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SUPPORTING INFORMATION of SYNTHESES and STRUCTURES

Synthesis and Molecular Structure of an Abnormal Carbene-Gallium Chloride Complex

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All reactions were performed under purified argon using Schlenk techniques and an inert atmosphere drybox (M-Braun LabMaster 130). Chemicals were purchased from commercial sources and used as received. Solvents were dried and distilled under argon from Na/benzophenone prior to use. N-heterocyclic carbene NHC (NHC = :C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$) and compound **2** was prepared according to the literature method.[1,2] ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer. ^{11}B NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer. X-ray intensity data for compound **4**, **5·THF** and **6·(toluene)$_{0.5}$** were collected on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), using the ω-scan technique.

Compound **4**: NHC:BEt_3 (NHC = :C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$) was prepared similarly according to the literature method reported for the synthesis of NHC:BH_3[3]: to a slurry of NHC carbene (10.0g, 25.732 mmol) in hexane (120 mL) was added BEt_3 (2.6g, 26.532 mmol) at ambient temperature. The mixture was stirred over one day and then the solution was filtered. The residue of NHC:BEt_3 was obtained after the volatiles were removed in vacuo. To a solution of L:BEt_3 (5.0g, 10.275 mmol) in THF (50 mL) was added 6.5 mL of nBuLi solution (1.6M, 10.4 mmol) at -78 °C. The mixture was allowed to warm to room temperature over night and the solvent was then removed in vacuo. The residue was recrystallized in THF giving X-ray quality colorless crystals of **4** (7.1g, 98% yield) at ambient temperature. Mp: gradually decomposed at 303 ºC and melt at 311 ºC. ^{1}H NMR (THF-d_8): δ = 0.16 [q, 6H, B(C*H*$_2$CH$_3$)$_3$], 0.46 [t, 9H, B(CH$_2$C*H*$_3$)$_3$], 1.08 [d, 6H, CH(C*H*$_3$)$_2$], 1.13 [d, 6H, CH(C*H*$_3$)$_2$], 1.30 [d, 12H, CH(C*H*$_3$)$_2$], 2.97 [m, 4H, C*H*(CH$_3$)$_2$], 6.08 (s, 1H, C*H*), 7.09-7.28 (m, 6H, Ar-*H*).^{13}C NMR (C_6D_6): δ = 13.4 [BCH$_2$*C*H$_3$], 23.5 [B*C*H$_2$CH$_3$], 23.8 [CH(*C*H$_3$)$_2$], 24.1 [CH(*C*H$_3$)$_2$], 26.5 [CH(*C*H$_3$)$_2$], 27.2 [CH(*C*H$_3$)$_2$], 27.4 [*C*H(CH$_3$)$_2$], 28.1 [*C*H(CH$_3$)$_2$], 29.9 [*C*H(CH$_3$)$_2$], 30.0 [*C*H(CH$_3$)$_2$], 132.4 (Li*C*CN), 141.1 (NC*C*H), 123.7, 124.0, 128.0, 129.3, 146.7, 147.0, 147.9 (Ar-*C*), 207.2 (N*C*HN). ^{11}B NMR (THF-d_8, 160.35 MHz): δ = -13.85. Anal. Calc. for **4** ($C_{45}H_{74}N_2O_3BLi$)**:** C, 76.25; H, 10.52; N, 3.95; Found: C, 76.19; H, 10.38; N, 4.06. Crystal data for **4**: $C_{45}H_{74}N_2O_3BLi$, fw = 708.81, orthorhombic, *Pca21* (No. 29), a = 23.735(2) Å, b = 10.4695(10) Å, c = 18.5654(17) Å, α = 90º, β = 90º, γ = 90º, V = 4613.4(7) Å^3, Z = 4, R1 = 0.0584 for 8405 data ($I > 2\sigma(I)$), wR_2 = 0.1268 (all data).

Compound **5**: To a solution of $GaCl_3$ (0.3g, 1.704mmol) in THF (20 mL) was slowly added a solution of compound **4** (1.2g, 1.693mmol) in THF (20 mL) at -78 °C. The mixture was allowed to warm to room temperature over night and then the solvent was removed in vacuo. The residue was recrystallized in mixture of THF/hexane giving X-ray quality colorless crystals of **5** (0.72g, 67% yield). Mp: gradually decomposed and melt at 140 ºC. ^{1}H NMR (THF-d_8): δ = 1.11 [d, 6H, CH(C*H*$_3$)$_2$], 1.21 [d, 6H, CH(C*H*$_3$)$_2$], 1.29

[d, 6H, CH(CH_3)$_2$], 2.50 (m, 2H, CH(CH$_3$)$_2$), 2.62 [m, 2H, CH(CH$_3$)$_2$], 7.34 (d, 2H, Ar-H), 7.42 (d, 2H, Ar-H), 7.50 (t, 1H, Ar-H), 7.57 (t, 1H, Ar-H), 7.91 (s, 1H, C=CH), 9.51 (s, 1H, NCHN). ^{13}C NMR (THF-d$_8$): δ = 23.5 [CH(CH$_3$)$_2$], 24.9 [CH(CH$_3$)$_2$], 25.7 [CH(CH$_3$)$_2$], 26.5 [CH(CH$_3$)$_2$], 27.2 [CH(CH$_3$)$_2$], 27.4 [CH(CH$_3$)$_2$], 30.5 [CH(CH$_3$)$_2$], 30.6 [CH(CH$_3$)$_2$], 134.1 (GaCCN), 142.3 (NCCH), 125.6, 126.2, 132.4, 132.9, 133.2, 134.0, 147.2, 147.4 (Ar), 207.2 (NCHN). Anal. Calc. for **5·THF** (C$_{31}$H$_{44}$N$_2$OGaCl$_3$)**:** C, 58.47; H, 6.97; N, 4.40; Found: C, 58.39; H, 7.06; N, 4.36. Crystal data for **5·THF**: C$_{31}$H$_{44}$N$_2$OGaCl$_3$, fw = 636.75, Orthorhombic, *P*bca (No. 61), a = 11.4236(6) Å, b = 20.7234(11) Å, c = 29.0681(16) Å, V = 6881.5(6) Å^3, Z = 8, R1 = 0.0470 for 7085 data ($I > 2\sigma(I)$), wR$_2$ = 0.1181 (all data).

Compound **6**: To a solution of GaCl$_3$ (0.323g, 1.835mmol) in THF (10 mL) was slowly added a solution of compound **2** (0.9g, 1.829mmol) in THF (30 mL) at -78 °C. The mixture was allowed to warm to room temperature over night and then the solvent was removed in vacuo. The residue was extracted using 30 mL of toluene. The filtrate was concentrated to ca. 5 mL in vacuo, to which 5 mL of hexane was then added. X-ray quality colorless crystals of **6** were observed over 5 days (0.78g, 76% yield). Mp: gradually decomposed and melt at 224 ºC. ^{1}H NMR (C$_6$D$_6$): δ = 0.73 [t, 6H, B(CH$_2$CH_3)$_2$], 0.86 [q, 4H, B(CH_2CH$_3$)$_2$], 0.93 [t, 12H, CH(CH_3)$_2$], 1.47 [t, 12H, CH(CH_3)$_2$], 2.66 [m, 2H, CH(CH$_3$)$_2$], 2.82 [m, 2H, CH(CH$_3$)$_2$], 7.08-7.29 (m, 6H, Ar-H), 7.45 (s, 1H, CH).^{13}C NMR (C$_6$D$_6$): δ = 8.2 [BCH$_2$$CH_3$], 22.1 [B$CH_2CH_3$], 23.9 [CH($CH_3$)$_2$], 24.2 [CH($CH_3$)$_2$], 25.3 [CH($CH_3$)$_2$], 25.8 [CH($CH_3$)$_2$], 28.8 [$C$H(CH$_3$)$_2$], 29.1 [$C$H(CH$_3$)$_2$], 67.5 (B$C$CN), 137.9 (NC$C$H), 124.2, 124.5, 131.3, 131.4, 144.9, 145.4 (Ar-C). ^{11}B NMR (C$_6$D$_6$, 160.35 MHz): δ = -14.75. Crystal data for **6·(toluene)$_{0.5}$**: C$_{69}$H$_{98}$N$_4$B$_2$Ga$_2$Cl$_6$, fw = 1357.27, Monoclinic, P2(1)/c (No. 14), a = 9.4189(15)Å, b = 20.580(3)Å, c = 19.841(3)Å, α= 90^o, β= 102.730(3)^o, γ = 90^o, V = 3751.4(10)Å^3, Z = 2, R1 = 0.0602 for 7389 data ($I > 2\sigma(I)$), wR$_2$ =0.1940 (all data).

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SUPPORTING INFORMATION OF X-RAY

Table 1. Crystallographic Data for Compounds 4, 5 and 6.

Compound	**4**	**5·THF**	**6·(toluene)$_{0.5}$**
Empirical formula	$C_{45}H_{74}N_2O_3BLi$	$C_{31}H_{44}N_2OGaCl_3$	$C_{34.5}H_{49}N_2B_1Ga_1Cl_3$
Formula weight	708.81	636.75	678.63
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Lattice parameters			
a (Å)	23.735(2)	11.4236(6)	9.4189(15)
b (Å)	10.4695(10)	20.7234(11)	20.580(3)
c (Å)	18.5654(17)	29.0681(16)	19.841(3)
α (deg)	90	90	90
β (deg)	90	90	102.730(3)
γ (deg)	90	90	90
V (Å^3)	4613.4(7)	6881.5(6)	3751.4(10)
Space group	Pca2(1)	Pbca	P21/c
Z value	4	8	2
ρ_{calc} (g / cm^3)	1.020	1.229	1.202
μ (Mo Kα) (mm^{-1})	0.061	1.057	0.971
Temperature (K)	296(2)	296(2)	296(2)
$2\Theta_{max}$ (°)	50.496	52.896	52.044
No. Obs. (I > 2σ(I))	8405	7085	7389
No. Parameters	662	347	431
Goodness of fit (GOF)	1.018	1.016	1.055
Max. shift in cycle	0.001	0.001	0.001
Residuals*: R1; wR2	0.0584; 0.1268	0.0470; 0.1181	0.0602; 0.1670
Absorption Correction, Max/min	Multi-scan 0.7454 / 0.6819	Multi-scan 0.7454 / 0.6288	Multi-scan 0.7454 / 0.5911
Largest peak in Final Diff. Map (e$^-$ / Å^3)	0.121	0.561	1.068

[a] $R = \Sigma_{hkl}(\,|\,|F_{obs}|-|F_{calc}|\,|)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/\Sigma_{hkl}wF^2_{obs}]^{1/2}$; $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

Compound **4**

Table 2. Bond lengths [A] and angles [deg] for **4**.

B(1)-C(32)	1.610(8)
B(1)-C(1)	1.676(7)
B(1)-C(28)	1.646(8)
B(1)-C(32')	1.632(18)
B(1)-C(30')	1.661(18)
B(1)-C(30)	1.671(8)
B(1)-C(28')	1.725(16)
Li(1)-O(1)	1.93(3)
Li(1)-O(3)	1.987(15)
Li(1)-O(1')	2.05(2)
Li(1)-O(2)	2.053(18)
Li(1)-O(2')	2.02(3)
Li(1)-C(3)	2.151(9)
Li(1)-O(3')	2.19(3)
N(1)-C(1)	1.366(5)
N(1)-C(2)	1.394(5)
N(1)-C(16)	1.442(5)
N(2)-C(1)	1.372(5)
N(2)-C(3)	1.420(6)
N(2)-C(4)	1.451(6)
C(2)-C(3)	1.363(7)
C(4)-C(5)	1.397(7)
C(4)-C(9)	1.392(7)
C(5)-C(6)	1.381(8)
C(5)-C(13)	1.505(7)
C(6)-C(7)	1.372(9)
C(7)-C(8)	1.382(9)
C(8)-C(9)	1.377(8)
C(9)-C(10)	1.520(8)
C(10)-C(11)	1.514(8)
C(10)-C(12)	1.532(9)
C(13)-C(14)	1.532(8)
C(13)-C(15)	1.509(8)
C(16)-C(21)	1.388(6)
C(16)-C(17)	1.401(7)
C(17)-C(18)	1.386(8)
C(17)-C(25)	1.505(7)
C(18)-C(19)	1.360(9)
C(19)-C(20)	1.367(9)
C(20)-C(21)	1.388(7)
C(21)-C(22)	1.503(7)
C(22)-C(23)	1.512(8)
C(22)-C(24)	1.531(7)

C(25)-C(26)	1.524(9)
C(25)-C(27)	1.535(8)
C(28)-C(29)	1.557(13)
C(30)-C(31)	1.513(10)
C(32)-C(33)	1.559(8)
C(28')-C(29')	1.530(18)
C(30')-C(31')	1.534(17)
C(32')-C(33')	1.530(19)
O(1)-C(34)	1.40(3)
O(1)-C(37)	1.41(3)
C(34)-C(35)	1.39(2)
C(35)-C(36)	1.26(2)
C(36)-C(37)	1.43(2)
O(1')-C(34')	1.41(2)
O(1')-C(37')	1.43(3)
C(34')-C(35')	1.379(17)
C(35')-C(36')	1.278(19)
C(36')-C(37')	1.439(19)
O(2)-C(38)	1.362(13)
O(2)-C(41)	1.433(14)
C(38)-C(39)	1.423(17)
C(39)-C(40)	1.305(18)
C(40)-C(41)	1.367(17)
O(2')-C(38')	1.37(2)
O(2')-C(41')	1.43(2)
C(38')-C(39')	1.39(2)
C(39')-C(40')	1.32(3)
C(40')-C(41')	1.35(3)
O(3)-C(45)	1.322(15)
O(3)-C(42)	1.451(16)
C(42)-C(43)	1.542(18)
C(43)-C(44)	1.53(2)
C(44)-C(45)	1.497(17)
O(3')-C(45')	1.34(3)
O(3')-C(42')	1.48(2)
C(42')-C(43')	1.53(3)
C(43')-C(44')	1.55(3)
C(44')-C(45')	1.50(3)

C(32)-B(1)-C(1)	112.3(4)
C(32)-B(1)-C(28)	112.3(5)
C(1)-B(1)-C(28)	109.6(4)
C(1)-B(1)-C(32')	118.7(8)
C(1)-B(1)-C(30')	111.9(9)
C(32')-B(1)-C(30')	113.4(13)
C(32)-B(1)-C(30)	110.6(5)
C(1)-B(1)-C(30)	107.1(4)
C(28)-B(1)-C(30)	104.5(4)
C(1)-B(1)-C(28')	111.3(11)
C(32')-B(1)-C(28')	103.1(14)

C(30')-B(1)-C(28')	95.4(13)
O(1)-Li(1)-O(3)	102.1(12)
O(1)-Li(1)-O(2)	93(3)
O(3)-Li(1)-O(2)	105.6(8)
O(1')-Li(1)-O(2')	110(2)
O(1)-Li(1)-C(3)	112.8(15)
O(3)-Li(1)-C(3)	127.1(6)
O(1')-Li(1)-C(3)	109.9(11)
O(2)-Li(1)-C(3)	110.8(6)
O(2')-Li(1)-C(3)	114.4(11)
O(1')-Li(1)-O(3')	112.7(15)
O(2')-Li(1)-O(3')	87.4(12)
C(3)-Li(1)-O(3')	120.2(12)
C(1)-N(1)-C(2)	110.4(4)
C(1)-N(1)-C(16)	131.4(4)
C(2)-N(1)-C(16)	118.2(4)
C(1)-N(2)-C(3)	116.3(4)
C(1)-N(2)-C(4)	126.1(4)
C(3)-N(2)-C(4)	117.6(4)
N(1)-C(1)-N(2)	101.7(4)
N(1)-C(1)-B(1)	127.1(4)
N(2)-C(1)-B(1)	131.2(4)
C(3)-C(2)-N(1)	111.6(4)
C(2)-C(3)-N(2)	99.9(4)
C(2)-C(3)-Li(1)	122.8(5)
N(2)-C(3)-Li(1)	137.3(4)
C(5)-C(4)-C(9)	122.8(5)
C(5)-C(4)-N(2)	118.6(4)
C(9)-C(4)-N(2)	118.4(4)
C(4)-C(5)-C(6)	116.6(5)
C(4)-C(5)-C(13)	123.1(5)
C(6)-C(5)-C(13)	120.3(5)
C(7)-C(6)-C(5)	121.6(6)
C(6)-C(7)-C(8)	120.6(6)
C(9)-C(8)-C(7)	120.2(6)
C(8)-C(9)-C(4)	118.2(5)
C(8)-C(9)-C(10)	119.0(5)
C(4)-C(9)-C(10)	122.9(5)
C(9)-C(10)-C(11)	112.8(5)
C(9)-C(10)-C(12)	111.6(5)
C(11)-C(10)-C(12)	108.8(5)
C(5)-C(13)-C(14)	112.5(5)
C(5)-C(13)-C(15)	111.5(5)
C(14)-C(13)-C(15)	109.8(5)
C(21)-C(16)-C(17)	121.5(4)
C(21)-C(16)-N(1)	119.3(4)
C(17)-C(16)-N(1)	118.4(4)
C(18)-C(17)-C(16)	118.0(5)
C(18)-C(17)-C(25)	118.3(5)
C(16)-C(17)-C(25)	123.6(5)

C(17)-C(18)-C(19)	120.7(6)
C(18)-C(19)-C(20)	120.9(5)
C(21)-C(20)-C(19)	120.9(6)
C(20)-C(21)-C(16)	117.9(5)
C(20)-C(21)-C(22)	119.4(5)
C(16)-C(21)-C(22)	122.7(4)
C(21)-C(22)-C(23)	109.9(4)
C(21)-C(22)-C(24)	112.8(5)
C(23)-C(22)-C(24)	110.1(5)
C(17)-C(25)-C(26)	110.9(5)
C(17)-C(25)-C(27)	112.2(5)
C(26)-C(25)-C(27)	110.6(6)
C(29)-C(28)-B(1)	116.2(7)
C(31)-C(30)-B(1)	118.3(6)
C(33)-C(32)-B(1)	113.1(6)
C(29')-C(28')-B(1)	113.7(18)
C(31')-C(30')-B(1)	116.1(17)
C(33')-C(32')-B(1)	117.9(16)
C(34)-O(1)-C(37)	96(3)
C(34)-O(1)-Li(1)	118(2)
C(37)-O(1)-Li(1)	136(3)
O(1)-C(34)-C(35)	112.1(18)
C(36)-C(35)-C(34)	110(2)
C(35)-C(36)-C(37)	104.1(19)
O(1)-C(37)-C(36)	112.5(17)
C(34')-O(1')-C(37')	103(2)
C(34')-O(1')-Li(1)	120.8(14)
C(37')-O(1')-Li(1)	133.0(17)
O(1')-C(34')-C(35')	110.7(13)
C(36')-C(35')-C(34')	106.4(17)
C(35')-C(36')-C(37')	112.2(15)
O(1')-C(37')-C(36')	104.4(13)
C(38)-O(2)-C(41)	104.4(11)
C(38)-O(2)-Li(1)	131.2(12)
C(41)-O(2)-Li(1)	124.4(12)
O(2)-C(38)-C(39)	104.9(12)
C(40)-C(39)-C(38)	112.7(15)
C(41)-C(40)-C(39)	105.0(14)
C(40)-C(41)-O(2)	109.6(12)
C(38')-O(2')-C(41')	105(2)
C(38')-O(2')-Li(1)	125(2)
C(41')-O(2')-Li(1)	130(2)
O(2')-C(38')-C(39')	109(2)
C(40')-C(39')-C(38')	109(2)
C(41')-C(40')-C(39')	109(2)
C(40')-C(41')-O(2')	109(2)
C(45)-O(3)-C(42)	109.1(10)
C(45)-O(3)-Li(1)	132.4(10)
C(42)-O(3)-Li(1)	118.5(11)
O(3)-C(42)-C(43)	105.7(12)

C(44)-C(43)-C(42)	100.5(13)
C(43)-C(44)-C(45)	106.7(13)
O(3)-C(45)-C(44)	109.1(12)
C(45')-O(3')-C(42')	108(2)
C(45')-O(3')-Li(1)	116(2)
C(42')-O(3')-Li(1)	135(2)
O(3')-C(42')-C(43')	100(2)
C(44')-C(43')-C(42')	94(3)
C(45')-C(44')-C(43')	99(2)
O(3')-C(45')-C(44')	108(2)

Symmetry transformations used to generate equivalent atoms:

Compound **5**

Table 3. Bond lengths [A] and angles [deg] for **5·THF**.

Ga(1)-C(3)	1.978(3)
Ga(1)-Cl(3)	2.1480(11)
Ga(1)-Cl(1)	2.1636(12)
Ga(1)-Cl(2)	2.1864(12)
N(1)-C(1)	1.321(4)
N(1)-C(2)	1.380(4)
N(1)-C(16)	1.457(3)
N(2)-C(1)	1.330(4)
N(2)-C(3)	1.404(4)
N(2)-C(4)	1.457(4)
C(2)-C(3)	1.350(4)
C(4)-C(5)	1.387(5)
C(4)-C(9)	1.388(5)
C(5)-C(6)	1.399(6)
C(5)-C(13)	1.510(6)
C(6)-C(7)	1.337(7)
C(7)-C(8)	1.360(7)
C(8)-C(9)	1.420(5)
C(9)-C(10)	1.514(6)
C(10)-C(12)	1.536(5)
C(10)-C(11)	1.528(6)
C(13)-C(14)	1.533(6)
C(13)-C(15)	1.528(6)
C(16)-C(17)	1.398(4)
C(16)-C(21)	1.386(4)
C(17)-C(18)	1.388(5)
C(17)-C(25)	1.515(5)
C(18)-C(19)	1.368(5)
C(19)-C(20)	1.360(5)
C(20)-C(21)	1.387(4)
C(21)-C(22)	1.518(5)
C(22)-C(24)	1.523(5)
C(22)-C(23)	1.523(5)
C(25)-C(27)	1.486(6)
C(25)-C(26)	1.513(7)
O(1)-C(31)	1.393(6)
O(1)-C(28)	1.399(7)
C(28)-C(29)	1.445(9)
C(29)-C(30)	1.415(9)
C(30)-C(31)	1.469(8)
C(3)-Ga(1)-Cl(3)	113.80(9)
C(3)-Ga(1)-Cl(1)	114.33(9)
Cl(3)-Ga(1)-Cl(1)	106.92(5)

C(3)-Ga(1)-Cl(2)	103.33(9)
Cl(3)-Ga(1)-Cl(2)	109.21(6)
Cl(1)-Ga(1)-Cl(2)	109.10(6)
C(1)-N(1)-C(2)	107.9(2)
C(1)-N(1)-C(16)	126.0(2)
C(2)-N(1)-C(16)	126.0(2)
C(1)-N(2)-C(3)	109.6(2)
C(1)-N(2)-C(4)	122.4(3)
C(3)-N(2)-C(4)	128.0(2)
N(1)-C(1)-N(2)	108.9(3)
C(3)-C(2)-N(1)	109.4(3)
C(2)-C(3)-N(2)	104.3(2)
C(2)-C(3)-Ga(1)	124.3(2)
N(2)-C(3)-Ga(1)	131.4(2)
C(5)-C(4)-C(9)	124.8(3)
C(5)-C(4)-N(2)	118.0(3)
C(9)-C(4)-N(2)	117.2(3)
C(4)-C(5)-C(6)	116.4(4)
C(4)-C(5)-C(13)	123.5(3)
C(6)-C(5)-C(13)	120.0(4)
C(7)-C(6)-C(5)	120.6(5)
C(6)-C(7)-C(8)	122.6(4)
C(7)-C(8)-C(9)	120.5(4)
C(4)-C(9)-C(8)	115.0(4)
C(4)-C(9)-C(10)	123.1(3)
C(8)-C(9)-C(10)	121.9(4)
C(9)-C(10)-C(12)	113.8(4)
C(9)-C(10)-C(11)	110.6(4)
C(12)-C(10)-C(11)	109.6(4)
C(5)-C(13)-C(14)	112.8(4)
C(5)-C(13)-C(15)	110.0(4)
C(14)-C(13)-C(15)	110.2(4)
C(17)-C(16)-C(21)	123.8(3)
C(17)-C(16)-N(1)	118.1(3)
C(21)-C(16)-N(1)	118.1(3)
C(16)-C(17)-C(18)	115.7(3)
C(16)-C(17)-C(25)	123.2(3)
C(18)-C(17)-C(25)	121.1(3)
C(19)-C(18)-C(17)	121.7(3)
C(18)-C(19)-C(20)	121.0(3)
C(19)-C(20)-C(21)	120.7(4)
C(16)-C(21)-C(20)	117.1(3)
C(16)-C(21)-C(22)	123.1(3)
C(20)-C(21)-C(22)	119.7(3)
C(21)-C(22)-C(24)	111.6(3)
C(21)-C(22)-C(23)	111.1(3)
C(24)-C(22)-C(23)	111.1(4)
C(27)-C(25)-C(17)	111.9(4)
C(27)-C(25)-C(26)	106.7(4)
C(17)-C(25)-C(26)	112.1(4)

C(31)-O(1)-C(28)	108.0(4)
O(1)-C(28)-C(29)	107.4(6)
C(28)-C(29)-C(30)	107.1(6)
C(31)-C(30)-C(29)	106.3(5)
O(1)-C(31)-C(30)	107.5(5)

Symmetry transformations used to generate equivalent atoms:

Compound **6**

Table 4. Bond lengths [A] and angles [deg] for compound **6·(toluene)**$_{0.5}$.

Ga(1)-C(1)	2.035(4)
Ga(1)-Cl(3)	2.185(3)
Ga(1)-Cl(1)	2.126(3)
Ga(1)-Cl(2)	2.141(4)
Ga(1')-Cl(1')	2.189(10)
Ga(1')-C(1)	2.019(5)
Ga(1')-Cl(2')	2.154(11)
Ga(1')-Cl(3')	2.100(10)
N(1)-C(1)	1.354(4)
N(1)-C(2)	1.362(4)
N(1)-C(16)	1.459(4)
N(2)-C(1)	1.341(4)
N(2)-C(3)	1.408(4)
N(2)-C(4)	1.458(4)
C(2)-C(3)	1.350(5)
C(3)-B(1)	1.576(5)
C(4)-C(9)	1.388(5)
C(4)-C(5)	1.396(5)
C(5)-C(6)	1.393(6)
C(5)-C(13)	1.513(6)
C(6)-C(7)	1.355(7)
C(7)-C(8)	1.363(7)
C(8)-C(9)	1.408(6)
C(9)-C(10)	1.496(6)
C(10)-C(11)	1.517(7)
C(10)-C(12)	1.511(8)
C(13)-C(14)	1.491(8)
C(13)-C(15)	1.497(7)
C(16)-C(21)	1.394(5)
C(16)-C(17)	1.392(5)
C(17)-C(18)	1.394(5)
C(17)-C(25)	1.508(6)
C(18)-C(19)	1.364(6)
C(19)-C(20)	1.347(7)
C(20)-C(21)	1.410(5)
C(21)-C(22)	1.507(6)
C(22)-C(24)	1.536(6)
C(22)-C(23)	1.544(6)
C(25)-C(27)	1.506(7)
C(25)-C(26)	1.534(8)
B(1)-C(31)	1.524(6)
B(1)-C(29)	1.572(7)
C(28)-C(29)	1.441(9)

C(30)-C(31)	1.503(6)
C(32)-C(33)	1.3900
C(32)-C(34)	1.3900
C(32)-C(35)	1.466(16)
C(33)-C(34A)	1.3900
C(34A)-C(32A)	1.3900
C(32A)-C(33A)	1.3900
C(33A)-C(34)	1.3900

C(1)-Ga(1)-Cl(3)	104.61(16)
C(1)-Ga(1)-Cl(1)	113.03(15)
Cl(3)-Ga(1)-Cl(1)	108.53(15)
C(1)-Ga(1)-Cl(2)	111.9(2)
Cl(3)-Ga(1)-Cl(2)	108.1(3)
Cl(1)-Ga(1)-Cl(2)	110.4(2)
Cl(1')-Ga(1')-C(1)	109.5(4)
Cl(1')-Ga(1')-Cl(2')	103.0(7)
C(1)-Ga(1')-Cl(2')	115.9(5)
Cl(1')-Ga(1')-Cl(3')	107.6(6)
C(1)-Ga(1')-Cl(3')	112.3(4)
Cl(2')-Ga(1')-Cl(3')	108.0(7)
C(1)-N(1)-C(2)	109.9(3)
C(1)-N(1)-C(16)	126.9(3)
C(2)-N(1)-C(16)	122.9(3)
C(1)-N(2)-C(3)	111.7(3)
C(1)-N(2)-C(4)	125.1(3)
C(3)-N(2)-C(4)	123.0(3)
N(2)-C(1)-N(1)	105.2(3)
N(2)-C(1)-Ga(1)	129.4(2)
N(1)-C(1)-Ga(1)	125.0(2)
N(2)-C(1)-Ga(1')	129.6(2)
N(1)-C(1)-Ga(1')	125.2(2)
N(1)-C(2)-C(3)	109.6(3)
C(2)-C(3)-N(2)	103.6(3)
C(2)-C(3)-B(1)	125.5(3)
N(2)-C(3)-B(1)	130.9(3)
C(9)-C(4)-C(5)	124.7(3)
C(9)-C(4)-N(2)	118.7(3)
C(5)-C(4)-N(2)	116.5(3)
C(6)-C(5)-C(4)	116.2(4)
C(6)-C(5)-C(13)	120.5(4)
C(4)-C(5)-C(13)	123.4(3)
C(7)-C(6)-C(5)	121.1(5)
C(6)-C(7)-C(8)	121.3(4)
C(7)-C(8)-C(9)	121.5(5)
C(4)-C(9)-C(8)	115.1(4)
C(4)-C(9)-C(10)	123.7(4)
C(8)-C(9)-C(10)	121.2(4)
C(9)-C(10)-C(11)	111.5(5)
C(9)-C(10)-C(12)	112.3(5)

C(11)-C(10)-C(12)	109.1(6)
C(14)-C(13)-C(15)	109.2(6)
C(14)-C(13)-C(5)	111.5(5)
C(15)-C(13)-C(5)	114.0(5)
C(21)-C(16)-C(17)	124.5(3)
C(21)-C(16)-N(1)	118.7(3)
C(17)-C(16)-N(1)	116.8(3)
C(16)-C(17)-C(18)	116.2(4)
C(16)-C(17)-C(25)	123.3(3)
C(18)-C(17)-C(25)	120.4(4)
C(19)-C(18)-C(17)	121.0(4)
C(20)-C(19)-C(18)	121.6(4)
C(19)-C(20)-C(21)	121.4(4)
C(16)-C(21)-C(20)	115.3(4)
C(16)-C(21)-C(22)	123.1(3)
C(20)-C(21)-C(22)	121.6(4)
C(24)-C(22)-C(21)	113.1(4)
C(24)-C(22)-C(23)	109.7(4)
C(21)-C(22)-C(23)	110.3(3)
C(17)-C(25)-C(27)	110.7(4)
C(17)-C(25)-C(26)	112.2(5)
C(27)-C(25)-C(26)	109.8(5)
C(31)-B(1)-C(3)	124.2(4)
C(31)-B(1)-C(29)	119.9(4)
C(3)-B(1)-C(29)	115.8(4)
C(28)-C(29)-B(1)	106.4(6)
B(1)-C(31)-C(30)	121.1(5)
C(33)-C(32)-C(34)	120.0
C(33)-C(32)-C(35)	121.0(15)
C(34)-C(32)-C(35)	118.9(15)
C(34A)-C(33)-C(32)	120.0
C(33)-C(34A)-C(32A)	120.0
C(34A)-C(32A)-C(33A)	120.0
C(32A)-C(33A)-C(34)	120.0
C(33A)-C(34)-C(32)	120.0

Symmetry transformations used to generate equivalent atoms:

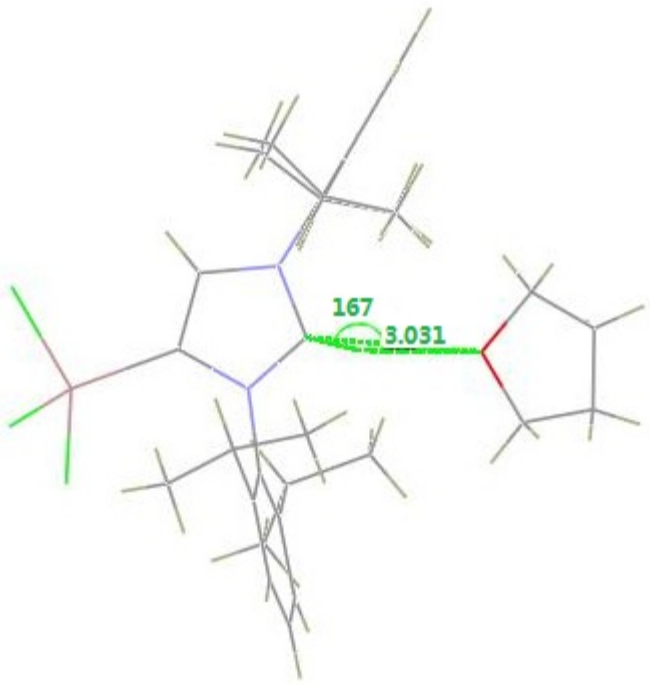

Figure 1. A moderate C–H···O hydrogen bond [distance (C···O) = 3.031 Å; C–H···O bond angle = 167°] between the C(1)–H(1A) unit of **5** and the O atom of THF solvent molecule.