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A Convenient Synthesis of Cyclopentadienylgallium – The Awakening of a Sleeping Beauty in Organometallic Chemistry

Christian Schenk,[a] Ralf Köppe,[b] Hansgeorg Schnöckel,*[b] and Andreas Schnepf*[c]

Dedicated to Professor Malcolm L. H. Green on the occasion of his 75th birthday

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Solid "GaI" reacts with NaCp to yield (η^5-cyclopentadienyl)gallium (GaCp) (**1**). During the synthesis the side product, $CpGa{\rightarrow}GaCp_2I$ (**2**), with a rare gallium–gallium donor–acceptor bond could be isolated. The reaction of **1** with $B(C_6F_5)_3$ affords $CpGa{\rightarrow}B(C_6F_5)_3$ (**4**). The molecular structures of **2** and **4**, which contain the first GaCp moieties, are presented. The convenient synthesis of **1** needs only standard laboratory equipment and certainly opens the door for **1** to become a versatile reagent in organometallic chemistry; awakening the sleeping beauty GaCp nearly twenty years after its initial discovery.

Introduction

The synthesis and structural characterization of $(Cp^*Al)_4$[1] ($Cp^* = C_5Me_5$) was a milestone in organometallic chemistry,[2] as this organometallic compound was the very first to contain aluminum in the oxidation state +1. The synthesis of $(Cp^*Al)_4$ was initially performed by using metastable AlX solutions (X = Cl, Br, I), which are available by a preparative co-condensation technology;[3,4] therefore, a highly sophisticated method had to be applied.[5] $(Cp^*Al)_4$ dissociates to monomers in an equilibrium reaction in solution and in the gas phase; the monomer was structurally characterized a couple of years later.[6] However, although monomeric AlCp* is an exciting reagent for organometallic chemistry, its application was only made possible by Roesky et al., who discovered the easier synthetic route of reducing Cp^*AlCl_2 with potassium.[7] From that point onward, AlCp* became a versatile reagent, leading to a highly productive chemistry;[8] for example, lately the ruthenium polyhydride complex with AlCp* moieties $[Cp^*RuH_2AlCp^*]_2$ could be synthesized by the reaction of AlCp* with $[H_2RuCp^*]$.[9] The heavier congener GaCp*, which was also initially synthesized – like AlCp* – from metastable GaX solutions (X = Cl, Br, I), has a similar story. GaCp* is hexameric in the solid state[10] and monomeric in the gas phase.[11] However, the chemistry of GaCp* also just began after a simple way to prepare it was discovered by Jutzi et al. using the reduction of Cp^*GaI_2 with potassium.[12] In addition, GaCp* can be obtained by the even more simple metathesis reaction of LiCp* with solid "GaI",[13] a subhalide that is surprisingly easily available by sonication of a 1:1 mixture of elemental gallium and elemental iodine, as discovered by Green et al. in 1990.[14,15] After the convenient access to GaCp* was discovered, its chemistry flourished, leading to fascinating results in cluster chemistry as well as coordination chemistry in recent years.[16] Hence, only the new simpler approaches without using complicated synthetic routes (co-condensation technology) paved the way to the application of these Al^I and Ga^I compounds as conventional reagents in organometallic chemistry.

Results and Discussion

With respect to AlCp* and GaCp*, the sterically less demanding compound GaCp ($Cp = C_5H_5$) (**1**) is still a Sleeping Beauty[17] since its discovery nearly twenty years ago, as it was up to now exclusively available by the reaction of metastable GaX solutions with, for example, LiCp.[18]

We now found a simpler route to GaCp (**1**): In a way similar to the synthetic route used for the synthesis of GaCp*,[13] we treated solid "GaI" with NaCp in toluene at low temperatures to obtain a colorless solution of GaCp (**1**) after filtration. The presence of **1** in solution was confirmed

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[a] School of Chemistry, Monash University,
P. O. Box 23, Victoria 3800, Australia
[b] Institut für Anorganische Chemie, Karlsruher Institut für Technologie, KIT-Campus Süd,
Postfach 6980, 76049 Karlsruhe, Germany
Fax: +49-721-608-44854
E-mail: hansgeorg.schnoeckel@kit.edu
[c] Institut für Anorganische Chemie, Universität Duisburg-Essen,
Universitätsstrasse 5-7, 45117 Essen, Germany
Fax: +49-201-183-2296
E-mail: andreas.schnepf@uni-due.de

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by Raman spectroscopy (262.1 cm^{-1}) and ^{71}Ga NMR spectroscopy (–708.4 ppm), whose results are in accordance with literature values[18] and DFT calculations.[19,20] However, we were unable to obtain a molecular structure for pure GaCp, as it decomposes upon concentration even at –78 °C. Nevertheless, during attempts to crystallize **1**, we gained a few yellow crystals of $CpGa{\rightarrow}GaCp_2I$ (**2**), the first structurally characterized molecule exhibiting a $Ga^{I}Cp$ moiety (Figure 1).[21]

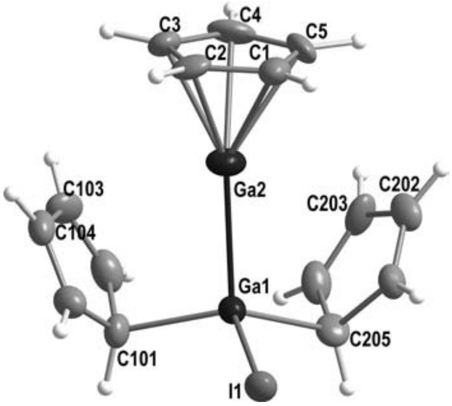

Figure 1. Molecular structure of $CpGa{\rightarrow}GaCp_2I$ (**2**) (thermal ellipsoids with 50% probability). Selected distances [pm] and angles [°]: Ga1–Ga2 246.90(17), Ga2–C1 230.5(12), Ga2–C2 229.4(10), Ga2–C3 224.0(9), Ga2–C4 223.8(11), Ga2–C5 228.6(10), Ga1–C101 204.6(12), Ga1–C205 202.6(10), Ga1–I1 262.52(13), Ga2–$Cp_{centroid}$ 193.4(1), Ga2–C103 316.6(11), Ga2–C104 324.1(10), Ga2–C202 342.5(11), Ga2–C203 356.6(12); Ga2–Ga1–C101 100.2(3), Ga2–Ga1–C205 106.1(3), Ga2–Ga1–I1 110.53(6), C101–Ga1–C205 125.1(5), C101–Ga1–I1 110.5(3), C205–Ga1–I1 103.6(3).

Compound **2** crystallizes in the $Pca2_1$ space group in the form of separate molecules, thus no further intermolecular Ga–Ga or Ga–I contacts are present in the solid state. The Ga–Ga bond in **2** (246.88 pm) is in the range of a normal Ga–Ga single bond, although it is better described as a donor–acceptor bond between the Lewis base GaCp and the Lewis acid $GaICp_2$. Hence, **2** is a rare example of a molecular compound containing a homonuclear dative bond between group 13 elements.[22] The hypothetical isomer Cp_2Ga–GaCpI (**2′**), having a normal Ga–Ga bond and both Ga atoms in the formal oxidation state +2, is less stable (**2′** → **2** +35.7 kJ/mol) according to quantum chemical calculations.[20]

Taking a closer look into the molecular structure of **2** shows additional contacts between the gallium atom in the formal oxidation state +1 (Ga2) and the σ-bound Cp ligands. The Ga–C contacts are between 317 and 366 pm, which is at the long-range end of Ga–C contacts found in benzene complexes of Ga^{I}, for example, the Ga–C distances in an (η^6-benzene)gallium(I) complex vary between 302 and 330 pm.[23] The formation of additional contacts in **2** is thereby similar to those, which have been found for the corresponding Cp* compound $Cp^*Ga{\rightarrow}GaCp^*I_2$ (**3**).[24] Due to the higher steric demand of the Cp* ligands in **3** only one σ-bound Cp* ligand is present, which also forms additional contacts to the gallium atom in the oxidation state +1.

The Ga–Ga bond in **3** (243.7 pm) is thereby 3.2 pm shorter than the one in **2**, which leads to the unusual situation that the ligand with the lower steric demand leads to the longer Ga–Ga bond, showing that the contacts to the σ-bound ligands at the Ga^{III} center significantly influence the bonding within **2** and **3**. The bonding to the η^5-bound ligand in **3** is thereby affected by the additional contacts, which results in a more bent arrangement (Ga–Ga–$Cp^*_{centroid}$ angle 137.3°) than the one in the structure of **2** (Ga–Ga–$Cp_{centroid}$ angle 169.1°), that is, the bonding between the Ga atom and the carbon atoms of the Cp ligand in **2** is closer to an ideal η^5 interaction.

These results show that the central metal–metal as well as the metal–ligand bonds in **2** and **3** can hardly be compared directly, as secondary interactions strongly influence the arrangement and consequently also the bonding in this section of the molecules. However, although the bonding between the Ga^{I} center and the Cp ligand is more ideal in **2** than in **3**, compound **2** is not very stable in solution: During recrystallization experiments with **2** in a few milliliters of mother solution just a gray precipitate and colorless crystals of $GaCp_3$ could be obtained even when working at –30 °C.[25] This result clearly hints to a higher reactivity of GaCp with respect to GaCp*, which is stable in the solid state and in solution even at elevated temperatures.[12]

Nevertheless, stable diluted solutions of GaCp (**1**) might be of use for further systematical reactions, making **1** a substance with great potential in the productive and widely used field of monodentate group 13 ligands. This general

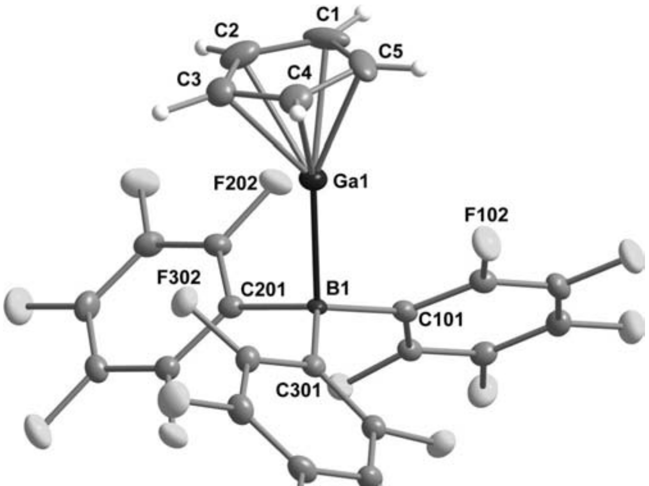

Figure 2. Molecular structure of $CpGa{\rightarrow}B(C_6F_5)_3$ (**4**) (thermal ellipsoids with 25% probability). Selected distances [pm] and angles [°]: Ga1–B1 215.4(3), Ga1–$Cp_{centroid}$ 188.4(17), Ga1–C1 220.1(4), Ga1–C2 224.4(4), Ga1–C3 226.0(4), Ga1–C4 223.0(3), Ga1–C5 219.6(4), Ga1–F102 289.5(6), Ga1–F202 294.0(8), Ga1–F302 304.8(9), B1–C101 163.6(4), B1–C201 164.9(4), B1–C301 161.0(4); B1–Ga1–$Cp_{centroid}$ 170.12(7), Ga1–B1–C101 105.53(16), Ga1–B1–C201 100.91(16), Ga1–B1–C301 103.61(15), C101–B1–C201 111.91(19), C201–B1–C301 116.1(2), C101–B1–C301 116.4(2), Σ°CBC 344.4(2).

Table 1. Selected distances [pm] and angles [°] for **2**, **3**, **4**, and **5** (E = B, Ga; Cp^a = Cp, Cp*).

Compound	Ga–$Cp^a_{centroid}$	Ga–E	Ga–C_{Cp^a} (min–max)	Ga–C_{Cp^a} (av.)	Σ°CBC	E–Ga–$Cp^a_{centroid}$
CpGa→$GaCp_2I$ (**2**)	191.7	246.9	223.8–230.5	227.3	–	169.2
Cp*Ga→GaCp*I_2 (**3**)	191.6	243.7	218.5–237.7	227.0	–	137.3
CpGa→$B(C_6F_5)_3$ (**4**)	188.4	215.4	219.6–226.0	222.6	344.4	170.1
Cp*Ga→$B(C_6F_5)_3$ (**5**)	186.5	216.1	221.7–223.8	222.7	342.1	176.7

applicability was subsequently proven by a projected reaction of **1** with $B(C_6F_5)_3$, which gave colorless crystals of CpGa→$B(C_6F_5)_3$ (**4**) in 45% yield. The molecular structure of **4**, determined by X-ray single-crystal structure analysis, is shown in Figure 2.

The Ga–B bond in **4** (215.4 pm) is identical within error bars with the Ga–B bond in the corresponding GaCp* compound Cp*Ga→$B(C_6F_5)_3$ (**5**) (see Table 1).[26] However, the B–Ga–$Cp_{centroid}$ angle in **4** is 170.1°, while it is considerably larger in **5** (176.7°). Thus in contrast to the comparison of **2** and **3**, the higher steric demand of the Cp* group in **5** forces a less bent orientation.

However, a closer inspection of the molecular structure of **4** shows that additional short intramolecular Ga···F contacts are present, where the shortest Ga–F distance (Ga1–F102 290 pm) is well within the range of the sum of the van der Waals radii (340 pm). This Ga···F interaction additionally leads to a bending of the Cp ligand and to a large variation in Ga–C bond lengths (220–226 pm).

Consequently, as in the case of **2**, secondary contacts significantly disturb the Ga–Cp interaction in **4** as well as the Ga–Cp* interaction in **5**, which makes a reasonable comparison of the central bonding parameters of the two compounds (**4** and **5**) nearly impossible.[27] However, there should be a difference between the donor abilities of GaCp and GaCp*, as the sum of the C–B–C bond angles (Σ°CBC) in **4** is 344.4° and the arrangement of $B(C_6F_5)_3$ is a bit closer to a trigonal planar relative to that in **5**, where the sum of the C–B–C bond angles is 342.1°. As the sum of the C–B–C bond angles in $B(C_6F_5)_3$ is a good indicator for the relative Lewis basicity of a bound donor – the more the sum of angles differs from 360° the stronger is the donor[28] – GaCp (**1**) is a slightly weaker donor compared to GaCp*.[29] The marginally stronger donor abilities of GaCp* do not come as a surprise, as a positive inductive effect can be expected of the five methyl groups. Nevertheless the differences are small, and therefore GaCp can be seen as a less sterically demanding analogue of GaCp* opening up a wide range of further applications, for example, in transition metal and rare earth chemistry.[30]

Conclusions

We presented an easy synthesis – that can be carried out with standard laboratory equipment – of GaCp (**1**), which is a promising reagent in organometallic chemistry; for example, it is less sterically demanding than the related Cp* compound and might therefore open the possibility of higher coordination numbers in coordination chemistry. Additionally Cp is in general a lot easier to obtain and a much more cost-efficient ligand than Cp*. This is certainly relevant for technical applications where the carbene-like character of **1** could be of use for various reactions, for example, with unsaturated compounds. Accordingly the presented convenient synthesis of GaCp might be the kiss to awake this sleeping beauty in organometallic chemistry.

Experimental Section

All manipulations were carried out under pure nitrogen by using standard Schlenk techniques. NaCp was prepared according to the literature.[31] $B(C_6F_5)_3$ was purchased from Sigma–Aldrich. The NMR spectra were recorded in $[D_6]$benzene with a Bruker AV 300 spectrometer (^1H 300.1 MHz, ^{11}B 96.3 MHz, ^{13}C 75.5 MHz, ^{19}F 282.4 MHz, ^{71}Ga 91.5 MHz). IR data were collected by using a Bruker IFS 113v Spectrometer. The samples were measured with the aid of an ATR unit. The Raman spectra were obtained with a Dilor XY800 spectrometer (CCD camera, Wright instruments, resolution 1.5 cm^{-1}), measured in dodecane in a sealed glass tube. EDX spectra were collected with an Ametek Genesis 4000 detector connected to a scanning electron microscope Zeiss Supra VP40.

GaCp (1): NaCp (0.09 g, 1 mmol) and GaI (0.18 g, 0.9 mmol) were suspended with cold toluene, benzene, pentane, or dodecane (20 mL in each case), leading to a pure white residue and a colorless solution. The cold solution was filtered and used right away without further manipulation. ^1H NMR (C_6D_6): δ = 5.8 (s, 5 H, Cp) ppm. ^{13}C NMR(C_6D_6): δ = 106.5 (s, Cp) ppm. ^{71}Ga NMR (C_6D_6): δ = –708.4 (br., GaCp) ppm. Raman (dodecane, 298 K): $\tilde{\nu}$ = 262.1 cm^{-1}.

CpGa→GaCp$_2$I (2): NaCp (0.2 g, 2.3 mmol) and GaI (0.41 g, 2.1 mmol) were suspended with cold toluene (30 mL), leading to a pure white residue and a colorless solution. The cold solution was filtered and layered with pentane (30 mL) at –30 °C. After a few hours, the solution turned yellow, and a few yellow crystals of **2** were obtained.

CpGa→B(C$_6$F$_5$)$_3$ (4): A solution of GaCp (0.15 g, 1.1 mmol) in cold toluene (–40 °C, 25 mL) was added to $B(C_6F_5)_3$ (0.5 g, 1 mmol). The reaction mixture was warmed slowly to room temperature under constant stirring overnight. The resulting bright yellow solution was filtered and concentrated in vacuo until the volume was ca. 10 mL. The toluene solution was then stored at –30 °C to give colorless crystals of **4** (0.31 g, 0.45 mmol, 45% yield). ^1H NMR (C_6D_6): δ = 5.74 (s, 5 H, Cp) ppm. ^{11}B NMR (C_6D_6): δ = –3 (br., w1/2 = 2100 Hz) ppm. ^{13}C NMR (C_6D_6): δ = 108.65 (s, Cp), 137.39 (dm, *J* = 250 Hz, *m*-C_6F_5), 142.79 (m, *p*-C_6F_5), 148.06 (dm, *J* = 260 Hz, *o*-C_6F_5) ppm. ^{19}F NMR (C_6D_6): δ = –128.9 (s, *m*-C_6F_5), –142.1 (s, *p*-C_6F_5), –161.6 (s, *o*-C_6F_5) ppm. IR (ATR unit, 298 K): $\tilde{\nu}$ = 443.6 (w), 472.5 (w), 559.3 (w), 615.3 (w), 655.8 (sh), 661.5 (m), 692.4 (w), 731.0 (w), 771.5 (m), 825.5 (m), 960.5 (s), 979.8 (s), 1008.7 (w), 1087.8 (sh), 1103.3 (m), 1284.6 (w), 1375.2 (w), 1460 (m), 1516.0 (m), 1645.2 (w) cm^{-1}.

Crystal Structure Data

CpGa→GaCp$_2$I (2): $IGa_2C_{15}H_{15}$ M_r = 461.6 $g\,mol^{-1}$, crystal dimensions $0.4\times0.3\times0.3\ mm^3$, orthorhombic, space group $Pca2_1$, a = 16.176(3) Å, b = 8.5188(17) Å, c = 11.319(2) Å, V = 1559.9(5) $Å^3$, Z = 4, ρ_{calcd} = 1.966 $g\,cm^{-3}$, μ_{Mo} = 5.414 mm^{-1}, $2\theta_{max}$ = 54.26°, 9155 measured, 1743 independent reflections (R_{int} = 0.0689); absorption correction: numerical (min./max. transmission 0.4143/0.5381), R_1 = 0.0313, wR_2 = 0.0553; STOE IPDS II diffractometer [Mo-K_a radiation (λ = 0.71073 Å), 150 K].

CpGa→B(C$_6$F$_5$)$_3$ (4): $GaF_{15}C_{23}BH_5$ M_r = 646.8 $g\,mol^{-1}$, crystal dimensions $0.3\times0.25\times0.2\ mm^3$, monoclinic, space group C_2/c, a = 18.288(4) Å, b = 12.382(3) Å, c = 20.547(4) Å, β = 108.96(3)°, V = 4400.3(15) $Å^3$, Z = 8, ρ_{calcd} = 1.953 $g\,cm^{-3}$, μ_{Mo} = 1.390 mm^{-1}, $2\theta_{max}$ = 53.48°, 11093 measured, 4649 independent reflections (R_{int} = 0.0770); absorption correction: numerical (min./max. transmission 0.8244/0.9006), R_1 = 0.0394, wR_2 = 0.0974; STOE IPDS II diffractometer [Mo-K_a radiation (λ = 0.71073 Å), 150 K]. The structures were solved by direct methods and refined against F^2 for all observed reflections. Programs used: SHELXS and SHELXL.[32]

CCDC-822364 (for **2**) and -822363 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.as.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): EDX, IR and Raman spectra.

Acknowledgments

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[29] This finding is in accordance with DFT calculations, where the bond enthalpy between GaCp and $B(C_6F_5)_3$ is calculated to be –9.4 kJ/mol in **4**, while it is –30.1 kJ/mol for **5** between GaCp* and $B(C_6F_5)_3$. Additionally, further calculations applying the less sterically demanding acceptor $GaMe_3$ also shows a small difference in donor strength between GaCp and GaCp*, as the reaction enthalpies for the formation of the donor–acceptor complex are nearly identical; that is, –15.3 kJ/mol for Cp and –20.6 kJ/mol for Cp*.

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