Reactivity Studies on a Versatile Bis(diaminogallyl)ferrocene

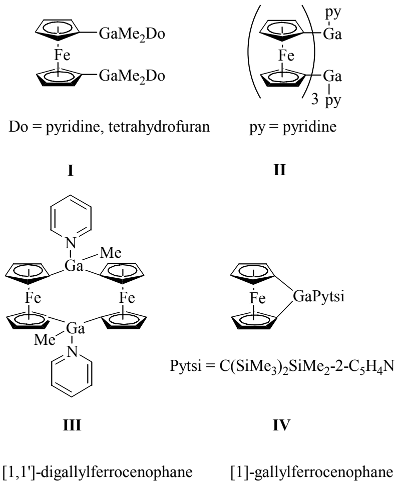
Ovidiu Feier-Iova and Gerald Linti*

Abstract—**With this paper we report on the synthesis, structure and spectroscopic characterization of new ferrocenyl-gallium compounds. They are synthesized starting from [1,1']-bis[bis(2.2.6.6-tetramethylpiperidino)gallyl]ferrocene, $[Fe\{(\eta^5-C_5H_4)Gatmp_2\}_2]$, (2). When (2) is reacted with CO_2, an insertion into all four gallium-nitrogen bonds yields in the formation of the carbamate (3). (4) was afforded by the reaction of (2) with acetic acid. An oligonuclear ferrocene system (5) where four ferrocendiyl units are fixed in an almost mutually coplanar geometry by a Ga_8O_{12} cage was synthesized. By the reaction of (2) with 1,2-catechol an unexpected five coordinated gallium derivatives was formed with cleavage of the gallium carbon bonds.**

Index Terms—**ferrocene, ferrocenophane, gallium, X-ray structure analysis, electrochemistry**

I. INTRODUCTION

Since the discovery of ferrocene [1] a very big family of ferrocenyl and ferrocenophane derivatives has been developed. We are especially interested in gallium organyls. Here, up to now, the gallylsubstituted ferrocenes have been studied les intensively. Only a few gallyl ferrocenenes have been synthesized in the last two decades and they can be classified in four distinctive groups (Scheme 1): the first is represented by donor adducts of type **I** [2] – [5], the second group includes gallium-bridged ferrocenophanes **II** [2], [5], the third group [1,1']-ferrocenophanes linked by Ga-Me and Ga-Aryl units **III** [2] – [5] and the last [1]-ferrocenophanes [6] – [8]. **IV** is the first example with a bridging gallium atom. Starting from these [1,1']-ferrocenophanes can be prepared via ring-opening polymerization reactions [9] – [13].



Scheme 1: Survey on gallyl- and digallylferrocenes.

Generally, ferrocenophanes show interesting electrical, magnetic, and optical properties as a result of electron delocalization [14]. A common route to polyferrocenyl species is based on the formation of donor-acceptor bonds between difunctional nitrogen bases and Lewis acidic substitutents at the ferrocene derivatives, i.e. $[Fe\{(\eta^5-C_5H_4)EMe_2\}_2L]$ (E = B [15], [16], Ga [3]; L = phenazine, 4,4'-bipyridyl, pyrazine etc.).

In this paper, we report on reactions of a bis(diaminogallyl)ferrocene **2** [17]. The derivatives obtained, were characterized by single crystal structure determination and spectroscopic and cyclovoltammetric methods.

II. RESULTS AND DISCUSSION

A. *Reactions*

By treatment of a solution of of bis(tmp)gallium chloride **1** (tmp = 2.2.6.6-tetramethylpiperidino) [18] with a solution of $[Li_2\{Fe(\eta^5-C_5H_4)_2\} \bullet 2/3\ tmeda]$ [19 in hexane the synthesis of [1,1']-bis[bis(2.2.6.6-tetramethylpiperidino)gallyl]ferrocene **2** [17]was achieved (eq. 1). **2** was obtained as red crystals in good yields. **2** reacts easily with an excess of CO_2. Insertion into all four gallium-nitrogen bonds affords the carbamate **3** [17] as yellow crystals (Scheme 2). Reactions of **2** with the Brønsted acids MeCOOH, $EtOH/H_2O$, and $C_6H_4(OH)_2$ lead to the formation of the ferrocenyl derivative $[tmpH_2]^+_2$ $[Fe\{(\eta^5-C_5H_4)Ga(OOC-Me)_3\}_2]^{2-}$ **4**, a gallium ferrocenophane

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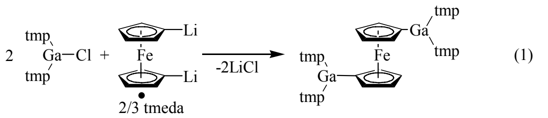

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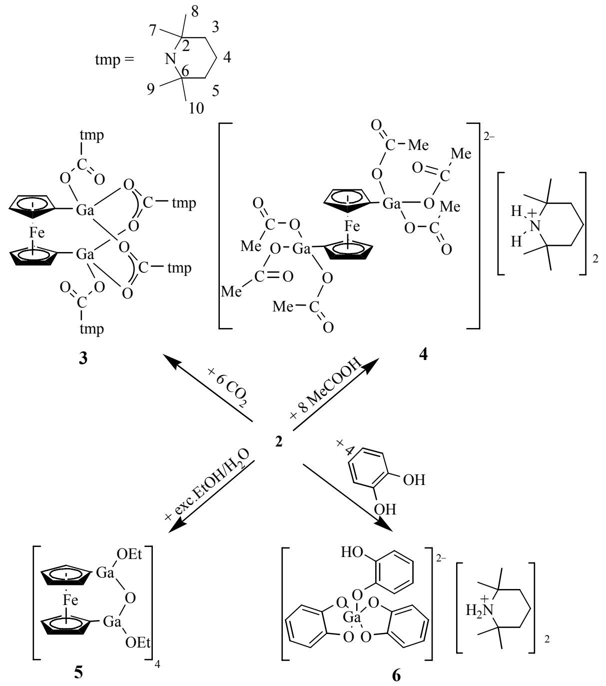

3 4 2 5 6

Scheme 2: Reactions of **2**

with four ferrocenyl units $[Fe\{(\eta^5\text{-}C_5H_4)GaOEt\}_2O]_4$ **5** and an catechol gallanate $[tmpH_2]^+{}_2[(C_6H_4O_2)_2Ga(OC_6H_4OH)]^{2-}$ **6** as main products were yielded (scheme 2).

B. Spectroscopic Characterization

All compounds described in this paper were characterized by means of ^1H and ^{13}C NMR spectroscopy.

The ferrocenyl derivatives **2** and **3** [17] give raise to two pseudo triplets for the protons of the Cp-rings (Cp = cyclopentadienyl) in the ^1H NMR spectra and three signals for the ring carbon atoms in the ^{13}C NMR spectra, respectively. A low field shift of the signals for the carbon atoms of the cyclopentadienyl rings in **2** compared to ferrocene ($\delta^{13}C = 68$) was observed [19] with the exception of the *ipso*-atoms in **3** [17]. For [1, 1']-bis(dimethylgallyl)ferrocene [3] a similar, but less strong low field shift is observed for the *ipso*-carbon atom ($\delta^{13}C = 76.2$).

The high field shift of the corresponding *ipso*-carbon atoms in **3** compared to ferrocene can be interpreted as a result of the higher coordination number of the attached gallium atoms (C.N. 4-5) compared to **2**. In organyl substituted [1, 1]-digallylferrocenophanes [20] the *ipso*-carbon atoms resonate at about $\delta = 70$. This is more similar to **3** than to **2** [1].

^1H and ^{13}C NMR spectra of **2** exhibit single signal sets for the tmp groups. This is a result of fast rotation of the tmp groups about the Ga-N bonds. In the ^{13}C-NMR spectra the signals for the C-2, 6 atoms of **2** are at higher field than those for **3** [1]. The shifts for **2** are in the typical region observed for other tmp_2Ga derivatives [18]. The difference of 3 ppm for the shifts of the quaternary carbon atoms hints to a more electronegative substituent at the nitrogen atom in **3** than in **2** [17]. The carbon atoms of the NCO_2 groups give raise to two signals ($\delta = 165.8$, 161.3), which signifies two different bonding modes. This finding is in agreement with the molecular structure in the solid state (see below). This is supported by two sets of signals for the tmp groups in **3**, too.

The ^1H NMR spectrum of **4** shows a single signal set for the 2.2.6.6-tetramethylpiperidinium ions, one singlet for the methyl groups of the acetates and two broad signals for the ring protons of the Cp rings. In the ^{13}C NMR spectrum only two signals for the carbon atoms of the Cp rings could be observed, the signal for the *ipso*-carbon atoms was too weak. All signals are shifted to lower field, compared to ferrocene [19], again. The acetate groups gave raise to three signals [$\delta = 23.6$ (CH_3), $\delta = 177.4$, 177.9 (H_3CCO_2)]. That is in line with the solid state structure, where two of the acetate groups are involved in hydrogen bonding.

6 gives raise to a broad signal corresponding to the proton of the –O*H* group ($\delta\ ^1H = 8.40$), three broad signals for the protons of the catecholate-rings in a ratio of 2:6:4 as well as signals for the 2.2.6.6-tetramethylpiperidinium ions and thf. For a structure **6,** as depicted in scheme 2, up to seven signals are expected for the catecholate moieties. In the ^{13}C spectrum the signals corresponding to the substituted carbon atoms of the aromatic-rings were observed at $\delta = 150.0$ and 145.2. Three signals for CH groups ($\delta = 120.3$, 117.7 and 114.2) were identified. That means again isochronic nuclei in different environment. This might be due to a migration of the proton between different oxygen atoms, the dynamics have to be investigated in future.

C. Electrochemistry

The cyclic voltammograms of **2**, **3**, **4**, and **5** were recorded in thf solution with NBu_4PF_6 as supporting electrolyte and decamethylcobaltocene/decamethylcobaltocenium as internal standard (Fig. 1). For all the compounds, reversible oxidation potentials were observed at: $E_{1/2} = -199$ mV (**2**) [17], $E_{1/2} = -196$ mV (**3**) [17], $E_{1/2} = -244$ mV (**4**) and $E_{1/2} = -153$ mV (**5** (vs ferrocene/ferricinium) with peak separations of 220 mV (**2**), 169 mV (**3**), 196 mV (**4**) and respectively 130 mV (**5**). Other gallyl substituted ferrocenes like $[Fe\{(\eta^5\text{-}C_5H_4)GaMe(py)\}_2]$ (py = pyridine) [2]-[5], [20], [21], described in literature, have lower oxidation potentials [$E_{1/2} = -370$ mV in pyridine]. This is an effect of the groups directed bounded to the gallium atoms which are less able to donate electrons into the ring, due to the electron withdrawing substituents at the gallium atoms and the influence of the solvent, of course. Mostly notable is, that for the tetranuclear species **5** only one redox peak is observed. The trinuclear ferrocenophane $[\{Fe\ (\eta^5\text{-}C_5H_4)_2\}_3Ga_2]$ [5] shows three peaks. This might mean that the ferrocendiyl units in **5** are well separated and no delocalization is possible. Further investigations are necessary.

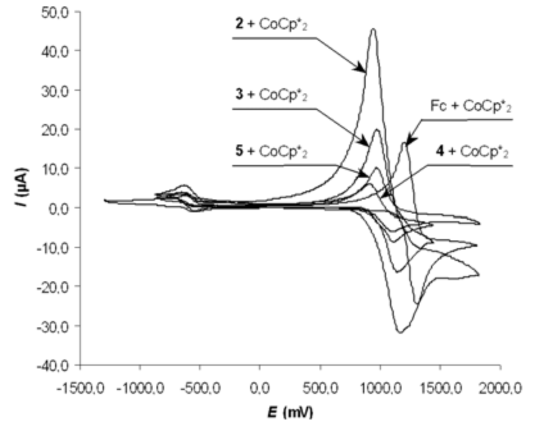

Fig. 1: Cyclic voltammograms of **2** [17], **3** [17], **4**, **5** and ferrocene (Fc) in thf; internal standard: CoCp*$_2$/CoCp*$_2^+$ (Cp* = pentamethylcyclopentadienyl).

D. *Crystal Structure Analyses*

4 (Fig. 2), crystallizing as pale yellow crystals of the triclinic system, space group $P\bar{1}$, is the 2,2,6,6-tetramethylpiperidinium salt of a 1,1'-bis(trisacetatogallyl)ferrocenate(2-). The anionic part shows in a centrosymmetric conformation eclipsed Cp rings with the substituents in *anti* position.The gallium atoms are surrounded distorted tetrahedrally by a Cp ring and three acetate groups. The OGaO bond angles are smaller (99.3° - 103.4°) than the tetrahedral angle. The OGaC angles are wider (107.6° - 121.6°). The Ga-O distances (d_{Ga-O} = 189.4 pm on an average) are typical for Ga-O distances with tetracoordinated gallium atoms. The second oxygen atoms of each carboxylate group have longer distances to the gallium atoms [d_{GaO} = 276.2 (O6), 318.7 (O4), 403.6 (O2) pm], which are to be regarded as non-bonding. The C-O bonds in the carboxylates are longer (d_{Ga-O} = 131.0 pm) for the gallium bonded oxygen atoms than for the other ones (d_{Ga-O} = 123.2 pm). The oxygen atoms O(2) and O(4) are involved in hydrogen bonding to the counter ions ($d_{O(2)-H(1)}$ = 192.1 pm, $d_{O(4)-H(2)}$ = 214.6 pm). The Ga-C bonds ($d_{Ga(1)-C(1)}$ = 194.3) are similar to those in **3** and shorter than those in **2**. This is a consequence of the more electronegative substituents at the gallium atoms in **3** and **4** and is in line with the Bent's rule.

5 (Fig. 3), crystallizing in needles of the monoclinic system, space group $P2_1$, together with two molecules of benzene, is formally a tetramer of [Fe{(η^5-C$_5$H$_4$)GaOEt}$_2$O]. Thus, the central core of **5** is a gallium-oxygen cage made up by eight gallium atoms and 12 oxygen atoms. Eight of these are part of ethoxy groups, the others are oxide ions. This cage shows two stacked boat-shaped Ga$_3$O$_3$ rings, which are linked by two Ga-O bonds. Thus, a distorted hexagonal prism is made up with six gallium atoms, two μ^2-OEt groups and four oxygen atoms. One of the side faces is part of an eight-membered ring of four gallium atoms, two oxygen atoms and two μ^2-OEt groups.

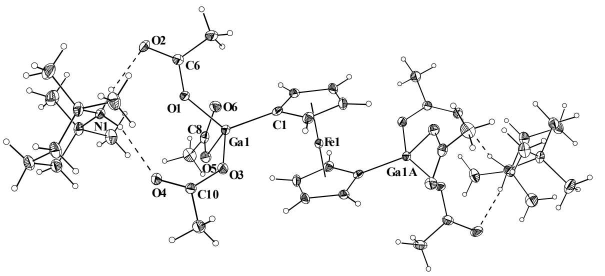

Fig. 2: View of **4**, showing the hydrogen bonds between cations and anion. Selected bond lengths [pm] and angles [°]: Ga(1)-C(1) 194.4(3) , Ga(1)-O(1) 189.5(2) , Ga(1)-O(3) 189.2(2) , Ga(1)-O(5) 189.4(2) , C(6)-O(1) 131.4(3), C(6)-O(2) 124.0(3), C(8)-O(5) 130.9(4), C(8)-O(6) 123.5(4), C(10)-O(3) 131.0(3), C(10)-O(4) 123.3(3); O(1)-Ga(1)-O(3) 101.95(9), O(1)-Ga(1)-O(5) 103.38(9), O(3)-Ga(1)-O(5) 99.3(1), O(1)-Ga(1)-C(1) 119.55(9), O(3)-Ga(1)-C(1) 107.6(1), O(5)-Ga(1)-C(1) 121.6(1), O(1)-C6)-O(2) 120.0(3)

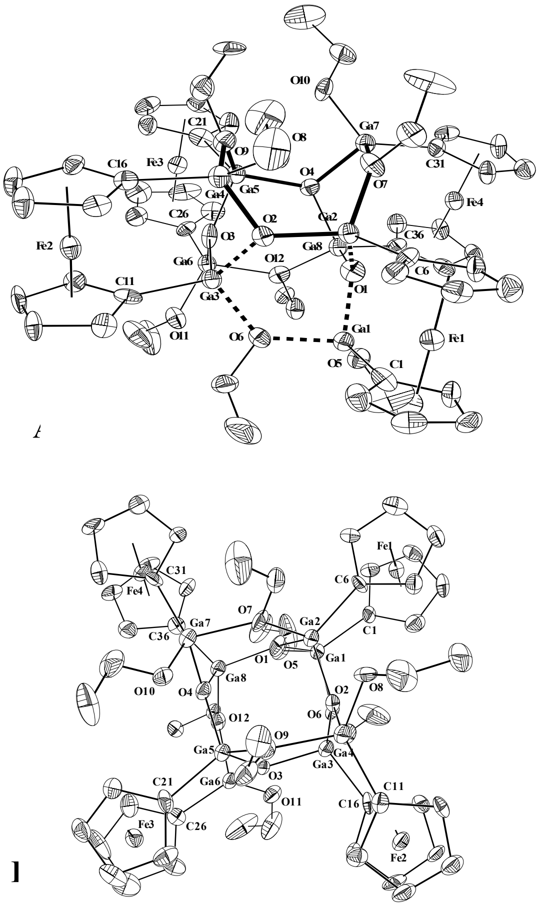

Fig. 3: View of a molecule of **5** (**A** = one side view, **B** = upper view). Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]:
Ga-O from 179.5(12) to 194.3(13), Ga-C from 192.3(19) to 199.3(19), O-Ga-O from 93.2(5) to 115.7(5), O-Ga-C from 106.5(6) to 122.6(7), Ga-O-Ga from 111.3(6) to 127.6(6), C-O-Ga from 113.7(11) to 126.3(18), C-C-Ga from 122.1(13) to 132.1(15), Ga-C-Fe from 123.1(10) to 126.9(9).

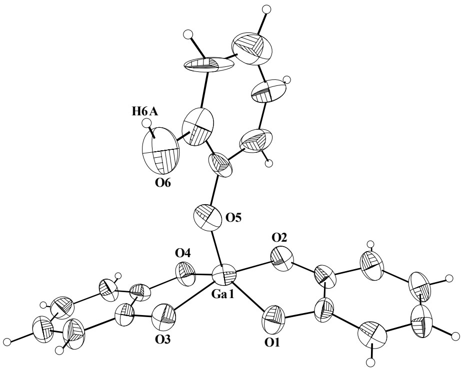

Fig.4: View of the anion of **6**. The tmpH_2^+ cations are omitted for clarity. Selected bond lengths [pm] and angels [°]: Ga(1)-O(1) 189.8(7), Ga(1)-O(2) 192.2(6), Ga(1)-O(3) 194.9(6), Ga(1)-O(4) 191.2(6), Ga(1)-O(5) 183.2(8); O(1)-Ga(1)-O(2) 84.4(3), O(1)-Ga(1)-O(3) 89.2(3), O(3)-Ga(1)-O(4) 83.0(3), O(1)-Ga(1)-O(5) 104.2(3), O(4)-Ga(1)-O(5) 113.0(3), O(3)-Ga(1)-O(5) 90.7(3)

The remaining four OEt groups are in terminal positions. Each of the gallium atoms is tetra-coordinated by three oxygen atoms of the cage and a carbon atom, which is part of a ferrocendiyl unit. The Ga-O distances in the cage cover a range from 179.5 to 194.0 pm. Here the terminal OEt groups with 2-coordinated oxygen atoms have the shortest bonds. The four ferrocendiyl units are arranged around this cage in a nearly mutually coplanar manner that means the Cp ring planes of different ferrocendiyl units intersect at angles between 5 and 17°. The iron atoms are separated by 730 to 780 pm. This is about 200 pm longer than in $[\{Fe(\eta^5\text{-}C_5H_4)_2\}_3Ga_2]$ [5]. This difference might explain the electrochemical behaviour of both compounds.

6 (Fig. 4) crystallizes in plates of the orthorhombic system, space group $P2_12_12_1$ together with a molecule of thf in the unit. Here, two 2,2,6,6-tetramethylpiperidinium cations balance the charge of a dianionic gallanate, whre a central gallium atom is coordinated square pyramidally by two chelating catecholate ligands and a further η^1-catecholate in axial position. The oxygen atom O(6) is protonated. The Ga-O bonds in the square base are between 189.7 and 194.9 pm. The axial Ga-O bond is shorter ($d_{Ga\text{-}O(5)}$ = 183.2 pm).

III. CONCLUSION

The bis(diaminogallyl)ferrocene **2**, which is straightforward to prepare, proved to be a valuable synthon for the preparation of other gallyl substituted ferrocenyl derivatives. Here the reactivity of the Ga-N bonds towards carbon dioxide, reacting with insertion to form a carbamato bridged ferrocenophane, and towards proton acidic reagents was used. Especially the tetranuclear ferrocene derivative prepared by mixed alcoholysis/hydrolysis, whose structure is determined by a gallium/oxo cage, represents a new type of ferrocenyl oligomers. Ongoing studies are directed to explore the properties of these compounds in the preparation of molecular magnets.

IV. EXPERIMENTAL SECTION

A. *General Remarks*

All manipulations were performed in vacuum or under argon using Schlenk techniques. Solvents were dried prior to use and stored under argon. The other chemicals were used without any further purification directly after purchasing. – NMR: Bruker ARX 200 and AV 400 spectrometers. Spectra were referenced to internal solvent peaks.- Mass spectra: JEOL JMS-700 (EI) and Finnigan TSQ 700 (ESI).- Elemental analyses were performed by the Microanalytical Laboratory of the Institut of Inorganic Chemistry, Heidelberg. The deviations which appeared in the results from calculated values are because of the extremely air-sensitive and hygroscopic nature of these complexes.- Melting points were determined with a Gallenkamp Melting Point Apparatus.- tmp_2GaCl [18], $[Li_2\{Fe(\eta^5\text{-}C_5H_4)_2\} \bullet 2/3\ tmeda]$ [19], **2**, and **3** [17] were prepared as described in the literature.

B. *Electrochemistry*

All electrochemical experiments were done with a Princeton Applied Research Potentiostat/Galvanostat Model 263A and the corresponding software PowerSuite 2.11. The three-electrode system was used. A glass carbon working electrode (2 mm diameter) was employed. The pseudo reference electrode was a silver wire immersed in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (NBu_4PF_6) in thf. Platinum wire was used as the auxiliary electrode. In each case, IR compensation was applied in order to reduce the thf resistance. The scan rate for all CVs measurements was 25 mV/s. The decamethylcobaltocenium tetrafluoroborate was added for each measurement as an internal standard. The measured redox potentials were later converted into ferrocene/ferrocenium ($[FeCp_2]/[FeCp_2]^+$) potentials ($E([CoCp^*_2])$ = -585 mV (in thf) vs. $[FeCp_2]/[FeCp_2]^+$; our own measurement). Experiments were performed under strict inert conditions. Measurements were taken at room temperature (23 °C) in thf as solvent with NBu_4PF_6 as supporting electrolyte.

C. *X-Ray crystallography*

X-ray crystallography. Crystallographic data are summarized in Table I.

Suitable crystals were mounted with a perfluorinated polyether oil on the tip of a glass fiber and cooled immediately on the goniometer head. Data collections were performed with Mo-K_α radiation (graphite monochromator) on a STOE IPDSI diffractometer. Structures were solved by Direct Methods and refined by full-matrix least-squares against F^2. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms at carbon atoms were included in calculated positions and refined using a *riding model*. The positions of other hydrogen atoms were taken from a differende Fourier map and refined freely with isotropic U. Calculations were performed using the SHELXTL package [22].

Table I. Crystal and Intensity Collection Data for Complexes **4**, **5** and **6**.

	4	**5**	**6**
Formula	$C_{40}H_{66}FeGa_2N_2O_{12}$	$C_{68}H_{84}Fe_4Ga_8O_{12}$	$C_{40}H_{57}GaN_2O_7$
Molar mass [g mol^{-1}]	962.26	1874.51	747.60
Crystal system	triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1$	$P2_12_12_1$
a [Å]	10.580(2)	12.646(3)	13.917(3)
b [Å]	11.072(2)	13.037(3)	14.254(3)
c [Å]	11.438(2)	22.861(5)	20.509(4)
α [°]	64.81(3)	90.00	90.00
β [°]	84.86(3)	104.41(3)	90.00
γ [°]	75.75(3)	90.00	90.00
Cell volume [Å^3]	1174.9(4)	3650.3(13)	4068.5(14)
Z	1	2	4
F(000) electrons	504	1880	1592
D_{calc} [g/cm^3]	1.360	1.705	1.221
Absorption coefficient [mm^{-1}]	1.500	3.725	0.724
θ range for data collection [°]	1.97 to 24.03	1.69 to 23.98	1.99 to 19.48
Crystal size [mm^3]	0.20 x 0.14 x 0.13	0.57 x 0.15 x 0.09	0.53 x 0.32 x 0.19
Index ranges	$-12 \le h \le 12$	$-14 \le h \le 13$	$-12 \le h \le 12$
	$-12 \le k \le 12$	$-14 \le k \le 14$	$-13 \le k \le 13$
	$-13 \le l \le 13$	$-26 \le l \le 26$	$-19\ l \le 19$
Reflections collected	7517	22714	14436
Independent reflections (R_{int})	3458 (0.048)	11199 (0.1208)	3479 (0.0724)
Refl. $I > 2\sigma(I)$	2501	6154	2914
Parameters	267	837	526
Goodness-of-Fit on F^2	0.828	0.861	1.030
Final R indices [$I > 2\sigma(I)$] R_1	0.028	0.071	0.056
wR_2	0.060	0.167	0.142
R indices (all data) R_1	0.044	0.123	0.068
wR_2	0.062	0.196	0.149
Largest diff. peak, hole [eÅ^{-3}]	0.37, -.38	1.01, -1.83	0.41, -0.23
Data collection temp [K]	200(2)	200(2)	200(2)

A. Synthesis routes

Synthesis of $[tmpH_2]^+_2[Fe\{(\eta^5\text{-}C_5H_4)Ga(O_2CMe)_3\}_2]^{2-}$ (4): Into a solution of 0.43 g **2** (0.49 mmol) in 20 ml of diethylether, cooled to –78 °C, a solution of 0.17 ml (waterfree H_3CCOOH 2.99 mmol) in 5 ml of diethylether was added dropwise. Within a few seconds the color changed from red-orange to yellow. Then the mixture was allowed to warm up slowly to ambient temperature and stirred for an additional hour. A deposition of a yellow precipitate was observed. All volatiles were removed in vacuum (0.01 mbar) and thE remaining solid was washed with hexane several times. Then the solid was dissolved in a 10:1 mixture of tetrahydofurane/hexane and stored at –32 °C for several days. 0.46 g **4** (97 %) as yellow crystals were collected.- M.p.: 132 – 135 °C.- ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.28 (br, H, Cp-*H*), 4.24 (br, 4 H, Cp-*H*), 2.10 (s, 18 H, O_2CCH_3), 1.82 (s, 4H, $tmpH_2^+$-γ-*CH₂*), 1.62 (s, 8H, $tmpH_2^+$-β-CH_2), 1.39 (s, 24H, $tmpH_2^+$-CH_3).- ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 177.8 (CO_2CH_3), 177.3 (CO_2CH_3), 75.0 (Cp-*CH*), 70.5 (s, Cp-*C*H), 55.7 (tmp-C^2/C^6), 35.2 (tmp-C^3/C^5), 27.5 (tmp-$C^7/C^8/C^9/C^{10}$), 23.6 (CO_2CH_3), 16.4 (tmp-C^4).- $C_{40}H_{66}FeGa_2N_2O_{12}$ (962.25): calcd. C 49.93, H 6.91, N 2.91, found C 50.25, H 7.06, N 3.05.- MS (ESI-MS, ^{69}Ga): m/z (%) = (–): 431 (100) $[Fe(\eta^5\text{-}C_5H_4)GaAc_3]^-$, 389 (53) $[Fe(\eta^5\text{-}C_5H_4)GaAc_2OH]^-$. (Ac = CH_3COO^-).

Synthesis of $[Fe\{(\eta^5\text{-}C_5H_4)Ga(OEt)\}_2O]_4$ (5): 0.64 g **2** (0.73 mmol) were dissolved in 20 ml of benzene at room temperature and 0.35 ml of 90%-ethanol (5.94 mmol) were added dropwise. Within a few seconds the color changed from red-orange to light yellow. Then the reaction mixture was stirred for another 15 minutes. The clear yellow solution was reduced to one-third of its original volume in vacuum and stored at –32 °C for several days. 0.22 g **5** (18 %) as yellow crystals precipitated.- M.p. : 119 – 123 °C, (240 °C dec.).- $C_{56}H_{72}Fe_4Ga_8O_{12}$ (1718.42): calcd. C 39.14, H 4.22, found C 36.22, H 4.43.- MS (70eV, EI-MS, ^{69}Ga): m/z (%) = 858 (0.2) $[M - 2\{Fe(C_5H_4)_2Ga_2(OEt)_4O\}]^{+\bullet}$, 186 (96) $[C_{10}H_{10}Fe]^{+\bullet}$, 121 (60) $[C_5H_5Fe]^+$, 69 (100) $[Ga]^+$, 56 (30) $[Fe]^{+\bullet}$.

Synthesis of $[tmp]^+_2[(C_6H_4O_2)_2Ga(OC_6H_4OH)]^{2-}$ (6): Into a solution of 0.36 g **2** (0.40 mmol) in 20 ml of thf, cooled to –78 °C, 0.18 g 1,2-dihydroxybenzene (1.66 mmol) dissolved in 5 ml of thf were added dropwise. The color changed immediately from red-orange to yellow and a white precipitate was formed. Then the reaction mixture was heated to reflux for 10 minutes and a clear yellow solution was obtained. The mixture was stirred for another 30 minutes at room temperature. The clear yellow solution was reduced to one-third of its original volume and stored at –32 °C for several days. 0.28 g **6** (93 %) as colorless crystals were formed.- M.p. : 247 – 250 °C (dec.).- ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.40 (br, 1 H, O*H*), 6.85 (br, 2 H, C*H*), 6.66 (br, 6 H, C*H*), 6.55 (br, 4 H, C*H*), 1.69 (m, 4H, tmp-γ-CH_2), 1.58 (m, 8 H, tmp-β-CH_2), 1.28 (s, 24 H, tmp-CH_3).- ^{13}C NMR (600 MHz, $CDCl_3$, 25 °C): δ = 150.0 (*C*OGa), 145.2 (*C*OH), 120.3 (o-*C*H), 117.7 (o-*C*H), 114.2 (m-*C*H), 56.0 (tmp-C^2/C^6), 35.8 (tmp-C^3/C^5), 27.9 (tmp-$C^7/C^8/C^9/C^{10}$), 16.1 (tmp-C^4).- $C_{40}H_{57}GaN_2O_7$ (747.61): calcd. C 64.26, H 7.68, N 3.75, found C 60.55, H 7.42, N 3.68.

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