

Synthesis and properties of pentafluorophenylgallium derivatives. The preparation of tris(pentafluorophenyl)gallium and its adducts, and of bis(pentafluorophenyl)gallium bromide, pentafluorophenylgallium dibromide, and tetrabutylammonium tetrakis(pentafluorophenyl)gallate *

Karl Ludovici, Wieland Tyrra and Dieter Naumann

Institut für Anorganische Chemie der Universität zu Köln, Greinstr. 6, W-5000 Köln 41 (Germany)

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Abstract

A complete series of mono-, bis-, tris- and tetrakis-(pentafluorophenyl)gallium compounds has been obtained from the reactions of GaCl_3 and GaBr_3 with $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$. The complexation behaviour of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ with N-donor molecules has been studied; 1:1 adducts with pyridine, diethylamine, tert/butyl amine and aniline as well as the uncomplexed $\text{Ga}(\text{C}_6\text{F}_5)_3$ and $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Ga}(\text{C}_6\text{F}_5)_4]$ have been obtained pure. All the compounds were characterized by NMR spectroscopy, mass spectrometry and elemental analysis, and some IR spectra were recorded.

Introduction

Although much is known about the synthesis and properties of organogallium derivatives [11] there have been only a few reports of perfluorinated analogues. The first perfluorinated organogallium derivative was prepared by Pohlmann and Brinckmann [2], who obtained $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ from the reaction of GaCl_3 with $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ in diethyl ether. Later, several groups made $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{As}(\text{C}_2\text{H}_5)_3$ [3] and $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{As}(\text{Si}(\text{CH}_3)_3)_3$ [4] by displacing the $(\text{C}_2\text{H}_5)_2\text{O}$ from the original complex by $\text{As}(\text{C}_2\text{H}_5)_3$ or $\text{As}(\text{Si}(\text{CH}_3)_3)_3$. The only mixed organoperfluoroorganogallium derivatives are $(\text{CH}_3)_2\text{Ga}(\text{C}_6\text{F}_5) \cdot \text{O}(\text{C}_2\text{H}_5)_2$ and the corresponding $\text{As}(\text{C}_2\text{H}_5)_3$ adduct [3].

Although the trifluoromethyl derivatives [5] as well as the phenyl derivatives of gallium [6] are well known and the pentafluorophenyl compounds of aluminium

Correspondence to: Professor D. Naumann.

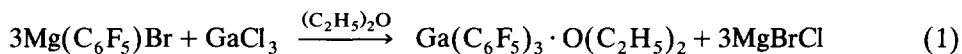
* Dedicated to Professor Ulrich Wannagat on the occasion of his 70th birthday.

and indium [7–10] have also been synthesized and characterized, neither pentafluorophenylgallium halides nor pentafluorophenylgallates have previously been reported. The work described below was carried out to complete this series.

Results and discussion

Preparation and characterization of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$

The adduct $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ was prepared by Pohlmann' and Brinckmann's method [2] (eq. 1).

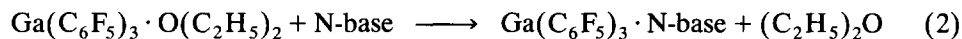


Only a melting point (169–171°C) and an elemental analysis were reported for the adduct. The white crystalline product we obtained melted at 241°C. This much higher melting point, together with a complete set of spectroscopic data suggests that $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ is pure. A crystal structure determination is in progress.

The mass spectra obtained at various electron energies reveal that in the first step, $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ loses diethyl ether. In a subsequent step $[\text{Ga}(\text{C}_6\text{F}_5)_3]^+$ undergoes fragmentation into $[\text{Ga}(\text{C}_6\text{F}_5)_2]^+$ and $[\text{C}_6\text{F}_5]^+$. Formation of $\text{Ga}(\text{C}_6\text{F}_5)$ fragments was not observed in any of the studies. The features of the mass spectra of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ are similar to those reported for the analogous non-fluorinated derivatives [6].

Reactions of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$

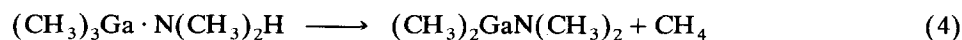
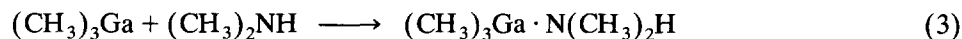
Exchange of the complex ligand. The reactions of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ with N-donor molecules such as amines or pyridine result in displacement of diethyl ether (eq. 2).



N-base: $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_6\text{H}_5\text{NH}_2$, $t\text{-C}_4\text{H}_9\text{NH}_2$, pyridine.

After evaporation of the excess of base, a crude solid was obtained which could be recrystallized from light petroleum. Stable light-yellow crystals were obtained in all cases.

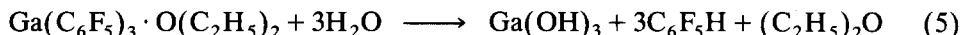
Dialkylamine complexes of unfluorinated trialkylgallium derivatives are known to react at higher temperature by cleavage of one carbon–gallium bond to give the corresponding dialkylgallium amide by loss of one alkane molecule [11–13] (eqs. 3 and 4).



In contrast to the reactions of the alkyl derivatives, tris(pentafluorophenyl)gallium amine complexes do not react with secondary or primary amines. Solutions of the amine adducts in boiling toluene contain no trace of pentafluorobenzene even after several days. Heating the neat complexes *in vacuo* does not give pentafluorophenylgallium amides, but at temperatures above the melting point an unselective decomposition occurs. We cannot at present account for this behaviour.

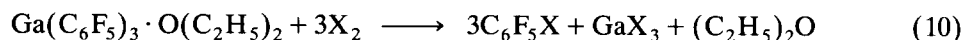
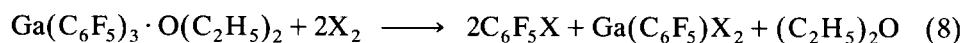
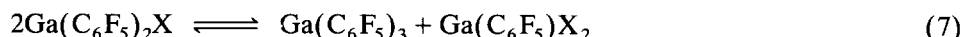
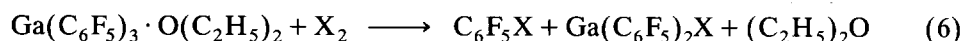
Hydrolysis. In acidic and basic aqueous solutions $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ is completely hydrolyzed within a few minutes to give $\text{Ga}(\text{OH})_3$ and $\text{C}_6\text{F}_5\text{H}$ without

any evidence of intermediates (eq. 5).



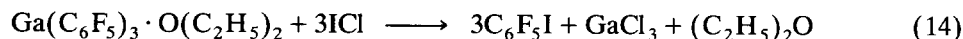
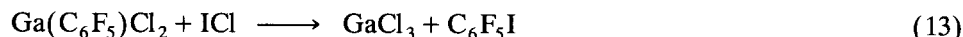
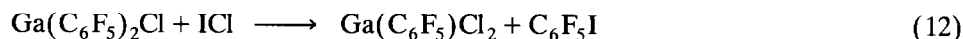
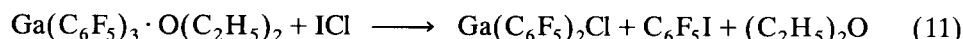
In contrast unfluorinated organogallium derivatives are partially hydrolyzed to give stable diorganogallium ions [12], but gallium trihalides, GaX_3 , are completely hydrolyzed to give $\text{Ga}(\text{OH})_3$ and HX [13]. Therefore the behaviour of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ towards water is more comparable with that of gallium trihalides than that of triorganogallium derivatives. This similarity is understandable on the assumption of comparable polarizations of the gallium-halogen bond in GaX_3 and the gallium-carbon bond in $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$.

Reactions with chlorine, bromine and iodine monochloride. The ^{19}F NMR spectra of the mixtures formed by treatment of the tris(pentafluorophenyl)gallium diethyl ether complex with a one molar equivalent of elemental chlorine or bromine show resonances from three pentafluorophenylgallium derivatives together with halogenopentafluorobenzene (Table 1). The resonances can be assigned to the corresponding mono- and bis-(pentafluorophenyl)gallium halides and tris(pentafluorophenyl)gallium. The $\text{Ga}(\text{C}_6\text{F}_5)_2\text{X}$ and $\text{Ga}(\text{C}_6\text{F}_5)\text{X}_2$ undergo redistribution to give finally $\text{Ga}(\text{C}_6\text{F}_5)_3$ and GaX_3 . (The redistribution was studied in the case of $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$ in toluene and basic aprotic solvents as outlined below.) When an excess of the halogen was used there was quantitative formation of the corresponding halogenopentafluorobenzene and the gallium trihalide (eqs. 6–10).

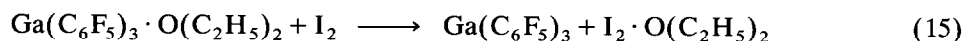


(X = Cl, Br)

A stepwise reaction also takes place in the reaction of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ with iodine monochloride (eqs. 11–14).



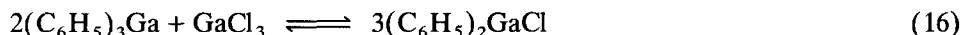
The reaction with elemental iodine. In contrast to the reactions of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ with Cl_2 , Br_2 and ICl , elemental iodine does not cause cleavage to give $\text{C}_6\text{F}_5\text{I}$. The reaction products were uncomplexed $\text{Ga}(\text{C}_6\text{F}_5)_3$ and an iodine-diethyl ether adduct (eq. 15).



The $\text{Ga}(\text{C}_6\text{F}_5)_3$ was isolated as colourless crystals with a melting point of 139°C . The ^{13}C NMR spectrum (Table 2) and the mass spectrum, as well as the elemental analysis, confirmed that the tris(pentafluorophenyl)gallium had been obtained in

an uncomplexed form. As expected, the uncomplexed derivative reacts with diethyl ether or pyridine to give a stable 1:1 adduct.

Redistribution reactions of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ with GaCl_3 . A convenient method of transforming triphenylgallium compounds into diphenylgallium halides involves redistribution with gallium trihalides [14] (eq. 16).



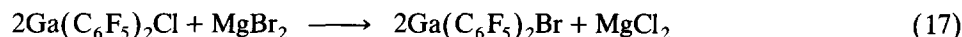
The analogous reaction for the pentafluorophenyl system led to exclusive formation of $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Cl}$ in CH_2Cl_2 solution, but exact stoichiometry and very long reaction time were required. Further attempts to obtain $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Cl}$ by the same method in other solvents were unsuccessful. In toluene, pentane or hexane, mixture containing $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Cl}$ and $\text{Ga}(\text{C}_6\text{F}_5)\text{Cl}_2$ along with the starting materials were obtained.

The reaction with HCl yielded only $\text{C}_6\text{F}_5\text{H}$ and GaCl_3 . Monitoring by ^{19}F NMR spectroscopy revealed only conversion of the starting material, $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ into the final product, $\text{C}_6\text{F}_5\text{H}$, with no evidence for the intermediates, $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Cl}$ or $\text{Ga}(\text{C}_6\text{F}_5)\text{Cl}_2$.

Preparation of $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$

As the pentafluorophenylgallium halides $\text{Ga}(\text{C}_6\text{F}_5)_2\text{X}$ and $\text{Ga}(\text{C}_6\text{F}_5)\text{X}_2$ could not be prepared by treatment of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ with halogens a new route was developed based on a controlled reaction with the appropriate Grignard reagent. The adduct $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ is formed quantitatively upon addition of GaCl_3 to a solution of $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ but it seems to be too stable to be completely transformed into $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Cl}$ by treatment with excess GaCl_3 . This is also the case when redistribution reactions are carried out separately. The formation of a bis(pentafluorophenyl)gallium derivative must therefore be brought about by kinetically controlled process. Thus a solution of $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ in $(\text{C}_2\text{H}_5)_2\text{O}$ was added dropwise to one of GaCl_3 in toluene and during the reaction $(\text{C}_2\text{H}_5)_2\text{O}$ was continually distilled off. In this way bis(pentafluorophenyl)gallium bromide, $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$, was isolated in 21% yield.

$\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$ is a white, air- and moisture-insensitive amorphous solid melting at $115\text{--}117^\circ\text{C}$ without decomposition. It was a surprise that the product was the bromide and not the expected chloride, but this can be attributed to the fact that the energy of the Mg--Cl bond is higher than that of the Mg--Br bond [15] (eq. 17).

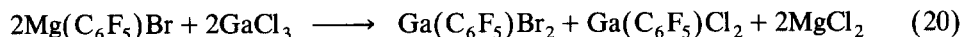
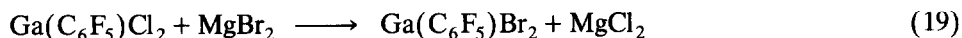


In toluene or basic aprotic solvents $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$ undergoes a slow dismutation to give $\text{Ga}(\text{C}_6\text{F}_5)_3$ and, finally, GaBr_3 . From the ^{13}C NMR spectra (Table 2) and the mass spectrum it is obvious that $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$ can be obtained in an uncomplexed form. The compound forms a stable 1:1 adduct with pyridine, and this was isolated and characterized spectroscopically and by elemental analysis.

Preparation of $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}_2$

Pentafluorophenylgallium dibromide was prepared by a similar method to that described above for $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$. It is important to use gallium tribromide instead

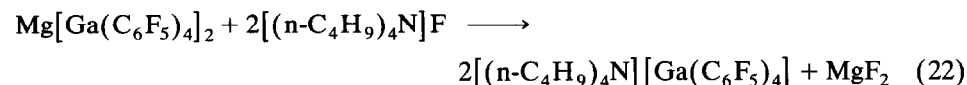
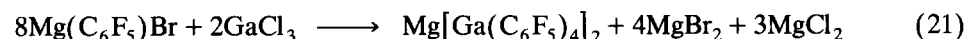
of the chloride as a starting material for this reaction because the use of GaCl_3 leads to a 1:1 mixture of $\text{Ga}(\text{C}_6\text{F}_5)\text{Br}_2$ and $\text{Ga}(\text{C}_6\text{F}_5)\text{Cl}_2$ (eqs. 18–20).



A 1:1-mixture of $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ and GaBr_3 gave the expected product, $\text{Ga}(\text{C}_6\text{F}_5)\text{Br}_2$. Because it is nearly insoluble in toluene, it was impossible to separate $\text{Ga}(\text{C}_6\text{F}_5)\text{Br}_2$ from the magnesium salts and obtain the compound in an uncomplexed form. After addition of pyridine to the precipitate, the adduct $\text{Ga}(\text{C}_6\text{F}_5)\text{Br}_2 \cdot \text{NC}_5\text{H}_5$ was isolated in 17% yield as a light-brown, air- and moisture-insensitive amorphous solid, which melts at 113°C and resolidifies unchanged on cooling.

Preparation of $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Ga}(\text{C}_6\text{F}_5)_4]$

The reaction of $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ with GaCl_3 in a molar ratio of 4:1 yielded $\text{Mg}[\text{Ga}(\text{C}_6\text{F}_5)_4]_2$. The latter could not be separated from the magnesium halides because the solubilities of $\text{Mg}[\text{Ga}(\text{C}_6\text{F}_5)_4]_2$, MgCl_2 , and MgBr_2 are too similar. However, addition of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{F}$ to the mixture gave $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Ga}(\text{C}_6\text{F}_5)_4]$ and MgF_2 . The salt $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Ga}(\text{C}_6\text{F}_5)_4]$ is readily soluble in organic solvents, whereas MgF_2 is insoluble (eqs. 21 and 22).



Comparison of the ^{71}Ga NMR data (Table 3) for $[\text{Ga}(\text{C}_6\text{F}_5)_4]^-$ with those for tetrahalogenogallates and $[\text{Ga}(\text{CF}_3)_4]^-$ shows that the electron densities at the gallium central atom are rather similar in both. The linewidth of approximately 3000 Hz may be related to the distorted tetrahedral molecular geometry, since the presence of four C_6F_5 groups prevents free rotation of all the pentafluorophenyl-groups around the $\text{Ga}-\text{C}(\text{ipso})$ bond. This distorted symmetry can also be deduced from the ^{19}F NMR spectra; the resonances of the 2,6-fluorine atoms are broadened due to the slowing of the quadrupole relaxation of the ^{69}Ga and ^{71}Ga nuclei and the resulting spin-spin interaction of the 2,6 fluorine atoms with the central gallium atom. Similar effects were observed for the isoelectronic $\text{Ge}(\text{C}_6\text{F}_5)_4$ [16].

Experimental

NMR spectra. Bruker FT NMR spectrometer AC-F 200; ^{19}F NMR: 188.3 MHz, ^{13}C NMR: 50.4 MHz. Bruker FT NMR spectrometer AMX 300; ^{71}Ga NMR: 91.5 MHz. Standards: CCl_3F (ext., ^{19}F), $\text{Si}(\text{CH}_3)_4$ (ext., ^{13}C), 1 M $\text{Ga}(\text{NO}_3)_3/\text{D}_2\text{O}$ (ext., ^{71}Ga). The NMR data are summarized in Tables 1–3. A negative chemical shift denotes a shift to low frequency (high field) of the reference compound.

Melting points. A HWS Mainz SG 2000 melting point apparatus, with samples in one-end open glass capillaries.

Table 1

¹⁹F NMR chemical shifts for pentafluorophenylgallium compounds

Compound	Solvent	$\delta(2,6-F)$	$\delta(3,5-F)$	$\delta(4-F)$
Ga(C ₆ F ₅) ₃	toluene	-125.1	-159.0	-148.4
Ga(C ₆ F ₅) ₃ ·O(C ₂ H ₅) ₂	toluene	-124.7	-161.2	-152.3
Ga(C ₆ F ₅) ₃ ·NH(C ₂ H ₅) ₂	toluene	-123.9	-160.5	-152.3
Ga(C ₆ F ₅) ₃ ·NH ₂ (C ₆ H ₅)	toluene	-123.5	-161.0	-152.9
Ga(C ₆ F ₅) ₃ ·NH ₂ (t-C ₄ H ₉)	toluene	-124.2	-160.0	-151.7
Ga(C ₆ F ₅) ₃ ·NC ₅ H ₅	CH ₃ CN	-124.1	-162.3	-156.2
Ga(C ₆ F ₅) ₂ Br	toluene	-123.7	-160.8	-151.8
Ga(C ₆ F ₅) ₂ Br·NC ₅ H ₅	CH ₃ CN	-123.7	-162.1	-156.4
Ga(C ₆ F ₅)Br ₂ ·NC ₅ H ₅	CH ₃ CN	-123.4	-163.8	-157.2
[(n-C ₄ H ₉) ₄ N][Ga(C ₆ F ₅) ₄]	toluene	-125.9	-167.3	-162.2

Table 2

¹³C NMR chemical shifts for some pentafluorophenylgallium derivatives

Compound	$\delta(1-C)$	$\delta(2,6-C)$	$\delta(3,5-C)$	$\delta(4-C)$
Ga(C ₆ F ₅) ₃ ^a	108.1	148.2	142.3	137.0
Ga(C ₆ F ₅) ₃ ·O(C ₂ H ₅) ₂ ^{a,b}	112.5	148.9	142.0	134.3
Ga(C ₆ F ₅) ₂ Br ^a	126.4	148.2	143.5	136.7
Ga(C ₆ F ₅) ₂ Br·NC ₅ H ₅ ^{c,d}	125.3	149.0	141.1	134.0
Ga(C ₆ F ₅)Br ₂ ·NC ₅ H ₅ ^{c,e}	126.0	148.2	141.1	134.0
[(C ₄ H ₉) ₄ N][Ga(C ₆ F ₅) ₄] ^{c,f}	121.5	149.8	141.0	137.1

^a Solvent CDCl₃. ^b Chemical shifts of complexing (C₂H₅)₂O: δ (OCH₂) 78.3 ppm; δ (CH₃) 13.1 ppm.^c Solvent CD₃CN. ^d Chemical shifts of complexing C₅H₅N: δ (2,6-C) 146.2 ppm; δ (3,5-C) 142.5 ppm; δ (4-C) 126.6 ppm. ^e Chemical shifts of complexing C₅H₅N: δ (2,6-C) 146.0 ppm; δ (3,5-C) 143.0 ppm; δ (4-C) 126.9 ppm. ^f Chemical shifts of the [(n-C₄H₉)₄N]⁺ cation: δ (α -CH₂) 59.2 ppm; δ (β -CH₂) 24.3 ppm; δ (γ -CH₂) 20.5 ppm; δ (CH₃) 13.5 ppm.

Table 3

⁷¹Ga NMR data for some gallates

Gallate	Solvent	$\delta(^{71}\text{Ga})$ (ppm)	Line width (Hz)
[GaCl ₄] ⁻ ^a	H ₂ O/HCl	+257	100
[Ga(C ₆ F ₅) ₄] ⁻	CD ₃ CN	+221	≈ 3000
[Ga(CF ₃) ₄] ⁻ ^b	CD ₃ CN	+171	high-resolved
[GaBr ₄] ⁻ ^a	H ₂ O/HBr	+69	100
[GaI ₄] ⁻ ^a	H ₂ O/HI	-450	100

^a From ref. 19. ^b From ref. 5.**Elemental analysis.** Ga, as described in ref. 17; F, as in ref. 18; Br, as in ref. 19.**IR and mass spectra.** Perkin-Elmer PE 580 B spectrometer and modified Varian MAT CH 5 respectively.**Preparations.** All reactions were carried out under dry nitrogen. Solvents were purified and dried by standard methods. GaBr₃ was prepared as described [20]. Mg(C₆F₅)Br was prepared in diethyl ether solution as described [2]. All other

Table 4

Yields, melting points and elemental analyses for the $\text{Ga}(\text{C}_6\text{F}_5)_3$ -derivatives

Compound	Yield (%)	m.p. (°C)	Elemental analysis (Found (calc.) (%))	
			Ga	F
$\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$	15 ^a	241	10.8 (10.8)	44.1 (44.2)
$\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{NH}(\text{C}_2\text{H}_5)_2$	65 ^b	143	10.8 (10.8)	44.0 (44.3)
$\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{NH}_2(\text{C}_6\text{H}_5)$	60 ^b	123	10.3 (10.5)	42.8 (42.9)
$\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{NH}_2(\text{t-C}_4\text{H}_9)$	70 ^b	176	10.7 (10.8)	43.8 (44.3)
$\text{Ga}(\text{C}_6\text{F}_5)_3$	90 ^b	139	12.2 (12.2)	45.0 (44.9)
$\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$ ^c	21 ^a	ca. 116	14.5 (14.4)	39.4 (39.3)
$\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br} \cdot \text{NC}_5\text{H}_5$ ^d	75 ^e	ca. 80	12.4 (12.2)	33.8 (33.6)
$\text{Ga}(\text{C}_6\text{F}_5)\text{Br}_2 \cdot \text{NC}_5\text{H}_5$ ^f	17 ^g	ca. 113	14.1 (14.6)	19.6 (19.9)
$[(\text{n-C}_4\text{H}_9)_4\text{N}][\text{Ga}(\text{C}_6\text{F}_5)_4]$	25 ^a	147	7.0 (7.1)	38.5 (38.7)

^a Rel. to GaCl_3 . ^b Rel. to $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. ^c Br: 16.1 (16.5%). ^d Br: 14.2 (14.4%). ^e Rel. to $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$. ^f Br: 31.8 (33.2%). ^g Rel. to GaBr_3 .

chemicals were purchased from Strem Chemicals (GaCl_3 , Ga), Yarsley Chemicals ($\text{C}_6\text{F}_5\text{Br}$), Merck (Mg), Riedel de Haen (Br_2) and Fluka (I_2 , $[(\text{n-C}_4\text{H}_9)_4\text{N}]\text{F}$).

The yields, melting points and elemental analyses are summarized in Table 4.

Preparation of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$

A solution of 17.0 mmol of $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ in 50 ml of $(\text{C}_2\text{H}_5)_2\text{O}$ was added dropwise with stirring during 10 min to a solution of 1.0 g (5.7 mmol) of GaCl_3 in 50 ml of toluene at -30°C . After 1 h stirring of the mixture at room temperature the temperature was raised to 100°C and kept there for an additional 2 h. The ether was then distilled off over a period of 3 h; grey magnesium halides separated and the solution became transparent and light-brown. The magnesium salts were filtered off hot and toluene distilled from the filtrate. The residual dark-brown solid was extracted with low-boiling light petroleum, from which $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ crystallized as fine colourless needles, m.p. 241°C .

Mass spectrum of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (only ^{69}Ga -containing fragments and base peak; 20 eV, 120°C , m/e): 570 ($[\text{Ga}(\text{C}_6\text{F}_5)_3]^+$; 100%); 477 ($[\text{Ga}(\text{C}_6\text{F}_5)_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2]^+$; 3%); 403 ($[\text{Ga}(\text{C}_6\text{F}_5)_2]^+$; 33%).

IR spectrum of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (Nujol): 490 w, 615w, 720 w, 855 w, 960 vs, 1008 w, 1055 s, 1070 s, 1273 w, 1368 vs, 1512 s, 1640 s, 2900 vs.

Preparation of 1:1 complexes of $\text{Ga}(\text{C}_6\text{F}_5)_3$ with N-donors

The adduct $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ was dissolved in freshly-distilled $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{t-C}_4\text{H}_9\text{NH}_2$, aniline, or pyridine at room temperature. After 1 hour the excess of amine was distilled off *in vacuo* and the residual complex was recrystallized from petroleum ether.

Mass spectrum of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{NH}(\text{C}_2\text{H}_5)_2$ (only ^{69}Ga -containing fragments and base peak; 20 eV, 180°C , m/e): 643 ($[\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{NH}(\text{C}_2\text{H}_5)_2]^+$; 35%), 570 ($[\text{Ga}(\text{C}_6\text{F}_5)_3]^+$; 40%), 167 ($[\text{C}_6\text{F}_5]^+$; 100%).

Mass spectrum of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{t-C}_4\text{H}_9\text{NH}_2$ (16 eV, 180°C , m/e): 570 ($[\text{Ga}(\text{C}_6\text{F}_5)_3]^+$; 40%), 476 ($[\text{Ga}(\text{C}_6\text{F}_5)_2 \cdot \text{t-C}_4\text{H}_9\text{NH}_2]^+$; 50%), 403 ($[\text{Ga}(\text{C}_6\text{F}_5)_2]^+$; 40%), 58 ($[\text{C}_4\text{H}_{10}]^+$; 100%).

Mass spectrum of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot (\text{C}_6\text{H}_5)\text{NH}_2$ (17 eV, 180°C, m/e): 570 ($[\text{Ga}(\text{C}_6\text{F}_5)_3]^+$; 50%), 403 ($[\text{Ga}(\text{C}_6\text{F}_5)_2]^+$; 40%), 93 ($[(\text{C}_6\text{H}_5)\text{NH}_2]^+$; 100%).

Preparation of non-complexed $\text{Ga}(\text{C}_6\text{F}_5)_3$

A solution of 0.30 g (0.46 mmol) of $\text{Ga}(\text{C}_6\text{F}_5)_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ and 0.12 g (0.47 mmol) of I_2 in 10 ml of toluene was boiled and the solvent and the iodine etherate condensed *in vacuo*. The residue was recrystallized from light petroleum to give $\text{Ga}(\text{C}_6\text{F}_5)_3$ as colourless crystals, m.p. 139°C.

Mass spectrum of $\text{Ga}(\text{C}_6\text{F}_5)_3$ (only ^{69}Ga -containing fragments and base peak; 20 eV, 100°C, m/e): 570 ($[\text{Ga}(\text{C}_6\text{F}_5)_3]^+$; 100%), 403 ($[\text{Ga}(\text{C}_6\text{F}_5)_2]^+$; 80%).

Preparation of $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$

GaCl_3 (1.00 g, 5.7 mmol) was dissolved in boiling toluene and a solution of 11.3 mmol of $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ in diethyl ether was added dropwise as the ether was continuously distilled off. After 2 h the magnesium salts were filtered off from the hot light-brown solution. Cooling of the filtrate to room temperature gave a precipitate of $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$ as a white amorphous powder.

Mass spectrum of $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$ (only ^{69}Ga - and ^{81}Br -containing fragments and base peak; 20 eV, 120°C, m/e): 570 ($[\text{Ga}(\text{C}_6\text{F}_5)_3]^+$; 1%), 484 ($[\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}]^+$; 4%), 403 ($[\text{Ga}(\text{C}_6\text{F}_5)_2]^+$; 4%), 398 ($[\text{Ga}(\text{C}_6\text{F}_5)\text{Br}_2]^+$; 2%), 317 ($[\text{Ga}(\text{C}_6\text{F}_5)\text{Br}]^+$; 3%), 167 ($[\text{C}_6\text{F}_5]^+$; 100%).

IR spectrum of $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}_2$ (Nujol): 240 w, 270 w, 290 w, 430 s, 490 w, 610 w, 650 s, 690 s, 760 w, 800 s, 960 s, 1020 w, 1070 s, 1160 w, 1220 w, 1260 w, 1510 s, 1620 s, 1640 s.

Preparation of $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br} \cdot \text{NC}_5\text{H}_5$

$\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br}$ (0.50 g, 1.03 mmol) was dissolved in 5 ml of freshly distilled pyridine at ambient temperature. After 1 hour the excess of pyridine was distilled off *in vacuo* and the brown residue recrystallized from light petroleum to give $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br} \cdot \text{NC}_5\text{H}_5$ as a pale-brown solid in 75% yield.

Mass spectrum of $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br} \cdot \text{NC}_5\text{H}_5$ (only ^{69}Ga - and ^{81}Br -containing fragments and base peak; 20 eV, 150°C, m/e): 570 ($[\text{Ga}(\text{C}_6\text{F}_5)_3]^+$; 1%), 563 ($[\text{Ga}(\text{C}_6\text{F}_5)_2\text{Br} \cdot \text{NC}_5\text{H}_5]^+$; 2%), 482 ($[\text{Ga}(\text{C}_6\text{F}_5)_2 \cdot \text{NC}_5\text{H}_5]^+$; 3%), 403 ($[\text{Ga}(\text{C}_6\text{F}_5)_2]^+$; 2%), 310 ($[\text{GaBr}_2 \cdot \text{NC}_5\text{H}_5]^+$; 8%), 231 ($[\text{GaBr}_2]^+$; 2%), 167 ($[\text{C}_6\text{F}_5]^+$; 20%), 79 ($[\text{C}_5\text{H}_5\text{N}]^+$; 100%).

Preparation of $\text{Ga}(\text{C}_6\text{F}_5)\text{Br}_2 \cdot \text{NC}_5\text{H}_5$

GaBr_3 (1.76 g, 5.7 mmol) was dissolved in boiling toluene. A solution of 5.7 mmol of $\text{Mg}(\text{C}_6\text{F}_5)\text{Br}$ was dropped as the diethyl ether was continuously distilled off. The mixture was then stirred for 2 h at 100°C, then 0.46 ml (5.7 mmol) of pyridine was added and the mixture was stirred for 60 min. The magnesium halides were filtered off from the hot suspension, and $\text{Ga}(\text{C}_6\text{F}_5)\text{Br}_2 \cdot \text{NC}_5\text{H}_5$ separated from the filtrate as a pale-brown solid.

Mass spectrum of $\text{Ga}(\text{C}_6\text{F}_5)\text{Br}_2 \cdot \text{NC}_5\text{H}_5$ (only ^{69}Ga - and ^{81}Br -containing fragments and base peak; 20 eV, 60°C, m/e): 398 ($[\text{Ga}(\text{C}_6\text{F}_5)\text{Br}_2]^+$; 21%), 312 ($[\text{GaBr}_3]^+$; 11%), 79 ($[\text{C}_5\text{H}_5\text{N}]^+$; 100%).

Preparation of $[(n-C_4H_9)_4N][Ga(C_6F_5)_4]$

A solution of 22.8 mmol of $Mg(C_6F_5)Br$ in $(C_2H_5)_2O$ was added dropwise during 10 min to a well-stirred solution of 1.0 g (5.7 mmol) of $GaCl_3$ in toluene at $-30^\circ C$. The mixture was warmed to room temperature, stirred for 1 h at ambient temperature, and heated under reflux for 1 h, and the ether was then distilled off over a period of 3 h to leave a brown suspension. Water was added to the suspension at room temperature and the mixture stirred for 1 h. The layers were then separated and 2.96 g (11.4 mmol) of $[(n-C_4H_9)_4N]F$ and 10 ml of $(C_2H_5)_2O$ were added to the aqueous layer and this mixture was stirred for 2 h at room temperature. The ether layer was then separated and dried over $CaCl_2$. After evaporation of a small amount of the $(C_2H_5)_2O$ light-brown crystals of $[(n-C_4H_9)_4N][Ga(C_6F_5)_4]$ separated. No further purification was necessary.

Mass spectra of $[(n-C_4H_9)_4N][Ga(C_6F_5)_4]$ obtained at 20 eV and $180^\circ C$ show the typical fragments of $Ga(C_6F_5)_3$ and $[(n-C_4H_9)_4N]^+$.

IR spectrum of $[(n-C_4H_9)_4N][Ga(C_6F_5)_4]$ (Nujol): 370 vw, 490 w, 720 vw, 740 vw, 790 vw, 885 w, 955 vs, 1035 s, 1060 w, 1070s, 1260 w, 1355 s, 1510 s, 1640 w.

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