Supporting Information

Azido- and Amido-substituted Gallium Hydrides Supported by *N*-Heterocyclic Carbenes

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Contents

Table S1. Crystallographic data for compound **1**

A. Crystal Data	
formula	$C_{24.50}H_{30}GaN_5$
formula weight	464.25
crystal dimensions (mm)	0.15×0.11×0.03
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	18.7477 (5)
b (Å)	8.4344 (2)
c (Å)	15.3559 (4)
β (deg)	95.0657 (17)
V (Å^3)	2418.68 (11)
Z	4
ρ_{calcd} (g cm^{-3})	1.275
μ (mm^{-1})	1.700
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	139.98
total data collected	15845 ($-18 \le h \le 21$, $-10 \le k \le 10$, $-18 \le l \le 18$)
independent reflections	4451 (R_{int} = 0.0706)
number of observed reflections (*NO*)	3400 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9950–0.7737
data/restraints/parameters	4451 / 0 / 308
goodness-of-fit (S)[e] [all data]	1.039
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0668
wR_2 [all data]	0.1905
largest difference peak and hole	1.249 and –0.629 e Å^{-3}

[a]Obtained from least-squares refinement of 5294 reflections with $9.48° < 2\theta < 136.10°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8. (*SHELXT-2014*)

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8. (*SHELXL-2014*)

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0962P)^2 + 2.9865P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S2. Crystallographic data for compound **2**

A. Crystal Data	
formula	$C_{23}H_{25}F_6GaN_2O_6S_2$
formula weight	673.29
crystal dimensions (mm)	0.25×0.16×0.10
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	12.2187 (10)
b (Å)	15.2841 (13)
c (Å)	15.7675 (13)
β (deg)	102.522 (4)
V (Å^3)	2874.6 (4)
Z	4
ρ_{calcd} (g cm^{-3})	1.556
μ (mm^{-1})	3.391
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	145.34
total data collected	19732 (-15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19)
independent reflections	5488 (R_{int} = 0.0240)
number of observed reflections (*NO*)	5048 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8317–0.5732
data/restraints/parameters	5488 / 0 / 371
goodness-of-fit (S)[e] [all data]	1.079
final R indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0330
wR_2 [all data]	0.0988
largest difference peak and hole	0.355 and –0.468 e Å^{-3}

[a]Obtained from least-squares refinement of 9649 reflections with 7.42° < 2θ < 145.14°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8. (*SHELXT-2014*)

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8. (*SHELXL-2014*)

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0518P)^2 + 1.8037P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S3. Crystallographic data for compound **3**

A. Crystal Data	
formula	$C_{27}H_{43.85}Cl_{0.15}GaN_3Si_2$
formula weight	541.72
crystal dimensions (mm)	0.37×0.24×0.12
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	9.3467 (2)
b (Å)	9.9910 (2)
c (Å)	18.9915 (4)
α (deg)	81.5099 (8)
β (deg)	79.0123 (7)
γ (deg)	62.4631 (8)
V (Å^3)	1540.13 (6)
Z	2
ρ_{calcd} (g cm^{-3})	1.168
μ (mm^{-1})	2.213
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	147.80
total data collected	11040 ($-11 \le h \le 11$, $-12 \le k \le 12$, $-23 \le l \le 23$)
independent reflections	5997 (R_{int} = 0.0124)
number of observed reflections (*NO*)	5883 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.5707–0.3806
data/restraints/parameters	5997 / 1[e] / 321
goodness-of-fit (*S*)[f] [all data]	1.061
final R indices[g]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0296
wR_2 [all data]	0.0828
largest difference peak and hole	0.305 and –0.255 e Å^{-3}

[a]Obtained from least-squares refinement of 9191 reflections with $11.16° < 2\theta < 147.66°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8. (*SHELXT-2014*)

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8. (*SHELXL-2014*)

[e]The Ga–H distances were restrained to be approximately the same by use of the *SHELXL* **SAME** instruction.

[f]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0417P)^2 + 0.7628P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S4. Crystallographic data for compound **4**

A. Crystal Data	
formula	$C_{40}H_{71.50}Cl_2GaN_3O_{1.75}Si_2$
formula weight	819.30
crystal dimensions (mm)	0.30×0.25×0.18
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	12.2392 (2)
b (Å)	36.3301 (7)
c (Å)	11.9340 (2)
β (deg)	117.5323 (6)
V (Å^3)	4705.51 (14)
Z	4
ρ_{calcd} (g cm^{-3})	1.156
μ (mm^{-1})	2.576
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	148.22
total data collected	33450 ($-15 \le h \le 15$, $-45 \le k \le 45$, $-14 \le l \le 14$)
independent reflections	9547 (R_{int} = 0.0171)
number of observed reflections (*NO*)	9244 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d,e])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7298–0.5798
data/restraints/parameters	9547 / 0 / 421
goodness-of-fit (*S*)[f] [all data]	1.112
final *R* indices[g]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0324
wR_2 [all data]	0.0807
largest difference peak and hole	0.312 and –0.229 e Å^{-3}

[a]Obtained from least-squares refinement of 9234 reflections with $9.50° < 2\theta < 147.56°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8. (*SHELXT-2014*)

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8. (*SHELXL-2014*)

[e]Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent diethylether oxygen or carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as implemented in *PLATON* (Spek, A. L. *Acta Crystallogr.* **2015**, *C71*, 9–18. *PLATON* - a multipurpose crystallographic tool. Utrecht University, Utrecht, The Netherlands). A total solvent-accessible void volume of 682 Å^3 with a total electron count of 132 (consistent with 3 molecules of solvent diethylether, or 0.75 molecules per formula unit of the Ga complex) was found in the unit cell.

[f]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0268P)^2 + 3.1744P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S5. Crystallographic data for compound **5**

A. Crystal Data	
formula	$C_{34}H_{54}ClF_3GaN_3O_3SSi_2$
formula weight	803.21
crystal dimensions (mm)	0.24×0.21×0.15
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	11.1905 (2)
b (Å)	22.5860 (4)
c (Å)	16.2428 (3)
β (deg)	91.6950 (12)
V (Å^3)	4103.55 (13)
Z	4
ρ_{calcd} (g cm^{-3})	1.300
μ (mm^{-1})	2.959
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	148.15
total data collected	26507 (-13 ≤ h ≤ 13, -28 ≤ k ≤ 28, -18 ≤ l ≤ 19)
independent reflections	8220 (R_{int} = 0.0581)
number of observed reflections (*NO*)	6507 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods/dual space (*SHELXD*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7568–0.5956
data/restraints/parameters	8220 / 23[e] / 475
goodness-of-fit (*S*)[f] [all data]	1.097
final R indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0552
wR_2 [all data]	0.1572
largest difference peak and hole	0.597 and –0.549 e Å^{-3}

[a]Obtained from least-squares refinement of 9974 reflections with 7.82° < 2θ < 147.72°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

(continued)

[c]Schneider, T. R.; Sheldrick, G. M. *Acta Crystallogr.* **2002**, *D58*, 1772-1779.

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

[e]Corresponding distances within the two components of the disordered GaCl{N(SiMe$_3$)$_2$} moiety were constrained to be equal (within 0.03 Å) during refinement: (GaA–ClA) = d(GaB–ClB); d(GaA–N3A) = d(GaB–N3B); d(Si1A–N3A) = d(Si1B–N3B); d(Si2A–N3A) = d(Si2B–N3B); d(Si1A–C5A) = d(Si1B–C5B); d(Si1A–C6A) = d(Si1B–C6B); d(Si1A–C7A) = d(Si1B–C7B); d(Si2A–C8A) = d(Si2B–C8B); d(Si2A–C9A) = d(Si2B–C9B); d(Si2A–C10A) = d(Si2B–C10B); d(Si1A···Si2A) = d(Si1B···Si2B); d(N3A···C5A) = d(N3B···C5B); d(N3A···C6A) = d(N3B···C6B); d(N3A···C7A) = d(N3B···C7B); d(N3A···C8A) = d(N3B···C8B); d(N3A···C9A) = d(N3B···C9B); d(N3A···C10A) = d(N3B···C10B); d(C5A···C6A) = d(C5B···C6B); d(C5A···C7A) = d(C5B···C7B); d(C6A···C7A) = d(C6B···C7B); d(C8A···C9A) = d(C8B···C9B); d(C8A···C10A) = d(C8B···C10B); d(C9A···C10A) = d(C9B···C10B).

[f]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0610P)^2 + 6.2812P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

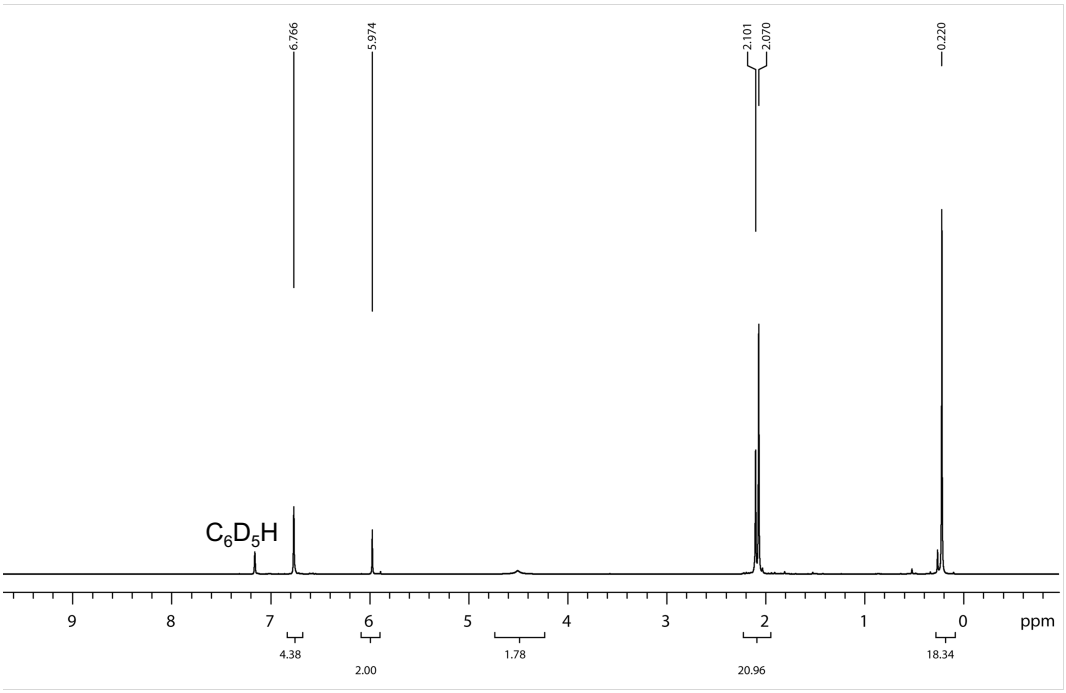

Figure S1: ^{1}H NMR spectrum of IMes•$GaH_2N(SiMe_3)_2$ in C_6D_6 (**3**).

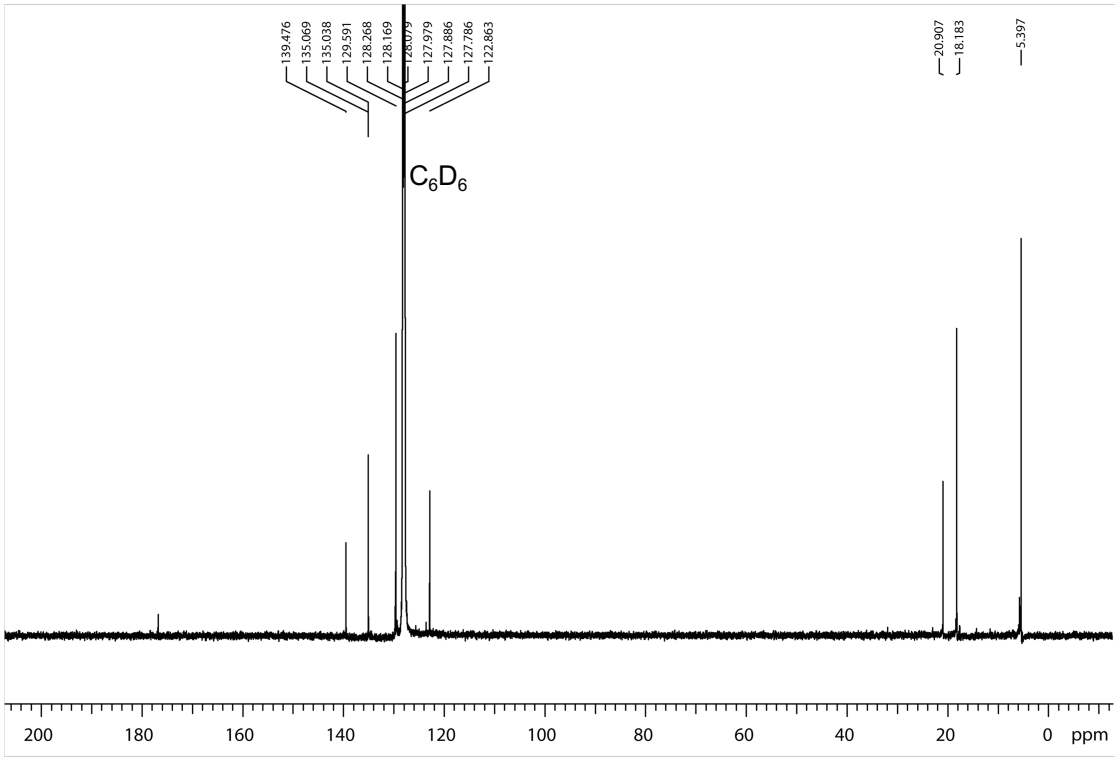

Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of IMes•$GaH_2N(SiMe_3)_2$ in C_6D_6 (**3**).