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A novel synthetic route to pentaalkylcyclopentadienylgallium(I) compounds

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Abstract

The reaction of ‘GaI’ with potassium cyclopentadienides allows a simple access to cyclopentadienylgallium(I)-complexes. Thus, the compounds Me_5C_5Ga **1** and Me_4EtC_5Ga **2** have been prepared in high yields. Performing the synthesis of ‘GaI’ under ultrasonic conditions not in toluene but in benzene as solvent, avoids the formation of benzyl iodide as side product. © 2002 Published by Elsevier Science B.V.

Keywords: Gallium; Green’s GaI; Me_5C_5Ga; Me_4EtC_5Ga

1. Introduction

The investigation of subvalent Group 13-element compounds MR (M = Group 13-element) has been in the center of extensive research during the last years [1]. For the stabilization of these low oxidation state species it is crucial to use substituents R with appropriate steric demands and electronic properties. In using the pentamethylcyclopentadienyl (Cp*) substituent, Schnöckel et al. were able to prepare the half-sandwich complex Cp*Ga **1** by reacting metastable solutions of Ga(I)Cl with the Cp* transfer agents Cp^*_2Mg or Cp*Li [2]. However, such metastable solutions are difficult to prepare, so that there was a demand for an easier synthesis of Cp*Ga. We were able to show, that the strategy to synthesize Cp* complexes of low-valent main-group elements by reductive dehalogenation of the corresponding $Cp^*_xElHal_y$ compounds could be applied also in gallium chemistry. Thus, the reductive dehalogenation of Cp^*GaI_2 led to the formation of **1** in good yield [3]. The synthetic potential of **1** meanwhile is well documented [4–8].

Here, we present an even more facile synthesis of Cp*Ga **1** and of the gallium(I)-cyclopentadienide Me_4EtC_5Ga **2**, which allows to prepare these compounds in large scale quantities. This route is based on the reaction of ‘GaI’ with the corresponding potassium cyclopentadienides.

2. Results and discussion

In 1990 a simple synthesis of ‘GaI’ was described by Green et al. [9]. A pale green powder is formed from the reaction of gallium metal with iodine in toluene under ultrasonic conditions at 35 °C; it is unsoluble in toluene, and separation from the protecting solvent leads to decomposition. The compound ‘GaI’ has not been structurally characterized so far. It undergoes reactions as expected for a gallium(I) halide. Thus, ‘GaI’ inserts into the metal–iodine bonds of $CpFe(CO)_2I$ and $(C_5H_4Me)Mo(CO)_3I$ [9]; the reaction with alkyl iodides (RI) leads to monoalkylgallium diiodides $RGaI_2$ in high yields (55–90%) [9]. In the presence of PEt_3 disproportionation is observed; beside gallium metal the donor stabilized species $Ga_2I_4(PEt_3)_2$ and $Ga_3I_5(PEt_3)_3$ have been isolated from the reaction mixture [10]. The reaction of ‘GaI’ with TpNa (Tp = tris(3,5-di-*tert*-butylpyrazolyl)hydroborato) leads to the formation of the complex TpGa [11]. In reacting ‘GaI’ with $(Me_3Si)_3Si$-, $(Me_3Si)_3C$-, $(Me_3C)_3Si$- and $(Me_3Si)_3Ge$-metal compounds, Linti et al. were able to

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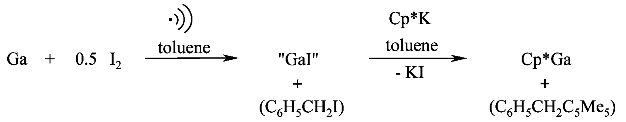
synthesize a series of neutral or anionic gallium clusters [1c,12]. Recently, the same research group described that Ga_4I_6 $[(Ga^+)_2(Ga_2I_6)^{2-}]$ is the major component of ‘GaI’ [13].

We now could demonstrate that ‘GaI’ is a useful starting material for the preparation of pentaalkylcyclopentadienylgallium(I)-compounds. Upon sonication of a mixture with equimolar amounts of gallium metal and iodine in toluene the initial violet color disappeared (iodine in toluene) and a pale green, unsoluble powder (‘GaI’) was obtained. After the subsequent addition of Cp*K, the color of the solution slowly turned to yellow, while a light grey precipitate was formed. After filtration, Cp*Ga **1** can be obtained as a yellow air-sensitive liquid by vacuum distillation (b.p.: 80 °C/8 Torr) in 52% yield.

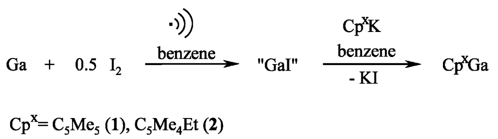
Surprisingly, a small amount of (benzyl)pentamethylcyclopentadiene was found in the crude reaction product before distillation; the formation of this side product might be caused by the reaction of benzyl iodide with Cp*K. In an independent experiment we were able to show, that benzyl iodide is formed from the ultrasound reaction of iodine and toluene, but only in the presence of gallium metal (Scheme 1).

This observation means that the unsoluble pale green compound cannot be a pure ‘GaI’ species since the amount of I_2 has been reduced by its concurrent reaction with the solvent. In order to increase the content of ‘GaI’ a solvent is needed which is not iodinated under ultrasonic conditions. Therefore, ‘GaI’ was prepared in benzene in a manner analogous to that described above. Subsequent addition of an equimolar amount of Me_5C_5K or Me_4EtC_5K at room temperature led to the formation of **1** and **2**, respectively. Compounds **1** and **2** were obtained in 60% yield by distillation in vacuo as slightly yellow, air-sensitive liquids, which solidified after several days during storage at 4 °C. Compared with the reaction carried out in toluene, the increase in yield (8%) corresponds to the prevention of the side reaction (Scheme 2).

The analytical data for **1** (^1H-, ^{13}C-, ^{71}Ga-NMR, MS) agree well with those reported by Schnöckel et al. [2]. The synthesis of **2** from metalstable ‘GaBr’ solutions (toluene–$^nBu_2O$ (7:1)) with $Mg(C_5Me_4Et)_2$ has already been mentioned in the doctoral thesis of C. Doriat from the research group of Schnöckel [14]. A full characterization of the compound was not given, but the NMR data correspond to those obtained for **2**. Thus, four signals could be detected in the ^1H-NMR spectrum. A triplet ($\delta = 1.04$ ($^3J_{H-H} = 7.5$ Hz)) and a quartet ($\delta = 2.38$ ($^3J_{H-H} = 7.5$ Hz)) represent the ethyl group of the Cp′ system; the remaining two singlet resonances ($\delta = 1.92$ and 1.93 ppm) are each caused by two chemically and magnetically equivalent methyl groups of the Cp ring. Correspondingly, in the ^{13}C-NMR spectrum four signals could be observed for the aliphatic carbon atoms ($\delta = 9.7$, 9.9, 17.6, 18.3) and three resonances for the ring carbon atoms ($\delta = 113.0$, 113.2). In the ^{71}Ga-NMR spectrum one signal at −650.7 ppm is found. This high-field resonance is typical for strongly shielded gallium nuclei and agrees well with those of other η^5-bondend Cp^xGa systems [2,15]. Compared with Cp*Ga **1** ($\omega_{1/2} = 700$ Hz) [2] the ^{71}Ga-NMR signal collected for compound **2** has a greater half band width ($\omega_{1/2} = 1.7$ kHz); this effect can be explained by the less symmetrical environment of the Ga atom compared with the situation in Cp*Ga **1**. Owing to its thermal stability, compound **2** could be characterized with standard EIMS techniques. The molecular ion is observed at 218 amu with the correct isotopic pattern; the fragmentation process is characterized by the loss of the gallium atom and further fragmentation of the remaining Cp′ ring.



Scheme 1.



Scheme 2.

In summary, we were able to develop a new method for the synthesis of pentaalkylcyclopentadienylgallium(I) compounds Cp^xGa ($Cp^x = C_5Me_5$ **1**, $Cp^x = C_5Me_4Et$ **2**) by reaction of ‘GaI’ with potassium cyclopentadienides. By performing the synthesis of ‘GaI’ under ultrasonic conditions not in toluene but in benzene, the side reaction of benzyl iodide formation is avoided.

3. Experimental

3.1. General

All manipulations were carried out under purified argon atmosphere using standard vacuum techniques. The solvents were commercially available, purified by conventional means and distilled immediately prior to use. Cp*K [16] and Cp′K [17] were prepared according to the literature. Gallium metal was purchased form Chemetal GmbH. Sonification experiments were performed using a Bandelin Sonorex Super 10 P ultrasonic bath (50% power). Elemental analyses were provided 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; $^{71}Ga\{^1H\}$ 91.5 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. Mass spectrometry was performed using a VG Autospec spectrometer. Only characteristic fragments and isotopes of the highest abundance are listed.

*3.2. Preparation of Cp*Ga in toluene*

A mixture of (2.00 g, 28 mmol) Ga particles (diameter: 1 mm) and I_2 (3.64 g, 14 mmol) in 40 ml of toluene was sonicated for 12 h at 50 °C. To the resulting pale green 'GaI' an equimolar amount of Cp*K (5.00 g, 28 mmol) was added. The reaction suspension was then stirred for 48 h. During this time the color of the toluene solution turned to yellow, while a light grey precipitate was formed. After filtration and extraction of the remaining grayish solid with 20 ml of toluene, the solvent was removed from the combined yellow solutions. The remaining oily reaction product contains (benzyl)pentamethylcyclopentadiene (0.43 g, 2 mmol) and Cp*Ga. Distillation at 80 °C (8 Torr) gives 3.06 g Cp*Ga (15 mmol) as a light yellow liquid in 52% yield.

Analytical data for **1** correspond to those reported in the literature [3]. Data for (benzyl)pentamethylcyclopentadiene [18]: ^{1}H-NMR (C_6D_6): δ 0.98 (s, 3H, $C_6H_5CH_2(C_5\mathit{Me}_5)$), 1.55 (s, 6 H, $C_6H_5CH_2(C_5\mathit{Me}_5)$), 1.75 (s, 6 H, $C_6H_5CH_2(C_5\mathit{Me}_5)$), 2.64 (s, 2 H, $C_6H_5C\mathit{H}_2(C_5Me_5)$), 7.03 (m, 5 H, $C_6\mathit{H}_5CH_2(C_5Me_5)$). ^{13}C-NMR ($C_6D_6$): δ 10.51, 10.93, 22.03, 41.72, 57.10, 126.05, 127.50, 128.87, 134.85, 138.96, 139.46. MS (EI, 70 eV) [m/z] (rel. int.): 226 [M^+ (53)], 203 [Cp^{*+} (100)], 121, [$Cp^{*+}-CH_2$ (41)], 119 [$Cp^{*+}-Me-H$ (31)], 105 [$Cp^{*+}-2$ Me (24)], 69 (Ga^+ (9)].

3.3. Isolation of $C_6H_5CH_2I$

A mixture of (2.00 g, 28 mmol) Ga particles (diameter: 1 mm) and I_2 (3.64 g, 14 mmol) in 40 ml of toluene was sonicated for 12 h at 50 °C. The resulting suspension was filtrated. After removing all volatile components a colorless powder was isolated, which was analyzed to be $C_6H_5CH_2I$, (0.43 g, 2 mmol).

Data for $C_6H_5CH_2I$ [19]: m.p. 27 °C. ^{1}H-NMR (C_6D_6): δ 3.96 (s, 2H, $C_6H_5C\mathit{H}_2I$), 6.89 (m, 5 H, $C_6\mathit{H}_5CH_2I$). ^{13}C-NMR (C_6D_6): δ 33.4 ($C_6H_5\mathit{C}H_2I$), 128.33/128.8/129.2/138.1 ($\mathit{C}_6H_5CH_2I$). IR (cm^{-1}, KBr): $v = 3023$ (w), 3011 (w), 2965 (w), 1490 (m), 1453 (m), 1266 (vs), 1221 (s), 1062 (m), 1043 (m), 910 (w), 821 (w), 763 (s), 694 (vs).

3.4. Preparation of Cp^xGa in benzene

A mixture of (2.00 g, 28 mmol) Ga particles (diameter: 1 mm) and I_2 (3.64 g, 14 mmol) in 40 ml of benzene was sonicated for 12 h at 50 °C. To the resulting pale green 'GaI' an equimolar amount of the corresponding potassium cyclopentadienide (Cp*K: 5.00 g, 28 mmol; Cp′K: 5.40 g, 28 mmol) was added. The reaction suspension was then stirred for 48 h. During this time the color of the benzene solution turned to yellow, while a light grey precipitate was formed. After filtration and extraction of the remaining grayish solid with 20 ml of benzene, the solvent was removed from the combined yellow solutions. The remaining oil was distilled at 80 °C (8 Torr) to give the corresponding gallium cyclopentadienide (Cp*Ga **1**: 3.53 g, 17 mmol; Cp′Ga **2**: 3.72 g, 17 mmol) as a light yellow liquid in about 60% yield.

Data for **2**: b.p. 80 °C (8 Torr). ^{1}H-NMR (C_6D_6): $\delta = 1.04$ (t, $^3J_{HH} = 7.5$ Hz, 3 H, $(C\mathit{H}_3CH_2)Me_4C_5$), 1.92 and 1.93 (s, 12 H, $(CH_3CH_2)\mathit{Me}_4C_5$), 2.38 (q, $^3J_{HH} = 7.5$ Hz, 2 H, $(C\mathit{H}_3C\mathit{H}_2)Me_4C_5$). ^{13}C-NMR ($C_6D_6$): $\delta = 9.7$ $((CH_3CH_2)\mathit{Me}_4C_5)$, 9.9 $((CH_3CH_2)\mathit{Me}_4C_5)$, 17.6 $((\mathit{C}H_3CH_2)Me_4C_5)$, 18.3 $((CH_3\mathit{C}H_2)Me_4C_5)$, 113.0 and 113.2 $((CH_3CH_2)Me_4\mathit{C}_5)$, 121.4 $((CH_3CH_2)Me_4C_5$–Ethyl–C). ^{71}Ga-NMR (C_6D_6): $\delta - 650.7$ ($\omega_{1/2} = 1.7$ kHz). MS (EI, 70 eV) [m/z] (rel. int.): 218 [M^+ (45)], 203 [M^+-Me (26)], 150 [$Cp'H^+$ (50)], 135, [Cp'^+-CH_2 (100)], 119 [Cp'^+-2 Me (62)], 105 [Cp'^+-2 Me$-CH_2$ (43)], 91 [Cp'^+-2 Me-2 CH_2 (53)], 69 (Ga^+ (65)]. Anal. Calc. for $C_{11}H_{17}Ga$ ($M = 218.98$ g mol^{-1}): C, 60.34; H, 7.83. Found: C, 60.57; H, 7.91%.

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