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Unexpected Reactivity of Cp*Ga toward Fe−Cl Bonds: Synthesis and Structure of Cp*(Cp*Ga)$_2$FeGaCl$_2$·THF and of Cp*(CO)$_2$FeGa(η^2-Cp*)Cl

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Summary: The complex Cp(Cp*Ga)$_2$FeGaCl$_2$·THF (**1**) was obtained in the reaction of FeCl$_2$ with 3 equiv of η^5-pentamethylcyclopentadienylgallium (Cp*Ga) in THF. For the formation of **1**, the following unprecedented reaction sequence is proposed: (I) coordination of Cp*Ga to the iron center; (II) insertion of Cp*Ga into the Fe−Cl bond; (III) Cp*/Cl-[1,2]^2-exchange; (IV) σ−π rearrangement of the Cp* ligand. A comparable insertion step could be observed in the reaction of Cp*Ga with Cp*(CO)$_2$FeCl where the compound Cp*(CO)$_2$FeGa(η^2-Cp*)Cl (**2**) was formed. **1** and **2** are characterized by NMR, IR, and X-ray crystallographic data and by elemental analysis.*

Introduction

The ligand potential of Cp*Ga in transition metal chemistry has been demonstrated in two recent reports.[1,2] It has been shown that the substitution of weakly bonded ligands (CO, olefins) against the two-electron donor Cp*Ga leads to the formation of complexes where Cp*Ga adopts terminal as well as bridging positions. Here, we report on a novel reactivity pattern of Cp*Ga: Insertion into a transition metal halide bond and a subsequent Cp*/Cl exchange process followed by σ/π rearrangement of the Cp* ligand has been observed in the reaction with FeCl$_2$, besides the expected ligand substitution step. Insertion without further rearrangement was observed in the reaction with the electronically saturated compound Cp*(CO)$_2$FeCl.

Results and Discussion

Reaction of FeCl$_2$ with 3 equiv of Cp*Ga in refluxing THF led to the formation of the complex Cp*(Cp*Ga)$_2$FeGaCl$_2$·THF (**1**), indicated by a color change from light yellow to violet (Scheme 1).

Cp*(Cp*Ga)$_2$FeGaCl$_2$·THF (**1**) could be isolated in 65% yield as air-sensitive crystals. Complex **1** readily dissolves in THF and melts at 143 °C under slow decomposition. Crystals suitable for an X-ray structure analysis were obtained by cooling a THF solution to −30 °C. The molecular structure of **1** is shown in Figure 1. Crystallographic data are given in Table 1, and selected bond lengths and angles are collected in Table 2.

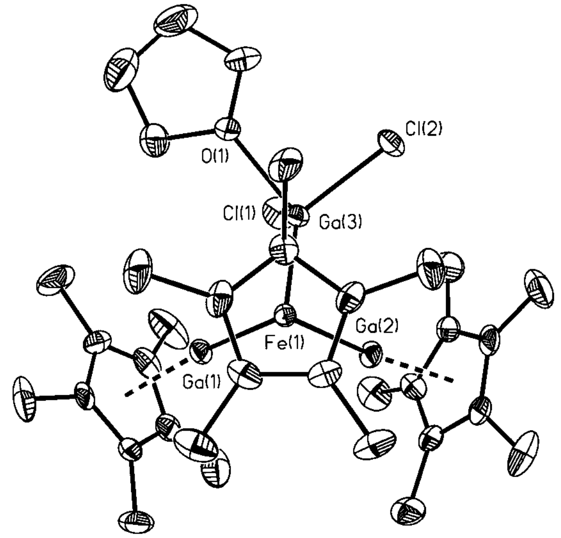

Figure 1. Molecular structure of Cp*(Cp*Ga)$_2$FeGaCl$_2$·THF (**1**).

Scheme 1

$$\mathrm{FeCl_2} + 3\ \mathrm{Cp^*Ga} \xrightarrow{\mathrm{THF}} \underset{\mathbf{1}}{\mathrm{Cp^*(Cp^*Ga)_2FeGaCl_2\cdot THF}}$$

In compound **1**, the iron atom is "pseudooctahedrally" coordinated by one η^5-bonded Cp* ring and by three gallium-containing fragments; two of them correspond to Cp*Ga molecules, while the remaining one corresponds to the GaCl$_2$·THF unit. The two Cp*Ga ligands are found in terminal positions with Ga−Fe distances of 2.2790(15) and 2.2764(15) Å. These values are in the same range as that observed for Fe(Cp*Ga)(CO)$_4$ (2.2731(4) Å)[1] and are significantly greater than that found in the "ferrogallyne" (C$_6$H$_3$Mes*$_2$)GaFe(CO)$_4$ (2.2248(7) Å).[3] Within the Cp*Ga units, the η^5-bonding mode of the Cp* ring is maintained, although small deviations from ideal η^5-bonding are observed (Table 2). The distance from the Fe center to the gallium atom of the GaCl$_2$·THF moiety (Ga(3)) is slightly longer (2.3208(17) Å). The geometry at the Ga(3) atom deviates considerably from tetrahedral arrangement (Cl−Ga(3)−O, 90.66(17)°, 90.89(15)°; Fe−Ga−Cl, 126.42(8)°, 121.63(8)°); a comparable situation is observed in other transition metal compounds containing a GaCl$_2$·THF unit.[4−6] Concerning the substituents at the Ga(3)−Fe unit, a sterically favored

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Table 1. Crystallographic Data for $Cp^*(Cp^*Ga)_2FeGaCl_2{\cdot}THF$ (1) and for $Cp^*(CO)_2FeGa(\eta^2\text{-}Cp^*)Cl$ (2)

empirical formula	$C_{34}H_{53}Cl_2FeGa_3O$ (**1**)	$C_{22}H_{30}ClFeGaO_2$ (**2**)
fw	813.67	487.48
cryst color, habit	violet, irregular	yellow, irregular
cryst size, mm^3	0.80 × 0.60 × 0.60	0.5 × 0.4 × 0.3
temp, K	173	
wavelength	Mo Kα 0.71073 Å	
space group	orthorhombic, *Pbca*	monoclinic P2(1)/c
unit cell dimens	$a = 11.344(4)$ Å $b = 19.122(9)$ Å $c = 33.030(19)$ Å	$a = 15.354(5)$ Å $b = 8.682(3)$ Å $c = 17.065(5)$ Å $\beta = 91.66(3)°$
V, Å^3	7165(6)	2274(1)
Z	8	4
density (calcd), Mg/m^3	1.509	1.424
θ range for data collection	2.13−27.00°	2.39−27.00°
no. of reflns collected	7824	5143
no. of ind reflns	7824	4960
abs corr	empirical from ψ-scans	
final R_F [$I > 2\sigma(I)$]	0.0699 [4334]	0.0538 [3157]
wR_{F^2} (all data)	0.1754	0.1185
no. of params	371	254
largest diff peak and hole, e Å^{-3}	0.881 and −1.054	0.527 and −0.400
diffractometer used	Siemens P2(1) diffractometer	
programs used	Siemens SHELXTL plus/SHELXL-97	
structure refinement	full-matrix least-squares on F^2	

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

Ga(1)−C(1)	2.273(8)	Fe(1)−C(21)	2.079(8)
Ga(1)−C(2)	2.308(8)	Fe(1)−C(22)	2.065(7)
Ga(1)−C(3)	2.320(8)	Fe(1)−C(23)	2.082(8)
Ga(1)−C(4)	2.393(7)	Fe(1)−C(24)	2.077(8)
Ga(1)−C(5)	2.398(7)	Fe(1)−C(25)	2.085(7)
Ga(2)−C(11)	2.291(7)	Ga(1)−Fe(1)	2.2790(15)
Ga(2)−C(12)	2.251(7)	Ga(2)−Fe(1)	2.2764(15)
Ga(2)−C(13)	2.307(8)	Ga(3)−Fe(1)	2.3208(17)
Ga(2)−C(14)	2.382(8)	Ga(3)−Cl(1)	2.272(3)
Ga(2)−C(15)	2.375(8)	Ga(3)−Cl(2)	2.286(2)
$Cp^*_{(centroid)}$−Ga(1)	2.007(7)	Ga(3)−O(1)	2.157(5)
$Cp^*_{(centroid)}$−Ga(2)	1.986(7)		
Fe(1)−Ga(3)−Cl(1)	126.42(8)	Ga(1)−Fe(1)−Ga(2)	92.93(5)
Fe(1)−Ga(3)−Cl(2)	121.63(8)	Ga(2)−Fe(1)−Ga(3)	82.86(5)
Fe(1)−Ga(3)−O(1)	118.22(16)	Ga(1)−Fe(1)−Ga(3)	88.97(6)
Cl(1)−Ga(3)−Cl(2)	100.01(9)		
O(1)−Ga(3)−Cl(1)	90.66(17)		
O(1)−Ga(3)−Cl(2)	90.89(15)		

staggered conformation is adopted. The Ga(3)−O(1) bond length (2.157(5) Å) is in a range typically observed for complexes with this subunit.[4−6]

In solution, fast dynamic processes within the Cp* units at the Ga atoms lead to averaged NMR signals (^1H, ^{13}C). The same phenomenon is observed for the Cp* ring located at the iron center. The NMR shifts of the THF protons in **1** differ (1.15/3.52 ppm) from those of noncoordinated THF (1.41/3.56 ppm) (solvent C_6D_6).

In the described reaction, a Cp* ring introduced by the Cp*Ga molecule is finally located at the iron center; the two chlorine atoms introduced by the $FeCl_2$ unit are finally bound to the Ga(3) atom. The following reaction sequence is proposed: In a first step, Cp*Ga molecules coordinate to the iron center of "$FeCl_2(THF)_x$".[7] In a second step, a Cp*Ga unit inserts into the Fe−Cl bond. This process is followed by a Cp*/Cl-[1,2]^2-exchange. Finally, ligand extrusion and σ/π rearrangement of the Cp* ring at the iron atom leads to the formation of **1**. The driving force for the reaction sequence discussed is the formation of the 18 valence electron complex **1**. The proposed key steps are shown in Scheme 2.

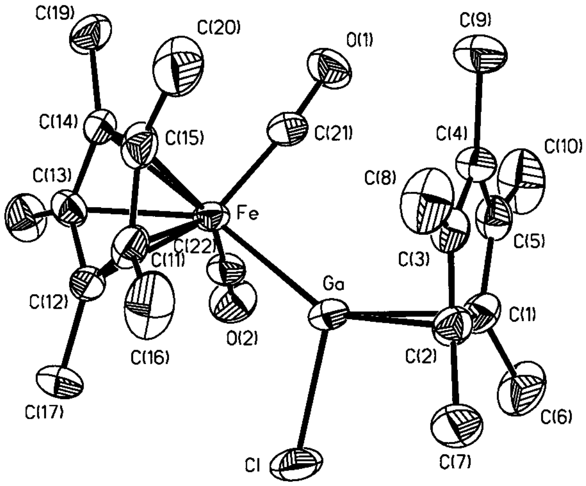
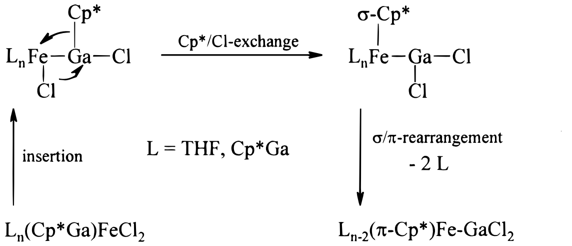
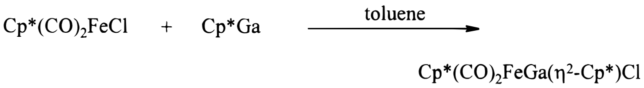


Figure 2. Molecular structure of $Cp^*(CO)_2FeGa(\eta^2\text{-}Cp^*)$-Cl (**2**).

Scheme 2



Scheme 3



2

A comparable insertion step could be observed in the reaction of Cp*Ga with the 18 valence electron complex $Cp^*(CO)_2FeCl$. Here, insertion without further rearrangements led to the formation of the complex $Cp^*(CO)_2FeGa(\eta^2\text{-}Cp^*)Cl$ (**2**). The air and moisture sensitive compound **2** melts at 163 °C but decomposes slowly under these conditions. The solid-state structure of **2** could be determined by X-ray diffraction studies and is shown in Figure 2. Crystallographic data are given in Table 1; selected bond lengths and angles are collected in Table 3.

In **2**, the configuration at the Fe center is comparable to that in **1**. The compound exhibits Fe−C(CO) distances of 1.745(4) and 1.765(4) Å and C−O distances of 1.148(5) and 1.166(6) Å. These bond lengths are shorter (Fe−C) and longer (C−O) than those of $Cp^*(CO)_2FeCl$,[8] indicating that the $Ga(\eta^2\text{-}Cp^*)Cl$ unit is a comparatively

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(7) The compound $FeCl_2(THF)_2$ has been isolated from THF solutions of $FeCl_2$: Herzog, S.; Gustav, K.; Krüger, E.; Berender, H.; Schuster, R. *Z. Chem.* **1963**, *11*, 428. The presence of "$FeCl_2(THF)_x$" in THF solution is assumed.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

Ga−C(1)	2.168(5)	C(1)−C(2)	1.450(6)
Ga−C(2)	2.212(4)	C(2)−C(3)	1.397(6)
Ga−C(3)	2.804(4)	C(3)−C(4)	1.407(6)
Ga−C(4)	3.083(4)	C(4)−C(5)	1.411(7)
Ga−C(5)	2.756(5)	C(5)−C(1)	1.405(6)
Fe−C(11)	2.126(5)	Fe−C(21)	1.765(4)
Fe−C(12)	2.107(4)	Fe−C(22)	1.745(5)
Fe−C(13)	2.114(5)	C(21)−O(1)	1.148(5)
Fe−C(14)	2.092(4)	C(22)−O(2)	1.166(6)
Fe−C(15)	2.097(5)	Ga−Cl	2.2861(15)
		Fe−Ga	2.3355(10)

C(1)−Ga−Fe	138.31(13)
C(2)−Ga−Fe	140.50(12)
C(21)−Fe−C(22)	95.3(2)
Cl−Ga−Fe	112.86(5)
$(\mathrm{Ga{-}C(1){-}C(2)})_{\mathrm{plane}}{-}\mathrm{Cp^*}_{\mathrm{plane}}$	93.6(4)

Table 4. Structural (Å) and IR Data ($\mathrm{cm^{-1}}$) for $\mathrm{Cp^*(CO)_2FeCl}$ and for 2

	d(Fe−C(CO))	*d*(C−O)	*ν*(CO)
$\mathrm{Cp^*(CO)_2FeCl}$	1.774(4)	1.055(5)	2024
	1.802(4)	1.132(5)	1967
$\mathrm{Cp^*(CO)_2FeGa(\eta^2\text{-}Cp^*)Cl}$ (**2**)	1.745(4)	1.148(5)	1978
	1.765(4)	1.166(6)	1924

better electron donor (see Table 4). The Fe−Ga bond length is 2.3355(10) Å; a similar distance is found in the compound $[\mathrm{Cp^*(CO)_2Fe(Cl)(\mu\text{-}O^iPr)}]_2$ (2.3669(9) Å).[9] Within the Ga(Cp*)Cl part, the Cp*−Ga interaction is best described as η^2-bonding.[10]

The static η^2-bonding of the Cp* unit in the Ga(Cp*)-Cl fragment observed in the solid state is not maintained in solution. Fast haptotropic shifts lead to averaged NMR signals (^{1}H, ^{13}C) for the Cp* methyl groups and for the Cp* ring atoms. The pronounced electron-donating effect of the Ga(η^2-Cp*)Cl unit is indicated in the IR spectrum of **2**. Here, two CO stretching vibrations are observed (1978, 1924 $\mathrm{cm^{-1}}$), which are shifted toward lower wavenumbers compared to those in $\mathrm{Cp^*(CO)_2FeCl}$[11] (Table 4).

A reaction sequence including Cp*Ga insertion and Cp*/Cl-[1,2]^2-exchange is unprecedented. Although insertions of RM fragments (M = group 13 element) have been reported in a few cases,[12] the insertion of Cp*Ga has never been observed before. It is intended to explore the reactivity of Cp*Ga toward other transition metal halide bonds. The described reaction sequence once more demonstrates the versatility of the Cp* system in main group chemistry.[13] In this context it is interesting to note that a similar Cp* migration has already been observed in phosphorus chemistry.[14]

Experimental Section

General Comments. All manipulations were carried out under a purified argon atmosphere using standard vacuum techniques. The solvents were purified by conventional means and distilled immediately prior to use. Cp*Ga[1] and $\mathrm{Cp^*(CO)_2FeCl}$[15] were prepared according to the literature. $\mathrm{FeCl_2}$ was purchased from Merck and used without further purification. The melting point determinations were performed using a Büchi 510 melting point apparatus. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld. The NMR spectra were recorded in benzene-d_6 using a Bruker Avance DRX 500 spectrometer (^{1}H 500.1 MHz; ^{13}C{^{1}H} 125.8 MHz). Chemical shifts are reported in ppm and were referenced to the solvent resonances as internal standard. IR data were collected using a Bruker Vektor 22-FT spectrometer. The samples were measured as KBr pellets.

Preparation of $\mathrm{Cp^*(Cp^*Ga)_2FeGaCl_2{\cdot}THF}$ (1). Cp*Ga (0.24 g, 1.18 mmol) in THF (5 mL) was added dropwise with stirring to a solution of $\mathrm{FeCl_2}$ (0.05 g, 0.39 mmol) in THF (30 mL). While the reaction mixture was stirred at reflux for 3 h, the color of the solution changed from initially light yellow to violet. After the mixture was cooled to room temperature, all volatile components were removed in vacuo. The red-violet residue was dissolved in THF and filtered. The filtrate was concentrated and cooled to −30 °C to yield 0.21 g of **1** (0.25 mmol, 65%) in form of violet crystals.

Mp: 143 °C (dec). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.15 (t, 4H, THF), 1.52 (s, 15 H, $\mathrm{Cp^*_{(Fe)}}$ methyl), 1.68 (s, 30 H, $\mathrm{Cp^*_{(Ga)}}$ methyl), 3.52 (t, 4H, THF). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 9.38 ($\mathrm{Cp^*_{(Ga)}}$ methyl), 10.53 ($\mathrm{Cp^*_{(Fe)}}$ methyl), 24.8 (THF), 68.1 (THF), 95.41 ($\mathrm{Cp^*_{(Fe)}}$ ring), 115.82 ($\mathrm{Cp^*_{(Ga)}}$ ring). IR ($\mathrm{cm^{-1}}$, KBr): 2958(w), 2906(m), 2855(m), 1422(w), 1375(w), 1098(w), 1015(w). Anal. Calcd for $\mathrm{C_{34}H_{53}Cl_2FeGa_3O}$ (M = 813.67 g $\mathrm{mol^{-1}}$): C, 50.18; H, 6.56. Found: C, 50.07; H, 6.30.

Preparation of $\mathrm{Cp^*(CO)_2FeGa(\eta^2\text{-}Cp^*)Cl}$ (2). Cp*Ga (0.16 g, 0.78 mmol) was added dropwise with stirring to a solution of $\mathrm{Cp^*(CO)_2FeCl}$ (0.22 g, 0.78 mmol) in toluene (30 mL). While the mixture was stirred at room temperature for 20 h, the color of the solution changed from initially red to orange-yellow. Subsequently, the solvent was removed in vacuo. The residual orange solid was dissolved in *n*-hexane and filtered. The filtrate was concentrated and cooled to −60 °C to yield 0.34 g of **2** (0.70 mmol, 90%) in the form of yellow crystals.

Mp: 163 °C (dec). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.50 (s, 15 H, $\mathrm{Cp^*_{(Fe)}}$ methyl), 2.09 (s, 15 H, $\mathrm{Cp^*_{(Ga)}}$ methyl). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 10.16 ($\mathrm{Cp^*_{(Fe)}}$ methyl), 12.02 ($\mathrm{Cp^*_{(Ga)}}$ methyl), 95.16 ($\mathrm{Cp^*_{(Fe)}}$ ring), 121.70 ($\mathrm{Cp^*_{(Ga)}}$ ring), 215.49 (CO). IR ($\mathrm{cm^{-1}}$, KBr): 2960(w), 2910(m), 2857(m), 1978(s), 1924(s), 1074(w), 1032(w). Anal. Calcd for $\mathrm{C_{22}H_{30}ClFeGaO_2}$ (M = 487.48 g $\mathrm{mol^{-1}}$): C, 54.20; H, 6.20. Found: C, 53.92; H, 6.03.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Alcoholysis of **2** with ^{i}PrOH leds to the formation of the compound $[\mathrm{Cp^*(CO)_2Fe(Cl)(\mu\text{-}O^iPr)}]_2$: Jutzi, P.; Schebaum, L. O., unpublished results.

(10) The bonding between the Cp* ring and the Ga atom in **2** has to be classified as a π-interaction. Remarkably, the Ga atom is found slightly outside the $\mathrm{C_5}$ cylinder (angle between the Cp* ring plane and the Ga−C(1)−C(2) triangle: 93.6(4)°). This situation is unique. As expected for a π-bonded Cp* ring, no bond length alternation inside the $\mathrm{C_5}$ perimeter is observed.

(11) Measured as KBr pellet.

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(15) $\mathrm{Cp^*(CO)_2FeCl}$[8] was prepared in a procedure analogous with $\mathrm{Cp(CO)_2FeCl}$: Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*. 3. Bd.; Stuttgart Enke, 1981; p 1954.