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Steric Demand of the Cp*Ga Ligand: Synthesis and Structure of Ni(Cp*Ga)$_4$ and of *cis*-M(Cp*Ga)$_2$(CO)$_4$ (M = Cr, Mo)

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*Summary: In the reaction of (η^5-pentamethylcyclopentadienyl)gallium (Cp*Ga) with Ni(COD)$_2$ (COD = 1,5-cyclooctadiene) and NorM(CO)$_4$ (Nor = norbornadiene; M = Cr, Mo) the complexes Ni(Cp*Ga)$_4$ (**1**) and cis-M(Cp*Ga)$_2$(CO)$_4$ (M = Cr (**2**), Mo (**3**)), respectively, were obtained. Compounds **1**−**3** were characterized by NMR and IR data and by elemental analysis. In addition, an X-ray crystal structure analysis was performed on complexes **1** and **3**. Cis-orientation of the Cp*Ga ligands is made possible by deviation of the Cp*$_{centroid}$−Ga−M vector from linearity. **1** is the first homoleptic complex with Cp*Ga as ligand.*

Introduction

Very recent investigations have shown that RGa fragments are interesting novel ligands in transition-metal chemistry.[1,2] In a preliminary report, we have shown that the reaction of Cp*Ga with Cr(CO)$_5$(C$_8$H$_{14}$) (C$_8$H$_{14}$ = *cis*-cyclooctene), Fe$_2$(CO)$_9$, Fe(CO)$_3$CHT (CHT = cycloheptatriene), Co$_2$(CO)$_8$, and Ni(CO)$_4$ leads to the complexes Cr(Cp*Ga)(CO)$_5$ (**4**), Fe(Cp*Ga)(CO)$_4$ (**5**), Fe$_2$(μ-Cp*Ga)$_3$(CO)$_6$ (**6**), Co$_2$(μ-Cp*Ga)$_2$(CO)$_6$ (**7**), and Ni$_4$(μ-Cp*Ga)$_4$(CO)$_6$ (**8**), respectively, where Cp*Ga adopts terminal as well as bridging positions.[2] The steric demand of this ligand can be estimated from its calculated cone angle;[3] from there the question arises how many Cp*Ga ligands can be fixed in terminal positions and in cis-orientation to a transition-metal center. In this context we report here on the synthesis and structure of the compounds Ni(Cp*Ga)$_4$ (**1**) and *cis*-M(Cp*Ga)$_2$(CO)$_4$ (M = Cr (**2**), Mo (**3**)).

Results and Discussion

Reaction of Ni(COD)$_2$ (COD = 1,5-cyclooctadiene) with 4 equiv of Cp*Ga in refluxing *n*-hexane led to a full substitution of COD by Cp*Ga ligands and to the formation of the homoleptic nickel complex Ni(Cp*Ga)$_4$ (**1**) (Scheme 1).

Scheme 1

$$\mathrm{Ni(COD)_2} + 4\ \mathrm{Cp^*Ga} \xrightarrow[\text{- 2 COD}]{\text{n-hexane}} \underset{\mathbf{1}}{\mathrm{Ni(Cp^*Ga)_4}}$$

(COD = 1,5-cyclooctadiene)

Scheme 2

$$\mathrm{NorM(CO)_4} + 2\ \mathrm{Cp^*Ga} \xrightarrow[\text{- Nor}]{\text{n-hexane}} \underset{\mathbf{2, 3}}{cis\text{-}\mathrm{M(Cp^*Ga)_2(CO)_4}}$$

(Nor = norbornadiene; M = Cr, Mo)

Ni(Cp*Ga)$_4$ (**1**) could be isolated in 60% yield as orange crystals. The compound is rather air-stable and can be handled in air for at least several hours. It melts at 192 °C but decomposes slowly under these conditions. The complex dissolves easily in aprotic organic solvents such as *n*-hexane and toluene.

The reaction of NorM(CO)$_4$ (Nor = norbornadiene, M = Cr, Mo) with 2 equiv of Cp*Ga resulted in the formation of the corresponding transition-metal complexes *cis*-M(Cp*Ga)$_2$(CO)$_4$ (M = Cr (**2**), Mo (**3**)) (Scheme 2), which could be isolated in high yield in the form of yellow crystals. They melt with decomposition at approximately 180 °C and are soluble in aprotic organic solvents.

Complexes **1**−**3** have been characterized by means of NMR and IR data and by elemental analysis. By repeated crystallization from toluene crystals suitable for an X-ray structure analysis were obtained for **1** and **3**.

The molecular structure of **1** is presented in Figure 1. Crystallographic data are given in Table 1, and selected bond lengths and angles are collected in Table 2.

Complex **1** crystallizes in the tetragonal space group $I\bar{4}$, showing the nickel atom tetrahedrally coordinated by four Ga atoms with Ga−Ni−Ga angles of 109.5°. The Ga−Ni bond length is 2.2188(5) Å; this distance is slightly shorter than those observed in Ni$_4$(Cp*Ga)$_4$(CO)$_6$.[4] The Cp*$_{centroid}$−Ga distance is 2.003(4) Å and is thus shortened by about 4% in comparison to the corresponding distance of Cp*Ga in the solid state[5] or

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[4] The Ga−Ni distances in Ni$_4$(Cp*Ga)$_4$(CO)$_6$[2] are found between 2.2933(11) and 2.8321(13) Å.

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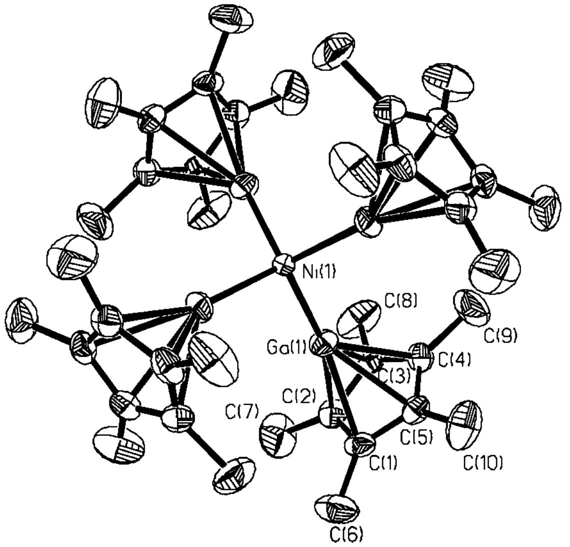

Figure 1. Molecular structure of $\mathrm{Ni(Cp^*Ga)_4}$ (**1**), with thermal ellipsoids at 50% probability.

Table 1. Crystallographic Data for $\mathrm{Ni(Cp^*Ga)_4}$ (1) and *cis*-$\mathrm{Mo(Cp^*Ga)_2(CO)_4}$ (3)

	$\mathrm{C_{40}H_{60}Ga_4Ni}$ (**1**)	$\mathrm{C_{24}H_{30}Ga_2MoO_4}$ (**3**)
fw	878.51	616.94
cryst color, habit	brown, octahedral	yellow, irregular
cryst size, mm^3	0.90 × 0.80 × 0.50	0.70 × 0.40 × 0.30
temp, K	173(2)	
wavelength	Mo Kα, 0.710 73 Å (graphite monochromator)	
space group	tetragonal, $I\bar{4}$	triclinic, $P\bar{1}$
unit cell dimens		
a, Å	12.110(2)	8.377(3)
b, Å	12.110(2)	9.397(3)
c, Å	14.955(4)	18.548(8)
α, deg	90	85.56(3)
β, deg	90	82.10(3)
γ, deg	90	66.34(3)
V, Å^3	2193.2(8)	1324.3(9)
Z	2	2
density (calcd), Mg/m^3	1.330	1.550
θ range for data collecn, deg	2−30	2−28.5
no. of rflns collected	3581	7144
no. of indep rflns	3180 (R_{Int} = 0.0641)	6699 (R_{Int} = 0.0382)
abs cor	empirical from *ψ*-scans	
final R_F [$I > 2\sigma(I)$]	0.0479 [2948]	0.0493 [4862]
$R_{\mathrm{w}F^2}$ (all data)	0.1212	0.1130
no. of params	107	326
largest diff peak and hole, e Å^{-3}	0.456 and −0.454	0.633 and −0.829
diffractometer used	Siemens P2(l) diffractometer	
programs used	Siemens SHELXTL plus/SHELXL-97	
structure refinement	full-matrix least squares on F^2	
remarks		displaced Cp* ring (78:22); rings adjusted using SAME

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

Ga(1)−C(1)	2.334(4)	Ga(1)−C(5)	2.351(4)
Ga(1)−C(2)	2.329(4)	Ga(1)−Ni(1)	2.2188(5)
Ga(1)−C(3)	2.331(4)	$\mathrm{Cp^*_{centroid}}$−Ga	2.003(4)
Ga(1)−C(4)	2.346(4)		
Ga−Ni(1)−Ga	109.46(15)	$\mathrm{Cp^*_{centroid}}$−Ga−Ni	164.70(10)

in the gas phase.[6] The Cp* moieties are nearly symmetrically η^5-bonded to the gallium centers, but a substantial deviation from linearity is observed for the $\mathrm{Cp^*_{centroid}}$−Ga−Ni vectors (165°). Repulsive intramolecular interactions between the Cp* methyl groups of different Cp*Ga ligands (cone angle *θ* 112°) are the main reason for the observed deviation; they would cause steric stress in case of a linear $\mathrm{Cp^*_{centroid}}$−Ga−Ni arrangement. The asymmetry within the Cp*GaNi moiety in the solid state is not maintained in solution. Here, fast haptotropic shifts in the Cp* part of the molecule lead to averaged NMR signals (^{1}H, ^{13}C) for the Cp* methyl groups and for the Cp* ring atoms, even at low temperature (−80 °C). In the IR spectrum, absorptions typical for the Cp* ring system (2958, 2906, and 2855 cm^{-1}) are detected. **1** is the first homoleptic complex with Cp*Ga as ligand and, except for $\mathrm{Ni[InC(SiMe_3)_3]_4}$,[7] is the only homoleptic transition-metal compound containing ElR ligands (El = group 13 element).

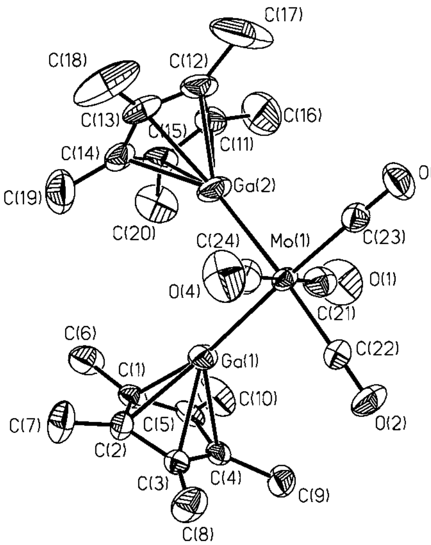

Figure 2. Molecular structure of *cis*-$\mathrm{Mo(Cp^*Ga)_2(CO)_4}$ (**3**), with thermal ellipsoids at 50% probability.

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

Ga(1)−C(1)	2.257(4)	Ga(2)−C(11)	2.253(8)
Ga(1)−C(2)	2.244(4)	Ga(2)−C(12)	2.268(7)
Ga(1)−C(3)	2.282(4)	Ga(2)−C(13)	2.276(6)
Ga(1)−C(4)	2.302(4)	Ga(2)−C(14)	2.286(7)
Ga(1)−C(5)	2.298(4)	Ga(2)−C(15)	2.314(11)
Ga(1)−Mo(1)	2.554(1)		
Ga(2)−Mo(1)	2.537(1)		
O(1)−C(21)	1.144(6)	Mo(1)−C(21)	2.037(6)
O(2)−C(22)	1.158(5)	Mo(1)−C(22)	1.972(4)
O(3)−C(23)	1.153(5)	Mo(1)−C(23)	1.977(5)
O(4)−C(24)	1.152(6)	Mo(1)−C(24)	2.046(6)
$\mathrm{Cp^*(1)_{centroid}}$−Ga(1)	1.928(6)		
$\mathrm{Cp^*(2)_{centroid}}$−Ga(2)	1.932(6)		
Ga(1)−Mo(1)−Ga(2)	90.34(4)		
$\mathrm{Cp^*(1)_{centroid}}$−Ga(1)−Mo(1)	160.8(6)		
$\mathrm{Cp^*(2)_{centroid}}$−Ga(2)−Mo(1)	172.2(6)		

The molecular structure of **3** in the solid state is shown in Figure 2. Crystal structure parameters are given in Table 1, and selected bond lengths and angles are collected in Table 3.

The structure of **3** contains two Cp*Ga units in cis-orientation to the molybdenum center with Ga−Mo

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Table 4. $Cp^*_{centroid}$−Ga Distances (Å) for Complexes with Terminal Cp*Ga Ligands

	$Cr(Cp^*Ga)(CO)_5$ (**4**) $Fe(Cp^*Ga)(CO)_4$ (**5**)	*cis*-$Mo(Cp^*Ga)_2(CO)_4$ (**3**)	$Ni(Cp^*Ga)_4$ (**1**)	Cp*Ga
$d(Cp^*_{centroid}-Ga)$	1.910(4) 1.863(4)	1.930(6)	2.003(4)	2.081(5)

distances of 2.5536(14) and 2.5373(11) Å, respectively; this interaction is similar to that in the only other structurally investigated example, $(\eta^5\text{-}C_5H_4Me)(CO)_3MoGaI_2\cdot Et_2O$ (2.582(2) Å).[8] The Ga−Mo−Ga angle is 90° within experimental error, and $Cp^*_{centroid}$−Ga distances are 1.928(6) and 1.932(6) Å, respectively. Similar to the situation in **1**, the Cp* ligands are nearly symmetrically η^5-bonded to the gallium atoms, but pronounced deviations from linearity are observed for the $Cp^*_{centroid}$−Ga−Mo vectors (160.8(6)/172.2(6)°). These deviations are necessary to allow the cis-orientation of two Cp*Ga units (cone angle θ 107°) at an octahedrally coordinated metal center. In the $Mo(CO)_4$ part of the molecule, the $Mo-CO_{axial}$ distances (2.042(6) Å, average) are greater than the $Mo-CO_{equatorial}$ (1.975(5) Å, average) distances, thus indicating pronounced back-bonding in positions with trans-oriented Cp*Ga ligands. Corresponding to a dynamic Cp* system, only one kind of methyl group is detected by NMR spectroscopy for **2** and **3**. The IR spectra show absorptions in the ν_{CO} region typical for terminal CO ligands (between 1986 and 1861 cm^{-1}).

It is interesting to compare the $Cp^*_{centroid}$−Ga distances in transition-metal compounds with respect to the character of the Ga−metal interaction. In Table 4 data are given for Cp*Ga and for complexes with terminal Cp*Ga ligands.

In all compounds the $Cp^*_{centroid}$−Ga distances are shortened in comparison to those of Cp*Ga in the solid state[5] or in the gas phase.[6] A reduced distance corresponds to a gallium atom in a comparatively higher oxidation state and indicates predominant σ-donor quality of the Cp*Ga fragment. The shortest $Cp^*_{centroid}$−Ga distances are observed in the monosubstituted complexes $Cr(Cp^*Ga)(CO)_5$ (**4**) and $Fe(Cp^*Ga)(CO)_4$ (**5**), indicating the most pronounced electron donation toward the transition-metal center. In **3**, the overall electron donation is less effective due to the presence of a second Cp*Ga ligand; this is documented by the comparatively longer $Cp^*_{centroid}$−Ga distances. The longest $Cp^*_{centroid}$−Ga distance in this series is found in the homoletic nickel complex **1**, thus indicating only weak electron transfer from each of the four Cp*Ga units.

From molecular models it can be concluded that it is difficult to prepare compounds with three terminal Cp*Ga ligands at an octahedrally coordinated metal center. In this context it is interesting to note that the reaction of $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo, W) with Cp*Ga proceeds with elimination of CH_3CN and results in the formation of compounds with the general composition $M_2(Cp^*Ga)_3(CO)_6$, where the Cp*Ga presumably adopts bridging positions. The structures of these complexes have not yet been fully defined.[9]

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. $Ni(COD)_2$ was commercially available; $NorM(CO)_4$ (M = Cr, Mo) was prepared according to literature methods.[10] 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 (^1H, 500.1 MHz; $^{13}C\{^1H\}$, 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 $Ni(Cp^*Ga)_4$ (1). A solution of Cp*Ga (0.63 g, 3.05 mmol) in *n*-hexane (5 mL) was added dropwise to a solution of $Ni(COD)_2$ (0.21 g, 0.76 mmol) in *n*-hexane (25 mL). While the reaction mixture was heated at reflux for 3 h, the color of the solution changed from initially yellow to red-brown. After the mixture was cooled to room temperature, all volatile components were removed in vacuo. The red-brown residue was dissolved in toluene and filtered. The filtrate was concentrated and cooled to −30 °C to yield 0.47 g of $Ni(Cp^*Ga)_4$ (0.53 mmol, 70%) in the form of orange crystals.

Mp: 192 °C dec. ^1H NMR (C_6D_6): δ 1.94 (s, 60 H, Cp* methyl). ^{13}C NMR (C_6D_6): δ 10.12 (Cp* methyl), 112.97 (Cp* ring). IR (cm^{-1}, KBr): 2958 (w), 2906 (m), 2855 (m), 1422 (w), 1375 (w), 1098 (w), 1015 (w). Anal. Calcd for $C_{40}H_{60}NiGa_4$ (M_r = 878.51): C, 54.68; H, 6.88. Found: C, 54.66; H, 6.72.

Preparation of *cis*-$Cr(Cp^*Ga)_2(CO)_4$ (2) and of *cis*-$Mo(Cp^*Ga)_2(CO)_4$ (3). In a typical experiment a solution of 1.5 mmol of Cp*Ga and 0.75 mmol of the corresponding $NorM(CO)_4$ (M = Cr, Mo) complex in *n*-hexane (20 mL) was refluxed for 3 h. After the mixture was cooled to room temperature, all volatile components were removed in vacuo and the yellow residue was crystallized from toluene to give *cis*-$M(Cp^*Ga)_2(CO)_4$ in about 80% yield.

Data for **2**: mp 170 °C dec; ^1H NMR (C_6D_6) δ 1.83 (s, 30 H, Cp* methyl); ^{13}C NMR (C_6D_6) δ 9.33 (Cp* methyl), 114.86 (Cp* ring), 223.35/230.77 ($CO_{ax/eq}$); IR (cm^{-1}, KBr) 2966 (w), 2922 (w), 2866 (w), 1986 (m), 1900 (s, sh), 1890 (s), 1861 (s), 1362 (w), 1101 (w), 799 (w), 669 (m), 644 (m). Anal. Calcd for $C_{24}H_{30}O_4CrGa_2$ (M_r = 573.94): C, 50.22; H, 5.26. Found: C, 49.97; H, 5.47.

Data for **3**: mp 190 °C dec; ^1H NMR (C_6D_6) δ 1.81 (s, 30 H, Cp* methyl); ^{13}C NMR (C_6D_6) δ 9.39 (Cp* methyl), 114.63 (Cp* ring), 211.25/216.10 ($CO_{ax/eq}$); IR (cm^{-1}, KBr) 2963 (w), 2922 (w), 2864 (w), 2009 (m), 1910 (s, sh), 1904 (s), 1872 (s), 1383 (w), 1097 (w), 1021 (w), 799 (w), 608 (m), 580 (m). Anal. Calcd for $C_{24}H_{30}O_4MoGa_2$ (M_r = 616.94): C, 46.64; H, 4.89. Found: C, 46.48; H, 4.80.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond lengths and angles for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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