  e Å<sup>-3</sup>, CCDC: 2144443.†

Crystal data for 2 at 100(2) K:  $C_{15}H_{23}Cl_2GaN_2$ ,  $M_r = 371.97$  g mol<sup>-1</sup>,  $0.462 \times 0.306 \times 0.060$  mm, monoclinic,  $C2/c$ ,  $a = 14.553(3)$  Å,  $b = 11.340(2)$  Å,  $c = 12.589(2)$  Å,  $\beta = 119.16(2)$ ,  $V = 1814.3(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Mo K}_\alpha) = 1.804$  mm<sup>-1</sup>,  $\theta_{\text{max}} = 26.408^\circ$ , 15 526 reflections measured, 1871 independent ( $R_{\text{int}} = 0.0267$ ),  $R_1 = 0.0208$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.0538$  (all data), res. density peaks: 0.390 to  $-0.345$  e Å<sup>-3</sup>, CCDC: 2144444.†

Crystal data for 2a at 100(2) K:  $C_{15}H_{25}Cl_4GaN_2$ ,  $M_r = 444.89$  g mol<sup>-1</sup>,  $0.387 \times 0.245 \times 0.238$  mm, orthorhombic,  $P2_12_12_1$ ,  $a = 8.412(2)$  Å,  $b = 15.856(3)$  Å,  $c = 15.903(3)$  Å,  $V = 2121.2(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Mo K}_\alpha) = 1.799$  mm<sup>-1</sup>,  $\theta_{\text{max}} = 26.355^\circ$ , 17 672 reflections measured, 4334 independent ( $R_{\text{int}} = 0.0223$ ),  $R_1 = 0.0175$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.0430$  (all data), res. density peaks: 0.482 to  $-0.322$  e Å<sup>-3</sup>, CCDC: 2144445.†

Crystal data for 3 at 100(2) K:  $C_{30}H_{46}Ga_2N_4$ ,  $M_r = 673.05$  g mol<sup>-1</sup>,  $0.376 \times 0.171 \times 0.163$  mm, monoclinic,  $C2/c$ ,  $a = 23.069(3)$  Å,  $b = 8.896(2)$  Å,  $c = 17.634(2)$  Å,  $\beta = 114.36(2)$ ,  $V = 3296.7(10)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Mo K}_\alpha) = 1.821$  mm<sup>-1</sup>,  $\theta_{\text{max}} = 26.475^\circ$ , 146 235 reflections measured, 3406 independent ( $R_{\text{int}} = 0.0776$ ),  $R_1 = 0.0337$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.0797$  (all data), res. density peaks: 0.505 to  $-0.350$  e Å<sup>-3</sup>, CCDC: 2144446.†

Crystal data for 4 at 100(2) K:  $C_{76}H_{94}Al_2I_2N_4$ ,  $M_r = 1371.31$  g mol<sup>-1</sup>,  $0.721 \times 0.714 \times 0.216$  mm, monoclinic,  $P2_1/c$ ,  $a = 14.825(2)$  Å,  $b = 10.706(2)$  Å,  $c = 22.175(3)$  Å,  $\beta = 93.54(2)$ ,  $V = 3512.8(9)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu(\text{Mo K}_\alpha) = 0.964$  mm<sup>-1</sup>,  $\theta_{\text{max}} = 26.374^\circ$ , 46 646 reflections measured, 7180 independent ( $R_{\text{int}} = 0.0248$ ),  $R_1 = 0.0225$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.0598$  (all data), res. density peaks: 0.756 to  $-0.383$  e Å<sup>-3</sup>, CCDC: 2144447.†

## Conflicts of interest

The authors declare no conflict of interest.

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