Synthesis and Characterization of (4-Fluorophenyl)amino-Based Amino- and Iminometallanes of Group 13. Crystal Structures of $(MeAlNR_f)_4$, $(MeMNR_f)_6 \cdot n$THF (M = Al, n = 2; M = Ga, n = 7), and $(MeIn(THF)NR_f)_4$ ($R_f = 4\text{-}C_6H_4F$)[†]

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The novel amino- and iminometallanes $(MeAlNR_f)_n$ **(1)** ($n = 4$, **1a**; $n = 6$, **1b**), $(Me_2GaN(H)R_f)_2$ **(2)**, $(MeGaNR_f)_6$ **(3)**, $(Me_2InN(H)R_f)_2$ **(4)**, and $(MeIn(THF)NR_f)_4$ **(5)** ($R_f = 4\text{-}C_6H_4F$) have been prepared in high yield by the reaction of $AlMe_3$, $GaMe_3$, and $InMe_3$, respectively, with 4-fluoroaniline. All of the products have been fully characterized by elemental analysis, IR, NMR, and mass spectroscopy. The crystal structures of **1a**, **1b**·2THF, **3**·7THF, and **5** have been determined. For the degree of oligomerization of compound **1** a solvent- and temperature-dependent influence is assumed. $(MeGaNR_f)_6$ **(3)** is the first hexameric iminogallane and $(MeIn(THF)NR_f)_4$ **(5)** is the second iminoindane described in the literature.

Introduction

The reactions of organometallic compounds of group 13 with primary amines have been studied for decades.[1] In the first step of the reaction aminometallanes $(R_2MN(H)R')_n$ (M = Al, Ga, In; n = 1, 2, 3)[2] are formed. Generally, the compounds have a core structure of a four-membered ring with alternating metal and nitrogen atoms. The thermolysis of the aminometallanes proceeds by two different routes. One possible pathway (a) is the intermolecular reaction of aminometallanes forming iminometallanes $(RMNR')_n$.[3] The degree of oligomerization in the resulting cage compounds is highly dependent on the metal and on the steric demand of the ligands. The second route (b) of the thermolysis of the aminometallanes takes place by intramolecular side chain elimination of hydrocarbons. Especially for the thermolysis of aminogallanes and -indanes route b is strongly favored due to the high temperatures needed for completing hydrocarbon elimination. Therefore only five iminogallanes[4a−d] and one iminoindane[4b] have been reported in the literature to date.

We have previously reported on the synthesis of the first iminogallane and -indane with heterocubane structures. In order to avoid side chain elimination, a perfluorinated aromatic amine was used.[4b]

As the number of electron-withdrawing fluorine atoms on the nitrogen ligand might affect the temperature of pyrolysis, we investigated the reactions of the trimethylmetallanes of aluminum, gallium, and indium using 4-fluoroaniline in which the steric influence of the fluorine atom is minimized for the degree of oligomerization of the products. In this paper we report the synthesis and characterization of the aminometallanes $(Me_2GaN(H)R_f)_2$ **(2)** and $(Me_2InN(H)R_f)_2$ **(4)** and the iminometallanes $(MeAlNR_f)_4$ **(1a)**, $(MeAlNR_f)_6$ **(1b)**, $(MeGaNR_f)_6$ **(3)**, and $(MeIn(THF)NR_f)_4$ **(5)**. The molecular structures of **1a**, **1b**·2THF, **3**·7THF, and **5** have been determined by X-ray diffraction studies at low temperature.

Experimental Section

General Considerations. All experiments were performed using standard Schlenk techniques under dry nitrogen atmosphere due to the extreme sensitivity of reactants and products toward air and moisture. A Braun MB 150-GI drybox was used to store the compounds and to prepare the samples for spectroscopic characterizations. All solvents were dried over sodium/benzophenone, freshly distilled and degassed prior to use. Trimethylalane and 4-fluoroaniline were purchased from Aldrich Chemical Co., and trimethylgallane was purchased from Strem Chemicals. Trimethylindane was prepared as described in the literature.[5a]

Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. As described in the literature[5b,c] elemental analy-

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[†] Dedicated to Professor Leopold Horner on the occasion of his 85th birthday.

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ses of metal–nitrogen compounds of group 13 are often not exact. Cause for this is an incomplete burning of the samples, due to the formation of metal carbides and nitrides already at low temperatures.

NMR spectra were recorded on a Bruker AM 250 and were externally referred to tetramethylsilane or $CFCl_3$, respectively. FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between KBr plates in the range 4000–400 cm^{-1} (only strong absorptions are given), and EI mass spectra, on Finnigan MAT 8230 or Varian MAT CH 5 instruments.

Preparation of $(MeAlN\text{-}4\text{-}C_6H_4F)_4$ (1a) and $(MeAlN\text{-}4\text{-}C_6H_4F)_6$ (1b). 4-Fluoroaniline (2.22 g, 20.0 mmol) in toluene (30 mL) was slowly added to a solution of trimethylalane (1.44 g, 20.0 mmol) in toluene (50 mL) at 0 °C. The reaction mixture was refluxed until gas evolution was finished (2 h). After removal of the solvent under reduced pressure the white solid was heated at 130 °C for 2 h. The residue was dissolved in *n*-hexane (100 mL) and filtered. Removal of the solvent *in vacuo* gave product **1** (2.16 g, 72%), mp 179 °C. ^1H NMR (250.13 MHz, THF-d_8): δ 7.35–6.65 (m, Ar-H), −0.94 (s, Al-(CH_3)) ppm. ^{19}F NMR (235.32 MHz, THF-d_8): δ −121.3 (s, Ar-F) ppm. MS (70 eV): *m/e* (%) 906 (($MeAlN\text{-}4\text{-}C_6H_4F)_6$, 100), 891 (($MeAlN\text{-}4\text{-}C_6H_4F)_6$ − Me, 82), 604 (($MeAlN\text{-}4\text{-}C_6H_4F)_4$, 4), 589 (($MeAlN\text{-}4\text{-}C_6H_4F)_4$ − Me, 6), 453 (($MeAlN\text{-}4\text{-}C_6H_4F)_3$, 10), 302 (($MeAlN\text{-}4\text{-}C_6H_4F)_2$, 20). IR (Nujol mull): 1506 (s), 1465 (s), 1232 (s), 1201 (s), 1158 (s), 1099 (s), 872 (s), 861 (s), 835 (s), 785 (s), 732 (s), 701 (s), 680 (s), 535 (s), 511 (s), 410 (s) cm^{-1}. Anal. Calcd for $(C_7H_7AlFN)_x$ (151.1): C, 55.6; H, 4.7; N, 9.3. Found: C, 53.7; H, 4.8; N, 8.9.

Crystals of the tetrameric product **1a** were obtained from *n*-hexane at −20 °C, whereas the crystallization in THF at room temperature afforded the hexameric compound **1b**·2THF.

Preparation of $(Me_2GaN(H)\text{-}4\text{-}C_6H_4F)_2$ (2). 4-Fluoroaniline (2.51 g, 22.6 mmol) dissolved in toluene (20 mL) was slowly added dropwise to a solution of trimethylgallane (2.59 g, 22.6 mmol) in toluene (20 mL) at room temperature. The reaction mixture was heated for 3 h under reflux. The solution was concentrated under reduced pressure (20 mL) and cooled overnight in a freezer (2 °C) to yield product **2** (4.07 g, 86%) as colorless crystals, mp 194 °C. ^1H NMR (200.13 MHz, THF-d_8): δ 6.94–6.90 (m, 8 H, Ar-H), 4.70 (s (br), 2 H, NH), −0.31 (s, 12 H, Ga($CH_3)_2$) ppm. ^{19}F NMR (188.32 MHz, THF-d_8): δ −123.8 (s, Ar-F) ppm. MS (70 eV): *m/e* (%) 420 (M, 10), 405 (M − Me, 15), 209 (M/2 − H, 100), 99 ($GaMe_2$, 90). IR (Nujol mull): 3287 (m, ν_{NH}), 1235 (s), 1226 (vs), 1209 (vs), 1197 (vs), 1154 (s), 871 (s), 836 (vs), 757 (vs), 739 (s), 705 (s), 584 (s), 546 (s), 538 (s), 462 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{22}F_2Ga_2N_2$ (419.8): C, 45.8; H, 5.3; N, 6.7. Found: C, 45.9; H, 5.3; N, 6.5.

Preparation of $(MeGaN\text{-}4\text{-}C_6H_4F)_6$ (3). Compound **2** (2.10 g, 5.0 mmol) was heated for 3 h to 205 °C for a quantitative elimination of methane. The pale yellow residue was washed with *n*-hexane (30 mL) and recrystallized from THF at −26 °C to yield product **3**·7THF. Removal of the solvent *in vacuo* gave the THF-free product **3** (1.24 g, 64%), mp 320 °C. ^1H NMR (200.13 MHz, THF-d_8): δ 6.98–6.82 (m, 24 H, Ar-H), −0.47 (s, 18 H, $GaCH_3$) ppm. ^{19}F NMR (188.32 MHz, THF-d_8): δ −122.3 (s, Ar-F) ppm. MS (70 ev): *m/e* (%) 1163 (M, 28), 776 ([$MeGaN\text{-}4\text{-}C_6H_4F]_4$, 10), 388 (M/3, 100), 194 (M/6, 10). IR (Nujol mull): 1499 (vs), 1467 (vs), 1378 (s), 1367 (s), 1200 (vs), 1153 (s), 839 (s), 790 (s), 780 (s) cm^{-1}. Anal. Calcd for $C_{42}H_{42}F_6Ga_6N_6$ (1163.2): C, 43.4; H, 3.6; N, 7.2. Found: C, 42.3; H, 3.8; N, 7.2.

Preparation of $(Me_2InN(H)\text{-}4\text{-}C_6H_4F)_2$ (4). 4-Fluoroaniline (2.34 g, 21.1 mmol) in toluene (20 mL) was slowly added to a solution of trimethylindane (3.37 g, 21.1 mmol) in toluene (20 mL). The reaction mixture was then heated under reflux for 3 h. Slowly cooling the mixture to room temperature yielded product **4** as colorless crystals (4.64 g, 86%), mp 202 °C. ^1H NMR (200.13 MHz, THF-d_8): δ 6.83–6.79 (m, 8 H, Ar-H), 4.06 (s (br), 2 H, NH), −0.24 (s, 12 H, In($CH_3)_2$) ppm. ^{19}F NMR (188.32 MHz, THF-d_8): δ −127.0 (s, Ar-F) ppm. MS (70 eV): *m/e* (%) 510 (M, 15), 495 (M − Me, 12), 400 (M − $HN\text{-}4\text{-}C_6H_4F$, 40), 255 (M/2, 25), 145 ($InMe_2$, 100), 115 (In, 55). IR (Nujol mull): 3283 (m, ν_{NH}), 1501 (vs), 1462 (s), 1441 (s), 1231 (s), 1203 (vs), 1152 (s), 838 (vs), 763 (vs), 730 (s), 707 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{22}F_2In_2N_2$ (510.0): C, 37.7; H, 4.4; N, 5.5. Found: C, 37.1; H, 4.2; N, 5.4.

Preparation of $(MeIn(THF)N\text{-}4\text{-}C_6H_4F)_4$ (5). Compound **4** (1.85 g, 3.63 mmol) was heated in an oil bath to 220 °C. After ca. 3 h gas evolution ceased and the reaction mixture resolidified. The yellow residue was washed with *n*-hexane (50 mL) and recrystallized from toluene (5 mL)/THF (5 mL) to give colorless crystals of product **5**, which were suitable for an X-ray diffraction analyses. These crystals partially lose the coordinated THF by removal of the solvent *in vacuo*, yielding $(MeInN\text{-}4\text{-}C_6H_4F)_4$·THF (1.25 g, 72%), mp 232 °C. ^1H NMR (200.13 MHz, THF-d_8): δ 6.76–6.69 (m, 16 H, Ar-H), 0.15 (s, 12 H, $InCH_3$) ppm. ^{19}F NMR (188.32 MHz, THF-d_8): δ −128.4 (s, Ar-F) ppm. MS (70 eV) *m/e* (%): 956 (M, 100), 115 (In, 66). IR (Nujol mull): 1487 (s), 1467 (s), 1200 (s), 832 (s), 781 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{28}F_4In_4N_4\cdot C_4H_8O$ (1027.9): C, 37.4; H, 3.5; N, 5.5. Found: C, 36.9; H, 3.5; N, 5.6.

X-ray Structure Determinations for 1a, 1b·2THF, 3·7THF, and 5. The highly unstable crystals of **3**·7THF and **5** were mounted in an oil drop on a glass fiber at low temperature.[6] Data for **1b**·2THF were collected at −80 °C on a Stoe-Siemens-Huber diffractometer with monochromated Mo Kα radiation (λ = 0.710 73 Å) using a SMART-CCD area detector. For the integration of intensities the program SAINT was used. Data for **1a**, **3**·7THF, and **5** were collected at low temperatures on a Stoe-Siemens-AED diffractometer with monochromated Mo Kα radiation (λ = 0.710 73 Å) using the learnt profile method.[7] A semiempirical absorption correction based on ψ-scans was employed for structure **3**·7THF. Due to the small number of strong reflections at a suitable χ angle, no ψ-scan absorption correction was possible in the case of **5**. All the structures were solved by direct methods using SHELXS-90/96.[8] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was used. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-93/96.[9] The *R* values are defined as $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$. The crystals of compound **1b**·2THF contain two disordered THF molecules per asymmetric unit. The crystals of compound **3**·7THF contain THF solvent in two different situations: One molecule occupies a general position within the asymmetric unit, showing discrete disorder among two partially occupied sites. The other THF molecule is disordered over a $\bar{3}$ axis, whose symmetry it is unable to fulfill. Thus, the asymmetric unit contains $^7/_6$ THF molecules plus one-sixth of compound **3**. In both cases, the refinement of the disordered solvent was carried out using distance and ADP restraints.

Results and Discussion

Addition of trimethylalane to 4-fluoroaniline leads to the formation of the iminoalane $(MeAlNR_f)_n$ **(1)** (Scheme 1). The intermediate aminoalane could not be isolated, possibly due to the electron-withdrawing properties of the fluorine atom as observed in the reaction of tri-

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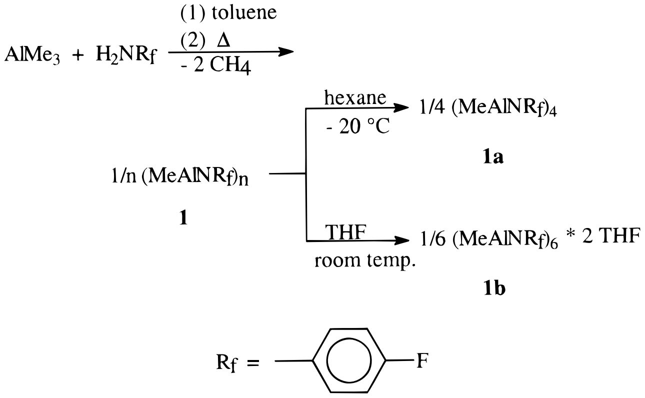
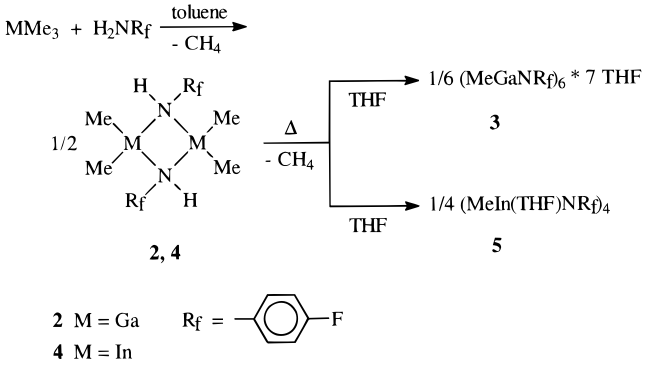
Scheme 1



Scheme 2



methylalane with pentafluoroaniline.[4c] In the mass spectra of $(MeAlNR_f)_n$ **(1)** fragment ions for the species with $n = 1$ to $n = 6$ could be detected. Crystallization of compound **1** afforded crystals of either tetrameric **1a** (hexane, −20 °C) or hexameric **1b**·2THF (THF, room temperature), depending on the temperature and solvent used (Scheme 1). When the solvent is removed from the crystals *in vacuo*, both compounds have identical spectroscopic data. We are currently studying whether the control of the oligomerization in the crystals is dependent on the crystallization temperature or the donor properties of the solvent used.

Interestingly, the formation of the iminoalane $(MeAlN\text{-}4\text{-}C_6H_4F)_n$ is complete within only 2 h, occurring at a low thermolysis temperature (130 °C), while the preparation of the analogous non-fluorine-containing compound $(MeAlNC_6H_5)_6$ requires 180 °C for 24 h.[10]

Reaction of trimethylgallane and -indane with 4-fluoroaniline in toluene leads to the formation of the corresponding dimeric aminometallanes $(Me_2GaN(H)\text{-}4\text{-}C_6H_4F)_2$ **(2)** and $(Me_2InN(H)\text{-}4\text{-}C_6H_4F)_2$ **(4)** in high yield (Scheme 2). The compounds are air- and moisture-sensitive white solids.

The EI mass spectra of **2** and **4** show the molecular ions of the dimeric species and their characteristic fragments. In the IR spectra the N−H vibrations are observed as sharp bands (3287 cm^{-1} for compound **2**, 3283 cm^{-1} for compound **4**). Only one sharp signal is observed in the ^1H NMR spectra for the methyl groups at the metal indicating that there is no *cis*/*trans* isomerization in solution as observed for other aminometallanes.[11]

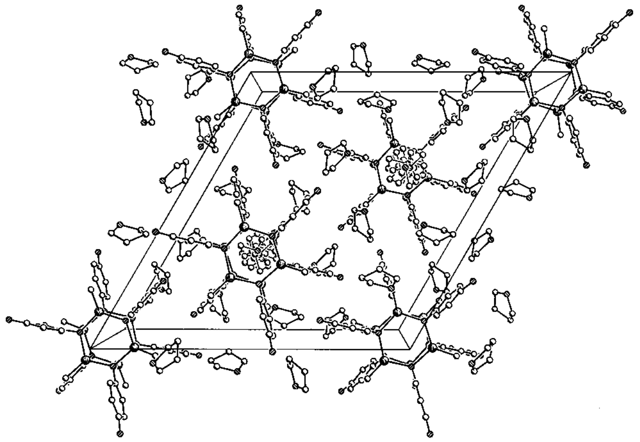


Figure 1. Packing diagram of **3**·7THF (view down the *c*-axis). One of the THF molecules is disordered on a $\bar{3}$-axis.

Further thermolysis of compound **2** and recrystallization from THF afford the hexakis(μ_3-((4-fluorophenyl)imino)methylgallane) **3**·7THF (Scheme 2), the first hexameric iminogallane characterized by X-ray diffraction. As in the case of the homologous aluminum compound **1** the EI mass spectrum shows also fragment ions of the tetrameric and dimeric iminometallanes. But in contrast to compound **1**, crystallization from solvents other than THF did not yield suitable crystals for an X-ray diffraction analysis. The crystals of **3** contain seven solvent molecules for each iminogallane molecule in the lattice, which are readily dissociated if the solvent is removed *in vacuo*. The packing diagram of compound **3** (view down the *c*-axis) is shown in Figure 1. One of the THF molecules is disordered on a $\bar{3}$-axis. Due to their high solvent content, the crystals immediately decay if allowed to warm above −20 °C. The temperature-dependent ^1H NMR spectra show no evidence for an equilibrium of different oligomers in solution.

Heating of the aminoindane **4** in an oil bath to 220 °C for 3 h and subsequent recrystallization from THF at −26 °C yields the tetrakis(μ_3-((4-fluorophenyl)imino)methylindane) tetrakis(tetrahydrofuran) adduct **5** (Scheme 2). However, the THF molecules are not strongly bonded, since the removal of the solvent *in vacuo* at room temperature leaves only one THF molecule in the compound as shown by elemental analysis and ^1H NMR spectroscopy. In the mass spectrum the molecular ion of the tetrameric iminoindane without THF was detected with an intensity of 100%, showing a high stability of this species even in the gas phase. Suitable crystals for an X-ray diffraction analysis of compound **5** could be obtained after 2 months at −26 °C from toluene/THF.

Crystal Structures of 1a, 1b·2THF, 3·7THF, and 5. The experimental details of the crystallographic study are summarized in Table 9. The crystal structure of **1a** contains two independent molecules in the asymmetric unit (Figure 2). The cage formed by the four aluminum and the four nitrogen atoms describes an almost perfect heterocubane, the largest deviation from the ideal 90° angle being 1.1°.

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Table 1. Selected Bond Lengths (Å) for $(MeAlNR_f)_4$ (1a)

Al(1)−N(1)	1.922(2)	N(4)−Al(2)	1.951(2)
Al(1)−N(2)	1.947(2)	N(4)−Al(3)	1.951(2)
Al(1)−N(3)	1.938(2)	N(4)−Al(4)	1.918(2)
Al(1)−C(1)	1.931(3)	N(4)−C(41)	1.435(3)

Table 2. Selected Bond Angles (deg) for $(MeAlNR_f)_4$ (1a)

N(1)−Al(1)−N(3)	89.32(10)	Al(2)−N(4)−Al(4)	90.06(10)
N(1)−Al(1)−N(2)	89.71	Al(3)−N(4)−Al(4)	90.72(10)
N(3)−Al(1)−N(2)	90.00(10)	Al(2)−N(4)−Al(3)	90.00(10)

Table 3. Selected Bond Lengths (Å) for $(MeAlNR_f)_6 \cdot 2THF$ (1b)

Al(1)−N(1)	1.909(3)	N(3)−Al(2)	1.905(3)
Al(1)−N(2)	1.907(3)	N(3)−Al(3)	1.913(3)
Al(1)−N(3)	1.952(3)	N(3)−C(31)	1.455(4)
Al(1)−C(10)	1.942(4)		

Table 4. Selected Bond Angles (deg) for $(MeAlNR_f)_6 \cdot 2THF$ (1b)

N(1)−Al(1)−N(2)	113.28(11)	Al(2)−N(3)−Al(3)	126.22(13)
N(1)−Al(1)−N(3)	90.59(11)	Al(1)−N(3)−Al(2)	89.55(11)
N(2)−Al(1)−N(3)	90.06(11)	Al(1)−N(3)−Al(3)	89.11(11)

Table 5. Selected Bond Lengths (Å) for $(MeGaNR_f)_6 \cdot 7THF$ (3)

Ga(1)−N(1)	1.967(43)	Ga(1)−N(1A)	2.033(4)
Ga(1)−N(1C)	1.971(3)	N(1)−Ga(1B)	2.033(4)
N(1)−Ga(1D)	1.971(3)	Ga(1)−C(10)	1.943(5)
N(1)−C(1)	1.452(6)	F(1)−C(4)	1.368(7)

Table 6. Selected Bond Angles (deg) for $(MeGaNR_f)_6 \cdot 7THF$ (3)

Ga(1)−N(1)−Ga(1B)	90.42(14)	Ga(1)−N(1)	125.87(18)
Ga(1B)−N(1)−Ga(1D)	90.30(14)	N(1)−Ga(1)−N(1A)	89.41(15)
N(1)−Ga(1)−N(1C)	114.05(18)	N(1A)−Ga(1)−N(1C)	89.28(15)
C(1)−N(1)−Ga(1)	112.1(3)	C(1)−N(1)−Ga(1B)	125.8(3)
C(1)−N(1)−Ga(1D)	110.8(3)	C(10)−Ga(1)−N(1)	117.8(2)
C(10)−Ga(1)−N(1A)	124.9(2)	C(10)−Ga(1)−N(1C)	116.0(2)

Table 7. Selected Bond Lengths (Å) for $(MeIn(THF)NR_f)_4$ (5)

In(1)−C(7)	2.117(7)	In(1)−N(1)	2.279(5)
In(1)−N(1A)	2.136(5)	In(1)−N(1B)	2.191(5)
N(1)−C(1)	1.415(8)	In(1)−O(1)	2.732(3)
F(1)−C(4)	1.363(8)		

The main difference between the two molecules is the orientation of the aromatic rings, which form two almost coplanar pairs in the first molecule, whereas only one pair of rings is coplanar in the other one.

Only in the first molecule, a contraction of the four Al−N bond distances between two of the four-membered Al_2N_2 rings can be noticed (average 1.918 Å, while the mean distance within the ring is 1.943 Å). This could be due to interactions with the π-electron system of the aromatic rings. The mean Al−N bond distance of 1.934 Å can be described in terms of the resonance hybrid between two covalent Al−N bonds, as found in monomeric three-coordinated aluminum amides $Al[N(i\text{-}Pr)_2]_3$[12a] and $(tBu)_2AlNMes_2$[12b] (1.81 Å, mean values) and as found in the pure donor bond compound $Me_3Al \cdot NMe_3$ (2.10 Å).[13]

The hexameric compound **1b**, which is formed along with the tetrameric species, has been also crystallized and structurally characterized. The structure of compound **1b** is shown in Figure 3. The N_6Al_6 core is a distorted hexagonal prism with approximate D_{3d} point group symmetry. The asymmetric unit contains two half-molecules, the other halves being generated by inversion centers. The N_3Al_3 rings are slightly bent into a chair conformation (mean torsion angle 8.3°). The N−Al−N angles within the six-membered ring vary between 112.8(1) and 113.7(1)° and within the four-membered ring between 90.1(1) and 90.9(1)°. The corresponding Al−N−Al angles are in the ranges 125.9(2)−127.3(2)° and 88.8(1)−89.6(1)°.

Table 8. Selected Bond Angles (deg) for $(MeIn(THF)NR_f)_4$ (5)

N(1)−In(1)−N(1A)	83.7(2)	N(1)−In(1)−N(1B)	85.2(2)
N(1A)−In(1)−N(1B)	85.8(2)	In(1)−N(1)−In(1B)	94.6(2)
In(1)−N(1)−In(1C)	93.7(2)	In(1B)−N(1)−In(1C)	96.3(2)
C(1)−N(1)−In(1)	123.8(4)	C(1)−N(1)−In(1B)	115.9(4)
C(1)−N(1)−In(1C)	125.3(4)	C(7)−In(1)−N(1)	111.9(3)
C(1)−In(1)−N(1A)	143.6(3)	C(7)−In(1)−N(1B)	126.7(3)

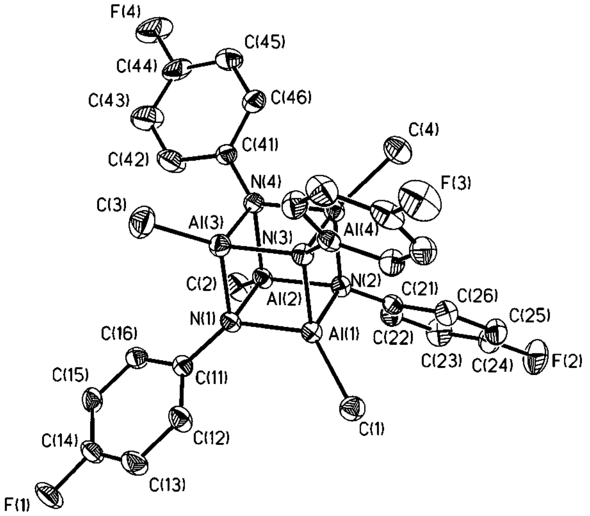

Figure 2. Crystal structure of **1a**, with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

The mean Al−N bond distance within the six-membered ring is 1.913 Å, whereas that in between the six-membered rings is 1.954 Å. This distortion can be explained as an effect of the repulsion between the aluminum centers, which thus is minimized for an Al···Al distance of 3.40 Å, whereas the undistorted structure would impose a shorter distance (3.31 Å). This accounts also for the 0.04 Å longer Al−N bond distance between the six-membered rings, where the resulting mean Al···Al distances are 2.71 Å.

The mean Al−N bond distance of 1.925 Å is in line with those found in other hexameric iminoalanes $\{HAlNCH(Me)(C_6F_5)\}_6$ (1.923 Å)[14] and $(HAlNiPr)_6$ (1.917 Å).[15]

The crystal structure of **3** (Figure 4) shows also a hexagonal prismatic Ga_6N_6 core. The asymmetric unit contains one-sixth of the iminogallane, along with a complete tetrahydrofuran molecule and one-sixth of a second one disordered on a $\bar{3}$-axis.

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Table 9. Crystallographic Data for 1a, 1b·2THF, 3·7THF, and 5

	compound			
	1a	**1b**·2THF	**3**·7THF	**5**
empirical formula	$C_{28}H_{28}Al_4F_4N_4$	$C_{42}H_{42}Al_6F_6N_6 + 2C_4H_8O$	$C_{42}H_{42}Ga_6F_6N_6 + 7C_4H_8O$	$C_{44}H_{60}F_4In_4N_4O_4$
fw	604.5	906.7 + 2 × 72.1	1163.2 + 7 × 72.1	1244.2
temp (K)	153(2)	193(2)	193(2)	193(2)
cryst size (mm)	0.40 × 0.35 × 0.35	0.40 × 0.40 × 0.40	0.50 × 0.50 × 0.50	0.40 × 0.20 × 0.20
cryst system	monoclinic	triclinic	rhombohedral	tetragonal
space group	$P2_1/n$	$P\bar{1}$	$R\bar{3}$	$P\bar{4}2_1c$
a (Å)	14.263(1)	12.155(3)	20.946(1)	15.031(2)
b (Å)	18.803(2)	12.397(3)	20.946(1)	15.031(2)
c (Å)	23.450(2)	19.270(4)	14.933(2)	10.932(2)
α (deg)	90(0)	94.64(3)	90(0)	90(0)
β (deg)	106.91(1)	107.04(3)	90(0)	90(0)
γ (deg)	90(0)	100.52(3)	120(0)	90(0)
cell vol V (Å^3)	6017(1)	2702(1)	5674(1)	2470(1)
Z	8	2	3	2
ρ_c (g·mm^{-3})	1.335	1.292	1.464	1.673
μ (mm^{-1})	0.205	0.183	2.174	1.901
F(000)	2496	1096	2568	1232
2θ range (deg)	5−45	4−50	5−45	8−50
data measd, unique	12 145, 7873 (R_{int} = 0.028)	21 632, 8648 (R_{int} = 0.044)	1909, 1644 (R_{int} = 0.020)	1352, 1229 (R_{int} = 0.066)
R,[a] w$R2$[b] ($I > 2\sigma(I)$)	0.039, 0.086	0.056, 0.136	0.039, 0.104	0.031, 0.067
R, w$R2$ (all data)	0.055, 0.095	0.070, 0.144	0.049, 0.112	0.036, 0.070
goodness of fit S [c]	1.066	1.064	1.093	1.082
weight factors a, b[d]	0.036, 4.993	0.046, 4.019	0.059, 12.541	0.034, 0.253
refined params	729	729	219	137
min/max transm factors			0.808/0.955	
restraints	0	466	230	0
largest diff peak/hole (e Å^{-3})	0.251/−0.268	0.425/−0.337	0.353/−0.323	0.595/−0.563

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

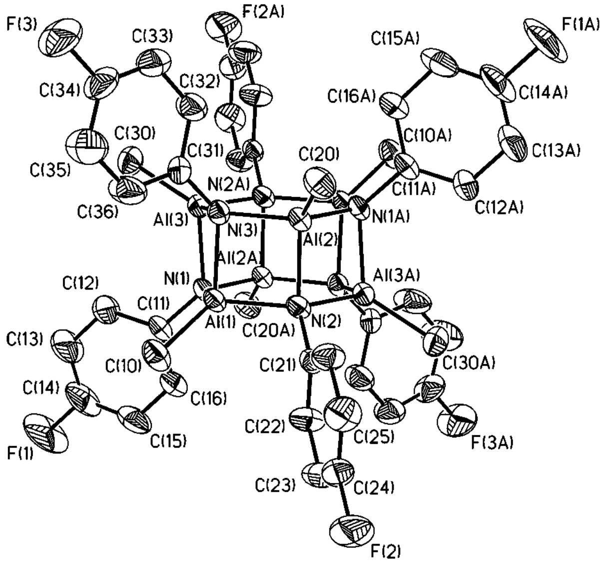

Figure 3. Crystal structure of **1b**·2THF, with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

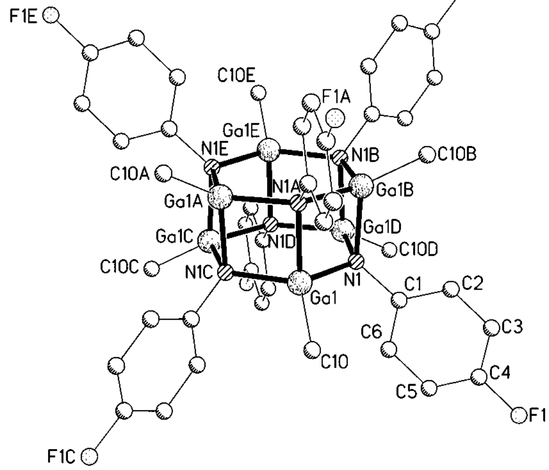

Figure 4. Crystal structure of **3**·7THF, with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

The molecule fulfills the S_6 point group symmetry, as imposed by the space group, with the 4-fluorophenyl ligands deviating from the higher D_{3d} symmetry. The same kind of distortion as in **1b** can be observed; the bond angles N−Ga−N and Ga−N−Ga within the six-membered ring are 114.1(2) and 125.9(2)°, respectively. This leads to Ga···Ga distances of 3.507(2) Å. The Ga−N distance between both six-membered rings is 0.064 Å longer than within the ring, with an average value of 1.990 Å, slightly shorter than in the reported tetrameric iminogallane{$MeGaNC_6F_5$}$_4$ (2.008 Å).[4c] There are no reported hexameric iminogallanes to date.

The longer M−N bond lengths between six-membered rings in **1b** and **3** are also consistent with a less effective overlap of the sp^3 hybridized orbitals, imposed by the more strained geometry, leading to weaker and thus longer bonds as compared to those within the six-membered rings.

The core of compound **5** consists of a distorted cube with In and N atoms at alternating corners. A methyl group and a THF molecule coordinate to each In atom, thus resulting in a 5-fold coordination of the metals (distorted trigonal bipyramid). The angle between the methyl group, the In atom, and the nitrogen trans to the THF molecule is 111.9(3)°. The 4-fold-coordinated N atoms bind a 4-fluorophenyl ligand each. The average In−N−In and N−In−N angles within the cube are 94.9

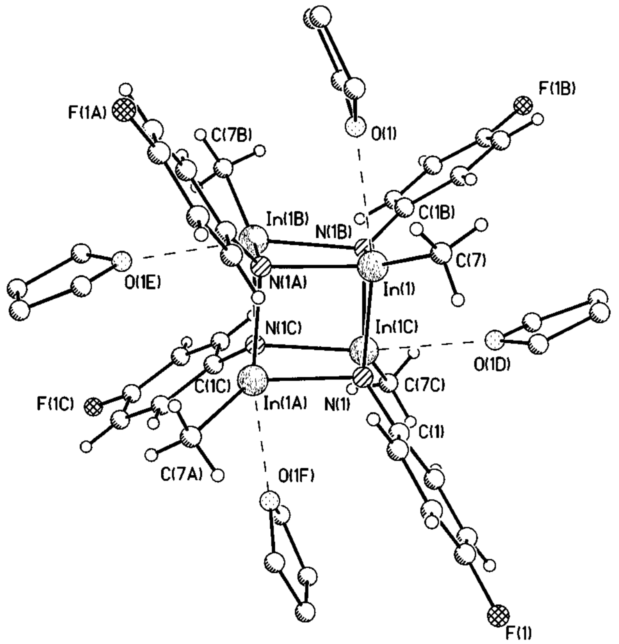

Figure 5. Crystal structure of **5**, with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

and 84.9°, respectively. These values are in good agreement with those observed for the related ((pentafluorophenyl)imino)methylindane[4b] (95.5 and 84.3°). The increased radius and soft character of the In atoms with respect to the Al ones account for the enhanced distortion of the cage with respect to that observed in compound **1a**. The In−N distances range from 2.136(5) to 2.279(5) Å. This difference is consistently bigger than that observed in the pentafluorophenyl analogue [In−N bond lengths in the range 2.167(1)−2.227(1) Å].[4b] This is most likely due to the presence of the coordinated THF molecule on each In atom. In fact of the three In−N bonds, the one trans to the THF molecule is the longest.

The In−O distance is 2.732(3) Å, which is relatively longer than those observed in other structurally characterized compounds showing In−THF interactions {2.257(9) Å in $InCl_3{\cdot}2THF$,[16] 2.414(4) Å in $InMes_3{\cdot}THF$,[17] and 2.309(5) and 2.416(5) Å in $[iPr_2In(THF)_2][BF_4]$}.[18]

Conclusions and Remarks

The introduction of fluorine into the 4-position of the phenyl ring resulted in new amino-based amino- and iminometallanes of group 13 that have unusual properties. Due to the lower basicity of the amine, the elimination of hydrocarbons occurred at lower temperatures giving products without major impurities. However, to our surprise, the stronger basic solvent (THF) gave hexameric **1b**·2THF while recrystallization from *n*-hexane afforded tetrameric **1a**. Obviously, in the more polar solvent (THF) the solubiltiy of the hexamer is less compared to the tetramer. It has to be taken in consideration however that the crystallization is a nonequilibrium process. The influence of the solvent has been nicely demonstrated by isolating the THF adduct of $(MeIn(THF)NR_f)_4$ **(5)**.

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Supporting Information Available: Tables of crystal data, non-hydrogen fractional coordinates and *U* values, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and *U* values of the structures **1a**, **1b**·2THF, **3**·7THF, and **5** (31 pages). Ordering information is given on any current masthead page.

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