

On the chemistry of gallium[☆]

Part 19. Synthesis and crystal structure analysis of novel complexes containing Ga–FeCp(CO)₂-fragments

Gerald Linti *, Guangming Li, Heinz Pritzkow

Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received 19 October 2000; received in revised form 21 November 2000; accepted 21 December 2000

Abstract

The gallium subhalides Ga₂Cl₄·2dioxane and sonochemically prepared GaI were reacted with the carbonyl ferrate K[Cp(CO)₂Fe] and the iron carbonyl dimer [Cp(CO)₂Fe]₂, respectively. In all the reactions performed, the gallium(I) and gallium(II) compounds disproportionated into elemental gallium and gallium(III) compounds. Several novel complexes containing Ga–FeCp(CO)₂ fragments were isolated and characterized spectroscopically and by X-ray crystal structure analysis. These are compounds of the types Cp(CO)₂FeGaX₂(B) [B = THF, dioxane, I[−][FeCp(C₇H₈)]⁺; X = Cl, I] and [Cp(CO)₂Fe]₂GaCl(B) [B = THF, 0.5 KCl]. In addition, the cage compounds [Cp(CO)₂FeGa]₆(μ₃-O)₄(μ-OH)₂I₂ and [Cp(CO)₂FeGa]₄FeK₂(OEt₂)₄(μ₃-O)₂(μ-Br)₄(μ₃-Br)₄ were isolated. In all these complexes the gallium atoms are surrounded tetrahedrally by substituents. Ga–Fe bond lengths are in the range of 231–239 pm. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gallium; Iron; Gallium–iron bond; Crystal structure analysis

1. Introduction

Complexes of transition metals with ligands having a Group 13 element atom as a ligating atom have gained interest during the past years [2–6]. This is mainly due to the use of such complexes as single-source precursor molecules in MOCVD [3]. On the other hand, the alleged analogy between CO and RE-fragments [E = Group 13 element] in their coordination properties has been discussed controversially [7–9]. Some of the structurally characterized complexes with Ga–Fe bonds are summarized in Table 1. Most of these compounds have been prepared starting from gallium(III) halide derivatives. However, having in mind the great variety of gallium cluster compounds [1,10–12] available from gallium subhalides by reaction with bulky alkalimetal silanides, reactions between carbonylmetalates and gallium subhalides seem rewarding. Herein, we report on

the reactions of the gallium halides “GaI” [13] and Ga₂X₄·2dioxane (X = Cl, Br) with K[FeCp(CO)₂] and [FeCp(CO)₂]₂.

2. Synthesis and reactions

In order to obtain compounds with Ga–Fe bonds, gallium halides may be treated with metal-bases like carbonyl ferrates. An alternative method to salt elimination reactions is a metathesis between compounds with Ga–Ga and Fe–Fe bonds: if Ga₂Cl₄·2dioxane is reacted with one equivalent of [FeCp(CO)₂]₂ in boiling toluene, yellow crystals of **1a** and **1b** are obtained in good yields by crystallization from a THF–ether mixture and toluene, respectively. Obviously, Ga₂Cl₄·2dioxane serves as a source for GaCl₂ (donor) radicals, which can combine with the 17 valence electron fragment FeCp(CO)₂ to form **1**. **1a** and **1b** are similar to [Cp(CO)₂FeGaCl₂(NMe₃)] [14], which was prepared from GaCl₃(NMe₃)₃ and K[FeCp(CO)₂] in THF at –78°C. A similar reaction using [Ru₃(CO)₁₂] afforded the RuGa₃ complex [(CO)₃Ru{GaCl(THF)₂}{GaCl₂(THF)₂}] [15].

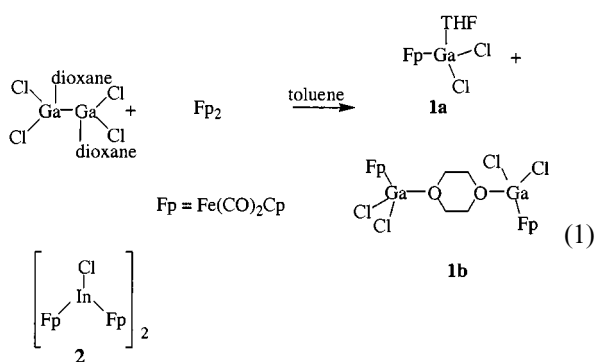
[☆] For Part 18, see Ref. [1].

* Corresponding author. Tel.: +49-6221-548529; Fax: +49-6221-546617.

E-mail address: gerald.linti@urz.uni-heidelberg.de (G. Linti).

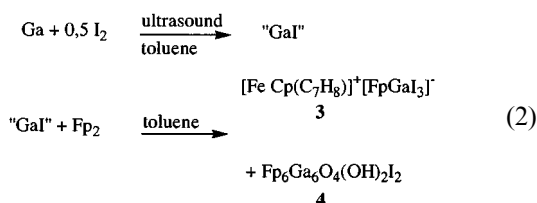
Table 1
Some structurally characterized compounds with Ga–Fe bonds

Complexes	$d(\text{Ga–Fe})$ (pm)	$\tilde{\nu}(\text{C–O})$ (cm^{-1})	References
$[(\text{CO})_4\text{Fe–GaAr}^*]$	222.48	2032(s), 1959(s), 1941(vs), 1929 (vs)	[32]
$[(\text{CO})_4\text{Fe–GaPh}^*]$	225.6	2038, 1985, 1959	[7]
$[(\text{CO})_4\text{Fe–GaCp}^*]$	227.71	2037(s), 1966(s), 1942(vs)	[33]
$[\text{Cp}(\text{CO})_2\text{FeGaS}]_2$	233.7	2001(s), 1993(vs), 1976(vs), 1923 (vs), 1986(vs)	[34]
$[(\text{CO})_4\text{Fe–GaCl}_2(\text{tmeda})]$	233.78	2011(vs), 1928(vs), 1881(vs)	[3,35]
$[\text{Cp}(\text{CO})_2\text{Fe–GaCl}(\text{NMe}_3)]$	236.18	1989(vs), 1934(vs)	[14]
$[\text{Cp}(\text{CO})_2\text{Fe–Ga}(\text{R}^N)(\text{BH}_4)]$	237.5	1975(vs), 1920 (vs)	[36]
$[\text{Fe}_2(\text{CO})_6\{\mu\text{-GaSi}(\text{SiMe}_3)_3\}_2]$	238.18	1964(s), 1921(s)	[27]
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_2\text{Ga}(\text{Bu})]$	240.6, 241.6	1978(vw, sh), 1967(vs), 1927(vs), 1915(vw)	[22]
$[(\text{CO})_4\text{Fe–Ga}(\text{Me})\text{-Fe}(\text{CO})_4]^{2-}$	241.58	1952(vs), 1874(vs, sh), 1851(vs), 1827(vs, sh)	[37]
$[\text{Cp}(\text{CO})_2\text{Fe–Ga}(\eta^1\text{-C}_5\text{H}_4\text{Me})_2(\text{NC}_5\text{H}_5)]$	242.72	–	[13,38]
$[\{\text{Cp}(\text{CO})_2\text{Fe}\}_3\text{Ga}]$	243.6–245.6	1987(m), 1965(s), 1929(s)	[17]
$[(\text{CO})_4\text{Fe–Ga}(\eta^1\text{-C}_2\text{H}_5)(\text{THF})_2]$	251.0	–	[39]



There is some resemblance of the reaction according to Eq. (1) to the reaction between InCl and $[\text{FeCp}(\text{CO})_2]_2$ [16]. Here, an oxidative addition of the Fe–Fe bond to the indium(I) fragment takes place to form **2**.

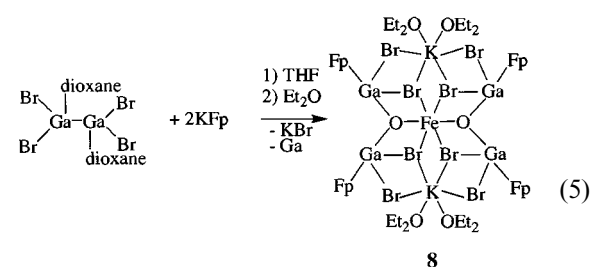
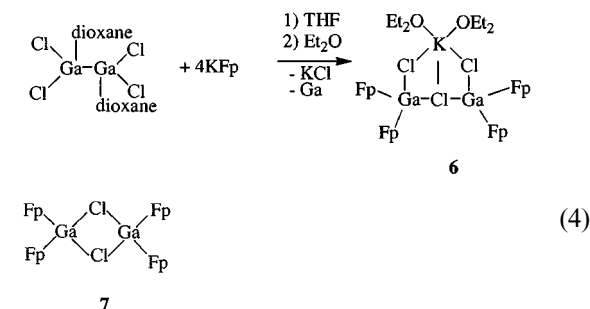
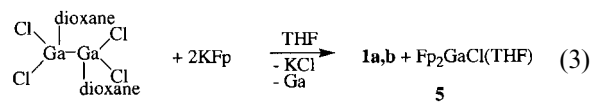
The analogous reaction (Eq. (2)) between Green's "GaI" and $[\text{FeCp}(\text{CO})_2]_2$ in toluene does not allow the isolation of $[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{GaI}$ although GaI insertion reactions into metal–halide bonds have been described [13]. This is understandable, because "GaI" consists predominantly of $(\text{Ga}^+)_2[\text{Ga}_2\text{I}_6]^{2-}$ [1]. Instead, the sandwich cation $[\text{CpFe}(\text{toluene})]^+$ as the $[\text{CpFe}(\text{CO})_2\text{GaI}_3]^-$ salt, **3**, is isolated in minor yield. In addition a $[\text{FeCp}(\text{CO})_2]$ substituted hexanuclear gallium oxo/hydroxo cage **4** is formed in this reaction by partial oxidative hydrolysis.



A salt elimination reaction between $\text{Ga}_2\text{Cl}_4 \cdot 2\text{dioxane}$ and two equivalents of $\text{K}[\text{FeCp}(\text{CO})_2]$ in THF at ambi-

ent temperatures affords **1a** and **b** (Eq. (3)), too. In addition, orange red crystals of **5** are isolated. During this reaction the deposition of elemental gallium is observed which indicates a disproportionation reaction.

If four equivalents of $\text{K}[\text{FeCp}(\text{CO})_2]$ are used in a similar reaction (Eq. (4)) no iron substituted digallane is isolated, either. The same kind of redox disproportionation takes place and well-shaped orange crystals of **6** are isolated.



(all equations are non-stoichiometric and are based on the stoichiometry used in the experiments)

Both **5** and **6** are Lewis-base adducts to $[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{GaCl}$, which is known as dimer **7** [17]. In **6**, the Lewis-base is a $\text{K}(\text{OEt})_2\text{Cl}$ unit, which links two

Table 2
Selected spectroscopic data for the complexes **1a**, **b**, **5**, **6** and **8**

	IR ($\nu_{\text{C-O}}$ (cm ⁻¹))	MS ^a	NMR (THF- <i>d</i> ₈)
1a	1990.4s, 1935.4s	316 (13) M ⁺ , 290 (27) [M-CO] ⁺	$\delta^1\text{H}$ (ppm) = 4.96 (s, 5H, C ₅ H ₅); $\delta^{13}\text{C}\{^1\text{H}\}$ (ppm) = 83.5 (C ₅ H ₅), 215.1 (CO)
1b	1989.6s, 1933.8s	318 (24) [(C ₅ H ₅) ₂ Fe(CO) ₂ GaCl ₂] ⁺ , 290 (31) [(C ₅ H ₅) ₂ Fe(CO) ₂ GaCl ₂ -CO] ⁺	$\delta^1\text{H}$ (ppm) = 4.96 (s, 5H, C ₅ H ₅); $\delta^{13}\text{C}\{^1\text{H}\}$ (ppm) = 83.5 (C ₅ H ₅), 215.1 (CO)
5	1992.1s, 1982.1s, 1971.4s, 1935.7s	458 (2) [M] ⁺ , 430 (22) [M-CO] ⁺	$\delta^1\text{H}$ (ppm) = 4.87 (s, 10H, C ₅ H ₅); $\delta^{13}\text{C}\{^1\text{H}\}$ (ppm) = 83.7 (C ₅ H ₅), 217.3 (CO)
6	2003.7s, 1933.7s	458 (7) [(C ₅ H ₅) ₂ Fe(CO) ₂ GaCl] ⁺ , 430 (55) [(C ₅ H ₅) ₂ Fe(CO) ₂ GaCl-CO] ⁺	$\delta^1\text{H}$ (ppm) = 4.86 (s, 10H, C ₅ H ₅); $\delta^{13}\text{C}\{^1\text{H}\}$ (ppm) = 83.7 (C ₅ H ₅), 217.3 (CO)
8	1997.5s, 1946.6s	406 (2) [GaBr ₂ C ₅ H ₅ Fe(CO) ₂] ⁺ , 378 (10) [GaBr ₂ C ₅ H ₅ Fe(CO) ₂ -CO] ⁺	$\delta^1\text{H}$ (ppm) = 5.10 (s, 5H, C ₅ H ₅); $\delta^{13}\text{C}\{^1\text{H}\}$ (ppm) = 84.1 (C ₅ H ₅)

^a Most intense *m/z* from the isotopic pattern.

[Cp(CO)₂Fe]₂GaCl molecules, forming a unique bicyclic KGa₂Cl₃ ring.

The analogous reaction (Eq. (5)) between Ga₂Br₄·2dioxane and two equivalents of K[FeCp(CO)₂] did not afford a bromine-analog to **1** or **5**. After work-up and crystallization from diethylether the only Ga-Fe compound isolated is the unexpected cage compound **8**.

3. Spectroscopic characterization

The IR spectra (KBr pellet) of compounds **1a**, **b**, **5**, **6** and **8** show the typical absorption bands for Cp(CO)₂Fe fragments (Table 2). The high-energy carbonyl vibrations in the Ga-Fe compounds are observed at higher wave numbers than in K[FeCp(CO)₂] [18], but they are in a similar region than that of [CpFe(CO)₂]₂ [19]. From a simple viewpoint this is in unison with the less ionic character of the Ga-Fe bond compared to the K-Fe interactions.

Because of their low solubility in less polar solvents, the NMR spectra of **1a**, **b**, **5** and **6** were recorded in THF. Consequently, the ¹H- and ¹³C-NMR spectra of **1a** and **b**, **5** and **6** are not distinguishable due to dioxane-THF and KCl-THF exchange, respectively.

The mass spectra (EI) of **1a** and **b** show the donor free [Cp(CO)₂FeGaCl₂]⁺ and its fragmentation. The spectrum of **1b** shows fragmentation of a dimer in low intensity, too. The mass spectra for **5** and **6** are very similar, exhibiting the fragmentation of [Cp(CO)₂Fe]₂GaCl. The cage compound **8** is degraded to Cp(CO)₂FeGaBr₂, the radical cation of which is observed as the highest mass peak.

4. Crystal structure analysis

1a crystallizes in the triclinic crystal system, space group *P* $\bar{1}$ (Table 3). Both independent molecules in the asymmetric unit are identical within the standard devia-

tions. The molecule of **1a** (Fig. 1) exhibits a gallium atom that is tetrahedrally coordinated by an iron, two chlorine atoms and one oxygen atom. The iron atom is further coordinated by a Cp-ring and two CO ligands. The bonding parameters of the Cp(CO)₂Fe fragment are in the normal range. The Ga-Fe bond length is 231.7 pm. This is 5 pm shorter than the Ga-Fe bond length in the related complex Cp(CO)₂FeGaCl₂(NMe₃) [14] (compare Table 1). This shortening of the Ga-Fe bond is caused by the replacement of the coordinated amine by a more electron withdrawing THF molecule. The dependence of the Ga-Fe bond length on the electronegativity of the substituents at the gallium center has already been proven in compounds of the type Cp(CO)₂FeGaX₂(NR₃) [3]. For X = halide, the Ga-Fe bond is up to 10 pm shorter than for X = alkyl. Obviously, the Ga-Fe bond resembles somewhat the Ga-Si bond, the length of which varies in compounds of the type (Me₃Si)₃SiGaX₂(THF) with the electronegativity of X [20]. (Me₃Si)₃SiGaCl₂(THF) in particular has very similar Ga-Cl and Ga-O bond lengths if compared to **1a**. The bond angles at the gallium center in both compounds are quite similar, too.

1b crystallizes in the triclinic space group *P* $\bar{1}$, too. The molecule of **1b** resides on a center of symmetry (Fig. 2). Thus, a dioxane molecule links two Cp(CO)₂FeGaCl₂ units. The Ga-Fe and Ga-Cl bonds, as well as the bond angles at the gallium center resemble those of **1a**. The main difference is the Ga-O distance, being 10 pm longer in **1b** than in **1a**, which demonstrates the different donor properties of THF and dioxane.

3 crystallizes in the triclinic space group *P* $\bar{1}$ with *Z* = 4.¹ Due to the extremely thin crystal plates the data set obtained is a very crude one. Therefore, the structural parameters are not to be discussed in detail. **3**

¹ In spite of the nearly monoclinic cell dimensions, structure solution and refinement was only possible in *P* $\bar{1}$.

(Fig. 3) is an ion pair of a CpFe(toluenes) sandwich cation. The anion is $[\text{Cp}(\text{CO})_2\text{FeGaI}_3]^-$. The Ga–Fe bond length is 236 pm. This is longer than in **1a** and **b**, but in the typical range for $\text{Cp}(\text{CO})_2\text{FeGaX}_2$ (donor) compounds.

5, the THF adduct of $[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{GaCl}$, crystallizes in the monoclinic space group $P2_1/n$ (Fig. 4). The central gallium atom is coordinated tetrahedrally by two iron atoms, one chlorine atom and one oxygen atom. The bond angles deviate markedly from the tetrahedral angle; i.e. the Fe(1)–Ga(1)–Fe(2) angle is very wide, due to the steric demand of the $\text{Cp}(\text{CO})_2\text{Fe}$ groups. In contrast, the O(5)–Ga(1)–Cl(1) angle is near 90° . This deformation of the coordination sphere around the gallium atom results in long Ga–O and Cl bonds. Compared to **1a**, the Ga–THF distance is lengthened by 23 pm. The Ga(1)–Cl(1) bond [$d_{\text{GaCl}} = 229.0(2)$ pm] is out of the typical range for terminal Ga–Cl bonds [$d_{\text{GaCl}} \leq 222$ pm], and is as long as the

bridging Cl–Ga distances in Ga_2Cl_6 [21]. The Ga–Fe distances are longer than in **1a**, yet similar to the ones in sterically strained $(\text{Cp}(\text{CO})_2\text{Fe})_2\text{Ga}^t\text{Bu}$ [22].

6 crystallizes in the monoclinic crystal system, space group $C2/c$. In analogy to **5**, it may be viewed upon as a Lewis-base adduct of $[\text{Cp}(\text{CO})_2\text{Fe}]_2\text{GaCl}$ (Fig. 5). This subunit consists of Ga(1), Fe(1), Fe(2) and Cl(2). The Ga–Fe and Ga–Cl bonds are similar to those in **5**. The same is true for the Fe(1)–Ga(1)–Fe(2) (130.9°), Fe(1)–Ga(1)–Cl(2) (109.5°) and Fe(2)–Ga(1)–Cl(2) (106.6°) angle. The Lewis-base is a $\text{K}(\text{OEt})_2\text{Cl}$ unit, which coordinates via its chlorine atom [Cl(1)] to Ga(1). This Ga(1)–Cl(1) contact is 25 pm longer than the Ga(1)–Cl(2) distance. In addition, Cl(2) coordinates to the potassium center. Thus, a four-membered, flat butterfly-type GaCl_2K ring results [torsion angle $\text{Cl}(1)\text{Ga}(1)\text{Cl}(2)\text{K}(1) = 11^\circ$]. Cl(1) does not coordinate to only one GaFe_2Cl unit; together with a second one, a bicyclo[2.2.0]hexane type structure results. One of the

Table 3
Crystal data and data collection parameters

	1a	1b	3	5	6	8	4
Formula	$\text{C}_{11}\text{H}_{13}\text{Cl}_2\text{Fe}-\text{GaO}_3$	$\text{C}_{18}\text{H}_{18}\text{Cl}_4\text{Fe}_2-\text{Ga}_2\text{O}_6$	$\text{C}_{19}\text{H}_{18}\text{I}_3\text{Fe}_2-\text{GaO}_2$	$\text{C}_{18}\text{H}_{18}\text{ClFe}_2-\text{GaO}_5$	$\text{C}_{36}\text{H}_{40}\text{Cl}_3\text{Fe}_4-\text{Ga}_2\text{KO}_{10} \cdot (\text{C}_4\text{H}_{10}\text{O})$	$\text{C}_{44}\text{H}_{60}\text{Br}_8\text{Fe}_5-\text{Ga}_4\text{K}_2\text{O}_{14}$	$\text{C}_{42}\text{H}_{32}\text{I}_2\text{Fe}_6-\text{Ga}_6\text{O}_{18} \cdot (\text{C}_4\text{H}_{10}\text{O})$
<i>M</i>	389.7	723.2	840.5	531.2	1141.0 (1215.1)	2088.5	1832.0 (1906.1)
Crystal size (mm ³)	$0.35 \times 0.35 \times 0.2$	$0.4 \times 0.3 \times 0.25$	$0.15 \times 0.1 \times 0.005$	$0.4 \times 0.2 \times 0.2$	$0.25 \times 0.25 \times 0.15$	$0.20 \times 0.15 \times 0.10$	$0.18 \times 0.12 \times 0.02$
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/n$
<i>a</i> (pm)	1090.8(2)	678.1(14)	1194.1(2)	795.4(2)	2003.3(4)	1288.3(3)	1248.3(1)
<i>b</i> (pm)	1163.5(2)	725.5(15)	1024.7(2)	1784.0(4)	1172.7(2)	2607.9(5)	1188.2(1)
<i>c</i> (pm)	1226.2(3)	1375.7(3)	2421.7(5)	1390.8(3)	2111.1(4)	2164.0(4)	1959.9(1)
α (°)	97.20(3)	104.8(3)	89.93(3)	90	90	90	90
β (°)	104.22(3)	94.02(3)	89.96(3)	96.64(3)	116.99(3)	104.23(3)	91.55(1)
γ (°)	93.23(3)	107.99(3)	86.74(3)	90	90	90	90
<i>V</i> (nm ³)	1.4905(5)	0.6141(2)	2.958(1)	1.9603(7)	4.419(1)	7.05(1)	2.906(1)
<i>Z</i>	4	1	4	4	4	4	2
$\rho_{\text{calc.}}$ (kg m ⁻³)	1.737	1.956	1.887	1.800	1.715	1.968	2.16
μ (mm ⁻¹)	3.134	3.795	5.011	2.987	2.807	7.205	5.31
<i>F</i> (000)	776	356	1560	1064	2288	4032	1808
Index range	$\pm h \pm k \pm l$	$\pm h \pm k \pm l$	$\pm h \pm k \pm l$	$hk \pm l$	$\pm hkl$	$\pm h \pm k \pm l$	$\pm hkl$
$2\theta_{\text{max}}$ (°)	50	52	52	50	50	52	51
<i>T</i> (K)	190	190	190	190	223	190	190
Reflections collected	5259	4759	21120	3978	3894	49965	5613
Reflections unique	5240	2198	10760	3431	3894	13097	5326
Reflections observed (4σ)	3991	2062	6593	3010	3349	8187	3913
Parameters	325	145	525	245	256	702	353
Weighting scheme x/y^a	0.1149/5.2444	0.111/0	0.1/0	0.0606/10.8833	0.0572/0	0.0481/0	0.0442/19.08
Goodness-of-fit on F^2	1.084	1.098	2.919	1.080	1.268	0.868	1.040
<i>R</i> (4σ)	0.067	0.061	0.171	0.052	0.035	0.042	0.041
<i>wR</i> ₂	0.205	0.156	0.492	0.140	0.105	0.098	0.100
Large res. peak (\AA^{-3})	1.26	1.40	8.1	2.53	0.73	0.76	1.65

^a $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

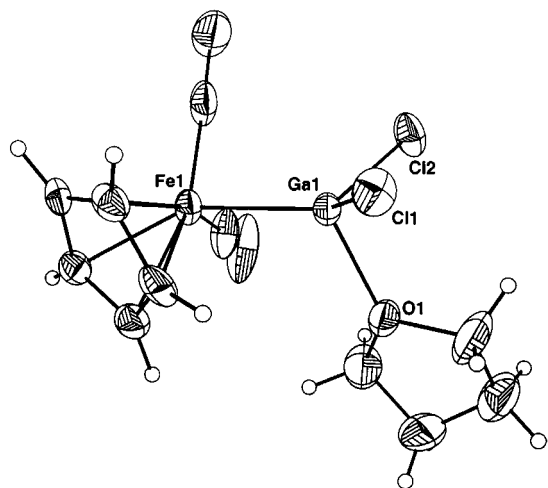


Fig. 1. View of a molecule of **1a**. Selected bond lengths (pm) and angles (°): Ga(1)–Fe(1) 231.7(1), Ga(1)–Cl(1) 222.0(2), Ga(1)–Cl(2) 222.0(2), Ga(1)–O(1) 199.7(5); Cl(1)–Ga(1)–Cl(2) 104.51(9), O(1)–Ga(1)–Cl(1) 95.0(2), O(1)–Ga(1)–Cl(2) 97.7(2), O(1)–Ga(1)–Fe(1) 115.7(1), Cl(1)–Ga(1)–Fe(1) 115.71(7), Cl(2)–Ga(1)–Fe(1) 119.44(7).

most striking features of this heterocycle is a T-shaped Ga₂ClK unit with a Ga(1)–Cl1–Ga(1) angle of 175.5° at the triple coordinated chlorine atom. The potassium center K(1) is penta-coordinated by three chlorine atoms and two oxygen atoms of two diethylether molecules. The K(1)–O(5) [O(5) #] distance is 261.8 pm, which is normal for K–O distances. The three K–Cl contacts are nearly equal and in the typical range.

The trigonal bipyramidal coordination polyhedron at the potassium center is severely distorted, i.e. the Cl(2)–K(1)–Cl(1) angle is not linear but equals

146.1°. This may be caused by two short K–H contacts ($d_{K-H} = 304$ pm) to methylene groups of the coordinated ether molecules. Quantum chemical calculations on the RI-DFT level with a def-SVP base and the BP86 functional [23] have been performed on a [H₂GaCl]₂K(H₂O)₂Cl model, **9**. The results of the calculation (Fig. 6) reveal a bicyclic structure similar to **6**. Especially the trend of the bond lengths, short and long GaCl contacts is confirmed. The main difference between **6** and **9** is the bond angle at Cl(1). In **9**, this angle is found to be 113°, far from linear. This is probably due to the substitution of the bulky Cp(CO)₂Fe groups by hydrogen.

8, the disproportionation product of the reaction between Ga₂Br₄·2dioxane and K[Cp(CO)₂Fe], crystallizes in the monoclinic space group *P*2₁/*n*. The complicated cage compound may be described as being built by two Cp(CO)₂FeGa(Br)–O–Ga(Br)Fe(CO)₂Cp molecules which are linked together by two K(OEt)₂Br units and a FeBr₂ unit (Fig. 7). This iron atom is coordinated octahedrally by four bromine atoms and the oxygen atoms of the digalloxane mentioned above. Each of the four bromine atoms coordinates to a gallium atom, which is tetracoordinated by a Cp(CO)₂Fe group, an oxygen atom and two bromine atoms. Both of the bromine atoms at a gallium center coordinate a potassium atom. The latter is hexacoordinated by four bromine atoms and two ether molecules. The K–Br and Fe–Br distances are in the expected range. The terminal Ga–Fe bonds [$d_{GaFe(aver.)} = 233$ pm] are short. This is consistent with the structural discussion for **1a** and **b**. The Ga–O distance [$d_{GaO} = 186.0(3) – 186.5(3)$ pm] is longer than in an other organometallic digalloxane; in [(CO)₅Mn–

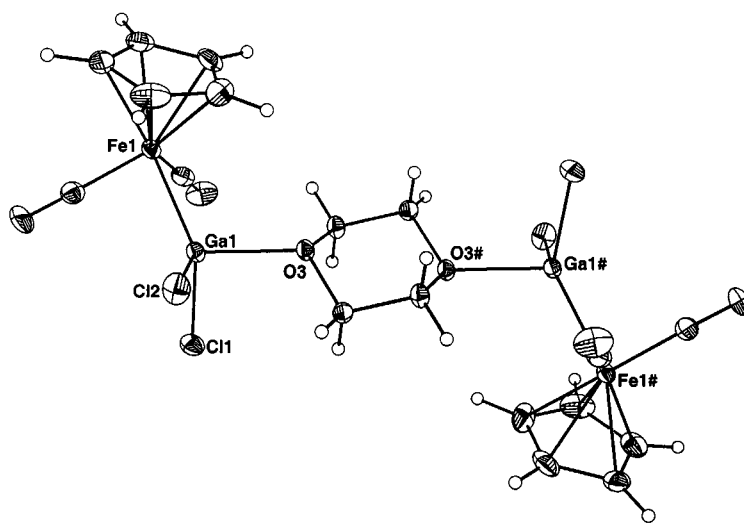


Fig. 2. View of a molecule of **1b**. Selected bond lengths (pm) and angles (°): Ga(1)–Fe(1) 231.64(9), Ga(1)–Cl(1) 222.8(1), Ga(1)–Cl(2) 220.2(1), Ga(1)–O(3) 209.6(2); Cl(1)–Ga(1)–Cl(2) 105.62(5), O(3)–Ga(1)–Cl(1) 95.02(7), O(3)–Ga(1)–Cl(2) 96.09(8), O(3)–Ga(1)–Fe(1) 112.03(8), Cl(1)–Ga(1)–Fe(1) 122.05(4), Cl(2)–Ga(1)–Fe(1) 120.19(4).

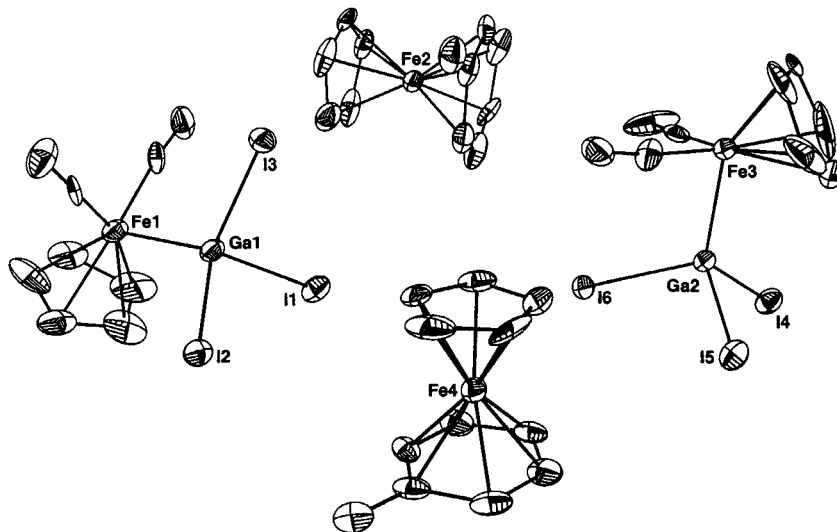


Fig. 3. View of the independent ion pairs **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (pm): Ga–Fe 236.1(7), Ga–I 262.9(5)–264.6(5).

$\text{Ga}(\text{C}_6\text{H}_5\text{Pr}_3)_2\text{O}$ the Ga–O distance is 179 pm [24]. This is not unexpected, because the oxo bridges in **8** [O(9),O(10)] are triple coordinated. Consequently, the Ga–O(9,10)–Ga angles are less wide (132°) than in the monomeric digalloxane [$\text{GaOGa} = 150.2(15)^\circ$].

By the reaction of “GaI” with $[\text{Cp}(\text{CO})_2\text{Fe}]_2$ **3** was obtained as well as the gallium oxo-/hydroxo cage compound **4** (Fig. 8). It crystallizes monoclinic, space group $P2_1/n$. The core of centrosymmetric **4** consists of six gallium and six oxygen atoms. Each of the tetracoordinated gallium atoms bears a $\text{Cp}(\text{CO})_2\text{Fe}$ group with a relatively short Ga–Fe distance. Ga(1) and Ga(2) are connected to three oxygen atoms. Therefore, their Ga–Fe bond [$d_{\text{GaFe}} = 233.5$ pm] is a bit shorter than that of Ga(3) [$d_{\text{GaFe}} = 234.4$ pm], having only two oxygen neighbors. Additionally, Ga(3) is bonded to an iodine atom. All Ga–O distances are similar ($d_{\text{GaO(aver.)}} = 191$ pm), unless the oxo atoms O(1) and O(2) bridge three gallium atoms and the hydroxo group O(2) only two. The Ga–O cage may be roughly described as a distorted hexagonal prism, because no bonding interaction between Ga(3) and O(2) # [Ga(3) # and O(2)] occurs. **4** represents a new type of Ga–O cages. Taking into account the empirical formula $\text{R}_6\text{Ga}_6\text{O}_4(\text{OH})_2\text{I}_2$, the compounds $\text{Mes}_6\text{Ga}_6\text{O}_4(\text{OH})_4$ [25] and $\text{Mes}_6\text{Ga}_6\text{O}_4\text{F}_4$ [26] seem to be closely related, but there is a striking difference. In both compounds, OH groups and fluorine atoms are μ_3 -bridging, while the iodine atoms in **4** are terminal and the hydroxo groups are of μ_2 -type. The consequence is a more open, less symmetric cage for **4** compared to the mesityl compounds. Other Ga–O cages are of adamantine type [27,28] or are higher nuclear cages like $\text{Ga}'_{12}\text{Bu}_{12}\text{O}_{10}(\text{OH})_4$ [29].

5. Conclusions

The reaction of $[\text{Cp}(\text{CO})_2\text{Fe}]_2$ as well as of $\text{K}[\text{Cp}(\text{CO})_2\text{Fe}]$ with gallium subhalides results in disproportionation reactions, yielding various $\text{Cp}(\text{CO})_2\text{Fe}$ -substituted gallium halide derivatives. The structural variety possible is documented with bicyclic **6** and the novel cage compounds **4** and **8**. Especially, the use of $\text{Ga}_2\text{X}_4 \cdot 2\text{donor}$ as a source for the $\text{GaX}_2(\text{donor})$ group will be explored further. The reaction with other metal–metal bonded complexes is to be examined, but

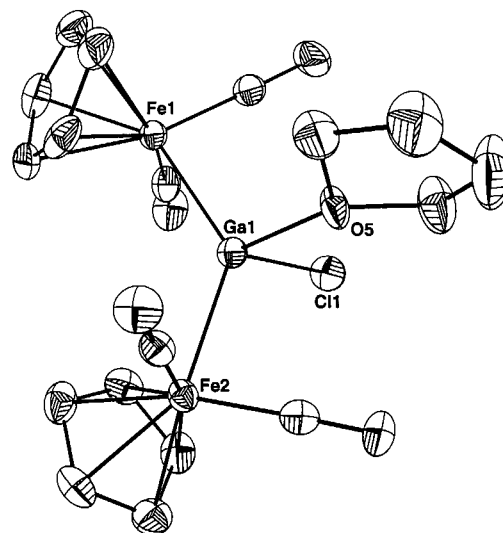


Fig. 4. View of a molecule of **5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (pm) and angles ($^\circ$): Ga(1)–Fe(1) 239.2(1), Ga(1)–Fe(2) 238.8(1), Ga(1)–Cl(1) 229.0(2), Ga(1)–O(5) 222.9(5); Fe(1)–Ga(1)–Fe(2) 129.51(4), Fe(1)–Ga(1)–Cl(1) 110.72(6), Fe(2)–Ga(1)–Cl(1) 108.53(6), Fe(1)–Ga(1)–O(5) 106.7(1), Fe(2)–Ga(1)–O(5) 101.9(2), O(5)–Ga(1)–Cl(1) 92.6(1).

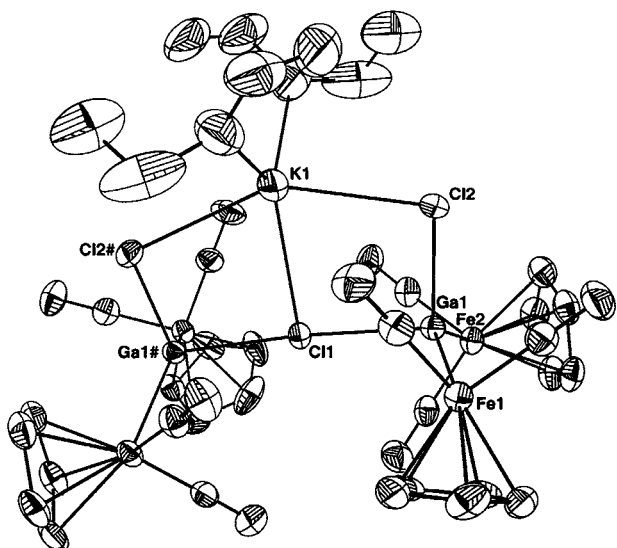


Fig. 5. View of a molecule of **6**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (pm) and angles ($^{\circ}$): Ga(1)–Fe(1) 237.70(8), Ga(1)–Fe(2) 237.7(1), Ga(1)–Cl(1) 258.19(6), Ga(1)–Cl(2) 233.5(1), K(1)–Cl(1) 306.1(2), K(1)–Cl(2) 304.9(1), K(1)–O(5) 261.8; Fe(1)–Ga(1)–Fe(2) 130.94(3), Cl(1)–Ga(1)–Cl(2) 95.26(4), Ga(1)–Cl(1)–Ga(1) $\#$ 175.51(6), Ga(1)–Cl(1)–K(1) 92.25(3).

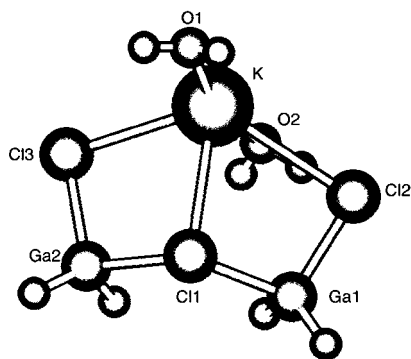


Fig. 6. View of the calculated structure **9**. Selected bond lengths (pm) and angles ($^{\circ}$): Ga(1)–Cl(1) 247.7, Ga(2)–Cl(1) 243.5, Cl(1)–K 322.9, Cl(2)–K 309.5, Cl(3)–K 327.6, Ga(1)–Cl(2) 227.8, Ga(2)–Cl(3) 230.3; Ga(1)–Cl(1)–Ga(2) 112.8.

particularly the investigation of oxidative additions of Ga–Ga bonds to unsaturated transition metal centers is a promising project.

6. Experimental

All procedures were performed under purified nitrogen or in vacuum using Schlenk techniques. NMR: Bruker ACP 200 and 250; MS were recorded on an Atlas CH7 or Varian MAT 711 machine. IR spectra were recorded from KBr pellets on a Bruker IFS 113v machine. Elemental analyses were done in the microanalytical laboratory of the Institute of Inorganic Chemistry of University Karlsruhe. X-ray crystallographic analy-

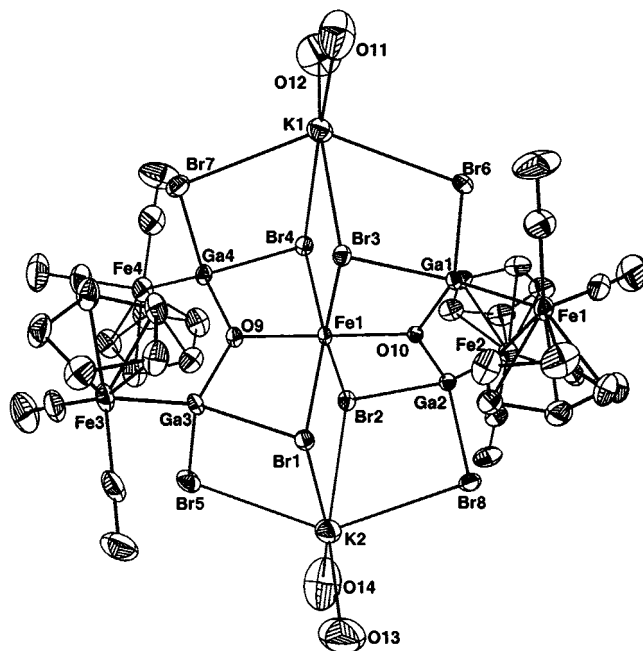


Fig. 7. View of a molecule of **8**. Hydrogen atoms and diethylether carbon atoms have been omitted for clarity. Selected bond lengths (pm) and angles ($^{\circ}$): Ga(1,2)–O(10) 186.5(3), Ga(3,4)–O(9) 186.0(3), 186.5(3), Ga–Fe 232.8(1)–233.1(1), Ga(1)–Br(3) 250.4(1), Ga(1)–Br(6) 243.2(1); Fe–Br(1–4) 277.7(1)–280.9(1), K(1)–Br(3,4) 328.9(2), K(1)–Br(6) 325.4(2); Fe–O(9,10) 194.9(3).

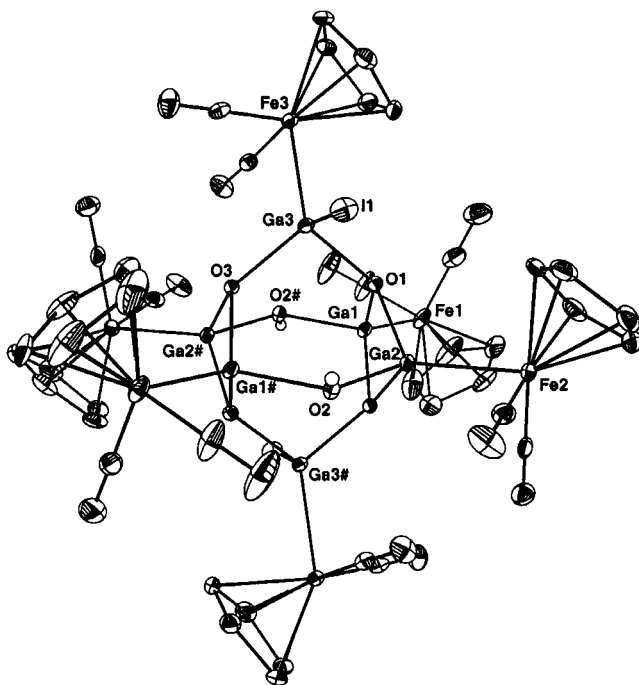


Fig. 8. View of a molecule of **4**. Carbon bonded hydrogen atoms have been omitted for clarity. Selected bond lengths (pm): Ga(1)–Fe(1) 233.2(1), Ga(2)–Fe(2) 233.8(1), Ga(3)–Fe(3) 234.4(1), Ga(1)–O(1) 192.0(5), Ga(1)–O(3) $\#$ 190.8(4), Ga(2)–O(1) 191.5(4), Ga(2)–O(3) $\#$ 193.1(4), Ga(2)–O(2) 191.9(4), Ga(1)–O(2) $\#$ 193.6(5), Ga(3)–I(1) 270.7(1).

ses: suitable single crystal were mounted with a perfluorated polyether oil on the top of a glass fiber and cooled immediately on the goniometer head. Data collections were performed with graphite monochromated MoK α radiation on Stoe IPDS (**3**, **8**), Stoe STADI4 (**1a**, **b**, **5**, **6**) and Bruker AXS (**4**) diffractometers using commercial software. Structures were solved and refined using the Bruker AXS SHELXTL (PC) package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon atoms were included as riding model with fixed isotropic U_s in the final refinement. OH atoms were taken from a difference Fourier map and refined isotropically. “GaI” [13], Ga₂Cl₄·2dioxane and Ga₂Br₄·2dioxan [30], [CpFe(CO)₂]₂ [18] and K[CpFe(CO)₂] [31] were prepared as described in the literature. Other chemicals were used as purchased.

6.1. Synthesis of (THF)GaCl₂[CpFe(CO)₂] (**1a**) and (dioxane){GaCl₂[CpFe(CO)₂]}₂ (**1b**)

A mixture of [CpFe(CO)₂]₂ (0.35 g, 1.00 mmol) and Ga₂Cl₄·2dioxan (0.46 g, 1.00 mmol) was heated to reflux in 30 ml of toluene for 2 h. The color of the mixture turned yellow and a gray precipitate formed at the end of the reaction. After filtration a yellow compound crystallized from the yellow toluene solution upon cooling to –4°C. The yellow crystalline compound was redissolved in 15 ml of a 5:1 mixture of ether and THF (5:1). Yellow single crystals of **1a** were obtained by over-laying the mixture of ether and THF with pentane at ambient temperature, yield: 0.62 g, **1a** (80% with respect to iron). Single crystals of **1b** (0.07 g, 18%) were isolated by cooling the toluene solution to –20°C — **1a**: ¹H-NMR (THF-*d*₈): δ = 4.96 (s, C₅H₅). — ¹³C-NMR (THF-*d*₈): δ = 83.5 (C₅H₅), 217.3 (CO). — IR (KBr, cm⁻¹): ν̄(C–O) 1990.4s, 1935.4s. — MS (70 eV, EI, M = GaCl₂C₅H₅Fe(CO)₂): *m/z* (%) = 318 (16) M⁺, 290(34) [M – CO]⁺, 262 (83) [M – 2CO]⁺, 225 (4) [M – 2CO – Cl]⁺, 186 (7) [(C₅H₅)₂Fe]⁺, 156 (100) [C₅H₅FeCl]⁺, 121 (41) [C₅H₅Fe]⁺. — Anal. Found: C 34.13, H 3.23. Calc. for C₁₁H₁₃Cl₂FeGaO₃ (389.7): C, 33.90; H, 3.36; — **1b**: ¹H-NMR (THF-*d*₈): δ = 4.96 (s, C₅H₅). — ¹³C-NMR (THF-*d*₈): δ = 83.5 (C₅H₅), 217.3 (CO). — IR (KBr, cm⁻¹): ν̄(C–O) 1989.6s, 1933.8s. — MS (70 eV, EI, M = GaCl₂C₅H₅Fe(CO)₂): *m/z* (%) = 580 (4) [2M – 2CO]⁺, 474 (13) [2M – GaCl – 2CO]⁺, 318 (24) M⁺, 290 (31) [M – CO]⁺, 262 (85) [M – 2CO]⁺, 225 (4) [M – 2CO – Cl]⁺, 186 (3) [(C₅H₅)₂Fe]⁺, 156 (100) [C₅H₅FeCl]⁺, 121 (33) [C₅H₅Fe]⁺. — Anal. Found: C, 29.47; H, 2.13. Calc. for C₁₈H₁₈Cl₄Fe₂Ga₂O₆ (723.3): C, 29.89; H, 2.51.

6.2. Synthesis of [CpFe(C₇H₈)] [Cp(CO)₂FeGaI₃] (**3**) and [Cp(CO)₂FeGa]₆O₄(OH)₂I₂ (**4**)

Solid [CpFe(CO)₂]₂ (0.35 g, 1.00 mmol) was added to a suspension of freshly prepared “GaI” (1.00 mmol) in 20 ml toluene at ambient temperature. The mixture was heated to reflux for 3 h. The color of the mixture turned reddish brown and some dark gray precipitate formed during the reaction. After filtration and removal of all volatiles in vacuo, the residue was extracted consecutively with 15 ml of ether and 15 ml of THF. Colorless crystals of **4** were obtained by cooling the ether solution to –4°C; yield: 0.22 g **4** (36% with respect to iron). Very thin yellow plates of **3** crystallized from the concentrated THF solution at –30°C; yield: 0.21 g **3** (25% with respect to iron). — **3**: ¹H-NMR (THF-*d*₈): δ = 7.10 (m, 5H, C₆H₅), 4.85 (s, 10H, C₅H₅), 2.27 (s, 3H, CH₃). — ¹³C-NMR (THF-*d*₈): δ = 25.3 (CH₃), 85.6 (C₅H₅), 128.8 (C₆H₅). — IR (KBr, cm⁻¹): ν̄(C–O) 1987.3s, 1980.3s, 1937.6s, 1924.8s. — MS (70 eV, EI): *m/z* (%) = 550 (2) [(C₅H₅)Fe(CO)₂]₂GaI⁺, 522 (100) [(C₅H₅)Fe(CO)₂]₂GaI – CO⁺, 494 (95) [(C₅H₅)₂Fe(CO)₂]₂GaI – 2CO⁺, 373 (52) [(C₅H₅)Fe(CO)₂GaI]⁺, 242 (10) [(C₅H₅)₂Fe]⁺, 213 (1) [C₅H₅FeC₇H₈]⁺, 186 (35) [(C₅H₅)₂Fe]⁺, 121 (43) [C₅H₅Fe]⁺. — Anal. Found: C, 27.40; H, 2.28. Calc. for C₁₉H₁₈I₃Fe₂GaO₂ (840.5): C, 27.15; H, 2.16. — **4**: NMR (THF-*d*₈): δ ¹H (ppm) = 5.18 (s, C₅H₅). — IR (KBr, cm⁻¹): ν̄(C–O) 1992.9s, 1938.3s. — MS (70 eV, EI): *m/z* (%) = 522 (26) [(C₅H₅)Fe(CO)₂]₂GaI – CO⁺, 494 (29) [(C₅H₅)Fe(CO)₂]₂GaI – 2CO⁺, 373 (11) [(C₅H₅)Fe(CO)₂GaI]⁺, 317 (13) [(C₅H₅)Fe(CO)₂GaI – 2CO]⁺, 248 (8) [(C₅H₅)Fe]⁺, 186 (39) [(C₅H₅)₂Fe]⁺, 121 (26) [C₅H₅Fe]⁺. — Anal. Found: C, 28.85; H, 2.64. Calc. for C₄₂H₃₂Fe₆Ga₆I₂O₁₈·C₄H₁₀O (1906.1): C, 28.99; H, 2.22.

6.3. Synthesis of GaCl[CpFe(CO)₂]₂ (**5**)

A solution of K[CpFe(CO)₂] (0.76 g, 3.50 mmol) in 20 ml of THF was added dropwise to a stirred solution of Ga₂Cl₄·2dioxane (0.80 g, 1.75 mmol) in 20 ml of THF at ambient temperature. The mixture was stirred for an additional 2 h at room temperature. The color of the mixture turned red and a gray precipitate formed at the end of the reaction. After filtration and removal of all volatiles in vacuo, the residue was redissolved in 15 ml of THF. Red crystals of **5** were obtained by over-laying the THF solution with pentane at –30°C; yield: 0.33 g (35% with respect to iron). — **5**: ¹H-NMR (THF-*d*₈): δ = 4.87 (s, C₅H₅). — ¹³C-NMR (THF-*d*₈): δ = 83.7 (C₅H₅), 217.3 (CO). — IR (KBr, cm⁻¹): ν̄(C–O) 1992.1s, 1982.1s, 1971.4s, 1935.7s. — MS (70 eV, EI, M = GaCl[(C₅H₅)Fe(CO)₂]₂): *m/z* (%) = 458 (1.6) [M]⁺, 430 (22) [M – CO]⁺, 402 (33) [M – 2CO]⁺, 242 (31) [(C₅H₅)₂Fe]⁺, 225 (25) [C₅H₅FeGaCl]⁺,

186 (100) $[(C_5H_5)_2Fe]^{+*}$, 121 (53) $[C_5H_5Fe]^+$. Anal. Found; C, 40.35; H, 3.27. Calc. for $C_{18}H_{18}ClFe_2GaO_5$ (531.2): C, 40.70; H, 3.42.

6.4. Synthesis of

$\{(Et_2O)_2K(\mu-Cl)_2(\mu_3-Cl)Ga_2[CpFe(CO)_2]_4\}$ (**6**)

A solution of $K[CpFe(CO)_2]$ (0.43 g, 2.00 mmol) in 20 ml of THF was added dropwise to a stirred solution of $Ga_2Cl_4 \cdot 2$ dioxane (0.22 g, 0.50 mmol) in 20 ml of THF at $-78^\circ C$. No color change was observed at $-78^\circ C$. The mixture was warmed to ambient temperature slowly and stirred for an additional 8 h. The color of the mixture turned yellowish brown and a gray precipitate formed at the end of the reaction. After the removal of all volatiles in vacuo, the residue was redissolved in 15 ml of ether. Well-shaped orange red crystals of **6** were obtained upon cooling the solution to $-4^\circ C$, yield 0.23 g **6** (40% with respect to iron). **6**: 1H -NMR (THF- d_6): $\delta = 4.86$ (s, C_5H_5). — ^{13}C -NMR (THF- d_6): $\delta = 83.7$ (C_5H_5). — IR (KBr, cm^{-1}): $\tilde{\nu}(C-O)$ 2003.7s, 1933.7s. — MS (70 eV, EI): m/z (%) = 458 (7.3) $\{[(C_5H_5)Fe(CO)_2]_2GaCl\}^{+*}$, 430 (55) $\{[(C_5H_5)Fe(CO)_2]_2GaCl - CO\}^{+*}$, 402 (50) $\{[(C_5H_5)Fe(CO)_2]_2GaCl - 2CO\}^{+*}$, 242 (52) $[(C_5H_5)_2Fe_2]^{+*}$, 225 (64) $[C_5H_5FeGaCl]^+$, 186 (100) $[(C_5H_5)_2Fe]^{+*}$, 121 (88) $[C_5H_5Fe]^+$. — Anal. Found: C, 35.33; H, 2.57. Calc. for $C_{28}H_{20}Cl_3Fe_4Ga_2KO_8 \cdot C_4H_{10}O$ (1066.8): C, 35.99; H, 2.81.

6.5. Synthesis of $(Et_2O)_4K_2(GaBr_2)_4FeO_2[(CpFe(CO)_2]_4$ (**8**)

$K[CpFe(CO)_2]$ (0.43 g, 2.00 mmol) was dissolved in 20 ml of THF and added dropwise to a vigorously stirred solution of $Ga_2Br_4 \cdot 2$ dioxane (0.63 g, 1.00 mmol) in 20 ml of THF. After warming to ambient temperature, the mixture was stirred for an additional 8 h. The color of the mixture turned to yellowish brown and a gray precipitate was formed. After the removal of all volatiles in vacuo, the residue was redissolved in 15 ml of ether. Pale yellow crystals of **8** were obtained by cooling the solution to $-4^\circ C$ for a few days; yield 0.32 g **8** (38% with respect to iron). **8**: 1H -NMR (THF- d_6): $\delta = 4.96$ (s, 20H, C_5H_5). — ^{13}C -NMR (THF- d_6): $\delta = 84.1$ (C_5H_5). — IR (KBr, cm^{-1}): $\tilde{\nu}(C-O)$ 1997.5s, 1946.6s. — MS (70 eV, EI): m/z (%) = 476 (9) $[Ga_2Br_2C_5H_5Fe(CO)_2]^+$, 448 (15) $[Ga_2Br_2C_5H_5Fe(CO)_2 - CO]^{+*}$, 406 (2) $[GaBr_2C_5H_5Fe(CO)_2]^{+*}$, 378 (10) $[GaBr_2C_5H_5Fe(CO)_2 - CO]^{+*}$, 350 (18) $[GaBr_2 - C_5H_5Fe(CO)_2 - 2CO]^{+*}$, 186 (96) $[(C_5H_5)_2Fe]^{+*}$, 200 (50) $[C_5H_5FeBr]^{+*}$, 121 (100) $[C_5H_5Fe]^+$. — Anal. Found: C, 24.86; H, 2.63. Calc. for $C_{44}H_{60}Br_8Fe_5Ga_4K_2O_4 \cdot (2088.5)$: C, 25.30; H, 2.90.

7. Supplementary material

For further details see Table 3, the crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150682 (**1a**), 150683 (**1b**), 150684 (**3**), 150685 (**4**), 150686 (**5**), 150687 (**6**), 150688 (**8**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

Acknowledgements

We thank Ms E. Möllhausen and Dr E. Baum (Universität Karlsruhe) for their assistance in X-ray data collection as well as Prof. Dr H. Schnöckel for diffractometer time. Financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and Chemetall GmbH is gratefully acknowledged.

References

- [1] G. Linti, M. Kehrwald, W. Köstler, A. Rodig, T. Blank, N. Wiberg, *Organometallics* (2000), in press.
- [2] G. Linti, H. Schnöckel, *Coord. Chem. Rev.* 206–207 (2000) 285.
- [3] R.A. Fischer, J. Weiß, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 2830.
- [4] N.A. Compton, R.J. Errington, N.C. Norman, *Adv. Organomet. Chem.* 31 (1990) 91.
- [5] K.H. Whitmire, *J. Coord. Chem. Sect. B* 17 (1988) 95.
- [6] P. Corradini, A. Sirigu, *Inorg. Chem.* 6 (1967) 601.
- [7] C. Böhme, G. Frenking, *Chem. Eur. J.* 5 (1999) 2184.
- [8] F.A. Cotton, X. Feng, *Organometallics* 17 (1998) 128.
- [9] R. Köppe, H. Schnöckel, *Z. anorg. allg. Chem.* 626 (2000) 1095.
- [10] G. Linti, W. Köstler, *Angew. Chem.* 109 (1997) 2758; *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2644.
- [11] G. Linti, A. Rodig, *Angew. Chem.* 112 (2000) 3076; *Angew. Chem. Int. Ed. Engl.* 39 (2000) 2952.
- [12] A. Schnepf, E. Weckert, G. Linti, H. Schnöckel, *Angew. Chem.* 111 (1999) 3578; *Angew. Chem. Int. Ed. Engl.* 38 (1999) 3381.
- [13] M.L.H. Green, P. Mountford, G.J. Smout, S.R. Speel, *Polyhedron* 9 (1990) 2763.
- [14] R.A. Fischer, A. Miehr, T. Priermeier, *Chem. Ber.* 128 (1995) 831.
- [15] G.N. Harakas, B.R. Whittlesey, *Inorg. Chem.* 36 (1997) 2704.
- [16] N.C. Norman, L.M. Clarkson, L.J. Farrugia, *Organometallics* 10 (1991) 1286.
- [17] R.M. Campbell, L.M. Clarkson, W. Clegg, D.C.R. Hockless, N.L. Pickett, N.C. Norman, *Chem. Ber.* 125 (1992) 55.
- [18] B.R. King, F.G.A. Stone, *Inorg. Synth.* 7 (1963) 110.
- [19] B.F. Hallam, P.L. Pauson, *J. Chem. Soc.* (1956) 3030.
- [20] G. Linti, R. Frey, W. Köstler, H. Urban, *Chem. Ber.* 129 (1996) 561.
- [21] A.F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1984.

- [22] X. He, R.A. Bartlett, P.P. Power, *Organometallics* 13 (1994) 548.
- [23] O. Treutler, R. Ahlrichs, *J. Chem. Phys.* 102 (1995) 346.
- [24] A.H. Cowley, A. Decken, C.A. Olazabal, N.C. Norman, *Inorg. Chem.* 33 (1994) 3435.
- [25] J. Store, T. Belgardt, D. Stalke, H.W. Roesky, *Angew. Chem.* 106 (1994) 1365; *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1244.
- [26] B. Neumüller, F. Gahlmann, *Angew. Chem.* 105 (1993) 1770; *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1701.
- [27] G. Linti, W. Köstler, *Chem. Eur. J.* 4 (1998) 942.
- [28] H.W. Schnitter, R.T. Albers, H.-G. Schmidt, C. Röpken, E. Parisini, G.M. Sheldrick, *Chem. Eur. J.* 3 (1997) 1783.
- [29] C.C. Landry, C.J. Harlan, S.G. Bott, A.R. Barron, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1201.
- [30] J.C. Beamish, M. Wilkinson, I.J. Worrall, *Inorg. Chem.* 17 (1978) 2026.
- [31] J.E. Ellis, E.A. Flom, *J. Organomet. Chem.* 99 (1975) 263.
- [32] R.C. Crittendon, X.-W. Li, J. Su, G.H. Robinson, *Organometallics* 16 (1997) 2443.
- [33] P. Jutzi, B. Neumann, G. Reumann, H.-G. Stämmler, *Organometallics* 17 (1998) 1305.
- [34] U. App, K. Merzweiler, *Z. anorg. allg. Chem.* 623 (1997) 478.
- [35] M.M. Schulte, Dissertation, Technische Universität München, 1996.
- [36] R.A. Fischer, T. Priermeier, W. Scherer, *J. Organomet. Chem.* 459 (1993) 65.
- [37] R.A. Fischer, M.M. Schulte, E. Herdtweck, M.R. Mattner, *Inorg. Chem.* 36 (1997) 2010.
- [38] J.J. Schneider, U. Denninger, J. Hagen, C. Krüger, D. Bläser, R. Boese, *Chem. Ber.* 120 (1997) 1876.
- [39] J.C. Vanderhoof, R.D. Ernst, F.W. Cagle, R.J. Neustadt, T.H. Cymbaluk, *Inorg. Chem.* 21 (1982) 1876.