Synthesis and Characterization of (Pentafluorophenyl)amino-Based Amino- and Iminometallanes. Crystal Structures of $(MeAlNC_6F_5)_4$ and $NHC_6F_5Ga(MesGa)_3(\mu_3\text{-}NC_6F_5)_4$ (Mes = 2,4,6-$Me_3C_6H_2$)

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The novel compounds $(MeAlNC_6F_5)_4$ **1**, $Mes_2AlNHC_6F_5$ **2**, $Mes_2GaNHC_6F_5$ **3**, and $NHC_6F_5Ga(MesGa)_3(\mu_3\text{-}NC_6F_5)_4$ **4** of group 13 have been prepared in high yields by the reaction of Me_3Al, Mes_3Al, and Mes_3Ga with pentafluoroaniline, respectively. **1–4** have been fully characterized by elemental analysis, IR, NMR, and mass spectrometry. The crystal structures of **1** and **4** have been determined. **1**·0.5hexane crystallizes in the space group $P\bar{1}$, $a = 1594.1(5)$ pm, $b = 1643.0(5)$ pm, $c = 1777.0(6)$ pm, $\alpha = 66.81(1)°$, $\beta = 63.77(1)°$, $\gamma = 64.16(1)°$, $V = 3.639(2)$ nm^3, $Z = 4$, and $R = 0.0507$ (wR2 = 0.1294); **4** crystallizes in the space group $C2/c$, $a = 4532.4(1)$ pm, $b = 1207.7(4)$ pm, $c = 2246.2(5)$ pm, $\alpha = \gamma = 90°$, $\beta = 91.92(3)$, $V = 12.288(6)$ nm^3, $Z = 8$, and $R = 0.0576$ (wR2 = 0.1172). The structure of **1** displays an almost perfect cube with alternating aluminum and nitrogen atoms. In contrast **4** consists of a distorted cube. **4** is the first example of an amino-substituted iminogallane containing a heterocubane structure. According to a modified Schomaker–Stevenson equation a bond order of 1 can be attributed to the exocyclic Ga(2)–N(5) bond length, whereas the Ga–N distances within the core have bond orders of $^2/_3$.

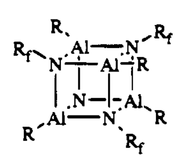
Introduction

The reactions of organometallic compounds of group 13 with primary and secondary amines have been studied for a long time.[1] The first step of this reaction affords aminometallanes $(R_2MNHR')_n$ (M = Al, Ga, In), which generally consist of four-membered rings with alternating metal and nitrogen atoms. It is remarkable that approximately 60 structurally characterized aminoalanes are known[2] whereas only 20 aminogallanes[3] and aminoindanes,[4] respectively, have been described thus far.

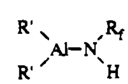
The second step, the thermolysis of the aminometallanes, proceeds via two different routes. One possible pathway is the intermolecular reaction of aminometallanes to form iminometallanes $(RMNR')_n$. With aluminum a dimeric,[5] a trimeric,[6] and tetrameric iminoalanes with an Al_4N_4 heterocubane core structure[7] are known as well as a few compounds with higher aggregation ($n = 6–16$).[8,9] The degree of oligomerization depends highly on the steric demand of the ligands at the metal and nitrogen atoms. The other route is thermolysis of aminometallanes while intramolecular side-chain elimination of hydrocarbons occurs.[3b] Iminogallanes and iminoindanes are almost unknown. To our knowledge only one iminogallane with a complex cage structure has been reported.[9]

Recently we found a method to avoid this intramolecular elimination. We were able to synthesize the first tetrameric iminogallane and iminoindane with heterocubane structure[10] by treatment of $GaMe_3$ and $InMe_3$ with pentafluroaniline each.

In this paper we report the synthesis and characterization of the tetrameric iminoalane $(MeAlNC_6F_5)_4$, **1**, isolated from the reaction of $AlMe_3$ with pentafluoroaniline, the two aminometallanes $Mes_2AlNHC_6F_5$, **2**, and $Mes_2GaNHC_6F_5$, **3**, and the aminoiminogallane $NHC_6F_5Ga(MesGa)_3(\mu_3\text{-}NC_6F_5)_4$ **4**. The molecular structures of **1** and **4** have been determined by X-ray diffraction at low temperatures.



1



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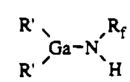

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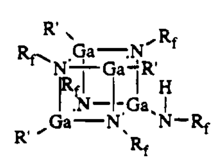

4

$R_f = C_6F_5$
R = Me
R' = Mes

Experimental Section

General Procedures. All experiments were performed using Schlenk techniques under dry nitrogen atmosphere due to the extreme sensitivity of reactants and products towards air and moisture. For storing the compounds and to prepare the samples for spectroscopic characterization a Braun MB 150-GI drybox was used. Trimethylalane

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Table 1. Selected Bond Lengths (pm) and Angles (deg)

For 1 with Averages for Chemical Equivalent Bonds (Esd's are Maximum Values)			
Al(1/8)−N(1/7)	191.2(4)	Al(1/8)−N(2/8)	196.1(4)
Al(1/8)−N(4/6)	194.7(4)	Al(2/5)−N(2/8)	194.0(4)
Al(2/5)−N(3/5)	196.8(4)	Al(2/5)−N(4/6)	192.0(4)
Al(3/7)−N(1/7)	194.4(4)	Al(3/7)−N(2/8)	191.2(4)
Al(3/7)−N(3/5)	194.5(4)	Al(4/6)−N(1/7)	194.6(4)
Al(4/6)−N(3/5)	191.0(4)	Al(4/6)−N(4/6)	194.9(4)
N−Al−N	87.2(2)−89.8(2)	Al−N−Al	90.4(2)−92.8(2)
For 4			
Ga(1)−C(1)	194.5(9)	Ga(1)−N(2)	200.1(6)
Ga(2)−N(5)	183.7(6)	Ga(3)−N(1)	202.3(7)
N(2)−Ga(1)−N(3)	87.9(2)	N(5)−Ga(2)−N(4)	134.5(3)
N(5)−Ga(2)−N(1)	117.7(3)	N(4)−Ga(2)−N(1)	87.9(3)

Table 2. Crystallographic Data for $(MeAlNC_6F_5)_4$, **1**

formula	$C_{28}H_{12}Al_4F_{20}N_4(C_6H_{14})_{0.5}$	V, nm^3	3.639(2)
fw	935.4	Z	4
cryst syst	triclinic	ρ_{calcd}, Mg m^3	1.707
space group	$P\bar{1}$ (No. 2)	2θ range, deg	8 − 45
a, pm	1594.1(5)	μ, nm^{-1}	0.263
b, pm	1643.0(5)	no. of reflcns	9451
c, pm	1777.0(6)	no. of restraints	607
α, deg	66.81(1)	no. of params	1134
β, deg	63.77(1)	R [$I > 2\sigma(I)$][a]	0.0507
γ, deg	64.16(1)	wR2 [all reflections][b]	0.1294
		weight factors:[c] a; b	0.063; 2.939

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [c] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [F_o^2 + 2F_c^2]/3$.

Table 3. Crystallographic Data for $NHC_6F_5Ga(MesGa)_3(\mu_3\text{-}NC_6F_5)_4$, **4**

formula	$C_{57}H_{34}F_{25}Ga_4$-$N_5(C_5H_{12})$	Z	8
		ρ_{calcd}, Mg m^3	1.746
fw	1614.9	2θ-range, deg	8 − 45
cryst system	monoclinic	μ, mm^{-1}	1.857
space group	$C2/c$ (No. 15)	no. of reflcns	8045
a, pm	4532.4(1)	no. of restraints	105
b, pm	1207.7(4)	no. of params	922
c, pm	2246.2(5)	R [I> 2σ(I)][a]	0.0576
β, deg	91.92(3)	wR2 [all reflections][b]	0.1172
V, nm^3	12.288(6)	weight factors:[c] a; b	0.061; 64.959

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [c] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [F_o^2 + 2F_c^2]/3$.

was purchased from Aldrich Chemical Co., pentafluoroaniline from Janssen Chimica and sublimed prior to use. Solvents were dried over sodium/benzophenone, freshly distilled and degassed prior to use. Trimesitylalane and -gallane were prepared as described in literature.[11,12] Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. NMR-spectra were recorded on a Bruker AM 250 and were externally referred to tetramethylsilane, hexafluorobenzene or $CFCl_3$, respectively. FT-IR spectra were measured on a Bio-Rad FTS 7 as nujol mulls in the range 4000−400 cm^{-1} and EI mass spectra on Finnigan MAT 8230 or Varian MAT CH 5 instruments.

Safety Notes. Compound **1** tends under circumstances not exactly determined to explode already at room temperature. $(MeAlNC_6F_5)_4$, **1**, should be prepared only in small amounts and should be handled with great caution.

Synthesis of $(MeAlNC_6F_5)_4$, 1. $AlMe_3$ (10.30 mL) (2 M in n-hexane, 20.6 mmol) was slowly added to a solution of $C_6F_5NH_2$ (3.77 g, 20.6 mmol) in (20 mL) n-hexane at room temperature and heated for 20 h under reflux. The solution was concentrated under reduced pressure to 10 mL and cooling overnight in a freezer (-25 °C) to yield product **1** (3.58 g, 78%) as colorless crystals, mp 175 °C. ^{1}H NMR (C_6D_6) δ −0.44 (sept, 12 H, AlCH_3). ^{19}F NMR (C_6D_6) δ −1.22 (m, 4 F , p-F), 0.82 (m, 8 F, o-F), 12.44 (m, 8 F, m-F). MS (70 eV): m/e (%) 892 (100) [M], 877 (12) [M-Me]. IR (Nujol mull): 1304 (m), 1260 (m), 1153 (s), 1025 (vs), 1006 (vs), 989 (vs), 799 (m), 740 (m), 706 (vs), 590 (s), 576 (m). Anal. Calcd for $C_{28}H_{12}Al_4F_{20}N_4$ (892.32): C, 37.65; H, 1.34; N, 6.28. Found C, 37.04; H, 1.40; N, 6.07.

Synthesis of $Mes_2AlNHC_6F_5$, 2. Mes_3Al (2.10 g, 5.5 mmol) dissolved in n-hexane (10 mL) was slowly added dropwise to a solution of $C_6F_5NH_2$ (1.0 g, 5.5 mmol) in n-hexane (10 mL) at room temperature. The reaction mixture was heated for 12 h under reflux. The solution was concentrated under reduced pressure to ~10 mL and cooling over night in a freezer (−25 °C) to yield product **2** (1.97 g, 81%) as colorless crystals, mp 184 °C (dec). ^{1}H NMR (CD_3CN) δ 2.18 (s, 6 H, p-CH_3), 2.30 (s, 12 H, o-CH_3), 3.62 (s (br), 1 H, N-H), 6.70 (s, 4 H, Mes-H). ^{19}F NMR (CD_3CN) δ - 17.95 (m, 1 F, p-F), −4.20 (m, 2 F, o-F), 2.15 (m, 2 F, m-F). MS (70 eV): m/e (%) 447 (36) [M], 265 (100) [M-C_6F_5-NH]. IR (Nujol mull): 3283 (m), 1603 (s), 1516 (vs), 1416 (w), 1261 (s), 1238 (m), 1094 (s), 1018 (s), 982 (vs), 801 (s), 632 (m), 605 (s), 585 (m), 559 (m), 542 (m), 494 (m), 471 (m). Anal. Calcd for $C_{24}H_{23}$-AlF_5N (447.43): C, 64.43; H, 5.14; N, 3.13. Found C, 64.01; H, 5.69; N, 2.96.

Synthesis of $Mes_2GaNHC_6F_5$, 3. Mes_3Ga (2.50 g, 6.0 mmol) dissolved in n-hexane (10 mL) was slowly added dropwise to a solution of $C_6F_5NH_2$ (1.10 g, 6.0 mmol) in n-hexane (10 mL) at room temperature. The reaction mixture was heated for 12 h under reflux. The solution was concentrated under reduced pressure to ~10 mL and cooling over night in a freezer (−25 °C) gave product **3** (1.40 g, 49%) as colorless crystals, mp 176−179 °C. ^{1}H NMR (CD_3CN) δ 2.20 (s, 6 H, p-CH_3), 2.31 (s, 12 H, o-CH_3), 3.72 (s, 1 H, N-H), 6.76 (s, 4 H, Mes-H). ^{19}F NMR (CD_3CN) δ −182.4 (m, 1 F, p-F), −167.8 (m, 2 F, m-F), −162.2 (m, 2 F, o-F). MS (70 eV): m/e (%) 489 (10) [M], 307 (100) [M-HNC_6F_5], 183 (6) [$H_2NC_6F_5$], 119 (5) [Mes], 69 (10) [Ga]. IR (Nujol mull): 3446 (m), 1661 (m), 1604 (m), 1524 (s), 1498 (s), 1301 (m), 1261 (m), 1168 (m),1143 (m), 1017 (vs), 1000 (vs), 947 (m), 849 (s), 797 (m), 736 (m), 721 (s), 666 (m), 588 (m), 526 (s). Anal. Calcd for $C_{24}H_{23}F_5GaN$ (490.11): C, 58.81; H, 4.73; N, 2.86. Found C, 57.20; H, 4.57; N, 3.00.

Synthesis of $NHC_6F_5Ga(MesGa)_3(\mu_3\text{-}NC_6F_5)_4$, 4. $Mes_2GaNHC_6F_5$ **3** (1.20 g, 2.5 mmol) was heated for 4 h to 200 °C; the mesitylene

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (pm^2 $\times$ 10^{-1}) for **1**[a]

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
Al(1)	7653(1)	4989(1)	8749(1)	26(1)	C(53)	5966(3)	10087(3)	6094(3)	33(1)
C(1)	7077(4)	4030(4)	9538(3)	40(1)	F(53)	5105(2)	9914(2)	6431(2)	47(1)
N(1)	7537(3)	6223(2)	8675(2)	25(1)	C(54)	6353(4)	10140(3)	6615(3)	35(1)
C(11)	6957(3)	6807(3)	9261(3)	30(1)	F(54)	5881(2)	10024(2)	7469(2)	53(1)
C(12)	6949(4)	7704(4)	9039(3)	36(1)	C(55)	7234(4)	10325(3)	6252(3)	34(1)
F(12)	7510(2)	8041(2)	8227(2)	50(1)	F(55)	7623(2)	10381(2)	6756(2)	51(1)
C(13)	6403(4)	8289(4)	9596(4)	48(1)	C(56)	7707(3)	10451(3)	5377(3)	29(1)
F(13)	6430(2)	9161(2)	9330(3)	74(1)	F(56)	8559(2)	10648(2)	5039(2)	41(1)
C(14)	5823(4)	7959(4)	10410(4)	51(2)	Al(6)	8963(1)	10911(1)	3168(1)	24(1)
F(14)	5264(2)	8535(3)	10949(2)	78(1)	C(6)	9960(3)	11165(3)	3284(3)	34(1)
C(15)	5787(4)	7089(4)	10657(4)	48(1)	N(6)	9341(2)	9990(2)	2548(2)	23(1)
F(15)	5219(2)	6760(3)	11445(2)	74(1)	C(61)	10361(3)	9501(3)	2220(3)	27(1)
C(16)	6344(4)	6514(4)	10090(3)	36(1)	C(62)	10801(3)	8566(3)	2525(3)	30(1)
F(16)	6295(2)	5651(2)	10355(2)	50(1)	F(62)	10254(2)	8057(2)	3183(2)	40(1)
Al(2)	9032(1)	5115(1)	7095(1)	27(1)	C(63)	11789(4)	8122(3)	2171(3)	39(1)
C(2)	10056(4)	4519(4)	6202(3)	43(1)	F(63)	12179(2)	7212(2)	2494(2)	59(1)
N(2)	9086(3)	4729(2)	8267(2)	25(1)	C(64)	12374(3)	8623(4)	1484(3)	41(1)
C(21)	9735(3)	3845(3)	8524(3)	24(1)	F(64)	13338(2)	8183(2)	1134(2)	65(1)
C(22)	10382(3)	3665(3)	8933(3)	26(1)	C(65)	11968(3)	9544(4)	1170(3)	36(1)
F(22)	10410(2)	4389(2)	9090(2)	38(1)	F(65)	12626(2)	10039(2)	502(2)	50(1)
C(23)	10994(3)	2792(3)	9190(3)	29(1)	C(66)	10985(3)	9974(3)	1536(3)	28(1)
F(23)	11591(2)	2664(2)	9595(2)	43(1)	F(66)	10592(2)	10905(2)	1220(2)	36(1)
C(24)	10981(3)	2034(3)	9039(3)	30(1)	Al(7)	7056(1)	11436(1)	3177(1)	24(1)
F(24)	11546(2)	1177(2)	9309(2)	42(1)	C(7)	5757(3)	12253(4)	3588(3)	41(2)
C(25)	10368(3)	2181(3)	8621(3)	30(1)	N(7)	8216(3)	11816(2)	2393(2)	23(1)
F(25)	10368(2)	1452(2)	8451(2)	40(1)	C(71)	8095(3)	12777(3)	2147(3)	22(1)
C(26)	9760(3)	2059(3)	8377(2)	28(1)	C(72)	8318(3)	13305(3)	1295(3)	26(1)
F(26)	9143(2)	3182(2)	7980(2)	37(1)	F(72)	8743(2)	12863(2)	656(2)	35(1)
Al(3)	8956(1)	5959(1)	8223(1)	26(1)	C(73)	8131(3)	14247(3)	1075(3)	29(1)
C(3)	9585(4)	6471(3)	8547(3)	37(1)	F(73)	8363(2)	14721(2)	237(2)	41(1)
N(3)	8869(3)	6387(3)	7058(2)	26(1)	C(74)	7708(3)	14720(3)	1706(3)	30(1)
C(31)	9532(3)	6835(3)	6357(3)	25(1)	F(74)	7510(2)	15646(2)	1496(2)	40(1)
C(32)	10538(3)	6432(3)	6183(3)	29(1)	C(75)	7495(3)	14228(3)	2567(3)	27(1)
F(32)	10872(2)	5627(2)	6738(2)	41(1)	F(75)	7093(2)	14676(2)	3188(2)	37(1)
C(33)	11214(3)	6816(3)	5485(3)	31(1)	C(76)	7699(3)	13288(3)	2754(3)	26(1)
F(33)	12176(2)	6389(2)	5360(2)	45(1)	F(76)	7482(2)	12804(2)	3604(2)	37(1)
C(34)	10888(4)	7633(4)	4922(3)	33(1)	Al(8)	8633(1)	10919(1)	1762(1)	24(1)
F(34)	11532(2)	8013(2)	4226(2)	46(1)	C(8)	8960(4)	10957(3)	573(3)	32(1)
C(35)	9900(4)	8076(3)	5088(3)	31(1)	N(8)	7481(3)	10518(2)	2567(2)	24(1)
F(35)	9569(2)	8902(2)	4559(2)	43(1)	C(81)	6932(3)	10508(3)	2132(3)	23(1)
C(36)	9234(3)	7679(3)	5790(3)	27(1)	C(82)	6435(3)	11321(3)	1657(3)	29(1)
F(36)	8269(2)	8138(2)	5932(2)	38(1)	F(82)	6470(2)	12142(2)	1640(2)	45(1)
Al(4)	7466(1)	6686(1)	7513(1)	27(1)	C(83)	5934(3)	11347(4)	1184(3)	34(1)
C(4)	6401(4)	7703(3)	7173(3)	39(1)	F(83)	5458(2)	12164(2)	743(2)	51(1)
N(4)	7633(3)	5420(3)	7561(2)	26(1)	C(84)	5918(3)	10525(4)	1171(3)	33(1)
C(41)	6924(3)	5288(3)	7388(3)	27(1)	F(84)	5438(2)	10527(2)	713(2)	48(1)
C(42)	5936(3)	5538(3)	7893(3)	30(1)	C(85)	6403(3)	9702(3)	1627(3)	32(1)
F(42)	5679(2)	5912(2)	8551(2)	30(1)	F(85)	6402(2)	8895(2)	1610(2)	52(1)
C(43)	5215(3)	5441(3)	7751(3)	34(1)	C(86)	6893(3)	9696(3)	2095(3)	27(1)
F(43)	4264(2)	5734(2)	8233(2)	45(1)	F(86)	7387(2)	8873(2)	2515(2)	39(1)
C(44)	5464(4)	5051(4)	7095(4)	45(1)	C(91)	12742(9)	3309(8)	6831(9)	89(4)
F(44)	4757(2)	4960(3)	6948(2)	69(1)	C(92)	13876(4)	3084(16)	6463(15)	235(13)
C(45)	6423(4)	4782(4)	6599(4)	54(2)	C(93)	14078(13)	3642(17)	5583(13)	238(12)
F(45)	6674(3)	4394(3)	5967(3)	99(2)	C(94)	15060(14)	3723(12)	5325(11)	186(8)
C(46)	7134(4)	4911(4)	6731(3)	43(1)	C(95)	15568(15)	2814(12)	5765(13)	166(8)
F(46)	8070(2)	4650(3)	6220(2)	64(1)	C(96)	15764(27)	2815(19)	6406(20)	226(13)
Al(5)	8209(1)	9576(1)	3321(1)	25(1)	C(91′)	12915(25)	3720(28)	5278(20)	221(17)
C(5)	8081(4)	8367(3)	3986(3)	38(1)	C(92′)	13051(17)	3435(21)	6081(20)	132(8)
N(5)	7828(3)	10531(2)	3918(2)	25(1)	C(93′)	13980(22)	2707(19)	6015(21)	178(10)
C(51)	7352(3)	10397(3)	4829(3)	26(1)	C(94′)	14658(16)	2973(25)	6085(19)	172(10)
C(52)	6469(3)	10202(3)	5220(3)	30(1)	C(95′)	14854(22)	2553(25)	6821(18)	180(11)
F(52)	6075(2)	10128(2)	4719(2)	39(1)	C(96′)	15852(21)	2421(24)	6750(22)	141(11)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

formed was condensed in a cooling-trap. Recrystallization of the residue from *n*-pentane (10 mL) gave colorless crystals of **4** (0.70 g, 72%), mp 287−290 °C. ^{1}H NMR (CD_3CN) δ 1.35 (s, 9 H, p-C*H*$_3$), 1.89 (s, 18 H, o-C*H*$_3$), 4.58 (s (br), 1 H, N-*H*), 6.47 (s, 6 H, Mes-*H*). ^{19}F NMR (CD_3CN) δ −10.9 (m, 1 F), −2.0 (m, 2 F), −0.9 (m, 3 F), −0.5 (m, 2 F), 0.25 (m, 10 F), 15.8 (m, 5 F), 19.8 (m, 2 F). MS (70 eV): *m*/*e* (%) 1543 (20) [M], 1361 (100) [M-HNC$_6$F$_5$], 740 (5) [(MesGaNC$_6$F$_5$)$_2$], 578 (17) [(MesGaN)$_2$C$_6$F$_5$], 307 (20) [MesGa], 183 (5) [H$_2$NC$_6$F$_5$], 119 (10) [Mes], 69 (12) [Ga]. IR (Nujol mull): 3447 (m), 1660 (m), 1603 (m), 1523 (vs), 1498 (vs), 1447 (s), 1301 (m), 1261 (m), 1166 (s), 1143 (m), 1018 (vs), 999 (vs), 947 (m), 850 (m), 797 (m), 735 (m) 676 (m), 588 (s), 571 (s), 541 (m), 526 (s), 479 (s), 439 (s). Anal. Calcd for $C_{57}H_{34}F_{25}Ga_4N_5$ (1542.77): C, 44.38; H, 2.22; N, 4.54. Found C, 43.41; H, 2.60; N, 4.03.

X-ray Measurements of 1 and 4. The intensities for the structures were collected on a Stoe-Siemens AED four-circle-diffractometer using graphite-monochromated MoK_α radiation (λ = 71.073 pm). The crystals were mounted on a glass fiber in a rapidly cooled polyfluoropolyether.[13] Data were collected at −120 °C with a profile-fitted method.[14] Both structures were solved by direct methods with

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **4**[a]

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
Ga(1)	877(1)	7862(1)	394(1)	33(1)	F(2)	2576(1)	8007(5)	563(2)	59(2)
C(1)	502(2)	8117(7)	−30(4)	41(2)	F(3)	2774(1)	6211(5)	1175(3)	73(2)
C(2)	238(2)	8332(7)	259(4)	40(2)	F(4)	2380(1)	4731(5)	1597(3)	80(2)
C(3)	−20(2)	8464(7)	−62(4)	48(2)	F(5)	1804(1)	5049(4)	1436(2)	61(2)
C(4)	−37(2)	8409(8)	−682(5)	56(3)	N(2)	1048(1)	7809(5)	1226(3)	32(2)
C(5)	222(2)	8205(7)	−959(4)	45(2)	C(50)	884(2)	8218(7)	1715(4)	37(2)
C(6)	490(2)	8077(7)	−656(4)	39(2)	C(51)	703(2)	7550(7)	2043(4)	41(2)
C(7)	236(2)	8389(9)	935(4)	58(3)	C(52)	537(2)	7953(9)	2489(4)	49(2)
C(8)	−325(2)	8501(9)	−1023(5)	72(3)	C(53)	544(2)	9065(9)	2629(4)	55(3)
C(9)	754(2)	7866(8)	−1025(4)	51(2)	C(54)	718(2)	9753(8)	2304(4)	49(2)
Ga(2)	1427(1)	7005(1)	2(1)	32(1)	C(55)	833(2)	9344(7)	1854(4)	43(2)
N(5)	1691(2)	6654(6)	−571(3)	37(2)	F(11)	682(1)	6481(4)	1914(2)	53(1)
C(11)	1777(2)	5647(7)	−781(4)	37(2)	F(12)	363(1)	7286(5)	2796(2)	72(2)
C(12)	1932(2)	5537(7)	−1300(4)	42(2)	F(13)	382(1)	9475(5)	3066(3)	86(2)
C(13)	2007(2)	4527(9)	−1527(4)	51(3)	F(14)	720(1)	10854(4)	2413(3)	69(2)
C(14)	1937(2)	3580(8)	−1241(4)	51(3)	F(15)	1033(1)	10060(4)	1523(2)	53(1)
C(15)	1783(2)	3655(8)	−735(4)	48(2)	N(3)	1260(1)	8514(5)	143(3)	31(2)
C(16)	1711(2)	4665(8)	−509(4)	42(2)	C(60)	1239(2)	9411(7)	−258(4)	35(2)
F(101)	2004(1)	6467(4)	−1592(2)	59(2)	C(61)	1423(2)	9587(7)	−732(4)	44(2)
F(102)	2154(1)	4480(5)	−2039(2)	78(2)	C(62)	1393(3)	10415(8)	−1126(4)	57(3)
F(103)	2012(2)	2588(5)	−1459(3)	83(2)	C(63)	1170(3)	11172(9)	−1064(5)	64(3)
F(104)	1706(1)	2722(5)	−446(3)	76(2)	C(64)	986(2)	11088(8)	−596(5)	57(3)
F(105)	1565(1)	4711(4)	12(2)	58(1)	C(65)	1023(2)	10212(7)	−217(4)	45(2)
Ga(3)	1200(1)	6219(1)	1126(1)	32(1)	F(21)	1652(1)	8890(4)	−798(2)	58(2)
C(21)	1198(2)	4923(6)	1658(3)	33(2)	F(22)	1575(2)	10531(5)	−1579(2)	84(2)
C(22)	1273(2)	5078(7)	2263(4)	40(2)	F(23)	1132(2)	12026(5)	−1454(3)	105(2)
C(23)	1320(2)	4159(8)	2627(4)	42(2)	F(24)	774(1)	11833(5)	−518(3)	85(2)
C(24)	1304(2)	3089(7)	2423(4)	41(2)	F(25)	850(1)	10175(4)	264(2)	52(1)
C(25)	1221(2)	2955(7)	1826(4)	45(2)	N(4)	1057(1)	6353(5)	261(3)	29(2)
C(26)	1171(2)	3843(7)	1447(4)	37(2)	C(70)	856(2)	5654(6)	−28(4)	32(2)
C(27)	1303(2)	6201(7)	2545(4)	52(3)	C(71)	599(2)	5295(7)	238(4)	40(2)
C(28)	1369(2)	2119(7)	2819(4)	58(3)	C(72)	402(2)	4590(7)	−23(4)	45(2)
C(29)	1071(2)	3565(8)	816(4)	57(3)	C(73)	444(2)	4195(8)	−583(4)	51(3)
Ga(4)	1433(1)	8527(1)	992(1)	33(1)	C(74)	692(2)	4528(8)	−871(4)	48(2)
C(31)	1691(2)	9605(7)	1412(3)	36(2)	C(75)	889(2)	5213(7)	−597(4)	38(2)
C(32)	1720(2)	10687(7)	1202(4)	40(2)	F(31)	554(1)	5673(4)	794(2)	52(1)
C(33)	1905(2)	11426(8)	1506(4)	51(2)	F(32)	170(1)	4241(5)	282(2)	67(2)
C(34)	2065(2)	11139(8)	2004(4)	50(3)	F(33)	251(1)	3502(5)	−853(3)	74(2)
C(35)	2035(2)	10057(8)	2213(4)	49(2)	F(34)	740(1)	4139(5)	−1419(2)	70(2)
C(36)	1850(2)	9306(7)	1922(4)	43(2)	F(35)	1129(1)	5510(4)	−900(2)	51(1)
C(37)	1562(2)	11087(8)	650(4)	60(3)	C(1P)	−514(8)	6095(47)	−2379(26)	252(9)
C(38)	2266(2)	11969(8)	2323(5)	66(3)	C(2P)	−219(7)	5907(41)	−2160(20)	253(9)
C(39)	1824(2)	8161(8)	2202(4)	65(3)	C(3P)	−1(7)	5979(26)	−2609(20)	254(9)
N(1)	1568(1)	6970(5)	840(3)	33(2)	C(4P)	295(7)	5757(37)	−2398(23)	254(9)
C(40)	1872(2)	6721(7)	931(3)	35(2)	C(5P)	518(8)	6355(43)	−2694(30)	253(9)
C(41)	2086(2)	7440(7)	706(3)	36(2)	C(6P)	2741(6)	14304(24)	174(18)	151(6)
C(42)	2384(2)	7283(8)	790(4)	43(2)	C(7P)	2509(7)	13736(21)	−140(19)	151(6)
C(43)	2486(2)	6385(9)	1093(4)	51(2)	C(8P)	2547(8)	12560(21)	−193(21)	150(6)
C(44)	2283(2)	5635(8)	1307(4)	50(3)	C(9P)	2374(7)	11915(21)	199(19)	150(6)
C(45)	1986(2)	5805(8)	1217(4)	44(2)	C(10P)	2402(7)	10736(23)	130(19)	148(6)
F(1)	1991(1)	8319(4)	382(2)	44(1)					

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

SHELXS-90[15] and refined against F^2 by full-matrix least-squares using SHELXL-93.[16] The hydrogen atoms were added in calculated positions and refined "riding" on their respective carbon atom; that bound to nitrogen (H5N) in **4** was refined freely. Absorption correction for **4** was applied using a semi-empirical method. The two structure refinements were complicated by disordered lattice solvent. The *n*-hexane molecule in **1** and the *n*-pentane molecule in **4** were refined applying similarity restraints for all chemically equivalent 1−2 and 1−3 distances.

Selected bond lengths and -angles are given in Table 1. Relevant crystallographic data of **1** and **4** are given in Tables 2 and 3, and fractional coordinates and equivalent isotropic displacement coefficients of **1** in Table 4 and of **4** in Table 5, respectively.

Results and Discussion

Addition of trimethylalane to pentafluoroaniline gives the tetrameric pentafluoroiminomethylalane ($(MeAlNC_6F_5)_4$), **1**, with elimination of methane. Compound **1** is a white solid sensitive

$$AlMe_3 + C_6F_5NH_2 \xrightarrow[-2CH_4]{} {}^1/_4(MeAlNC_6F_5)_4 \quad \mathbf{1} \qquad (1)$$

to moisture and air. In the ^1H NMR spectrum of **1** a septet is observed for the methyl protons at aluminum, which is assigned to long-range coupling with the *ortho*-positioned fluorine atoms of three of the four pentafluorophenyl substituents. It is remarkable that an intermediate aminoalane could not be observed. This behavior may result from electron withdrawing properties of the fluorine atoms. To prove this assumption of electronic rather than bulk properties, we reacted $AlMes_3$, instead of $AlMe_3$, with pentafluoroaniline. In this reaction an intermediate $Mes_2AlNHC_6F_5$, **2**, precipitated from the reaction

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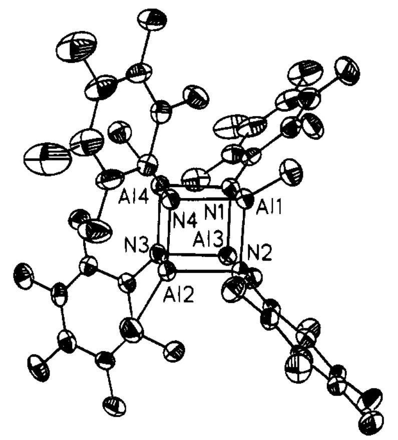

Figure 1. Molecular structure of 1 giving the numbering scheme used in Tables 1 and 4 (anisotropic displacement ellipsoids are drawn at the 50% probability level).

mixture. The same behavior is found with Mes_3Ga, forming $Mes_2GaNHC_6F_5$ **3**. **2** and **3** are white solids, sensitive to moisture

$$MMes_3 + C_6F_5NH_2 \xrightarrow[-\,MesH]{} Mes_2M{-}N(C_6F_5)H \quad (\mathbf{2, 3}) \qquad M = Al, Ga \qquad (2)$$

and air. In the EI mass spectra of **2** and **3** only the molecular ions and fragments for the monomeric compounds are observed, in contrast to dimeric aminometallanes where fragments tentatively assigned to dimeric species have been detected.[10] This indicates that **2** and **3** could be monomeric species, due to the sterical requirements of the ligands at the metal and the nitrogen atoms. Similar properties were observed for example with $Trip_2MN(H)Dipp$ (M = Al, Ga; Trip = 2,4,6-i-$Pr_3C_6H_2$; Dipp = 2,6-i-$Pr_2C_6H_3$).[17]

Thermolysis of compound **3** affords the tetrakis(pentafluoroimino)pentafluoroaminotrimesitylgallane **4** in contrast to the expected $(MesGaNC_6F_5)_4$. The bulky substutients are obviously responsible for the functionalization of the cubane in **4**. Compound **4** is an example of an amino-substituted iminogallane having a heterocubane core.

$$5\ Mes_2Ga{-}N(C_6F_5)H\ (\mathbf{3}) \xrightarrow[-4\,MesH,\ -GaMes_3]{\Delta} NHC_6F_5Ga(MesGa)_3(\mu_3\text{-}NC_6F_5)_4\ (\mathbf{4}) \qquad (3)$$

Crystal Structure of 1. Two independent molecules of $(MeAlNC_6F_5)_4$ heterocubanes and a single n-hexane molecule are present in the asymmetric unit of **1**. Structural parameters discussed in the text are given as averages of chemically corresponding values in the two heterocubanes. In Figure 1 a single molecule of **1** is depicted.

Basic structural features (Table 1), like i.e. the Al−N distances, are in good agreement with those of other known $(AlN)_4$-heterocubanes.[7a,8d] However, it seems noteworthy that **1** is the first example where the N−Al−N angle is more acute than 90° (86−89°) while the Al−N−Al angle is wider than 90° (91−92°).

On first glance the Al−N−Al and N−Al−N angles in all $(AlN)_4$-heterocubanes from geometrical considerations need to be more or less 90°. The nitrogen atom can be considered to bind the three adjacent aluminum atoms through p-orbitals. Electron releasing substituents at the nitrogen atom like silyl groups[7d] increase electron density on N, resulting in a higher N···N repulsion. This demonstrates that the nitrogen atoms are located above each Al_3-triangle of the Al_4 tetrahedron , giving rise to a more acute Al−N−Al angle and a wider N−Al−N angle, respectively. Electron withdrawing substituents like the C_6F_5 group lower the electron density at the nitrogen atoms, N···N repulsion is less pronounced and they are located closer to the Al_3 triangle, giving Al−N−Al angles wider than 90°.

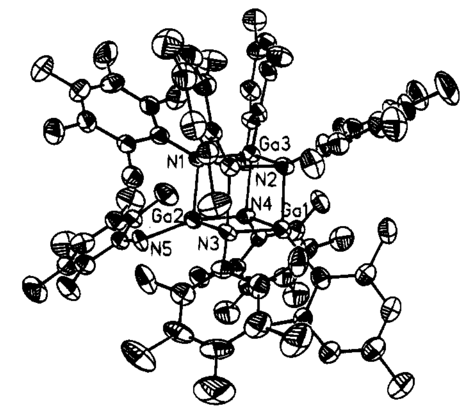

Figure 2. Molecular structure of 4 giving the numbering scheme used in Tables 1 and 5 (anisotropic displacement ellipsoids are drawn at the 50% probability level).

Crystal Structure of 4. The heterocubane structure of **4** is depicted in Figure 2. Within the $(GaN)_4$ core the N−Ga−N angles are more acute (85−89°) while the Ga−N−Ga angles are wider than 90°. The basic structural parameters are in agreement with those of the only other known $(GaN)_4$ heterocubane.[10] Important bond distances and angles are given in Table 1.

According to a modified Schomaker−Stevenson equation[18] a value of 180.4 pm would be expected for a Ga−N single bond. This value is nearly matched by the exocyclic Ga2−N5 distance of 184 pm. Different to the three other Ga atoms Ga2 is not coordinated to a mesityl ligand but by a F_5C_6NH amide. However, the Ga−N distances within the core are considerably longer ranging from 196 to 206 pm. Thus they can be regarded as having a bond order of $^2/_3$, because the correlation function of the bond valence method[19] yields 200 pm for a $^2/_3$ bond valence of Ga−N.

Conclusion

The reactions of perfluorinated amines with metal organyles represent a facile route for synthesizing iminoalanes and iminogallanes. The products have been obtained in high yields. The electron withdrawing properties of the perfluorinated group seems to be important for getting clean reaction products. Using alkyl or aryl substituents of comparable size leads to C−H activated products.

The bond orders of heterocubane metal−nitrogen bonds can be described as having a bond order of $^2/_3$, whereas metal−nitrogen single bonds having a bond order of 1.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, and bond lengths and angles, fully labeled figures of **1** and **4** of 50% probability of anisotropic displacement parameters, and tables of anisotropic displacement parameters and hydrogen atoms for both **1** and **4** (26 pages). Ordering information is given on any current masthead page.

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