Supporting Information

Synthesis and computational aspects of Al(II)- Al(II) and Ga(II)-Ga(II) dihalides based on an amidinate scaffold

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Experimental

Materials and methods

All reactions and handling of reagents were performed using standard Schlenk and glovebox techniques under an atmosphere of high purity N_2. Commercial reagents were purchased from Aldrich, Acros, or Alfa-Aesar Chemical Co. and used as received. Compound **2** was synthesised via reported procedure.[1]Toluene, was distilled over Na/K alloy (25 : 75) and diethyl ether was distilled over potassium mirror. C_6D_6 was dried by stirring for 2 days over Na/K alloy followed by distillation in a vacuum and degassed. ^1H, $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance 400, and Bruker Avance 500 MHz NMR spectrometers and were referenced to the TMS. Elemental analysis was performed by the Analytisches Labor für Anorganische Chemie at the university of Göttingen.

Compound 3

Compound **2** (1.5 g, 4 mmol) and KC_8 (1.08 g, 8 mmol) was placed in a 100 mL Schlenk flask and 50 mL of toluene was added at −78 °C, the reaction mixture was then allowed to warm to room temperature and stirred for another 12 h. After filtration of the insoluble residue, the solution was concentrated to 5 mL under vacuum, which gave white coloured single crystals of **3** at −30 °C (yield 1.5 g, 56%).

Elemental Analysis (%) calculated for $C_{30}H_{46}Cl_2Ga_2N_4$: C, 53.54; H, 6.89; N, 8.32; found: C, 53.29; H, 6.97; N, 8.17. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 1.28ppm (s, 18H, ^{t}Bu), 7.06–7.5 ppm (m, 5H, Ph). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 25 °C): δ 31.1 (^{t}Bu), 34.5 (^{t}Bu),51.5 (^{t}Bu), 127.3, 127.6, 127.9, 130.9(Ph), 176.1 ppm (NCN).

Compound 4

PhLi (4 mL, 10 mmol, 2.5 molar in dibutyl ether) was added to a solution of bis(2,6-diisopropylphenyl)carbodiimide (3.62 g, 10 mmol) in 50 mL diethyl ether at −78 °C under nitrogen atmosphere. The reaction mixture was then allowed to come to ambient temperature. This reaction mixture was then added to the Et_2O solution of AlI_3 (4.07 g, 10 mmol) at −78 °C. The resultant reaction mixture was stirred overnight and allowed to achieve room

temperature. The precipitate of LiI was filtered off. After removal of all the volatiles, *ca.* 10 mL solution was stored at −4 °C in a freezer for 1 day to afford colourless crystals of **1**. Compound **1** (2 g, 2 mmol) and KC_8 (540 mg, 4 mmol) was placed in a 100 mL Schlenk flask and 40 mL of toluene was added at −78 °C, the reaction mixture was then allowed to warm to room temperature and stirred for 12 h. After filtration of the insoluble residue, the solution was concentrated to 5 mL under vacuum, which gave white coloured single crystals of **4** at −30 °C (yield 1.6 g, 67%).

Elemental Analysis (%) calculated for $C_{62}H_{78}Al_2I_2N_4$: C, 62.73; H, 6.62; N, 4.72; found: C, 62.52; H, 6.83; N, 4.61. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.84 ppm (d, 12H, Dipp) 1.35 ppm (d, 12H, Dipp), 3.67 (sep,4H, Dipp C-H), 6.47– 6.58 ppm (m, 3H, Dipp), 6.95 ppm (d, 1H, Dipp), 6.98 ppm (s, 2H, Dipp), 7.04 – 7.10 (m, 5H, Ph). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 25 °C): δ 26.9 (*i*pr), 28.7 (*i*pr), 124.28,127.35,127.67,128.0,130.5,131.8,135.24(Ph), 144.10 ppm (NCN).

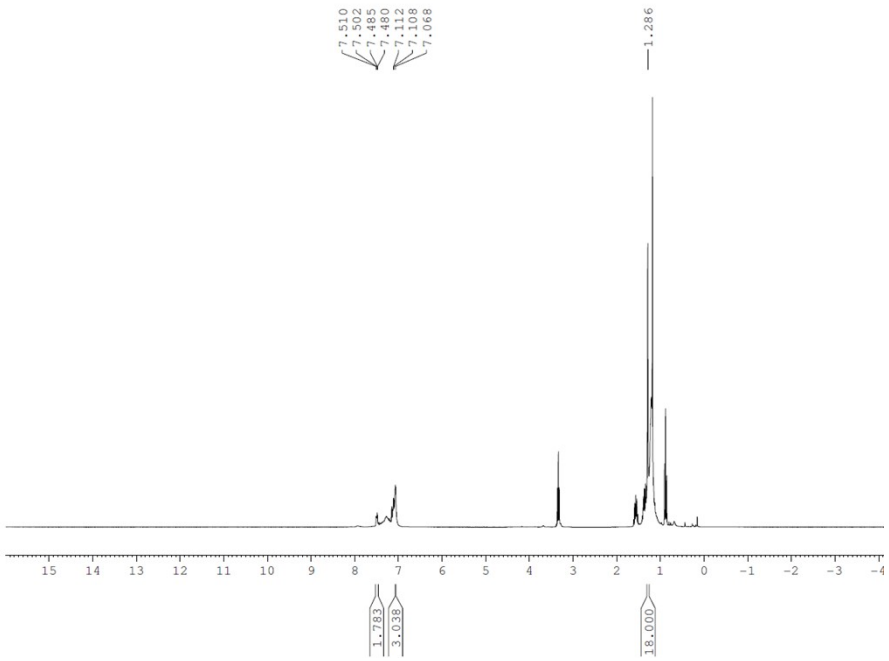


Figure S1: ^{1}H NMR spectrum of compound **3.**

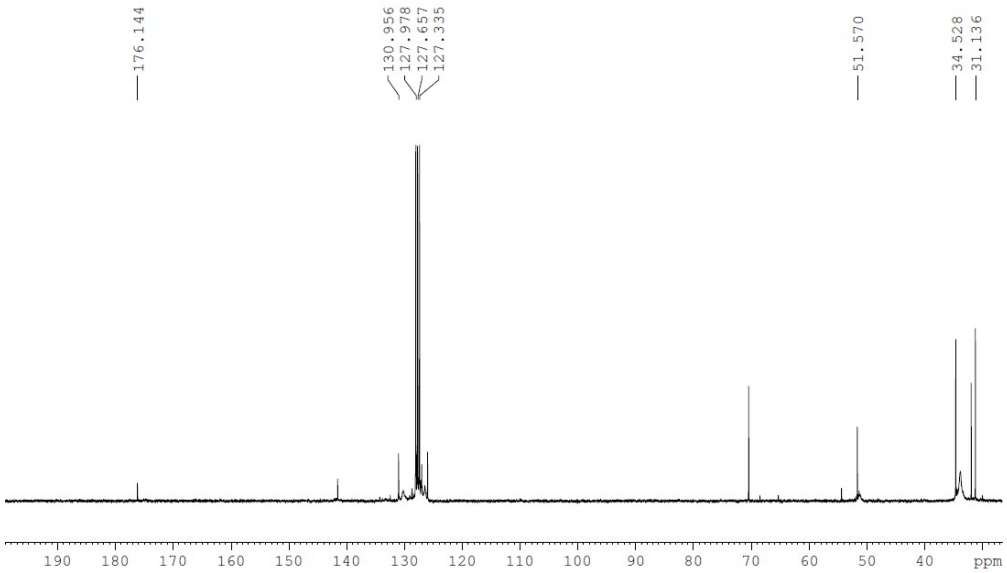


Figure S2: ^{13}C NMR spectrum of compound **3**.

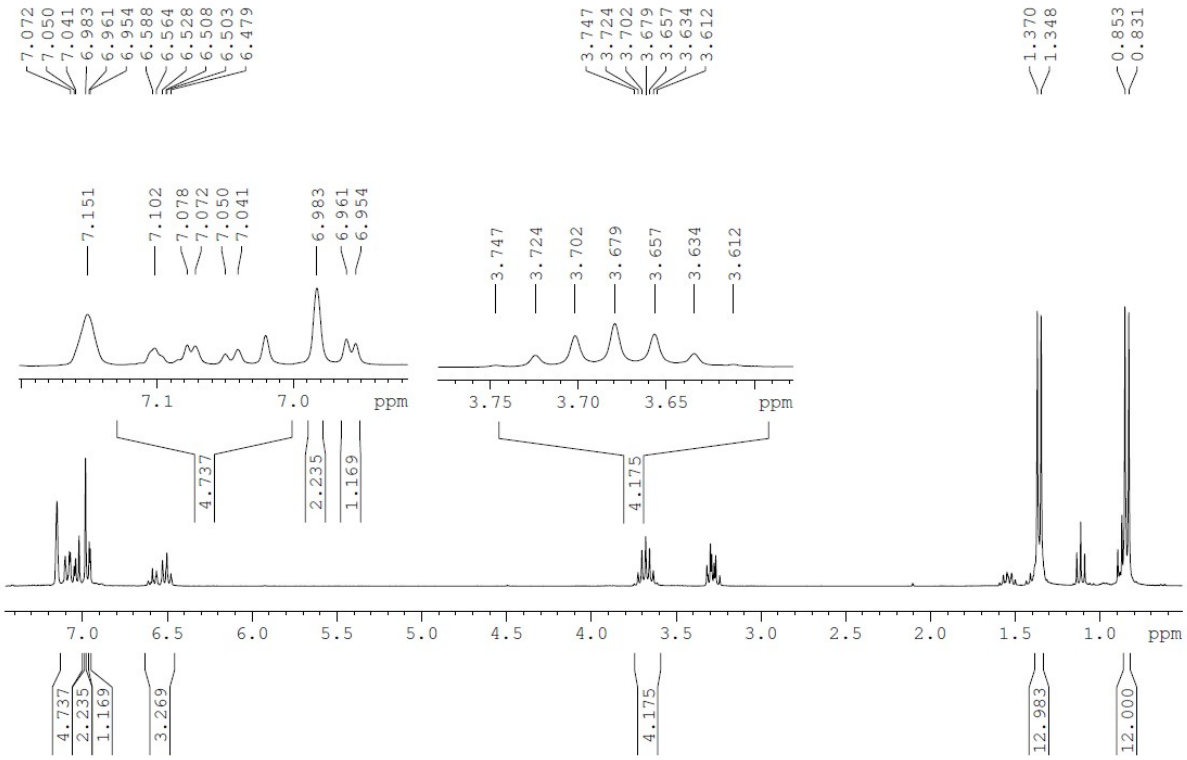


Figure S3: ^{1}H NMR spectrum of compound **4. (**Unassigned resonances in the aliphatic region belongs to dibutyl ether protons)

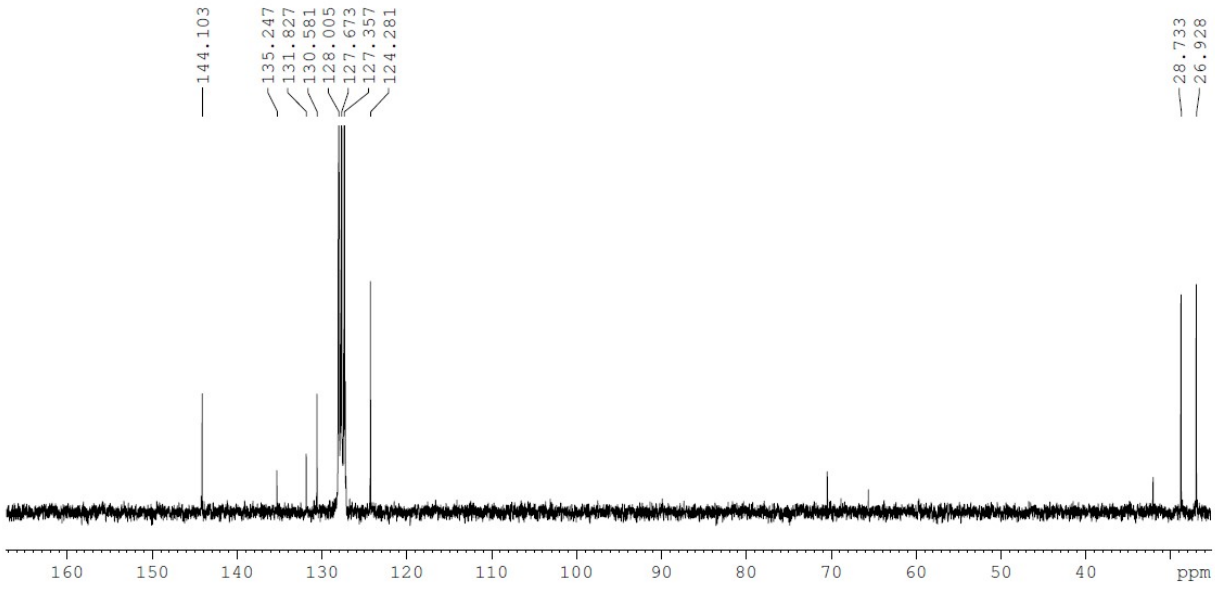


Figure S4: ^{13}C NMR spectrum of compound **4**

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 (λ=0.71073).[2] The data were integrated with SAINT[3] and an empirical absorption correction with SADABS[4] was applied. For **2** and **3** TWINABS[5] was used. The structures were solved by SHELXT[6] and refined on F^2 using SHELXL[7] in the graphical user interface ShelXle.[8] All non-hydrogen atoms were refined with anisotropic-displacement parameters. The hydrogen atoms were refined using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms unless stated otherwise.

The Crystallographic Information Files (CIF) can be obtained free of charge from the Cambridge Crystallographic Data Centre using the reference numbers 2144443-2144447

Table S1: Crystal data and structure refinement of **1**-**4**.

Compound	**1**	**2**	**2a**	**3**	**4**
Empirical formula	$C_{31}H_{39}AlI_2N_2$	$C_{15}H_{23}Cl_2GaN_2$	$C_{15}H_{25}Cl_4GaN_2$	$C_{30}H_{46}Cl_2Ga_2N_4$	$C_{76}H_{94}Al_2I_2N_4$
CCDC number	2144443	2144444	2144445	2144446	2144447
Formula weight	720.42	371.97	444.89	673.05	1371.31
Temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Trigonal	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P3_121$	$C2/c$	$P2_12_12_1$	$C2/c$	$P2_1/c$
a [Å]	15.276(3)	14.553(3)	8.412(2)	23.069(3)	14.825(2)
b [Å]		11.340(2)	15.856(3)	8.896(2)	10.706(2)
c [Å]	12.183(2)	12.589(2)	15.903(3)	17.634(2)	22.175(3)
β [°]		119.16(2)		114.36(2)	93.54(2)
V [Å^3]	2462.1(10)	1814.3(6)	2121.2(8)	3296.7(10)	3512.8(9)
Z	3	4	4	4	2
ρ [Mgm^{-3}]	1.458	1.362	1.393	1.356	1.297
μ [mm^{-1}]	1.963	1.804	1.799	1.821	0.964
F (000)	1074	768	912	1400	1420
Crystal size [mm]	0.251 x 0.213 x 0.190	0.462 x 0.306 x 0.060	0.387 x 0.245 x 0.238	0.376 x 0.171 x 0.163	0.721 x 0.714 x 0.216
θ-area [°]	1.539 to 26.425	2.407 to 26.408	1.814 to 26.355	1.938 to 26.475	1.376 to 26.374
Index ranges	$-17 \le h \le 19$, $-19 \le k \le 16$, $-15 \le l \le 15$	$-18 \le h \le 18$, $-14 \le k \le 14$, $-15 \le l \le 15$	$-10 \le h \le 10$, $-19 \le k \le 17$, $-19 \le l \le 19$	$-28 \le h \le 28$, $-11 \le k \le 11$, $-22 \le l \le 22$	$-18 \le h \le 18$, $-13 \le k \le 13$, $-27 \le l \le 27$
Total number reflect.	29077	15526	17672	146235	46646
Unique	3387	1871	4334	3406	7180

reflections					
R_{int}	0.0273	0.0267	0.0223	0.0776	0.0248
Max. and min. transmission	0.4296 and 0.3434	0.7454 and 0.5437	0.7454 and 0.6200	0.7454 and 0.5216	0.4296 and 0.3390
Data / restraints / parameters	3387 / 0 / 169	1871/ 135 / 128	4334 / 1 / 213	3406 / 0 / 178	7180 / 0 / 388
Goodness-of-fit on F^2	1.061	1.081	1.025	1.114	1.075
$R1$ [$I>2\sigma(I)$]	0.0157	0.0208	0.0175	0.0337	0.0225
$wR2$[$I>2\sigma(I)$]	0.0365	0.0531	0.0429	0.0768	0.0590
$R1$ [all data]	0.0164	0.0217	0.0182	0.0409	0.0240
$wR2$ [all data]	0.0369	0.0538	0.0430	0.0797	0.0598
Absolute structure parameter[9]	-0.022(6)	-	0.007(3)		
Largest diff. peak and hole [e·Å^{-3}]	0.389 to -0.220	0.390 to -0.345	0.482 to -0.322	0.505 and -0.350	0.756 to -0.383

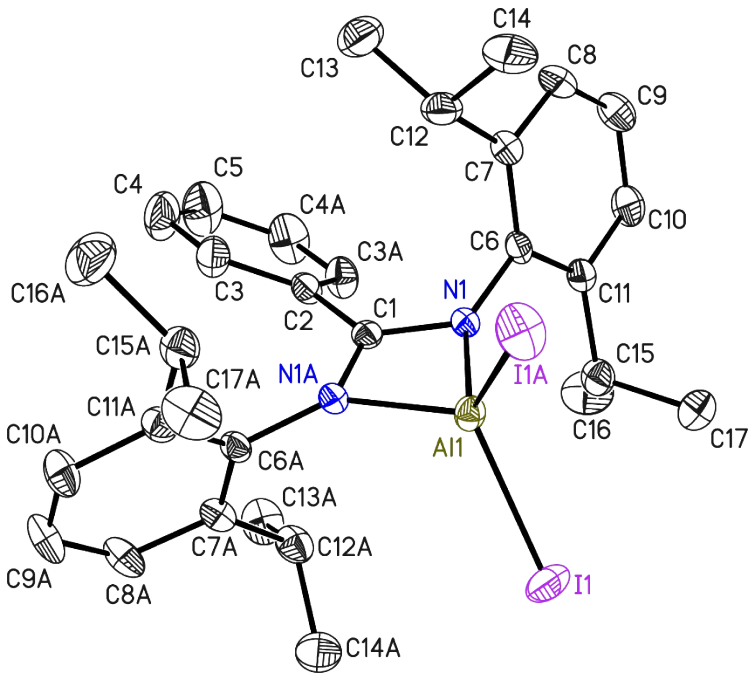


Figure S5: Molecular unit of **1**. The anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity.

Table S2: Bond lengths [Å] and angles [°] for **1**.

I(1)-Al(1)	2.4700(7)	C(1)-N(1)-Al(1)	89.80(16)
Al(1)-N(1)	1.890(2)	C(6)-N(1)-Al(1)	142.71(16)
Al(1)-C(1)	2.314(4)	N(1)#1-C(1)-N(1)	109.5(3)
N(1)-C(1)	1.341(3)	N(1)-C(1)-C(2)	125.23(15)
N(1)-C(6)	1.433(3)	N(1)-C(1)-Al(1)	54.77(15)
C(1)-C(2)	1.475(5)	C(2)-C(1)-Al(1)	180.0
C(2)-C(3)	1.389(3)	C(3)-C(2)-C(3)#1	119.4(4)
C(3)-C(4)	1.384(4)	C(3)-C(2)-C(1)	120.31(18)
C(4)-C(5)	1.374(4)	C(4)-C(3)-C(2)	120.1(3)
C(6)-C(11)	1.398(3)	C(5)-C(4)-C(3)	119.8(3)
C(6)-C(7)	1.408(3)	C(4)#1-C(5)-C(4)	120.8(4)
C(7)-C(8)	1.393(4)	C(11)-C(6)-C(7)	121.8(2)
C(7)-C(12)	1.517(4)	C(11)-C(6)-N(1)	118.8(2)
C(8)-C(9)	1.377(4)	C(7)-C(6)-N(1)	119.4(2)
C(9)-C(10)	1.378(4)	C(8)-C(7)-C(6)	117.1(3)
C(10)-C(11)	1.390(4)	C(8)-C(7)-C(12)	119.0(2)
C(11)-C(15)	1.521(4)	C(6)-C(7)-C(12)	123.8(2)
C(12)-C(14)	1.536(4)	C(9)-C(8)-C(7)	121.9(3)
C(12)-C(13)	1.536(4)	C(8)-C(9)-C(10)	119.7(3)
C(15)-C(16)	1.530(4)	C(9)-C(10)-C(11)	121.3(3)
C(15)-C(17)	1.530(4)	C(10)-C(11)-C(6)	118.1(2)
		C(10)-C(11)-C(15)	119.9(2)
N(1)-Al(1)-N(1)#1	70.86(12)	C(6)-C(11)-C(15)	122.0(2)
N(1)-Al(1)-C(1)	35.43(6)	C(7)-C(12)-C(14)	109.9(2)
N(1)-Al(1)-I(1)	117.49(6)	C(7)-C(12)-C(13)	112.0(2)
N(1)#1-Al(1)-I(1)	115.24(6)	C(14)-C(12)-C(13)	111.1(2)
C(1)-Al(1)-I(1)	123.02(2)	C(11)-C(15)-C(16)	113.3(2)
I(1)-Al(1)-I(1)#1	113.96(4)	C(11)-C(15)-C(17)	110.0(2)
C(1)-N(1)-C(6)	125.0(2)	C(16)-C(15)-C(17)	110.0(3)

Symmetry transformations used to generate equivalent atoms:

#1 x-y,-y,-z+2/3

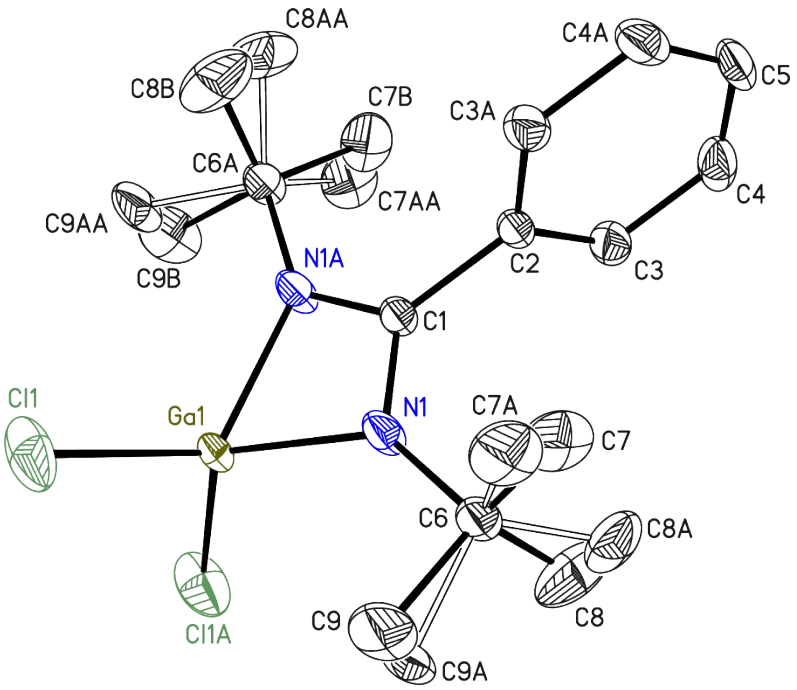


Figure S6: Molecular unit of **2**. The anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity.

The data were collected on a non-merohedral twin. The twin law is a two-fold rotation along (1 0 -1). The fractional contribution of the minor twin domain refined to 0.1416(16). Parts of the molecule (*t*Bu group: C7–C9) were disordered about two positions. The occupancy of the minor position refined to 0.429(18). All disordered groups were refined with distance restraints and restraints for the anisotropic displacement parameters.

Table S3: Bond lengths [Å] and angles [°] for **2**.

Ga(1)-N(1)	1.9415(12)	N(1)-Ga(1)-Cl(1)	118.55(5)
Ga(1)-Cl(1)	2.1424(5)	N(1)#1-Ga(1)-Cl(1)	118.90(5)
Ga(1)-C(1)	2.3729(19)	Cl(1)-Ga(1)-Cl(1)#1	109.10(3)
N(1)-C(1)	1.3288(16)	N(1)-Ga(1)-C(1)	34.05(4)
N(1)-C(6)	1.4805(19)	Cl(1)-Ga(1)-C(1)	125.452(14)
C(1)-C(2)	1.501(3)	C(1)-N(1)-C(6)	131.72(13)
C(2)-C(3)	1.3878(19)	C(1)-N(1)-Ga(1)	91.06(9)
C(3)-C(4)	1.397(2)	C(6)-N(1)-Ga(1)	137.02(10)
C(4)-C(5)	1.375(2)	N(1)-C(1)-N(1)#1	109.78(17)
C(6)-C(8)	1.489(8)	N(1)-C(1)-C(2)	125.11(8)
C(6)-C(7A)	1.512(7)	N(1)-C(1)-Ga(1)	54.89(8)
C(6)-C(7)	1.519(7)	C(2)-C(1)-Ga(1)	180.0
C(6)-C(9A)	1.531(5)	C(3)-C(2)-C(3)#1	120.2(2)
C(6)-C(8A)	1.533(5)	C(3)-C(2)-C(1)	119.91(10)
C(6)-C(9)	1.533(8)	C(2)-C(3)-C(4)	119.52(16)
		C(5)-C(4)-C(3)	120.17(17)
N(1)-Ga(1)-N(1)#1	68.10(7)	C(4)-C(5)-C(4)#1	120.4(2)

N(1)-C(6)-C(8)	106.5(4)	N(1)-C(6)-C(8A)	113.7(3)
N(1)-C(6)-C(7A)	109.4(4)	C(7A)-C(6)-C(8A)	110.2(3)
N(1)-C(6)-C(7)	113.7(4)	C(9A)-C(6)-C(8A)	107.5(4)
C(8)-C(6)-C(7)	112.6(4)	N(1)-C(6)-C(9)	103.6(4)
N(1)-C(6)-C(9A)	106.3(3)	C(8)-C(6)-C(9)	113.2(5)
C(7A)-C(6)-C(9A)	109.5(4)	C(7)-C(6)-C(9)	107.1(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2

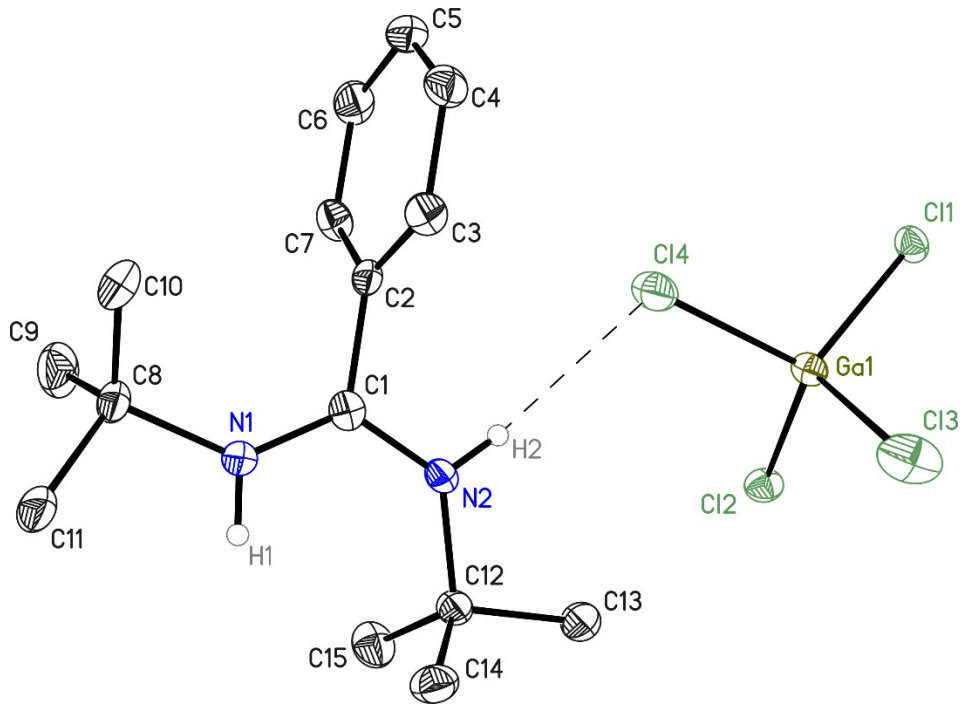


Figure S7: Asymmetric unit of **2a**. The anisotropic displacement parameters are depicted at the 50% probability level. Except for N-bound the hydrogen atoms are omitted for clarity.

Hydrogen atoms H1 and H2 were refined freely. All other hydrogen atoms were refined using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms.

Table S4: Bond lengths [Å] and angles [°] for **2a**.

Ga(1)-Cl(2)	2.1687(6)	C(1)-C(2)	1.495(3)
Ga(1)-Cl(1)	2.1712(6)	N(2)-H(2)	0.823(19)
Ga(1)-Cl(3)	2.1747(7)	N(2)-C(12)	1.501(3)
Ga(1)-Cl(4)	2.1786(7)	C(2)-C(7)	1.385(3)
N(1)-H(1)	0.83(2)	C(2)-C(3)	1.391(3)
N(1)-C(1)	1.315(3)	C(3)-C(4)	1.390(3)
N(1)-C(8)	1.512(3)	C(4)-C(5)	1.387(3)
C(1)-N(2)	1.318(3)	C(5)-C(6)	1.387(3)

C(6)-C(7)	1.389(3)	C(1)-N(2)-C(12)	130.75(18)
C(8)-C(9)	1.519(3)	C(7)-C(2)-C(3)	120.62(19)
C(8)-C(10)	1.520(3)	C(7)-C(2)-C(1)	119.92(18)
C(8)-C(11)	1.522(3)	C(3)-C(2)-C(1)	119.43(19)
C(12)-C(14)	1.523(3)	C(4)-C(3)-C(2)	119.28(19)
C(12)-C(13)	1.529(3)	C(5)-C(4)-C(3)	120.3(2)
C(12)-C(15)	1.536(3)	C(4)-C(5)-C(6)	120.0(2)
		C(5)-C(6)-C(7)	120.1(2)
Cl(2)-Ga(1)-Cl(1)	109.90(3)	C(2)-C(7)-C(6)	119.7(2)
Cl(2)-Ga(1)-Cl(3)	108.96(2)	N(1)-C(8)-C(9)	108.69(19)
Cl(1)-Ga(1)-Cl(3)	109.49(3)	N(1)-C(8)-C(10)	113.00(18)
Cl(2)-Ga(1)-Cl(4)	109.42(3)	C(9)-C(8)-C(10)	111.16(19)
Cl(1)-Ga(1)-Cl(4)	109.66(2)	N(1)-C(8)-C(11)	103.58(17)
Cl(3)-Ga(1)-Cl(4)	109.40(3)	C(9)-C(8)-C(11)	111.0(2)
H(1)-N(1)-C(1)	114.3(19)	C(10)-C(8)-C(11)	109.2(2)
H(1)-N(1)-C(8)	113.2(19)	N(2)-C(12)-C(14)	111.09(17)
C(1)-N(1)-C(8)	132.52(19)	N(2)-C(12)-C(13)	104.54(16)
N(1)-C(1)-N(2)	122.80(19)	C(14)-C(12)-C(13)	109.6(2)
N(1)-C(1)-C(2)	121.88(19)	N(2)-C(12)-C(15)	109.90(18)
N(2)-C(1)-C(2)	115.32(18)	C(14)-C(12)-C(15)	112.03(18)
H(2)-N(2)-C(1)	112.6(16)	C(13)-C(12)-C(15)	109.45(17)
H(2)-N(2)-C(12)	116.2(16)		

Table S5: Hydrogen bonds for **2a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...Cl(4)	0.823(19)	2.587(19)	3.406(2)	173(2)

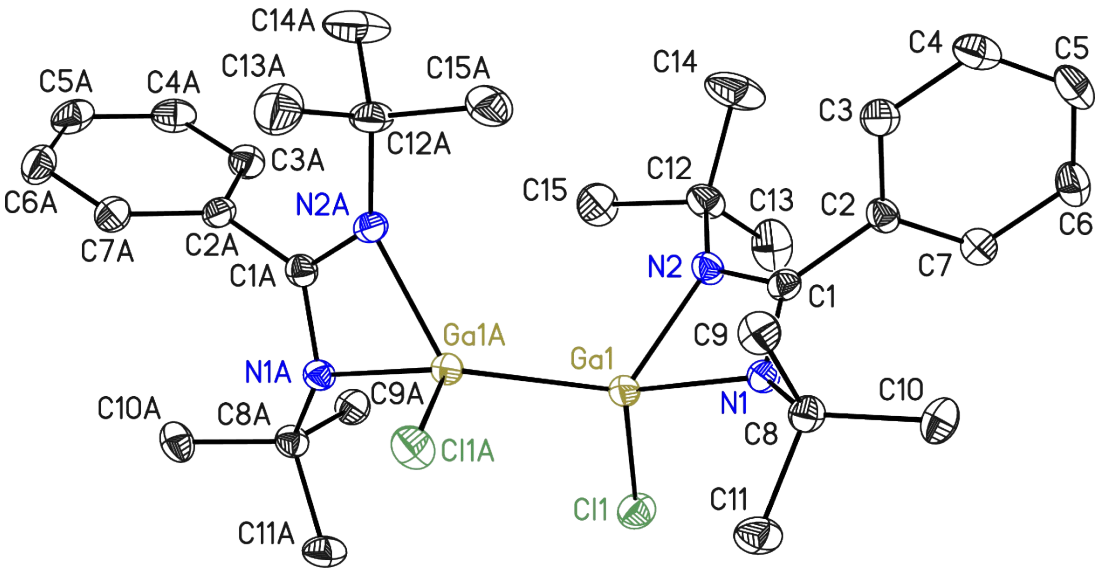


Figure S8: Molecular unit of **3**. The anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity.

Data were collected on a split crystal with three components. The final refinement was done on untwinned merged data from all domains.

Table S6: Bond lengths [Å] and angles [°] for **3**.

Ga(1)-N(2)	1.9795(19)		
Ga(1)-N(1)	1.9807(19)	N(2)-Ga(1)-N(1)	67.26(8)
Ga(1)-Cl(1)	2.2126(8)	N(2)-Ga(1)-Cl(1)	109.22(6)
Ga(1)-Ga(1)#1	2.4053(6)	N(1)-Ga(1)-Cl(1)	111.23(6)
Ga(1)-C(1)	2.413(2)	N(2)-Ga(1)-Ga(1)#1	121.11(6)
N(1)-C(1)	1.344(3)	N(1)-Ga(1)-Ga(1)#1	122.66(6)
N(1)-C(8)	1.482(3)	Cl(1)-Ga(1)-Ga(1)#1	116.01(3)
N(2)-C(1)	1.331(3)	N(2)-Ga(1)-C(1)	33.46(8)
N(2)-C(12)	1.474(3)	N(1)-Ga(1)-C(1)	33.85(7)
C(1)-C(2)	1.493(3)	Cl(1)-Ga(1)-C(1)	115.96(6)
C(2)-C(7)	1.389(3)	Ga(1)#1-Ga(1)-C(1)	127.93(5)
C(2)-C(3)	1.394(3)	C(1)-N(1)-C(8)	128.81(19)
C(3)-C(4)	1.386(3)	C(1)-N(1)-Ga(1)	90.98(14)
C(4)-C(5)	1.383(4)	C(8)-N(1)-Ga(1)	133.63(15)
C(5)-C(6)	1.385(4)	C(1)-N(2)-C(12)	131.0(2)
C(6)-C(7)	1.387(3)	C(1)-N(2)-Ga(1)	91.43(14)
C(8)-C(11)	1.528(3)	C(12)-N(2)-Ga(1)	136.52(15)
C(8)-C(9)	1.529(3)	N(2)-C(1)-N(1)	110.2(2)
C(8)-C(10)	1.531(3)	N(2)-C(1)-C(2)	125.6(2)
C(12)-C(14)	1.520(4)	N(1)-C(1)-C(2)	124.3(2)
C(12)-C(15)	1.528(3)	N(2)-C(1)-Ga(1)	55.11(12)
C(12)-C(13)	1.530(4)	N(1)-C(1)-Ga(1)	55.17(11)

C(2)-C(1)-Ga(1)	177.17(17)
C(7)-C(2)-C(3)	119.8(2)
C(7)-C(2)-C(1)	119.8(2)
C(3)-C(2)-C(1)	120.4(2)
C(4)-C(3)-C(2)	120.0(2)
C(5)-C(4)-C(3)	119.9(2)
C(4)-C(5)-C(6)	120.3(2)
C(5)-C(6)-C(7)	120.1(2)
C(6)-C(7)-C(2)	119.9(2)
N(1)-C(8)-C(11)	105.12(18)
N(1)-C(8)-C(9)	109.53(19)
C(11)-C(8)-C(9)	109.3(2)
N(1)-C(8)-C(10)	113.3(2)
C(11)-C(8)-C(10)	108.6(2)
C(9)-C(8)-C(10)	110.8(2)
N(2)-C(12)-C(14)	113.3(2)
N(2)-C(12)-C(15)	104.9(2)
C(14)-C(12)-C(15)	108.7(2)
N(2)-C(12)-C(13)	109.8(2)
C(14)-C(12)-C(13)	110.7(2)
C(15)-C(12)-C(13)	109.2(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

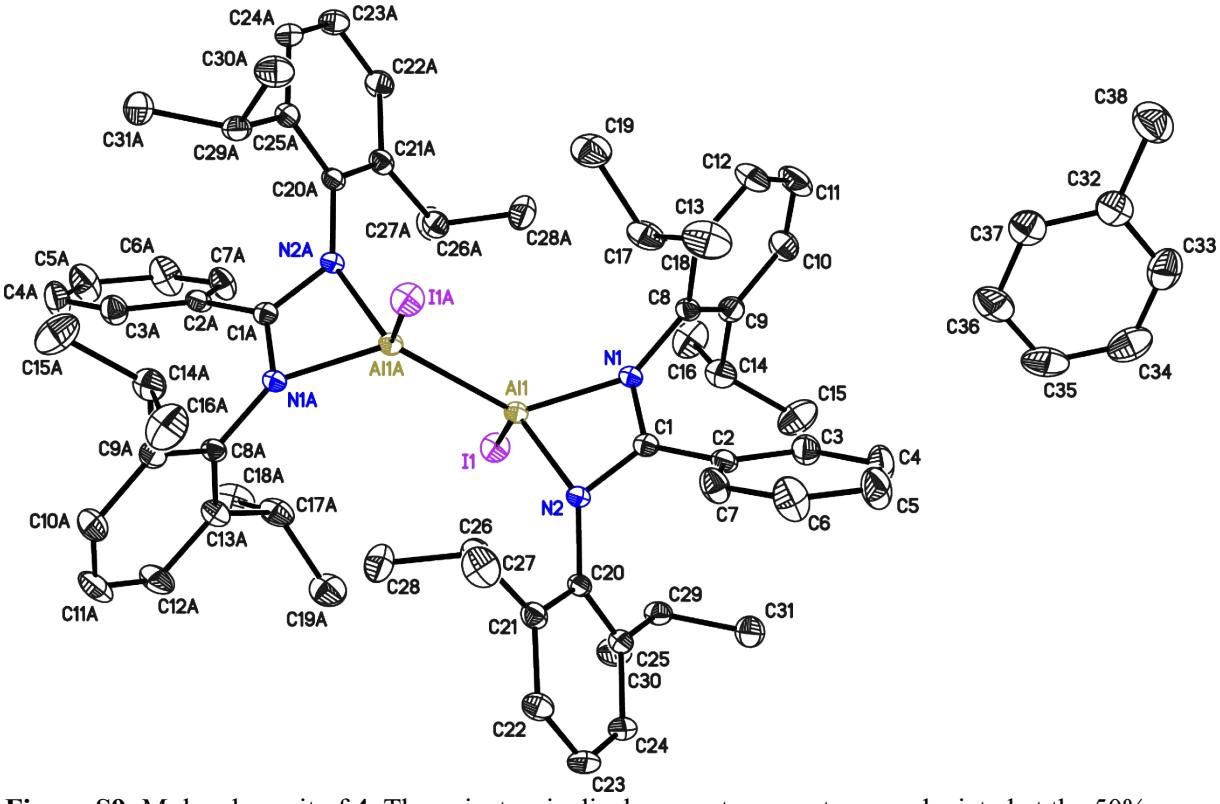


Figure S9: Molecular unit of **4**. The anisotropic displacement parameters are depicted at the 50% probability level. The hydrogen atoms are omitted for clarity.

Table S7: Bond lengths [Å] and angles [°] for **4.**

I(1)-Al(1)	2.5469(6)	C(9)-C(10)	1.396(2)
Al(1)-N(2)	1.9145(14)	C(9)-C(14)	1.525(2)
Al(1)-N(1)	1.9466(14)	C(10)-C(11)	1.380(3)
Al(1)-C(1)	2.3521(16)	C(11)-C(12)	1.378(3)
Al(1)-Al(1)#1	2.5803(10)	C(12)-C(13)	1.400(2)
N(1)-C(1)	1.341(2)	C(13)-C(17)	1.517(2)
N(1)-C(8)	1.439(2)	C(14)-C(16)	1.531(3)
C(1)-N(2)	1.344(2)	C(14)-C(15)	1.535(3)
C(1)-C(2)	1.486(2)	C(17)-C(19)	1.537(3)
N(2)-C(20)	1.4321(19)	C(17)-C(18)	1.537(3)
C(2)-C(3)	1.391(2)	C(20)-C(25)	1.407(2)
C(2)-C(7)	1.395(2)	C(20)-C(21)	1.410(2)
C(3)-C(4)	1.392(3)	C(21)-C(22)	1.397(2)
C(4)-C(5)	1.379(3)	C(21)-C(26)	1.516(2)
C(5)-C(6)	1.390(3)	C(22)-C(23)	1.379(3)
C(6)-C(7)	1.388(3)	C(23)-C(24)	1.386(3)
C(8)-C(13)	1.406(2)	C(24)-C(25)	1.404(2)
C(8)-C(9)	1.412(2)	C(25)-C(29)	1.521(2)

C(26)-C(27)	1.531(2)	C(4)-C(5)-C(6)	119.83(17)
C(26)-C(28)	1.541(2)	C(7)-C(6)-C(5)	120.11(18)
C(29)-C(31)	1.533(2)	C(6)-C(7)-C(2)	120.20(17)
C(29)-C(30)	1.536(2)	C(13)-C(8)-C(9)	120.94(14)
C(32)-C(37)	1.390(3)	C(13)-C(8)-N(1)	120.64(14)
C(32)-C(33)	1.399(3)	C(9)-C(8)-N(1)	118.36(14)
C(32)-C(38)	1.499(3)	C(10)-C(9)-C(8)	118.32(16)
C(33)-C(34)	1.380(3)	C(10)-C(9)-C(14)	118.77(16)
C(34)-C(35)	1.386(4)	C(8)-C(9)-C(14)	122.91(15)
C(35)-C(36)	1.381(3)	C(11)-C(10)-C(9)	121.29(17)
C(36)-C(37)	1.379(3)	C(12)-C(11)-C(10)	119.84(16)
		C(11)-C(12)-C(13)	121.54(18)
N(2)-Al(1)-N(1)	69.39(6)	C(12)-C(13)-C(8)	118.05(16)
N(2)-Al(1)-C(1)	34.85(5)	C(12)-C(13)-C(17)	118.63(16)
N(1)-Al(1)-C(1)	34.77(5)	C(8)-C(13)-C(17)	123.32(14)
N(2)-Al(1)-I(1)	113.53(4)	C(9)-C(14)-C(16)	111.51(16)
N(1)-Al(1)-I(1)	109.92(4)	C(9)-C(14)-C(15)	112.37(16)
C(1)-Al(1)-I(1)	119.76(4)	C(16)-C(14)-C(15)	108.75(15)
N(2)-Al(1)-Al(1)#1	115.03(5)	C(13)-C(17)-C(19)	111.38(16)
N(1)-Al(1)-Al(1)#1	121.48(5)	C(13)-C(17)-C(18)	111.47(17)
C(1)-Al(1)-Al(1)#1	122.09(5)	C(19)-C(17)-C(18)	110.15(16)
I(1)-Al(1)-Al(1)#1	118.11(3)	C(25)-C(20)-C(21)	121.21(14)
C(1)-N(1)-C(8)	124.89(13)	C(25)-C(20)-N(2)	119.08(14)
C(1)-N(1)-Al(1)	89.38(9)	C(21)-C(20)-N(2)	119.64(14)
C(8)-N(1)-Al(1)	144.90(10)	C(22)-C(21)-C(20)	118.19(15)
N(1)-C(1)-N(2)	109.85(13)	C(22)-C(21)-C(26)	120.29(15)
N(1)-C(1)-C(2)	126.03(14)	C(20)-C(21)-C(26)	121.42(14)
N(2)-C(1)-C(2)	123.89(14)	C(23)-C(22)-C(21)	121.31(16)
N(1)-C(1)-Al(1)	55.85(8)	C(22)-C(23)-C(24)	120.02(16)
N(2)-C(1)-Al(1)	54.48(8)	C(23)-C(24)-C(25)	121.06(16)
C(2)-C(1)-Al(1)	169.34(12)	C(24)-C(25)-C(20)	118.02(15)
C(1)-N(2)-C(20)	124.05(13)	C(24)-C(25)-C(29)	119.06(15)
C(1)-N(2)-Al(1)	90.67(10)	C(20)-C(25)-C(29)	122.88(14)
C(20)-N(2)-Al(1)	144.47(11)	C(21)-C(26)-C(27)	113.95(15)
C(3)-C(2)-C(7)	119.36(16)	C(21)-C(26)-C(28)	109.05(14)
C(3)-C(2)-C(1)	122.51(15)	C(27)-C(26)-C(28)	110.62(15)
C(7)-C(2)-C(1)	118.08(15)	C(25)-C(29)-C(31)	112.02(14)
C(2)-C(3)-C(4)	120.03(17)	C(25)-C(29)-C(30)	110.96(14)
C(5)-C(4)-C(3)	120.43(18)	C(31)-C(29)-C(30)	110.27(15)

C(37)-C(32)-C(33)	118.1(2)	C(33)-C(34)-C(35)	119.9(2)
C(37)-C(32)-C(38)	121.0(2)	C(36)-C(35)-C(34)	119.9(2)
C(33)-C(32)-C(38)	120.9(2)	C(37)-C(36)-C(35)	120.1(2)
C(34)-C(33)-C(32)	120.9(2)	C(36)-C(37)-C(32)	121.1(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1

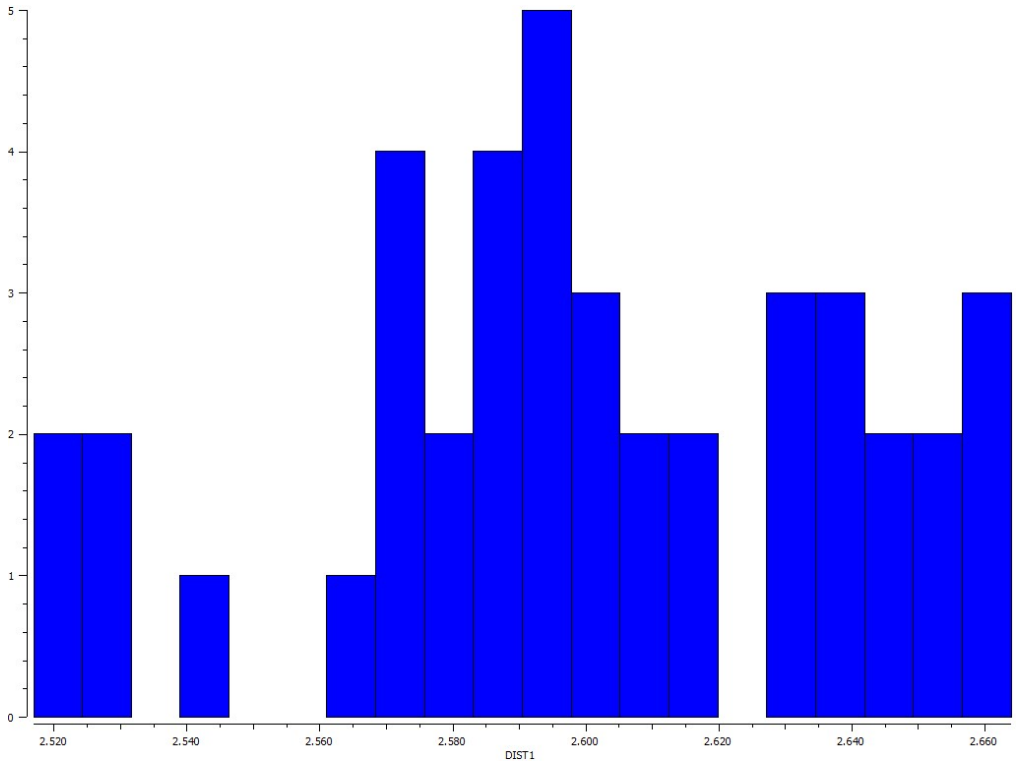


Figure S10: Histogram of all Al-Al single bonds between Al atoms that are fourfold coordinated and are not bound to other metals or hydrogen as listed in the CSD (version 5.43).[10]

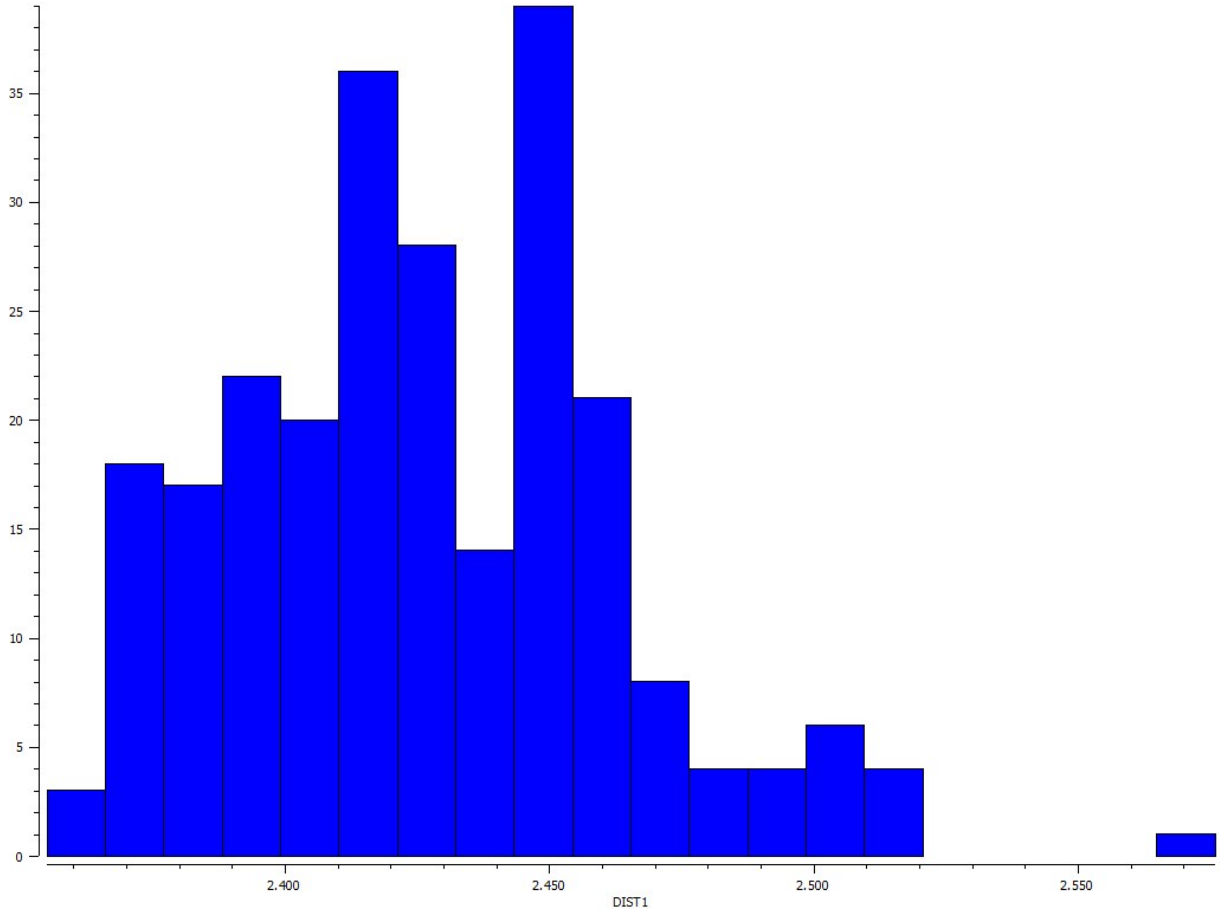


Figure S11: Histogram of all Ga-Ga single bonds between Ga atoms that are fourfold coordinated and are not bound to other metals or hydrogen as listed in the CSD (version 5.43).[10]

Computational details

Density functional theoretical (DFT) calculations were carried out for the systems **1-4** at B3LYP/ECP(I),6-311++G**[11-14] level of theory where the effective core potential (ECP) with double-ζ LANL2DZ was used for iodine and the 6-311++G** basis set was used for the other atoms. The optimized geometry was characterized as a minimum by computing harmonic vibrational frequencies at the same level of theory. To understand the nature of bonding in these compounds, natural bond orbital (NBO) analysis [15] was carried out at the optimized geometries. QTAIM (quantum theory of atoms in molecules) calculations were also employed to characterize the electron distribution around selected bonds in **1-4**. All the calculations were carried out using Gaussian 16 suite of programs.[16] Multiwfn software was employed to do the QTAIM analysis.[17]

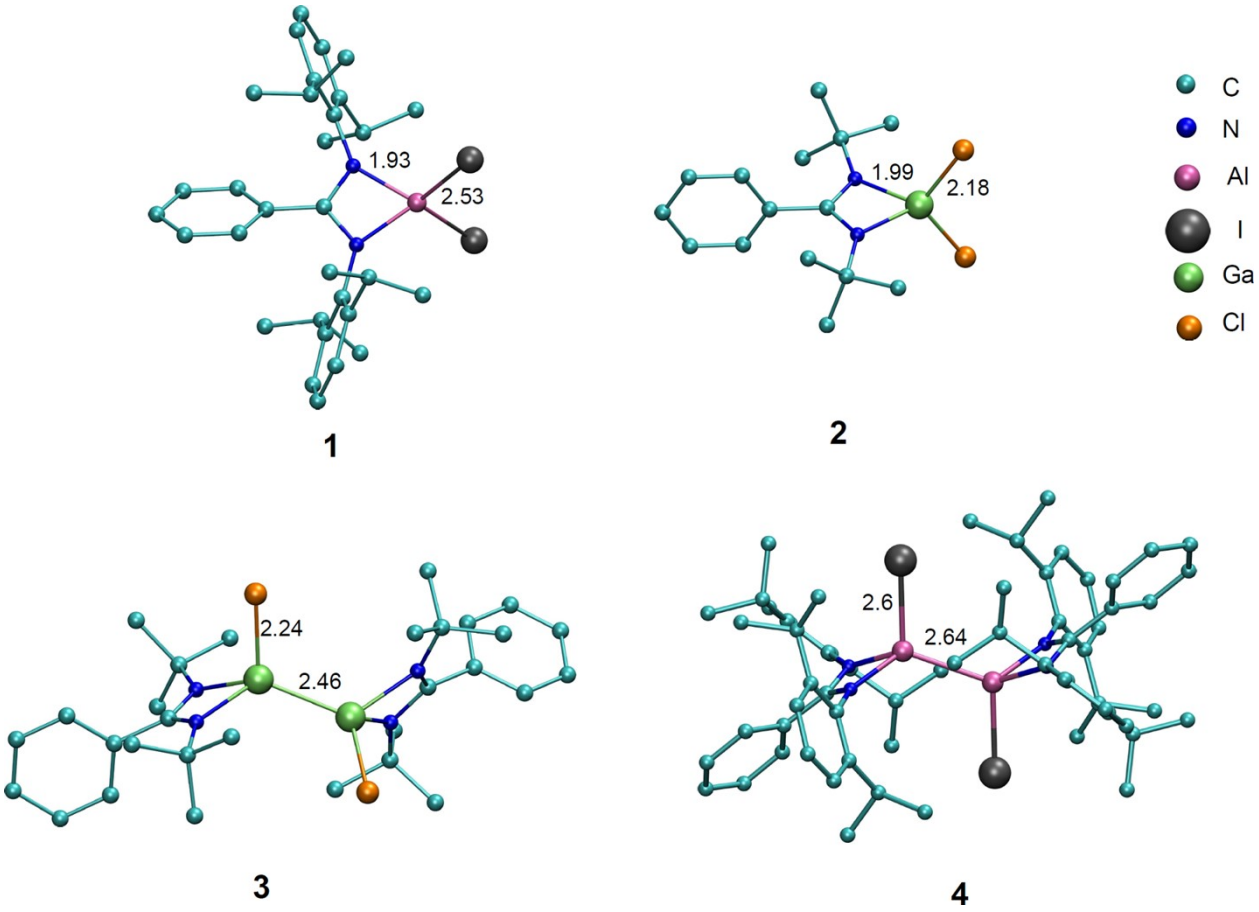
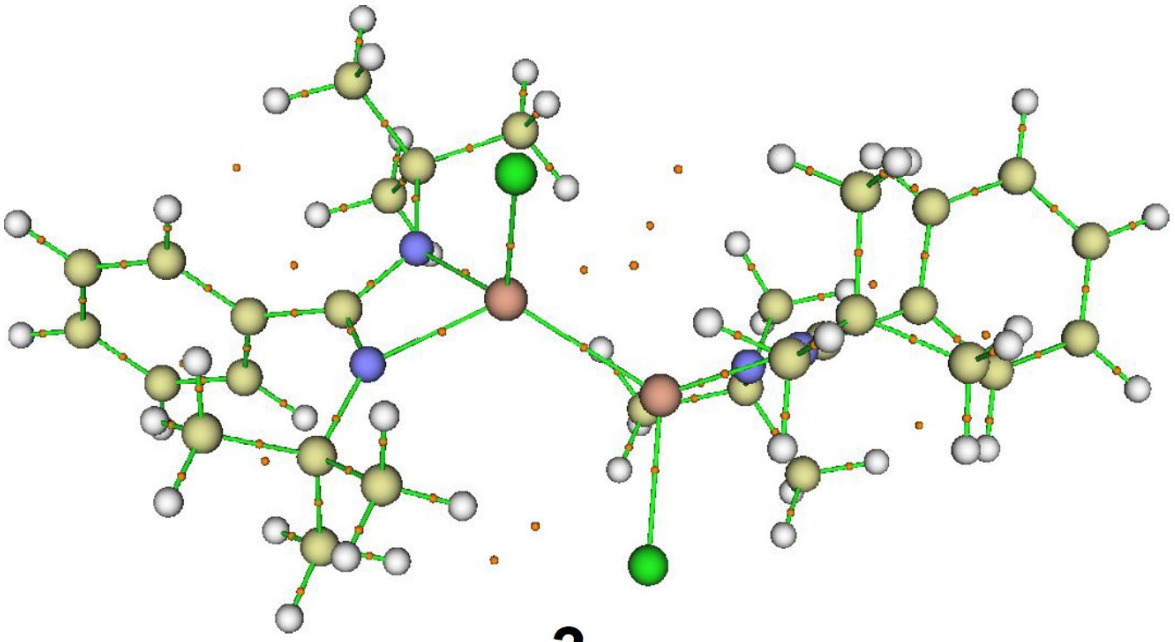


Figure S12. Optimized geometries of molecules **1, 2, 3,** and **4** obtained at the B3LYP/ECP(I),6-311++G** level of theory. The hydrogen atoms are not shown for clarity. The important bond distances are indicated in Angstrom units.



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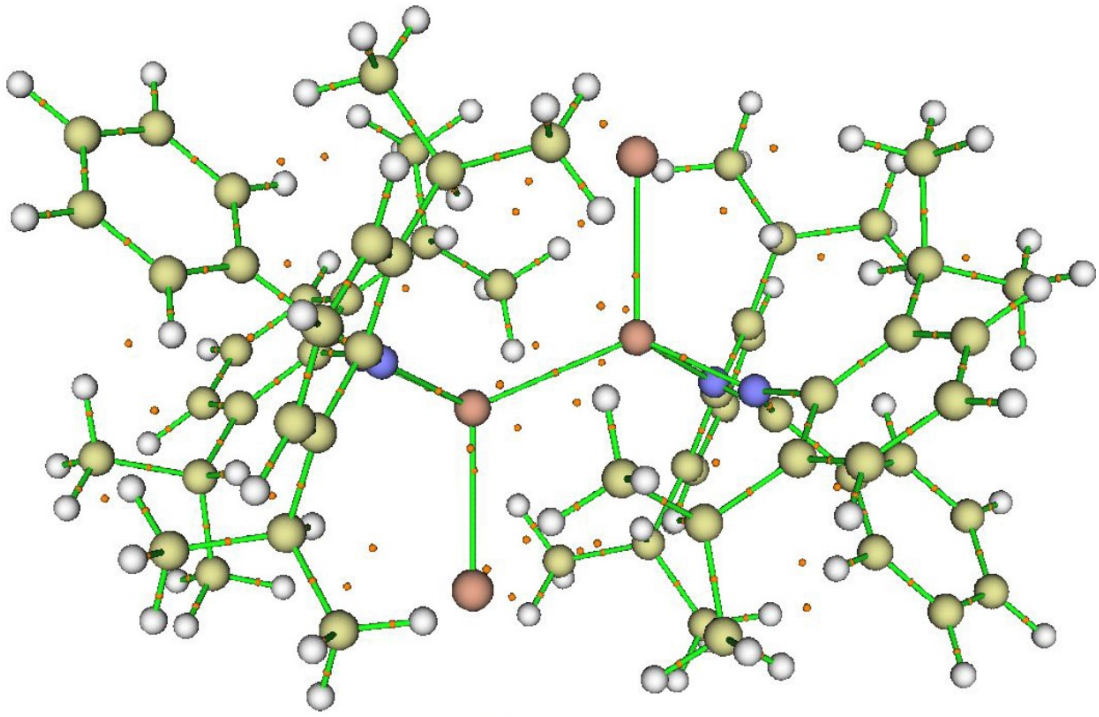

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Figure S13. The location of (3,-1) BCPs in the molecule **3** and **4** obtained at B3LYP/ECP(I),6-311++G** level of theory.

Table S8. Comparison of important geometrical parameters of molecules **1**, **2**, **3** and **4** obtained from experiments and calculations. r is for distance (Angs), ∠ is for angle and d is for dihedral.

Molecule	Geometrical Parameter	Crystal Structure	Calculated
1	r Al-I(1)	2.47	2.53
	r (Al-I2)	2.47	2.53
	r (Al-N1)	1.89	1.93
	r (Al-N2)	1.89	1.93
	∠ (I1-Al-I2)	114.0	111.9
2	r (Ga-Cl1)	2.14	2.18
	r (Ga-Cl2)	2.14	2.18
	r (Ga-N1)	1.94	1.99
	r (Ga-N2)	1.94	1.99
	∠ (Cl1-Ga-Cl2)	109.1	114.5
3	r (Ga1-Ga2)	2.41	2.46
	r (Ga1-Cl1)	2.21	2.24
	r (Ga2-Cl2)	2.21	2.24
	r (Ga1-N1)	1.98	2.02
	r (Ga1-N2)	1.98	2.02
	r (Ga2-N3)	1.98	2.02
	r (Ga2-N4)	1.98	2.02

	∠ (Cl1-Ga1-Ga2)	116.0	115.1
	∠ (Cl2-Ga2-Ga1)	116.0	115.1
	d (Cl1-Ga1-Ga2-Cl2)	100.8	121.2
4	r (Al1-Al2)	2.58	2.64
	r (Al1-I1)	2.55	2.60
	r (Al2-I2)	2.55	2.60
	r (Al1-N1)	1.91	1.96
	r (Al1-N2)	1.95	1.99
	r (Al2-N3)	1.91	1.96
	r (AL2-N4)	1.95	1.99
	∠ (I1-Al1-Al2)	118.1	112.0
	∠ (I2-Al2-Al1)	118.1	112.0
	d (I1-Ga1-Ga2-I2)	180.0	180.0

Table S9. Results of NBO analysis obtained at the B3LYP/ECP(I),6-311++G** level of theory.

Molecule	**Bond**	**Occupancy (*e*)**	**Atomic contribution**
1	Al-I σ	1.957	Al: s(27.38%) p(70.93%) d(1.69%) I: s(20.24%) p(79.76%)

2	Ga-Cl σ	1.964	Ga: s(27.03%) p(72.37%) d(0.60%) Cl: s(22.44%) p(77.36%) d(0.20%)
3	Ga-Ga σ	1.890	Ga1: s(41.89%) p(57.81%) d(0.30%) Ga2: s(41.89%) p(57.81%) d(0.30%)
	Ga-Cl σ	1.965	Ga1: s(20.0%) p(79.27%) d(0.74%) Cl1: s(26.08%) p(73.78%) d(0.14%)
4	Al-Al σ	1.821	Al1: s(40.59%) p(59.01%) d(0.41%) Al2: s(40.70%) p(58.90%) d(0.41%)
	Al-I σ	1.936	Al1: s(18.45%) p(79.34%) d(2.21%) I1: s(27.89%) p(72.11%)

Table S10. Natural charges of important atoms in the molecules **1**, **2**, **3** and **4** at B3LYP/ECP(I),6-311++G** level of theory.

Molecule	**Atom**	**NPA charges**
1	Al	+1.199
	I1	-0.306
	I2	-0.306
	N1	-0.824
	N2	-0.824
2	Ga	+1.394
	Cl1	-0.478

	Cl2	-0.478
	N1	-0.751
	N2	-0.751
3	Ga1	+1.005
	Ga2	+1.005
	Cl1	-0.535
	Cl2	-0.535
	N1	-0.743
	N2	-0.757
	N3	-0.743
	N4	-0.757
4	Al1	+1.084
	Al2	+1.084
	I1	-0.435
	I2	-0.435
	N1	-0.838
	N2	-0.859
	N3	-0.838
	N4	-0.859

Table S11. The electron density ($\rho(r)$), Laplacian ($[\nabla^2\rho(r)]$), and ellipticity (ε) at the (3,-1) BCPs in **1**, **2**, **3** and **4** obtained from QTAIM calculations at the B3LYP/ECP(I),6-311++G** level of theory.

Molecule	Bond	$\rho(r)$	$[\nabla^2\rho(r)]$	ε
1	Al-I1	0.055	+0.752	0.003
2	Ga-Cl1	0.089	+0.172	0.001
3	Ga1-Ga2	0.068	-0.023	0.008
	Ga1-Cl1	0.078	+0.146	0.011
4	Al1-Al2	0.057	-0.081	0.022
	Al1-I1	0.047	+0.060	0.040

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