Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Lewis Acid-Base Adducts of $Al(N(C_6F_5)_2)_3$ and $Ga(N(C_6F_5)_2)_3$ – Structural Features and Dissociation Enthalpies.

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Crystallographic Details

IPDS II or IPDS 2T (Stoe) diffractometers were used for data collection by the x-ray department at the Philipps-Universität Marburg (Dr. K. Harms, M. Marsch, and R. Riedel). Data collection, reduction and cell refinement were performed with Stoe IPDS Software. Structures were solved with direct methods using SHELXS-97,[1] SIR92[2] or SIR2004[3] and refined against F^2 with SHELXL-97,[4] all within the user interface of WinGX. Furthermore, the programs Mercury 3.1[5] and Platon[6] were used during refinement. Absorption correction was performed with semi-empirical methods within WinGX (multi-scan or Gaussian[7]).

Hydrogen atoms were calculated in their idealized positions and refined with fixed isotropic thermal parameters. All molecular structures were illustrated with Diamond 3[8] using thermal ellipsoids at the 30% probability level.

Crystal data and experimental conditions of molecular structures presented in the main manuscript are listed in Table S1 and S2. The corresponding CIF files providing full information concerning the molecular structures and experimental conditions are deposited at the Cambridge Crystallographic Data Center (CCDC numbers 2012101-2012106).

Table S1. Crystal data and experimental conditions.

	$Al(N(C_6F_5)_2)_3$ ·NCMe	**$Al(N(C_6F_5)_2)_3$ ·CN*t*Bu**	**$Ga(N(C_6F_5)_2)_3$ ·NCMe**
empirical formula	$C_{76}H_6Al_2F_{60}N_8$, C_7H_8	$C_{41}H_9AlF_{30}N_4$	$2(C_{38}H_3F_{30}GaN_4)$, C_7H_8
mol. weight [g mol^{-1}]	2316.98	1154.50	2402.46
crystal habit	colorless nugget	colorless prism	colorless block
crystal size [mm^3]	0.60 · 0.30 · 0.25	0.33 · 0.21 · 0.15	0.2 · 0.15 · 0.09
crystal system	triclinic	triclinic	triclinic
space group	*P*-1	*P*-1	*P*-1
a [Å]	11.5512(14)	11.0496(7)	11.5100(18)
b [Å]	13.7744(15)	11.2003(7)	13.793(2)
c [Å]	14.3749(17)	19.9634(13)	14.2825(19)
α [°]	84.728(13)	76.132(5)	84.719(11)
β [°]	71.409(14)	83.514(5)	71.532(11)
γ [°]	71.218(13)	61.578(5)	71.500(11)
volume [$Å^3$]	2052.3(4)	2109.5(2)	2039.4(5)
Z	1	2	1
density [g cm^{-3}]	1.875	1.818	1.968
T [K]	193(2)	193(2)	100(2)
absorption coeff. [mm^{-1}]	0.227	0.221	0.854
Θ range [°]	2.0 to 26.0	2.1 to 26.2	1.5 to 26.0
index ranges	-14 <= h <= 14, -16 <= k <= 16, -17 <= l <= 17	-13 <= h <= 13, -13 <= k <= 13, -24 <= l <= 24	-14 <= h <= 14, -16 <= k <= 17, -17 <= l <= 17
reflns collected	20413	31007	19267
independent reflns	7521 [R(int) = 0.0385]	8435 [R(int) = 0.0255]	8051 [R(int) = 0.0943]
absorption correction	gaussian	multi-scan	multi-scan
max. and min. transmission	0.9635 and 0.9167	0.9659 and 0.9336	1.1269 and 0.754
transmissiondata/restraints /parameters	7521 / 46 / 675	8435 / 3 / 683	8051 / 1 / 675
goodness-of-fit on F^2	1.013	1.038	0.733
final R indices [I>2s(I)]	R1 = 0.0398	R1 = 0.0380	R1 = 0.0504
R indices (all data)	wR2 = 0.1104	wR2 = 0.1044	wR2 = 0.1239
larg. diff. peak/hole [e $Å^{-3}$]	0.390 / -0.493	0.424 / -0.462	0.774 / -1.117
treatment of H atoms	constr.	constr.	constr.
CCDC number	2012101	2012102	2012103

Table S2. Crystal data and experimental conditions.

	$Ga(N(C_6F_5)_2)_3$ ·CN*t*Bu	**$Ga(N(C_6F_5)_2)_3$ ·THF**	**$Ga(N(C_6F_5)_2)_3$ ·PMe_3**
empirical formula	$C_{41}H_9F_{30}GaN_4$	$C_{40}H_8F_{30}GaN_3O$, C_7H_8	$C_{39}H_9F_{30}GaN_3P$, 0.09($C_{42}H_{48}$)
mol. weight [g mol^{-1}]	1197.24	1278.35	1237.17
crystal habit	colorless prism	colorless prism	colorless block
crystal size [mm^3]	0.36 · 0.08 · 0.05	0.29 · 0.20 · 0.11	0.18 · 0.17 · 0.13
crystal system	triclinic	monoclinic	hexagonal
space group	*P*-1	*P*21/*n*	*R*-3*c*
a [Å]	11.0023(4)	17.1941(7)	13.1449(5)
b [Å]	11.1257(5)	12.3834(3)	13.1449(5)
c [Å]	19.8025(8)	21.3791(7)	86.201(4)
α [°]	76.581(3)	90	90
β [°]	83.893(3)	102.734(3)	90
γ [°]	61.802(3)	90	120
volume [$Å^3$]	2077.97(15)	4440.1(3)	12899(1)
Z	2	4	12
density [g cm^{-3}]	1.913	1.912	1.910
T [K]	100(2)	100(2)	100(2)
absorption coeff. [mm^{-1}]	0.837	0.792	0.848
Θ range [°]	2.1 to 26.8	1.4 to 26.8	1.4 to 26.8
index ranges	-13 <= h <= 13, -14 <= k <= 14, -22 <= l <= 25	-21 <= h <= 21, -15 <= k <= 15, -27 <= l <= 25	-16 <= h <= 16, -16 <= k <= 16, -108 <= l <= 96
reflns collected	25604	27479	45151
independent reflns	8782 [R(int) = 0.0452]	9388 [R(int) = 0.0467]	3062 [R(int) = 0.0859]
absorption correction	multi-scan	multi-scan	multi-scan
max. and min. transmission	0.9015 and 0.8675	0.9711 and 0.7957	1.0402 and 0.7711
transmissiondata/restraints /parameters	8782 / 18 / 683	9388 / 0 / 740	3062 / 42 / 241
goodness-of-fit on F^2	0.860	0.805	0.927
final R indices [I>2s(I)]	R1 = 0.0323	R1 = 0.0294	R1 = 0.0358
R indices (all data)	wR2 = 0.0610	wR2 = 0.0592	wR2 = 0.0759
larg. diff. peak/hole [e $Å^{-3}$]	0.471 / -0.585	0.421 / -0.284	0.659 and -0.318
treatment of H atoms	constr.	constr.	constr.
CCDC number	2012104	2012105	2012106

NMR Spectra

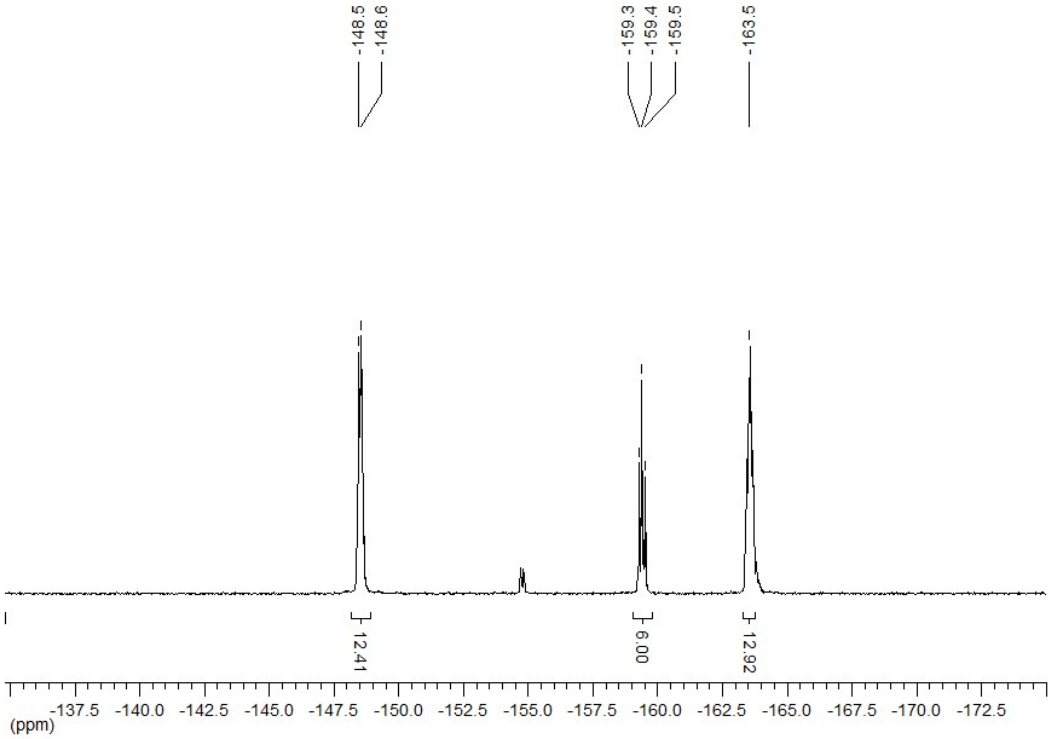

Figure S1. ^{19}F NMR spectrum of Al(N(C_6F_5)$_2$)$_3$·NCMe (**1**·NCMe) (188 MHz, [D_6]benzene, 25 °C). The spectrum reveals the presence of a small amount of HN(C_6F_5)$_2$, presumably as a consequence of partial hydrolysis (see Figure S3).

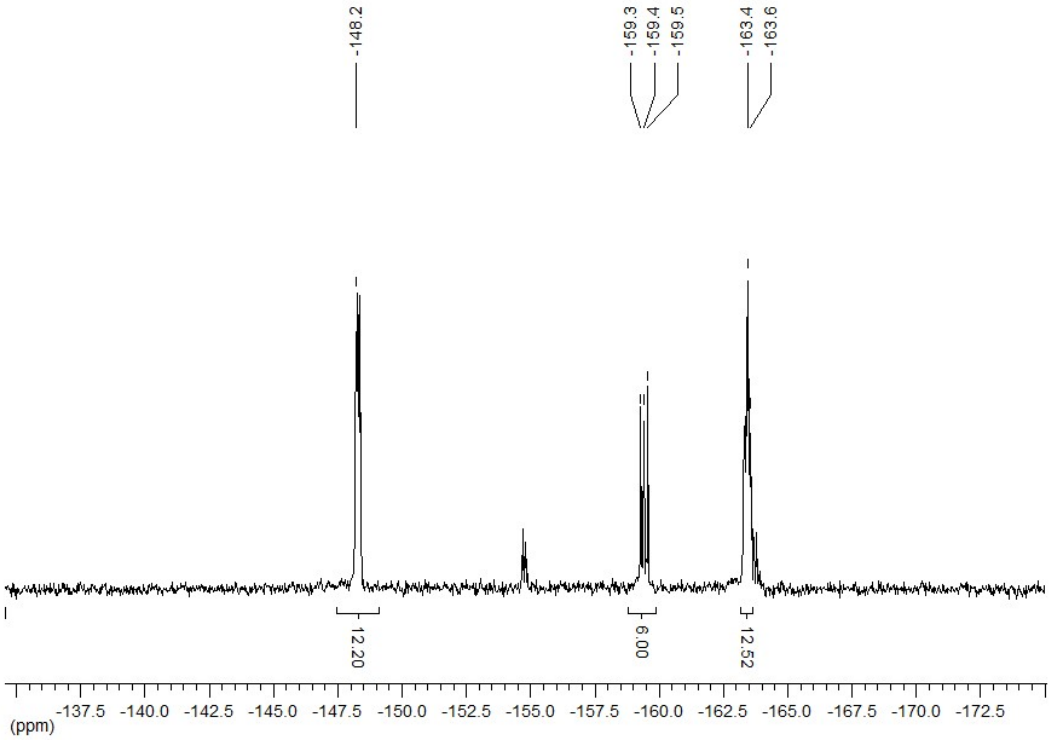

Figure S2. ^{19}F NMR spectrum of Al(N(C_6F_5)$_2$)$_3$·CN*t*Bu (**1**·CN*t*Bu) (188 MHz, [D_6]benzene, 25 °C). The spectrum reveals the presence of a small amount of HN(C_6F_5)$_2$, presumably as a consequence of partial hydrolysis (see Figure S3).

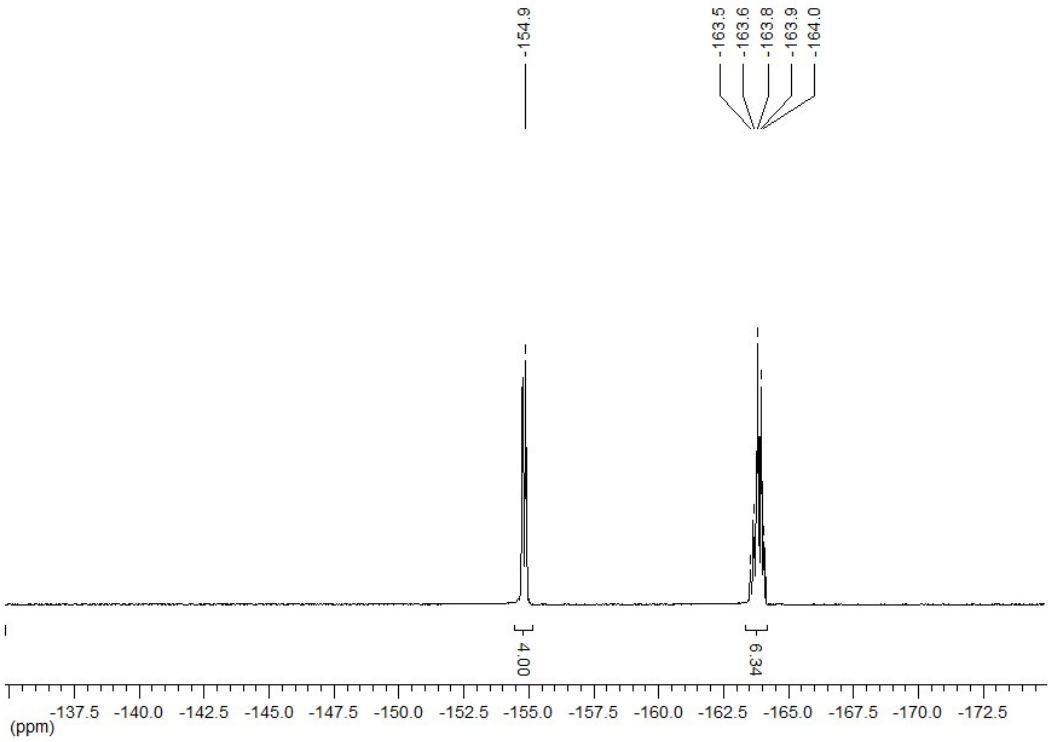

Figure S3. ^{19}F NMR spectrum of $H(N(C_6F_5)_2$ (188 MHz, $[D_6]$benzene, 25 °C).

Quantumchemical Calculations

The theoretical calculations of the dissociation enthalpies of the six Lewis acid base adducts were calculated as described in the related work on the two Lewis acids $Al(N(C_6F_5)_2)_3$ and $Ga(N(C_6F_5)_2)_3$.[9]

The molecular structures obtained by XRD analysis were used as the basis for the theoretical calculations. DFT optimizations were carried out with TURBOMOLE[10,11] at the (RI-)BP86[12,13,14]/def-TZVP[15], with RI-J auxiliary bases[16,17,18] and D3[19] dispersion correction. Vibrational frequencies were calculated analytically with the AOFORCE[20,21] module and all structures represented true minima without imaginary frequencies on the respective hypersurface. Thermal contributions to *ab initio* reaction energies (see below) were calculated with inclusion of zero point energy, thermal contributions to the enthalpy/entropy (FREEH tool; unscaled[22] BP86/def-TZVP/D3 vibrational frequencies).

RI-MP2 structure optimizations were carried out with TURBOMOLE[10] and def2-QZVPP[15] basis sets and corresponding RI-C auxiliary bases[12] for all atoms. Frozen core: 1s for 2nd row elements, 1s2s2p for Al, none for H, 1s2s2p3s3p for Ga.

MP2 and CCSD(T) single point calculations with correlation-consistent basis sets were done with Gaussian 03.[23] Basis set extrapolation was done with the following formula:

$$\Delta E_{CCSD(T)/A'VQZ} \approx \Delta E_{compound} = \Delta E_{CCSD(T)/A'VDZ} + \Delta E_{MP2/A'VQZ} - \Delta E_{MP2/A'VDZ}$$

with A'VXZ = cc-pVXZ for H[24], aug-cc-pV(X+d)Z for Al[25], aug-cc-pwCVXZ-PP for Ga[26], aug-cc-pVXZ for 2nd row elements [27] (X = D, Q).

Frozen core: 1s for 2nd row elements, 1s2s2p for Al, none for H and Ga.

Thermal contributions to reaction energies were calculated with BP86-D3/def-TZVP at 1 bar, 298.15 K:

$\Delta U° = \Delta E_{QM.} + \Delta E_{vrt}$

($\Delta E_{QM} = \Delta E_{SCF}$ for DFT, $\Delta E_{compound}$ for ab-initio calculations; ΔE_{vrt} = sum of translational, rotational, and vibrational energy incl. zero point vibrational energy)

$\Delta H° = \Delta U° + \Delta n\, RT$ (Δn = particle number change in reaction equation)

$\Delta G° = \Delta H° - 298.15\ K \cdot \Delta S°$

Table S3. Details on ab initio calculations (with thermal corrections at BP86-D3/def-TZVP level).

Compound	CCSD(T)/A'VDZ [H]	MP2/A'VDZ [H]	MP2/A'VQZ [H]	E_{comp} [kJ mol^{-1}]	H° [kJ mol^{-1}]	G° [kJ mol^{-1}]
MeCN	-132,4196669	-132,3806952	-132,5341215	-348070,66	-347943,15	-348015,74
*t*BuNC	-250,0063768	-249,9105911	-250,2133618	-657186,67	-656833,58	-656933,10
Me_3P	-460,2722395	-460,1873474	-460,4083507	-1209025,01	-1208717,28	-1208812,17
THF	-231,8566862	-231,7771111	-232,0633718	-609491,31	-609178,63	-609267,53
AlF_3	-541,2162733	-541,1989255	-541,5560525	-1421900,96	-1421867,26	-1421950,52
GaF_3	-557,7289951	-557,7178246	-558,3544499	-1465988,94	-1465957,94	-1466045,63
AlF_3·NCMe	-673,6851857	-673,628417	-674,140663	-1770105,357	-1769938,157	-1770056,296
AlF_3·CN*t*Bu	-791,2765248	-791,1648647	-791,8255492	-2079231,143	-2078837,403	-2078980,268
GaF_3·NCMe	-690,1922281	-690,1420866	-690,9335129	-1814177,585	-1814013,415	-1814137,901
GaF_3·CN*t*Bu	-807,7872829	-807,6826995	-808,6230837	-2123314,49	-2122923,68	-2123072,695
GaF_3·THF	-789,6433804	-789,5518229	-790,4737929	-2075629,327	-2075277,927	-2075413,675
GaF_3·PMe_3	-1018,062206	-1017,968022	-1018,826449	-2675176,121	-2674829,751	-2674976,044

Table S4. Details on BP86-D3/def-TZVP calculations.

Compound	SCF [H]	E_{vrt} [kJ mol^{-1}]	S° [kJ mol^{-1} K^{-1}]	H° [kJ mol^{-1}]	G° [kJ mol^{-1}]
MeCN	-132,8083861	125,03	0,24347	-348560,9076	-348633,4982
*t*BuNC	-250,7668404	350,61	0,33381	-658035,2495	-658134,775
Me_3P	-461,1936042	305,25	0,31826	-1210556,078	-1210650,967
THF	-232,5480851	310,2	0,29817	-610242,3173	-610331,2167
AlF_3	-542,338235	31,22	0,27925	-1423875,336	-1423958,594
GaF_3	-2224,913325	28,52	0,29413	-5841478,936	-5841566,631
$Al(N(C_6F_5)_2)_3$	-4775,69126	965,88	1,49104	-12537609,04	-12538053,6
$Ga(N(C_6F_5)_2)_3$	-6458,327682	966,81	1,48051	-16955370,04	-16955811,45
AlF_3·NCMe	-675,1962116	164,72	0,39624	-1772560,453	-1772678,592
AlF_3·CN*t*Bu	-793,1617568	391,26	0,47917	-2082052,452	-2082195,317
GaF_3·NCMe	-2357,763023	161,69	0,41753	-6190142,646	-6190267,133
GaF_3·CN*t*Bu	-2475,732674	388,33	0,4998	-6499645,327	-6499794,342
GaF_3·THF	-2457,514998	348,92	0,4553	-6451854,228	-6451989,976
GaF_3·PMe_3	-2686,171113	343,89	0,49067	-7052195,887	-7052342,18
$Al(N(C_6F_5)_2)_3$·NCMe	-4908,546243	1100,36	1,55516	-12886285,32	-12886748,99
$Al(N(C_6F_5)_2)_3$·CN*t*Bu	-5026,517168	1327,39	1,63319	-13195790,95	-13196277,89
$Ga(N(C_6F_5)_2)_3$·NCMe	-6591,160035	1098,3	1,57196	-17303989,89	-17304458,57
$Ga(N(C_6F_5)_2)_3$·CN*t*Bu	-6709,13513	1325,3	1,65196	-17613506,5	-17613999,04
$Ga(N(C_6F_5)_2)_3$·THF	-6690,909923	1287,76	1,58031	-17565693,76	-17566164,93
$Ga(N(C_6F_5)_2)_3$·PMe_3	-6919,577661	1283,06	1,56811	-18166065,61	-18166533,14

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