The First 1,1′-Digallylferrocene and a Rodlike, Polymeric Donor−Acceptor Complex: Synthesis, Properties, and Structure of $[Fe(\eta^5-C_5H_4GaMe_2)_2]_n$ and $[Fe(\eta^5-C_5H_4GaMe_2)_2(C_{12}H_8N_2)]_n$[†,1]

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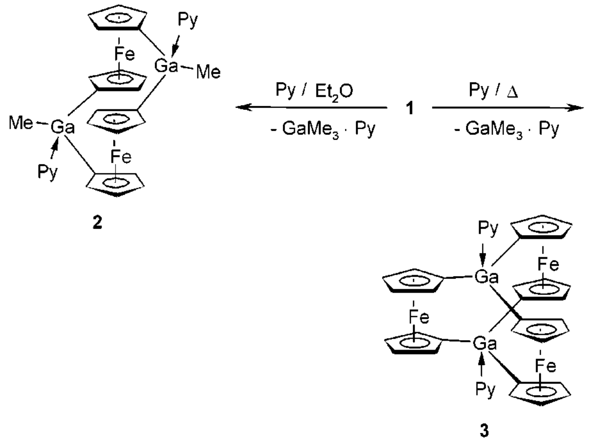
The reaction of 1,1′-bis(trichlorostannyl)ferrocene with trimethylgallium results in the formation of $Fe(C_5H_4GaMe_2)_2$ (**1**), the first digallylferrocene. An X-ray crystal structure analysis of **1** reveals a polymeric structure. NMR data confirm a monomeric structure of [**1**·2 donor] in donor solvents. The reaction of **1** with phenazine results in the formation of the supramolecular polyferrocene [**1**·phenazine]$_n$. Its rodlike structure is proven by X-ray crystallography.

Introduction

Although ferrocene chemistry is by now a well-developed area, the literature reveals only a few ferrocene derivatives bearing group 13 element alkyl substituents. Among these are two ferrocenylboranes, $(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4BMe_2)$ and $Fe(\eta^5-C_5H_4BMe_2)_2$,[1,2] and a few ferrocenylalanes, $[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_3Al_2Me_3Cl)]_2$ and $(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4Al_2R_4Cl)$ (R = Me, Et).[3] Only two ferrocenylgallanes have been reported, $[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4GaMe_2)]_2$ and $\{(\eta^5-C_5H_5)Fe[\eta^5-C_5H_3(GaMe_2)(CH_2NMe_2)]\}_2$;[4] these compounds were shown by X-ray crystallography to consist of molecular species in the solid state. Until recently ferrocene derivates with ElR_2 groups (El = Al, Ga, In, Tl) in 1,1′-position were unknown. In a preliminary report, we have described 1,1′-bis(dimethylgallyl)ferrocene **1** as a starting material for the synthesis of the novel gallaferrocenophanes [**2**·2Py] and [**3**·2Py] (eq 1).[5] Complex [**2**·2Py] is the first [1.1]ferrocenophane with group 13 elements in the bridging positions. [**3**·2Py] is the first member of a new class of compounds with a "carousel structure". Note that since we published the synthesis of [**2**·2Py], the alkylgallium-bridged [1.1]ferrocenophane $[\{Fe(C_5H_4)_2\}_2\{GaCH(SiMe_3)_2\}_2]$ has also been reported.[6]



(1)

The favorable electrochemical properties make ferrocene molecules especially promising candidates for the incorporation into polymer chains. Such materials have been shown to possess interesting electrical, magnetic, and optical properties as a result of electron delocalization.[7] So far, four major pathways to poly(ferrocenes) have been developed: polycondensation reactions using difunctional ferrocenes,[7] the polymerization of ferrocene derivatives bearing polymerizable substituents,[7] thermal[8] or catalytic[9] ring-opening polymerization of strained [1]- and [2]-ferrocenophanes, and coordination polymer synthesis.[10] The last method is based on the formation of donor−acceptor bonds between difunctional nitrogen

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[†] Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday.

[1] Herein we use the terms "gallyl" and "galla" (analogous to corresponding terms, e.g., for the element tin "stannyl", "stanna"), which are not recommended in the IUPAC rules for the nomenclature of organometallic compounds.

[2] (a) Renk, T.; Ruf, W.; Siebert, W. *J. Organomet. Chem.* **1976**, *120*, 1. (b) Renk, T.; Ruf, W.; Siebert, W. *Z. Naturforsch.* **1976**, *31b*, 1028.

[3] (a) Atwood, J. L.; Bailey, B. L.; Kindberg, B. L.; Cook, W. J. *Aust. J. Chem.* **1973**, *26*, 2297. (b) Atwood, J. L.; Shoemaker; A. L. *J. Chem. Soc., Chem. Commun.* **1976**, 536. (c) Rogers, R. D.; Cook, W. J.; Atwood, J. L. *Inorg. Chem.* **1979**, *18*, 279. (d) Robinson, G. H.; Bott, S. G.; Atwood, J. L. *J. Coord. Chem.* **1987**, *16*, 219.

[4] (a) Lee, B.; Pennington, W. T.; Laske, J. A.; Robinson, G. H. *Organometallics* **1990**, *9*, 2864. (b) Hecht, E. *Z. Anorg. Allg. Chem.* **2000**, *626*, 759.

[5] Jutzi, P.; Lenze, N.; Neumann, B.; Stammler, H.-G. *Angew. Chem.* **2001**, *113*, 1470; *Angew. Chem., Int. Ed.* **2001**, *40*, 1424.

[6] Uhl, W.; Hahn, I.; Jantschak, A.; Spies, T. *J. Organomet. Chem.* **2001**, *637−639*, 300.

[7] Manners, I. *Angew. Chem.* **1996**, *108*, 1712; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.

[8] (a) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246. (b) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131.

[9] Sheridan, J. B.; Temple, K.; Lough, A. J.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1997**, 711.

[10] (a) Fontani, M.; Peters, F.; Scherer, W.; Wachter, W.; Wagner, M.; Zanello, P. *Eur. J. Inorg. Chem.* **1998**, 1453. (b) Grosche, M.; Herdtweck, E.; Peters, F.; Wagner, M. *Organometallics* **1999**, *18*, 4669. (c) Dinnebier, R. E.; Wagner, M.; Peters, F.; Shankland, K. David, W. I. F. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1400.

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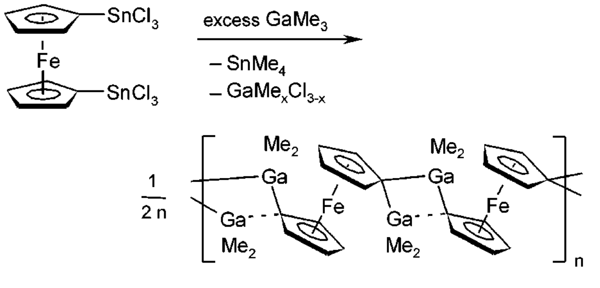
bases and $Fe(\eta^5\text{-}C_5H_4BMe_2)_2$ units. Among these substances, the compounds $[Fe(\eta^5\text{-}C_5H_4BMe_2)_2L]_n$ (L = 4,4′-bipyridyl and pyrazine) have been structurally characterized.[10b,c] We were interested in finding new ferrocene-based precursors for the formation of novel coordination polymers.

Results and Discussion

Synthesis of 1,1′-Bis(dimethylgallyl)ferrocene (1). Compound 1,1′-bis(dimethylgallyl)ferrocene **1** was prepared in good yield as an orange solid by the reaction of 1,1′-bis(trichlorostannyl)ferrocene with an excess of trimethylgallium (eq 2).[5,11] **1** is sparingly soluble in nondonor solvents and is extremely air sensitive. In the reaction mixture, methylgallium chlorides and tetramethylstannane were identified by NMR spectroscopy.



(2)

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Two possible reaction pathways may be discussed. The first begins with the substitution of $SnCl_3$ by $GaMe_2$ groups with elimination of trichloromethylstannane. In the next steps trichloromethylstannane reacts with excess trimethylgallium to form methylgallium chlorides and tetramethylstannane. The other possible reaction sequence begins with the methylation of 1,1′-bis(trichlorostannyl)ferrocene to 1,1′-bis(trimethylstannyl)ferrocene, followed by a substitution of the $SnMe_3$ by $GaMe_2$ groups. We could show in a separate control that trimethylgallium does not react with 1,1′-bis(trimethylstannyl)ferrocene. Thus we can exclude this pathway. The first step in the observed sequence corresponds to an electrophilic substitution reaction at a trichlorostannyl-substituted carbon center of the ferrocene unit.

Structural Features of 1. Yellow-orange crystals of **1** were grown from toluene/trimethylgallium solution at room temperature. **1** crystallizes in the triclinic space group $P\bar{1}$. The compound is a polymer that consists of ferrocenediyl fragments bridged by $GaMe_2$ groups. The molecular $Fe(C_5H_4GaMe_2)_2$ units are present in trans-conformation; this orientation allows the formation of polymer strands which are arranged parallel to each other and which are aligned parallel to the crystallographic *a*-axis. Each strand is surrounded by six other strands. A drawing of the structure of **1** including the unit cell is presented in Figure 1; two molecular $Fe(C_5H_4GaMe_2)_2$ units from the polymeric structure of **1** are presented in Figure 2 as thermal ellipsoid plots. Crystallographic data for **1** are collected in Table 1; selected bond length and bond angles are given in Table 2.

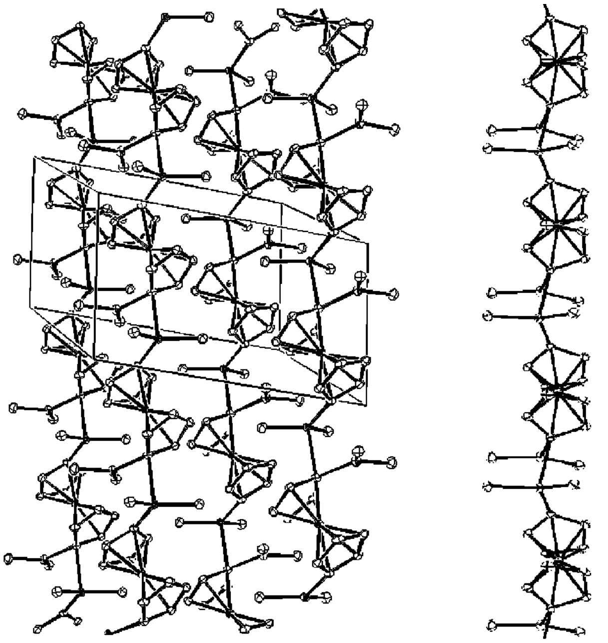

Figure 1. Solid state structure of **1**, including the unit cell.

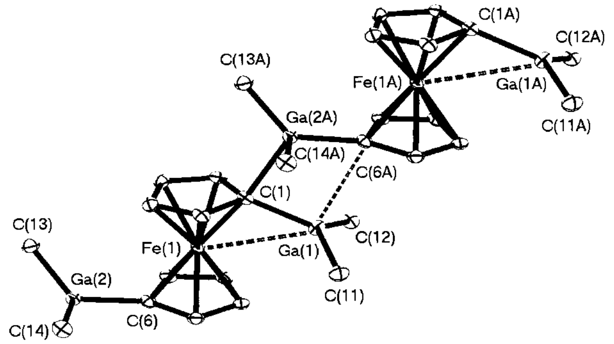

Figure 2. Part of the solid state structure of **1**, thermal ellipsoids at 50% probability.

It is interesting to regard in more detail the bridging $GaMe_2$ units in order to compare the bonding situation in polymeric **1** with that of dimeric $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{-}GaMe_2)]_2$.[4a] In the latter, two ferrocenyl groups are bridged by two $GaMe_2$ units via carbon atoms of the substituted cyclopentadienyl ring. A closer inspection shows the presence of a weakly bonded dimer with two short (1.992(5) Å) and two long (2.587(5) Å) Ga–C bonds. In contrast, an even more weakly bonded dimer with a highly asymmetric Ga_2C_2 unit is present in **1** (see Figure 2). The Ga–Ga distance of 3.044 Å does not indicate significant metal–metal interaction.

Regarding the Ga(1)Me_2 group a strong bending of the Ga(1)–C(1) vector out of the Cp plane (dip angle $\alpha = 25.7°$; see Figure 3) is observed. The Ga(1)–Fe(1) distance of 3.112(3) Å indicates attractive interactions between the electron-rich Fe(1) atom and the electron-deficient Ga(1) atom (empty p orbital). The Fe–Ga interaction can be compared with Fe–B interactions in borylferrocenes[12] and with Fe–C^+ interactions in ferrocenyl carbocations[13] (Table 3). In comparison, the Ga(1)–C(1) vector of **1** shows the greatest dip angle. The

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(11) An excess of trimethylgallium has been used to inhibit thermolysis reaction of **1** by elimination of trimethylgallium.[5]

(12) (a) Wrackmeyer, B.; Dörfler, U.; Milius, W.; Herberhold, M. *Polyhedron* **1995**, *11*, 1425. (b) Appel, A.; Jäkle, F.; Priemeier, T.; Schmid, R.; Wagner, M. *Organometallics* **1996**, *15*, 1188.

Table 1. Crystallographic Data for 1 and [1·Phenazine]$_n$

	1	[**1**·phenazine]
empirical formula	$C_{14}H_{20}FeGa_2$	$C_{26}H_{28}FeGa_2N_2$
fw	383.59	563.79
cryst color, habit	yellow-orange needles	green plate
cryst size, mm^3	0.16 × 0.06 × 0.04	0.27 × 0.12 × 0.02
temperature, K	100(2)	100(2)
wavelength, Å	0.71073	0.71073
cryst syst, space group	triclinic $P\bar{1}$	triclinic $P\bar{1}$
unit cell dimens	$a = 7.28300(10)$ Å $b = 8.7910(2)$ Å $c = 12.3490(3)$ Å $\alpha = 74.3810(8)°$ $\beta = 82.8000(8)°$ $\gamma = 68.5920(10)°$	$a = 7.5320(5)$ Å $b = 8.9050(5)$ Å $c = 9.7850(6)$ Å $\alpha = 64.861(4)°$ $\beta = 76.416(3)°$ $\gamma = 73.120(3)°$
volume, Å^3	708.59(3)	563.81(6)
Z	2	1
density (calcd), Mg/m^3	1.798	1.660
θ range for data collection, deg	3.01−29.95	3.27−24.96
no. of reflns collected	8073	3657
no. of indep reflns	4101 ($R_{int} = 0.0304$)	1947 ($R_{int} = 0.049$)
final R indices [$I > 2\sigma(I)$]	R1 = 0.0293, wR2 = 0.0576	R1 = 0.0370, wR2 = 0.0798
no. of reflns with $I > 2\sigma(I)$	3199	1537
R indices (all data)	R1 = 0.0488, wR2 = 0.0632	R1 = 0.0539, wR2 = 0.0869
no. of params	234	144
largest diff peak and hole, e Å^{-3}	0.837 and −0.5	0.426 and −0.481
remarks	hydrogens were refined isotropically	

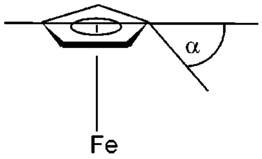


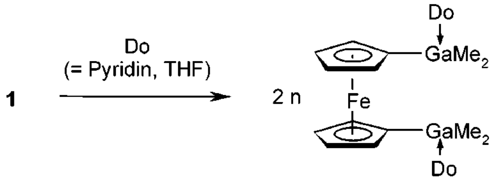
Figure 3. Dip angle α.

Ga(1)−C(1) bond distance of 1.978(2) Å and the Ga−C$_{Me}$ bond distances are typical for gallium organyls.[14] The Ga(1)−C(6A) distance of 2.775(2) Å indicates only a very weak interaction between these two atoms, if at all. Consequently, the C−Ga(1)−C angle sum is 359°, as expected for a gallium atom that remains coordinated in a trigonal planar fashion (sp^2-hybridization). We assume that the electron deficiency at Ga(1) is compensated by electron donation from the Fe(1) center. With reference to the Ga(1)−C(1) bond distance and the dip angle, there may be only negligible electon donation from the Cp π-system (C(1)−C(5)).

Regarding the Ga(2)Me$_2$ group, we follow Figure 2 and look in more detail at the environment of the equivalent Ga(2A)Me$_2$ group. One can observe a comparably weaker bending of the Ga(2A)−C(6A) vector out of the Cp plane (dip angle α = 11.6°) and a longer Ga(2A)−Fe(1A) distance of 3.419(3) Å. This finding indicates a weaker Fe(1A)−Ga(2A) interaction than observed for Fe(1)−Ga(1). The Ga(2A)−C(6A) bond distance of 1.989(2) Å and the Ga−C$_{Me}$ bond distances are typical for gallium organyls.[14] The Ga(2A)−C(1) bond distance (2.410(2) Å) is among the longest gallium−carbon distances reported. The Ga(2A) atom is distorted tetrahedrally coordinated (C(6A)−Ga(2A)−C(13A)/C(14A) angle sum 352°; ideal tetrahedral angle sum = 328.5°). We assume that the electron deficiency at Ga(2A) is compensated to a small extent by electron donation from the Fe(1A) atom.

The C(1)−Ga(2A)−C(6A) unit is mainly responsible for the intermolecular contact between the ferrocenediyl units and represents an asymmetric electron-deficient bond. The molecular structure of **1** may even be interpreted to possess only one bridging GaMe$_2$ unit, as demonstrated by the inspection of bond length and bond angles within the CpGaMe$_2$ units.

NMR Spectroscopy of 1. The solubility of **1** in donor solvents (Do), for example pyridine and THF, stems from the formation of monomeric adducts [**1**·2Do], which have been characterized using NMR spectroscopy (eq 3). ^{1}H NMR spectroscopic data for [**1**·2Py] and [**1**·2THF] are given in Table 4.



[1 · 2 Do] (3)

Electrochemistry of 1. A cyclic voltammogram of [**1**·2Py] was recorded using pyridine as solvent and the supporting electrolyte tetrabutylammonium fluoride (TBAPF). The reversible oxidation potential of [**1**·2Py] in pyridine is $E_{1/2} = -370$ mV, and the peak separation is 165 mV. The corresponding boron compound Fe(η^5-$C_5H_4BMe_2)_2$ has a lower oxidation potential of $E_{1/2} = -510$ mV in pyridine.[15] This effect can be explained by the higher electron-donating ability of the BMe$_2$·Py group compared with that of the GaMe$_2$·Py group. While the electron-donating ability of the BMe$_2$·Py group is approximately equal to the positive inductive effect of the five methyl groups in the pentamethylcyclopentadienyl (Cp*) ligand,[10a] the GaMe$_2$·Py group is a considerably weaker electron donor.

Synthesis and Structural Features of [1·Phenazine]$_n$. The coordination polymer [**1**·phenazine]$_n$ was prepared from stoichiometric amounts of **1** and phenazine. On heating in toluene, a yellow solution was formed, which presumably contains the monomeric compound [**1**·phenazine] and some oligomeric species. Because of the very low solubility of **1** in toluene, the reaction had to be carried out in dilute solution. After cooling to room temperature, the color of the solution changed to green and small quantities of dark green crystals were formed during a few days (eq 4).

[**1**·phenazine]$_n$ crystallizes in the triclinic space group $P\bar{1}$. A drawing of the structure of [**1**·phenazine]$_n$ including the unit cell is presented in Figure 4. Figure 5 shows the repeating unit of the polymer structure represented by one phenazine and by one digallylferrocene molecule.

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[13] Kreidlin, A. Z.; Dolgushin, F. M.; Yanovsky, A. I.; Kerzina, Z. A.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **2000**, *616*, 106.

[14] Cambridge Crystallographic Structure Database.

[15] Fe(η^5-$C_5H_4BMe_2)_2$ was prepared using a literature procedure.[2b] Electrochemical analysis was effected as described in the general comments of the Experimental Section.

Table 2. Selected Distances (Å) and Angles (deg) for 1

Ga(1)−C(1)	1.978(2)	C(1)−Ga(1)−C(11)	115.47(10)
Ga(1)−C(6A)	2.775(2)	C(1)−Ga(1)−C(12)	117.61(10)
Ga(1)−C(11)	1.965(3)	C(11)−Ga(1)−C(12)	125.64(12)
Ga(1)−C(12)	1.957(2)	C(6A)−Ga(2A)−C(13A)	117.35(11)
Ga(1)−Fe(1)	3.112(3)	C(6A)−Ga(2A)−C(14A)	113.20(10)
Ga(2A)−C(1)	2.410(2)	C(13A)−Ga(2A)−C(14A)	121.65(12)
Ga(2A)−C(A6)	1.989(2)	∑C−Ga(1)−C	359
Ga(2A)−C(A13)	1.969(2)	∑C−Ga(2A)−C	352
Ga(2A)−C(A14)	1.974(2)	Ga(1)−C(1)−$Cp_{Centroid}$	25.7(1)
Ga(2A)−Fe(1A)	3.419(3)	Ga(2A)−C(6A)−$Cp_{Centroid}$	11.6(1)
Fe−C	2.052(2)−2.077(2)		
Ga−Ga	3.044(3)		

Table 3. Dip Angle α

	1 Ga(1)	**1** Ga(2)	$CpFe(C_5H_4BBr_2)$	$Fe(C_5H_4BBr_2)_2$	$CpFe(C_5H_4CH_2)^+ BF_4^-$
α	25.7°	11.6°	18.9°	10.2°	23.6°

Table 4. ^{1}H NMR Data

compound	solvent	δ(Ga−Me)	δ(C_{Cp}−H)	δ(C_{Cp}−H)
1·2Py-d_5	pyridine-d_5	0.19	4.38	4.58
1·2THF-d_8	THF-d_8	−0.27	3.86	4.08

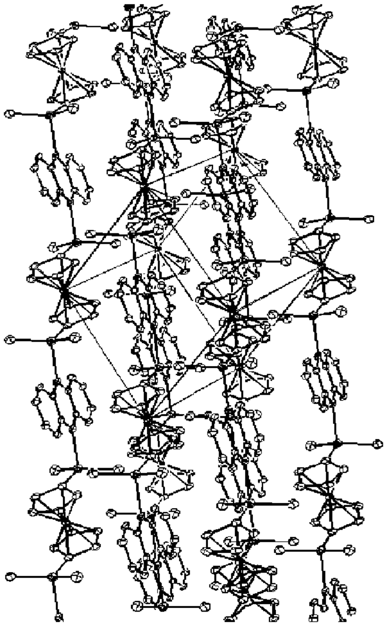
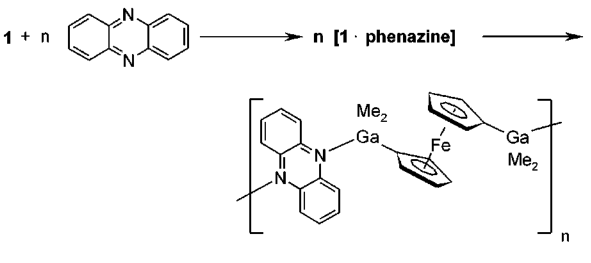


Figure 4. Solid state structure of [**1**·phenazine]$_n$, including the unit cell.



(4)

[1 · phenazine]$_n$

Crystallographic data for [**1**·phenazine]$_n$ are collected in Table 1; selected bond length and bond angles are given in Table 5.

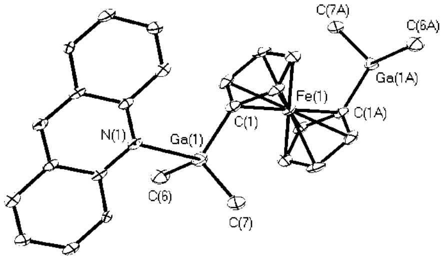


Figure 5. Part of the solid state structure of [**1**·phenazine]$_n$, thermal ellipsoids at 50% probability.

Table 5. Selected Distances (Å) and Angles (deg) for [1·Phenazine]$_n$

Ga(1)−C(1)	1.971(4)	C(1)−Ga(1)−C(6)	112.51(19)
Ga(1)−C(6)	1.980(4)	C(1)−Ga(1)−C(7)	115.48(17)
Ga(1)−C(7)	1.975(4)	C(6)−Ga(1)−C(7)	120.69(19)
Ga(1)−N(1)	2.408(3)	N(1)−Ga(1)−C(1)	106.95(14)
Fe−C	2.047(4)−2.070(4)	N(1)−Ga(1)−C(6)	98.56(16)
		N(1)−Ga(1)−C(7)	98.81(15)
		∑C−Ga(1)−C	349
		Ga(1)−C(1)−$Cp_{Centroid}$	9.5(2)

[**1**·phenazine]$_n$ consists of polymer strands arranged parallel to each other and aligned parallel to the crystallographic *a*−*c*-diagonal. The ferrocenediyl units are fixed in *trans* conformation. Each strand is surrounded by four other polymer strands. The strands are displaced in such a way that each phenazine ring is surrounded by ferrocenediyl units, so that π-stacking interactions between the phenazine rings cannot arise.

The Ga−C_{Me} bond distances are comparable to those in **1**. The Ga−N bond distance of 2.408(3) Å is longer than that found in other donor−acceptor adducts formed from sp^2-nitrogen donors and three-coordinated gallium acceptors.[14] This finding is consistent with the low basicity of phenazine (pK_a = 1.39; in water 15 °C).[16] The angle sum of 349° within the GaC_3 unit reveals only a small degree of pyramidalization of the Ga centers (ideal tetrahedral angle sum = 328.5°). This observation also explains the weak Ga−N interaction. The Ga(1)−C(9A)−$Cp_{centroid}$ dip angle α = 9.5(2)° indicates attractive Ga−Fe interactions. Competition between Ga−Fe and Ga−N interactions may be another cause for the observed small pyramidalization.

[**1**·phenazine]$_n$ (green) shows a clearly different color in comparison with **1** (orange). This effect may be caused by charge-transfer interactions between the ferrocenediyl units and the phenazine units. A similar phenomenon has been observed for Fe(η^5-$C_5H_4BMe_2$)$_2$ (red-brown) and for the polymeric compounds [Fe(η^5-C_5H_4-BMe_2)$_2$L]$_n$ (L = 4,4′-bipyridyl (purple) and pyrazine (green)).[10a,b]

Summary. Compound **1** was prepared from the reaction of 1,1′-bis(trichlorostannyl)ferrocene with an

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[16] Perkampus, H.-H.; Rössel, T. *Z. Elektrochem.* **1958**, *62*, 94.

excess of trimethylgallium. Our findings show that **1** is a polymer in which ferrocendiyl units and dimethylgallium groups are connected by electron-deficient bonds. As indicated by the formation of the coordination polymer [**1**·phenazine]$_n$, **1** can serve as a novel component in supramolecular chemistry. A similarity in the coordination behavior of **1** and Fe(η^5-$C_5H_4BMe_2$)$_2$ can be expected.[10]

We are currently trying to prepare supramolecular structures using **1**, **2**, and **3** as building blocks. First results show that all three compounds can successfully be used in coordination polymer synthesis.

Experimental Section

General Comments. All manipulations were carried out under purified argon atmosphere using standard Schlenk techniques. The solvents were commercially available, purified by conventional means, and distilled immediately prior to use. The NMR spectra were recorded using a Bruker Avance DRX 500 spectrometer (^{1}H 500.1 MHz, ^{13}C 125.8 MHz, ^{119}Sn 186.5 MHz). Chemical shifts are reported in ppm and were referenced to the solvent resonances as internal standard. The elemental analyses were performed by the Microanalytical Laboratory Beller, Göttingen. The cyclic voltammogram was recorded on an EG&G potentiostat, Model 273A, controlled by M 250/270 software. The supporting electrolyte was tetrabutylammonium fluoride (TBAPF), which was purchased from Fluka and used without further purification. The electrolyte concentration was 0.1 M. The voltammetric measurements were performed using a platinum-disk electrode ($d = 2$ mm), which was polished prior to use. Potentials were calibrated by the method of Gagné and are quoted versus the ferrocenium−ferrocene couple as internal standard.[17] A platinum wire was used as a counter electrode.

Starting Materials. 1,1′-Bis(trichlorostannyl)ferrocene was prepared using a literature procedure.[18]

Preparation of 1,1′-Bis(dimethylgallyl)ferrocene (1). Trimethylgallium ((pyrophoric!) 4.17 g, 36.3 mmol) was added to a suspension of 1,1′-bis(trichlorostannyl)ferrocene (2.30 g, 3.63 mmol) in toluene (5 mL) in a Schlenk flask. The reaction mixture was heated to 68 °C in the tightly closed flask until all components had dissolved. On cooling to room temperature, **1** formed as an orange, microcrystalline solid. The supernatant solution was decanted, and the solid residue was washed with hexane (or toluene) and dried in a vacuum, yield 1.20 g (3.13 mmol; 86%). ^{1}H NMR (pyridine-d_5): δ 0.19 (12 H; CH_3), 4.38 (4 H; ring C2/5-H or C3/4-H), 4.58 (4 H; ring C2/5-H or C3/4-H). ^{1}H NMR (THF-d_8): δ −0.27 (12 H; CH_3), 3.86 (4 H; ring C2/5-H or C3/4-H), 4.08 (4 H; ring C2/5-H or C3/4-H). ^{13}C NMR (pyridine-d_5): δ 6.6 (CH_3), 70.8 (ring C2/5 or C3/4), 75.3 (ring C2/5 or C3/4), 76.2 (C1−$GaMe_2$). Anal. Calcd for $C_{14}H_{20}FeGa_2$ ($M = 383.59$ g mol^{-1}): C, 43.84; H, 5.26. Found: C, 42.47; H, 4.77.[19] CV: $E_{1/2} = -370$ mV (peak separation 165 mV). Compound **1** is very air sensitive.

$SnMe_4$ and Me_xGaCl_{3-x} could be identified in the reaction mixture by NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ 0.14 ($SnMe_4$), 0.26 (br, Me_2GaCl/$MeGaCl_2$). ^{119}Sn NMR ($CDCl_3$): δ 0.8 ($SnMe_4$).

Preparation of [1·Phenazine]$_n$. Phenazine (47 mg, 0.26 mmol) and **1** (100 mg, 0.26 mmol) were charged in a Schlenk flask. Toluene (10 mL) was added, and the suspension was heated to ca. 100 °C until a yellow solution had formed. The reaction mixture was allowed to cool to room temperature. After a few days the color of the solution changed to green, and dark green, X-ray quality crystals formed, yield 31 mg (0.05 mmol; 21%).[20] The crystals were insoluble in all nondonor solvents. Anal. Calcd for $C_{26}H_{28}N_2FeGa_2$ ($M = 563.81$ g mol^{-1}): C, 55.39; H, 5.01; N, 4.97. Found: C, 55.42; H, 5.13; N, 4.89.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond lengths and angles; ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

[18] Herberhold, M.; Milius, W.; Steffl, U.; Vitzithum, K.; Wrackmeyer, B.; Herber, R. H.; Fontani, M.; Zanello, P. *Eur. J. Inorg. Chem.* **1999**, 145.

[19] The reactivity of **1** toward air and moisture contributes to the less than ideal elemental analysis (the same problem has been observed for dimethylgallylferrocene[4a]). In the MS of **1**, the M$^+$ peak was not observed; interestingly, the condensation product **3**$^+$ could be detected. The purity of **1** was established by high-resolution ^{1}H and ^{13}C NMR spectroscopy in donor solvents.

[20] No attempt to optimize the reaction has been made.