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Cp^*GaCl_2 and Cp^*_2GaCl ($Cp^* = \eta^1$-C_5Me_5) as starting materials for novel Group 13 element complexes

E. Leiner, M. Scheer *

Institute of Inorganic Chemistry, University of Karlsruhe, Geb. 30.45, Engesserstrasse, D-76128 Karlsruhe, Germany

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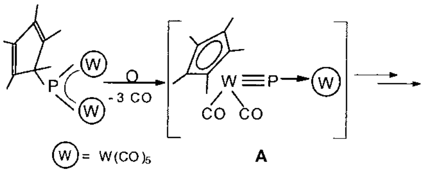
Abstract

Reactions of Cp^*GaCl_2 and Cp^*_2GaCl ($Cp^* = \eta^1$-C_5Me_5), respectively, with different carbonylmetalate anions are compared to yield the transition-metal–gallium complexes [(η^5-Cp*Ga)W(CO)$_5$] (**1**), [Fe$_2$(CO)$_6${μ-(η^5-Cp*Ga)}$_2${μ-(η^3-Cp*Ga)}] (**2**), [Ga{Mn(CO)$_5$}$_3$] (**3**), [Cp$^*_2$Ga{Mn(CO)$_5$}] (**4**), [Co$_2$(CO)$_6${μ-(η^5-Cp*Ga)}$_2$Co(CO)$_3$] (**5**) and [{(η^5-Cp)Fe(CO)}$_2$(μ-CO){μ$_2$-(η^5-Cp*Ga}] (**6**). The results show that both starting materials offer an alternative synthetic route to subvalent Cp*Ga(I) compounds via reductive dehalogenation reactions in comparison to the previously used reactions starting from Cp*Ga itself. Starting from Cp^*_2GaCl, Cp* elimination reactions are observed additionally, a process which dominates much more in the case of Cp^*InCl_2 as a starting material. In these reactions with $[CpFe(CO)_2]^-$ and $[CpW(CO)_3]^-$, [In{CpFe(CO)$_2$}$_3$] (**7**) and [In{CpW(CO)$_3$}$_3$] (**8**), respectively, are obtained in good yield. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gallium; Indium; Metathesis; Cyclopentadienes; Transition metal

1. Introduction

Recently, we developed a concept to generate complexes with a metal–phosphorus-triple bond of the type [Cp*(CO)$_2$W≡P→W(CO)$_5$] **A** as highly reactive intermediates [1]. By thermolysis of the phosphinidene complex Cp*P{W(CO)$_5$}$_2$ ($Cp^* = \eta^1$-C_5Me_5) a Cp* migration occurs from the σ-bound phosphorus atom to a tungsten atom in a η^5-coordination mode to form the intermediate **A**. This synthetic approach offers promising synthetic routes to a large variety of unprecedented phosphametallocycles. Accordingly, the trapping reaction of **A** with phosphaalkynes [1] and alkynes [2] proceeds via formal [2 + 2] cycloaddition reactions to form novel main-group-element–transition-metal cage compounds.



To extend the concept of the Cp* migration, we tried to incorporate Group 13 elements to synthesise complexes of the type Cp*E(ML$_n$)$_2$ (E = Ga, In) as possible starting materials for this purpose. However, in our investigations of the reactions of Cp^*GaCl_2 and Cp^*_2GaCl, respectively, with various metallates of transition metal carbonyls, we observed different reaction pathways, which resulted in a large number of novel transition-metal–gallium complexes.

In general, studies in the literature of neutral Ga compounds of the type RGa(ML$_n$)$_2$ and R$_2$Ga(ML$_n$) without any metal–metal bond are rare [3] and have been limited to the complexes [Mes*Ga{Co(CO)$_4$}$_2$] (Mes* = 2,4,6-t-Bu$_3$C$_6$H$_2$) [4], [{(CO)$_4$Fe}$_2$Ga(CH)$_3$] [3–5], [(t-Bu)$_2$Ga{Fe(CO)$_2$Cp}] [6], [(t-Bu)Ga{Fe(CO)$_2$Cp}$_2$] [6], [(CH$_3$)$_2$Ga{W(CO)$_3$Cp}] [7]; complexes of these types with R = Cp* have so far not been described.

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* Corresponding author. Tel.: +49-721-6083088; fax: +49-721-6087021.

E-mail address: mascheer@chemie.uni-karlsruhe.de (M. Scheer).

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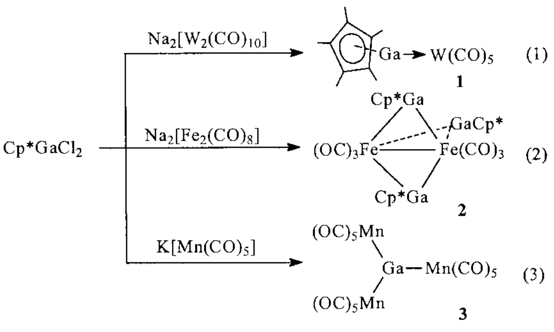
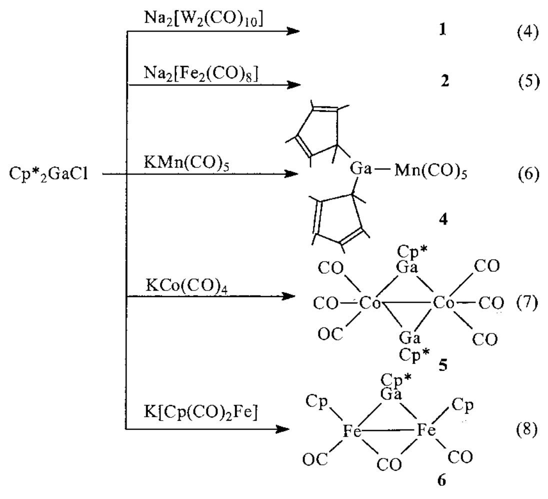
2. Results and discussion

2.1. Synthesis

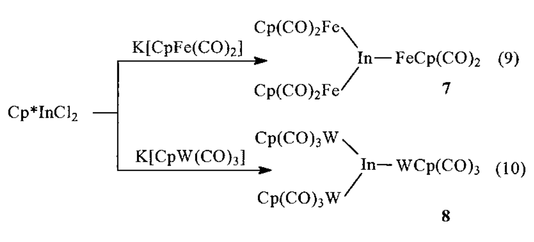
The reaction of Cp^*GaCl_2 with $Na_2[W_2(CO)_{10}]$ in *n*-hexane at low temperatures leads to $[(\eta^5\text{-}Cp^*Ga)W(CO)_5]$ (**1**), which can be regarded as a derivative of the tungstenhexacarbonyl, in which one of the CO units is replaced by a Cp*Ga ligand (Eq. (1)). In a similar experiment, where Cp^*GaCl_2 was replaced by Cp^*_2GaCl, the same product **1** could be obtained (Eq. (4)). Introducing $Na_2[Fe_2(CO)_8]$ into the reaction with Cp^*GaCl_2 under similar conditions, $[Fe_2(CO)_6\{\mu\text{-}(\eta^5\text{-}Cp^*Ga)_2\mu\text{-}(\eta^3\text{-}Cp^*Ga)\}]$ (**2**) is obtained in 30% yield (Eq. (2)). By replacement of Cp^*GaCl_2 by Cp^*_2GaCl, the same product **2** was formed (Eq. (5)). The reaction between Cp^*GaCl_2 and $K[Mn(CO)_5]$ in *n*-hexane at room temperature yields the complex $[Ga\{Mn(CO)_5\}_3]$ (**3**) in almost quantitative yield (Eq. (3)). In contrast, the use of Cp^*_2GaCl in the reaction with $K[Mn(CO)_5]$ yields the yellow crystalline complex $[Cp^*_2Ga\{Mn(CO)_5\}]$ (**4**) in 40% yield (Eq. (6)).



Scheme 1.



Scheme 2.



Scheme 3.

However, the reaction of Cp^*_2GaCl with $K[Co(CO)_4]$ leads to the complex $[Co_2(CO)_6\{\mu\text{-}(\eta^5\text{-}Cp^*Ga)\}_2]$ (**5**) in 60% yield [8a], which can be described as a derivative of the cobalt carbonyl complex $[Co_2(CO)_8]$, in which two of the CO units are replaced by the two bridging Cp*Ga ligands (Eq. (7)). The reaction of Cp^*_2GaCl with $K[CpFe(CO)_2]$ ($Cp = \eta^5\text{-}C_5H_5$) in toluene results in the formation of the dinuclear iron complex $[\{CpFe(CO)\}_2\text{-}(\mu\text{-}CO)\{\mu\text{-}(GaCp^*)\}]$ (**6**) in 75% yield (Eq. (8)).

In order to compare the observed reactivity patterns of the above gallium reagents with those of the indium analogues, similar reactions were carried out with Cp^*InCl_2. It was found that the reaction between Cp^*InCl_2 and $K[(CO)_2FeCp]$ led to $[\{(CO)_2FeCp\}_3In]$ (**7**) (Eq. (9)), whereas with $K[(CO)_3WCp]$, $[\{(CO)_3WCp\}_3In]$ (**8**) was obtained (Eq. (10)) [8b].

2.2. Spectroscopic and structural characterisation

In their EI–MS spectra, all compounds show the appropriate molecular ion peaks and fragmentation patterns, characterised by the subsequent loss of the CO ligands. Only for **4**, the highest mass peak corresponds to the molecular ion reduced by CH_3. In the IR spectra of all products, CO stretching frequencies were observed for terminal CO ligands. For **6**, an additional absorption at 1744 cm^{-1} for a bridging CO ligand was found. The obtained NMR and IR data of **2**, **3**, **5**, **7** and **8** are in good agreement with the published data, since **2** and **5** have previously been prepared by Jutzi et al. via the reaction of Cp*Ga with $Fe(CO)_3CHT$ (CHT = cycloheptatriene) and $[Co_2(CO)_8]$ [9], respectively. Complex **3** was first prepared by Norman et al. via metathetical reaction of $GaCl_3$ with $Na[Mn(CO)_5]$ [10] and was, furthermore, obtained by Cowley et al. via the reaction between Mes^*GaCl_2 ($Mes^* = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$) and $Na[Mn(CO)_5]$ [11]. Complexes **7** and **8** were prepared by the reaction of $InCl_3$ with $Na[Fe(CO)_2Cp]$ [12] and $Na[CpW(CO)_3]$ [13], respectively.

The ^1H-NMR spectrum of **1** reveals a singlet at 1.61 ppm for the η^5-bound Cp* group as has also been observed in the X-ray structure analysis of **1** (Fig. 1). Crystallographic data are given in Table 4, and selected bond lengths and angles are summarised in Table 1. In **1**, the tungsten atom lies in a distorted octahedral geometry and is surrounded by five CO groups and one Cp*Ga moiety as terminal ligands. The Ga–W bond length in **1** (2.566(1) Å) is shorter than the Ga–W bond lengths in $[\{CpW(CO)_3\}GaMe_2]$ (2.708(3) Å) [14] and

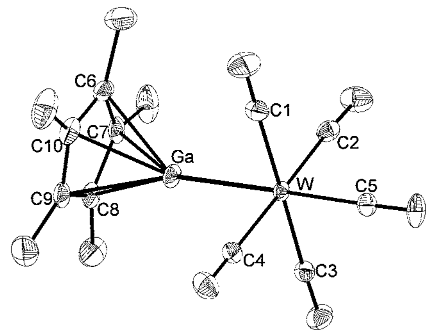


Fig. 1. Molecular structure of [(Cp*Ga)W(CO)$_5$] (**1**) in the crystal and selected atom labelling scheme (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity).

Table 1
Selected bond lengths (Å) and angles (°) for [(Cp*Ga)W(CO)$_5$] (**1**)

Bond lengths			
Ga–W	2.566(1)	Ga–C6	2.275(6)
W–CS	2.008(5)	Ga–C7	2.249(5)
W–C1	2.040(7)	Ga–C8	2.243(4)
W–C2	2.049(6)	Ga–C9	2.262(5)
W–C3	2.036(6)	Ga–ClO	2.280(5)
W–C4	2.059(6)		
Bond angles			
Ga–W–C2	89.4(2)	Ga–W–CS	179.3(2)

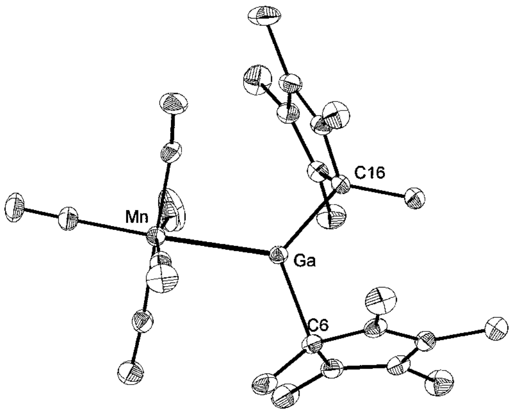


Fig. 2. Molecular structure of [Cp$^*_2$Ga{Mn(CO)$_5$}] (**4**) in the crystal and selected atom labelling scheme (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity).

Table 2
Selected bond lengths (Å) and angles (°) for [Cp$^*_2$Ga{Mn(CO)$_5$}] (**4**)

Bond lengths	
Ga–Mn	2.548(1)
Ga–C16	2.046(4)
Ga–C6	2.077(4)
Bond angles	
Mn–Ga–C16	120.4(1)
Mn–Ga–C6	117.7(1)
C6–Ga–C16	121.9(2)
Mn–C6–C16–Ga	0.33(1)

[{CpW(CO)$_3$}$_3$Ga] (2.739(3) Å) [14] and similar to the Ga–W bond length calculated by Frenking et al. in [{(OC)$_5$W}GaN(SiMe$_3$)$_2$] (2.551 Å) [15]. Complex **1** is isostructural with the Cr compound [(η^5-Cp*Ga)Cr(CO)$_5$], which was synthesised by Jutzi et al. via the direct use of Cp*Ga in its reaction with [Cr(CO)$_5$(C$_8$H$_{14}$)] [9].

The iron complex **2** was characterised structurally by the Jutzi group in the *monoclinic* space group $P2_1/m$. We obtained crystals for **2** from *n*-hexane in the *triclinic* space group $P\bar{1}$. However, the bond distances and angles found for **2** are similar to the published data [9].

Compound **4** represents the only example of a gallium complex of the general type R$_2$GaML$_n$, where the transition metal possesses only carbonyl ligands. Extending to all kinds of ligands, the complex [(*t*-Bu)$_2$Ga{Fe(CO)$_2$Cp}], synthesised by Power et al. [16], is comparable. Crystals suitable for an X-ray crystal structure analysis of **4** were obtained by crystallisation from *n*-hexane. The molecular structure of **4** is shown in Fig. 2, and selected bond lengths and angles are summarised in Table 2. The observed Ga–Mn bond length in the trigonal planar complex **4** (2.548(1) Å) lies between the reported values for [GaMes*(Cl){Mn-(CO)$_5$}] (Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$) (2.495(4) Å) [11] and [Mn$_2$(CO)$_8${μ-GaMn(CO)$_5$}$_2$] (2.455(1) Å) [17] on one side and [Mn$_3$(CO)$_{12}$(μ-GaCl$_2$)]$^{2-}$ (2.691(4) Å) [18] on the other. In **4**, the steric repulsion of the σ-bound Cp* ligands are apparently responsible for the lengthening. The slightly different Ga–C bond distances in **4** (2.046(4) and 2.077(4) Å) are in the range of Ga–C$_{Cp*}$ σ-bonds, found e.g. in Cp*GaCl$_2$ (1.97(1) Å) and Cp$^*_2$GaCl (2.03(2) and 1.96(2) Å) [19].

The η^1-bonding situation of the Cp* substituents observed for [Cp$^*_2$Ga{Mn(CO)$_5$}] (**4**) in the solid state is not maintained in solution. Thus, the ^{1}H-NMR spectrum of **4** shows only a singlet at 1.81 ppm for the Cp* protons at room temperature. At −80 °C (toluene-d_8), only a broadening of the signal is observed, indicating fast sigmatropic rearrangements as dynamic processes still occur at this temperature.

In the ^{1}H-NMR spectrum of **6**, two singlets at 2.03 and 4.20 ppm of the Cp* and Cp protons, respectively, are observed, which corresponds in principle with its solid-state structure (Fig. 3 and Table 3). The crystal structure analysis of **6** reveals that each complex consists of two CpFe(CO) units and the Fe–Fe bond is bridged by a CO ligand and a Cp*Ga ligand. Formally, the structure can be regarded as a derivative of the dinuclear iron complex [CpFe(CO)$_2$]$_2$, where one bridging CO is replaced by a Cp*Ga unit. The scrambling process of the ligands in [CpFe(CO)$_2$]$_2$ favours usually the *trans*-arrangement of the Cp-ligands [20]. However, the *cis*-complex crystallises at low temperatures only from its solutions [21]. In **6**, the assembly of all the

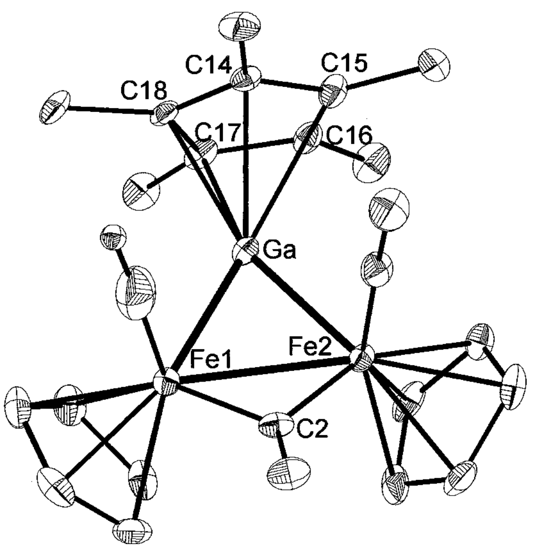


Fig. 3. Molecular structure of [{CpFe(CO)}$_2$(μ-CO)(μ-GaCp*)] (**6**) in the crystal and selected atom labelling scheme (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity).

Table 3
Selected bond lengths (Å) and angles (°) for [{CpFe(CO)}$_2$(μ-CO){μ-(Cp*Ga)}] (**6**)

Bond lengths			
Ga–Fel	2.383(1)	Ga–C17	2.222(7)
Ga–Fe2	2.350(1)	Ga–C18	2.206(8)
Fe–Fe	2.676(2)	Ga–C14	2.362(8)
Fel–C2	1.917(8)	Ga–C15	2.522(9)
Fe2–C2	1.952(9)	Ga–C16	2.447(8)
Bond angles			
Fel–Ga–Fe2	68.9(1)	Ga–Fe2–C2	98.9(2)
Fel–C2–Fe2	87.5(3)	Ga–Fe2–C2–Fel	19.9(0)
Ga–Fel–C2	98.8(3)		

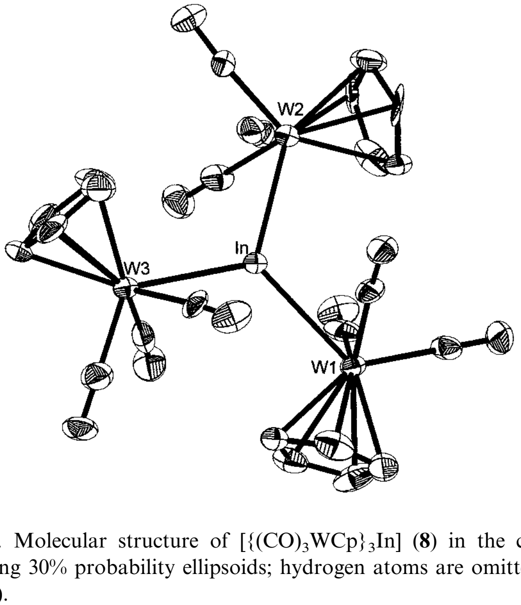


Fig. 4. Molecular structure of [{(CO)$_3$WCp}$_3$In] (**8**) in the crystal (showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity).

Table 4
Selected bond lengths (Å) and angles (°) for [{(CO)$_3$WCp}$_3$In] (**8**)

Bond lengths	
In–W1	2.894(2)
In–W2	2.889(1)
In–W3	2.868(2)
Bond angles	
W1–In–W2	120.40(5)
W2–In–W3	120.13(5)
W3–In–Wl	119.44(5)
W1–W2–W3–In	−0.95(1)

ligands requires a *cis*-arrangement of the Cp-ligands at the Fe atoms. Due to the steric repulsion of all substituents, the Cp* ligand at the Ga atom deviates from the ideal η^5-coordination to a more η^2:η^3 coordination mode (Table 3). Furthermore, the Fe–C2 distances of complex **6** (1.917(8) and 1.952(9) Å) indicate deviations and, along with the distortion of the Cp* coordination mode at the Ga atom, prohibit a molecular symmetry of the overall complex with a C_2 axis along the Ga–C2 vector. Therefore, **6** crystallises in the unusual space group *C*/*c*. The Fe–Ga distances of complex **6** (2.383(1) and 2.350(1) Å) are close to the lower limit of reported Fe–Ga single bonds (2.29–2.59 Å) [22]. The Fe–Fe bond distance of **6** (2.676(2) Å) is elongated in comparison to *cis*-[CpFe(CO)$_2$]$_2$ (2.531(2) Å) [21], but the Fe–Fe bond distance and the Fel–Ga–Fe2 angle are comparable to those of similar complexes, e.g. [{Fe(CO)$_3$}$_2${μ-GaSi(SiMe$_3$)$_3$}$_2$(μ-CO)] (2.6804(8) Å, 73.57(13)°) [23] and [{CpFe(CO)}$_2$(μ-CO)(μ-GaMes)] (Mes = 2,4,6-$Me_3C_6H_2$) (2.6526(6) Å, 68.84(2)°) [22].

The yellow crystalline complex **8** (Fig. 4 and Table 4) is isostructural with the Mo analogue [In{Mo(CO)$_3$Cp}$_3$] [13]. In **8**, the In atom is trigonal planar surrounded by three [W(CO)$_3$Cp] units. The In–W bond lengths (2.8678(17)–2.8942(15) Å) are slightly lengthened in comparison to 2.783(2) Å found in [HB(3,5-Me$_2$pz)$_3$]InW(CO)$_5$ (pz = pyrazolyl) [24]. Two C atoms of the carbonyl groups of each CpW(CO)$_3$ moiety are coordinated weekly to the central In atom (2.742–2.801 Å).

2.3. Conclusions

Although the initial aim to obtain complexes of the formula [Cp*Ga(ML$_n$)$_2$] was not achieved, the formation of the complexes **1**, **2**, **5** and **6** demonstrates that the reactions between Cp*GaCl$_2$ and Cp^*_2GaCl, respectively, with the corresponding metallates can be considered to be reductive dehalogenation of the Ga(III) compounds to form Cp*Ga containing complexes with Ga in the formal oxidation state +1. Reductive dehalogenation reactions of Cp*EX$_2$ are known for E = Al and B, e.g. the reported synthesis of

[(η^5-Cp*E)Fe(CO)$_4$] (E = B, Al) by the reaction of Cp*ECl$_2$ with Na$_2$[Fe(CO)$_4$] [25,26]. Thus, the applied reactions of Cp$_2^*$GaCl/Cp*GaCl$_2$ with metallates seem to be an alternative synthetic route to Cp*Ga containing complexes of formally monovalent gallium as shown by Jutzi et al. using Cp*Ga.

On the other hand, the reactions of Cp*GaCl$_2$ with K[Mn(CO)$_5$] to [Ga{Mn(CO)$_5$}$_3$] (**3**) is in accordance with the fact that compounds of the general types RGa(ML$_n$)$_2$ and R$_2$Ga(ML$_n$), without any metal–metal-bond, tend to give symmetrisation reactions to form complexes of the type Ga(ML$_n$)$_3$ [3]. Furthermore, the reactions (4), (5), (7) and (8) starting from Cp$_2^*$GaCl as well as the reaction (3) demonstrate the leaving group character of the Cp* ligand and, therefore, the competition problems observed in chloride elimination reactions [27]. This tendency is much more evident for the In complexes due to the lower In–C bond energies in comparison to the Ga–C bonds. Thus, starting from Cp*InCl$_2$, only **7** and **8**, respectively, are obtained, where the Cp* ligand is completely eliminated.

In summary, in comparison to Cp*GaCl$_2$, Cp$_2^*$GaCl can be regarded to be the more effective starting material for the synthesis of organometallic-gallium–transition-metal complexes of the formula Cp*Ga(ML$_n$)$_2$.

3. Experimental

All manipulations were performed under an atmosphere of dry N$_2$ using standard Schlenk techniques. All solvents were dried by common methods and freshly distilled prior to use. Gallium trichloride was obtained commercially and used without further purification. The starting materials Cp*GaCl$_2$ and Cp$_2^*$GaCl [19] and the compounds K[CpFe(CO)$_2$] [28], K[Mn(CO)$_5$] [29], K[Co(CO)$_4$] [30], Na$_2$[W$_2$(CO)$_{10}$] [31], Na$_2$[Fe$_2$(CO)$_8$] [32] were prepared according to methods described in the literature. ^{1}H-NMR spectra were recorded on a Bruker AC 250 and the IR spectra on a Bruker IFS 28. Mass spectroscopy was carried out on a Varian MAT 711.

*3.1. Preparation of [(η^5-Cp*Ga)W(CO)$_5$] (**1**)*

Cp*GaCl$_2$ (0.552 g, 2 mmol) or Cp$_2^*$GaCl (0.750 g, 2 mmol) was added to a slurry of Na$_2$[W$_2$(CO)$_{10}$] (0.463 g, 2 mmol) in 50-ml *n*-hexane at 0 °C. The reaction mixture was stirred at r.t. for 1 day. After filtering, the resulting orange solution was reduced in volume to 2 ml and stored at −30 °C. After a few days, [Cp*GaW(CO)$_5$] (**1**) (0.423 g, 40%) was crystallised as colourless crystals. Crystals suitable for an X-ray structure analysis of complex **1** were obtained from an *n*-hexane solution. ^{1}H-NMR (C$_6$D$_6$, 295 K, δ ppm): 1.61 (s, 15 H, Cp*). IR (KBr, cm^{-1}): $\tilde{\nu}$(C=O) 2065 (w), 1986 (m), 1910 (br). MS (EI, 70 eV, 60 °C, *m*/*z* (%)): 529.9 (100) [M$^+$], 473.9 (32) [M$^+$ − 2(CO)], 446.9 (53) [M$^+$ − 3(CO)], 417.9 (44) [M$^+$ − 4(CO)], 387.9 (84) [M$^+$ − 5(CO)], 203.9 (52) [Cp*Ga$^+$], 135.0 (4) [Cp*$^+$], 119.0 (16) [Cp*H$^+$ − CH$_3$], 68.9 (74) [Ga$^+$].

*3.2. Preparation of [(CO)$_3$Fe{μ-(η^5-Cp*Ga)$_2$}{μ-(η^3-Cp*Ga)}Fe(CO)$_3$] (**2**)*

Cp*GaCl$_2$ (0.138 g, 0.5 mmol) or Cp$_2^*$GaCl (0.188 g, 0.5 mmol) was added to a slurry of Na$_2$[Fe$_2$(CO)$_8$] (0.191 g, 0.5 mmol) in 20-ml *n*-hexane at −78 °C. The reaction mixture was allowed to warm up to r.t. and was stirred for 2 days further during which the colour of the solution changed to brown. After filtration and reducing the volume of the solution to 2 ml, orange crystals of **2** were isolated at −30 °C. ^{1}H-NMR (C$_6$D$_6$, 295 K, δ ppm): 2.05 (s, 15 H, Cp*). IR: $\tilde{\nu}$(C=O) (cm^{-1}, KBr): 1951, 1923. MS (EI, 70 eV, 130 °C, *m*/*z* (%)): 894 (19) [M$^+$], 606 (53) [M$^+$ − 3(CO) − GaCp*], 494 (21) [M$^+$ − 5(CO)], 204 (80) [Cp*Ga$^+$], 136 (100) [Cp*$^+$], 119 (60) [Cp*H$^+$ − CH$_3$], 69 (40) [Ga$^+$].

*3.3. Preparation of [Cp$_2^*$Ga{Mn(CO)$_5$}] (**4**)*

Cp$_2^*$GaCl (0.188 g, 0.5 mmol) was added to a slurry of K[Mn(CO)$_5$] (0.234 g, 1 mmol) in *n*-hexane at −78 °C. The resulting yellow solution was allowed to warm up to r.t. and was stirred for 3 days further. After filtering, the solution was reduced in volume to 2 ml and stored at −30 °C, where yellow crystals of **4** were obtained (70 mg, 40%). ^{1}H-NMR (toluene-*d*$_8$, 295 K, δ ppm): 1.81 (s, 30 H, Cp*). IR: $\tilde{\nu}$(C=O) (cm^{-1}, KBr): 2099 (m), 1969 (br), 1905 (sh). MS (EI, 70 eV, 90 °C, *m*/*z* (%)): 519 (0.5) [M$^+$ − CH$_3$], 399 (100) [M$^+$ − Cp*], 371(82) [M$^+$ − Cp* − CO], 343 (6) [M$^+$ − Cp* − 2(CO)], 316 (87) [M$^+$ − Cp* − 3(CO)], 287 (71) [M$^+$ − Cp* − 4(CO)], 259 (98) [M$^+$ − Cp* − 5(CO)], 204 (90) [Cp*Ga$^+$], 135 (86) [Cp*$^+$], 69 (66) [Ga$^+$], 55 (52) [Mn$^+$].

*3.4. Preparation of [(CO)$_3$Co[μ-(η^5-Cp*Ga)]$_2$Co(CO)$_3$] (**5**)*

Cp$_2^*$GaCl (0.413 g, 1.1 mmol) was added to a slurry of K[Co(CO)$_4$] (0.231 g, 1.1 mmol) in Et$_2$O (15 ml) at −78 °C. The resulting yellow solution was allowed to warm up to r.t. and was stirred for 12 h further during which the colour changed to orange. After filtering, all volatiles were removed in vacuo and the yellow residue was extracted twice with 15-ml aliquots of toluene and filtered. The solution was reduced in volume to 2 ml, and yellow crystals of **5** (124 mg, 40%) were obtained at −30 °C. ^{1}H-NMR (C$_6$D$_6$, 295 K, δ ppm): 1.91 (s, 15 H, Cp* methyl). IR: $\tilde{\nu}$ (C=O) (cm^{-1}, KBr): 2023 (s), 1989 (s), 1946 (br). MS (EI, 70 eV, 130 °C, m/z (%)): 696 (100) [M^+], 668 (32) [$M^+ - CO$], 640 (15) [$M^+ - 2(CO)$], 584 (100) [$M^+ - 4(CO)$], 556 (11) [$M^+ - 5(CO)$], 526 (53) [overlapping of $M^+ - 6(CO)$ and $M^+ - 4(CO) - Co$], 204 (3) [Cp^*Ga^+], 119 (6) [$Cp^*H^+ - CH_3$], 69 (6) [Ga^+].

*3.5. Preparation of $[\{(\eta^5\text{-}Cp)Fe(CO)\}_2\{\mu\text{-}(\eta^5\text{-}Cp^*Ga)\}(\mu\text{-}CO)]$ (**6**)*

To a slurry of $K[CpFe(CO)_2]$ (0.172 g, 0.8 mmol) in toluene (20 ml) at −78 °C, Cp^*_2GaCl (0.150 g, 0.4 mmol) was added. The reaction mixture was allowed to warm up to r.t. and was stirred for another day. After filtering, the resulting intensively red–brown solution was reduced in volume to 2 ml and stored at −30 °C. After a few days, brown crystals of **6** were obtained (131 mg, 75%). ^{1}H-NMR (C_6D_6, 295 K, δ ppm): δ 2.03 (s, 15 H, Cp* methyl), δ 4.2 (s, 10 H, Cp). IR (cm^{-1}, KBr): 1986, 1915, 1885, 1744. MS (EI, 70 eV, m/z (%)): 530 (22) [M^+], 502 (12) [$M^+ - CO$], 474 (7) [$M^+ - 2(CO)$], 446 (8) [$M^+ - 3(CO)$], 325 (76) [$Cp^*GaFeCp^+$], 256 (100) [Cp^*FeCp^+], 204 (31) [Cp^*Ga^+], 186 (90) [Cp_2Fe^+], 69 (35) [Ga^+].

*3.6. Preparation of $[\{(CO)_2FeCp\}_3In]$ (**7**)*

To a slurry of $K[CpFe(CO)_2]$ (0.172 g, 0.8 mmol) in n-hexane (20 ml) at −78 °C, Cp^*InCl_2 (0.128 g, 0.4 mmol) was added. The reaction mixture was allowed to warm up to r.t. and was stirred for 2 h further. After filtering, all volatiles were removed in vacuo, and the yellow residue was extracted twice with 15-ml aliquots of toluene and filtered. The solution was concentrated in volume to 2 ml, and yellow crystals of **7** (181 mg, 70%) were isolated at −30 °C. The spectroscopic data obtained for **7** are in accordance with the published ones [12].

*3.7. Preparation of $[\{(CO)_3WCp\}_3In]$ (**8**)*

To a slurry of $K[CpW(CO)_3]$ (0.297 g, 0.8 mmol) in n-hexane (20 ml) at −78 °C, Cp^*InCl_2 (0.128 g, 0.4 mmol) was added. The resulting reaction mixture was

Table 5
Crystallographic data for **1**, **2**, **4**, **6** and **8**

	1	**2**	**4**	**6**	**8**
Empirical formula	$C_{15}H_{15}GaO_5W$	$C_{36}H_{45}Fe_2Ga_3O_6$	$C_{25}H_{30}GaMnO_5$	$C_{23}H_{25}Fe_2GaO_3$	$C_{24}H_{15}InO_9W_3$
Formula weight	528.84	894.58	535.15	530.85	1113.73
Temperature (K)	200(1)	200(1)	203(2)	293(1)	213(2)
λ (Mo–K$_\alpha$)	0.71069	0.71069	0.56087 [a]	0.71069	0.56087 [a]
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Spacegroup	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	C/c	$P2_1/n$
Unit cell dimensions					
a (Å)	9.054(2)	11.639(2)	8.7300(17)	16.843(3)	11.395(2)
b (Å)	9.651(2)	11.862(2)	31.683(6)	9.2831(19)	17.667(4)
c (Å)	10.780(2)	16.116(3)	9.3220(19)	15.281(3)	13.415(3)
α (°)	73.43(3)	73.50(3)	90	90	90
β (°)	89.39(3)	82.53(3)	105.57(3)	116.34(3)	102.01(3)
γ (°)	75.77(3)	61.60(3)	90	90	90
V (Å^3)	873.3(3)	1876.6(6)	2483.8(9)	2141.2(8)	2641.5(9)
Z	2	2	4	4	4
μ (mm^{-1})	8.140	2.922	0.854	2.607	2.800
D_{calc} (g cm^{-3})	2.011	1.583	1.431	1.647	7.499
F(000)	500	908	1104	1080	2008
Θ-Range (°)	1.98 25.88	1.99 23.23	1.98 20.00	2.58 25.97	1.70 24.17
Index ranges	$-11 \le h \le 11$	$-12 \le h \le 12$	$-10 \le h \le 10$	$-19 \le h \le 20$	$-13 \le h \le 16$
	$-11 \le k \le 11$	$-13 \le k \le 13$	$-38 \le k \le 38$	$-10 \le k \le 11$	$-25 \le k \le 25$
	$-13 \le l \le 13$	$-17 \le l \le 17$	$-11 \le l \le 11$	$-18 \le l \le 18$	$-19 \le l \le 14$
R_{int}	0.0571	0.0621	0.0605	0.0501	0.1451
Reflections measured	6501	10 366	12 536	5338	18 623
Independent reflections	3134	5055	4532	3647	7801
Parameters	204	439	299	262	334
Goodness-of-fit on F^2	1.023	0.790	1.102	0.922	1.263
Reflections with [$I > 2\sigma(I)$]	2905	3071	3571	2793	4342
Final R_1, wR_2 [($I > 2\sigma(I)$)] (all data)	0.0300, 0.0733	0.0373, 0.0696	0.0610, 0.1459	0.0456, 0.0963	0.0895, 0.2131
	0.0319, 0.0741	0.0782, 0.0773	0.0778, 0.1566	0.0666, 0.1033	0.1514, 0.2565
Largest difference peak and hole (e Å^{-3})	2.092	0.369	1.223	0.795	3.567
	−2.247	−0.671	−0.784	−0.781	−5.916

[a] μ(Ag–K$_\alpha$)/mm^{-1}.

allowed to warm up to r.t. and was stirred for 2 h. After filtering, all volatiles were removed in vacuo, and the yellow residue was extracted twice with 15-ml aliquots of toluene and filtered. The solution was concentrated in volume to 2 ml, and yellow crystals of **8** (312 mg, 70%) were isolated at -30 °C. ^{1}H-NMR (C_6D_6): δ 5.02 (s, 15 H, Cp). IR (cm^{-1}, KBr): 1968, 1873, 1855. MS (EI, 70 eV) m/z (%): 1114 (0.2) [M^+], 1030 (4) [$M^+ - 3(CO)$], 918 (2) [$M^+ - 7(CO)$], 890 (4) [$M^+ - 8(CO)$], 862 (2) [$M^+ - 9(CO)$], 781(100) [$M^+ - \{WCp(CO)_3\}$], 725 (28) [$M^+ - 2(CO) - \{WCp(CO)_3\}$], 448 (1) [$M^+ - 2\{WCp(CO)_3\}$], 333 (9) [$WCp(CO)_3^+$], 115 (88) [$In^+$].

4. X-ray structure determinations for complexes 1, 2, 4, 6 and 8

Crystals of the compounds were mounted at low temperature in inert oil on a glass fiber. Data were collected on STOE IPDS diffractometers with Mo–K_α radiation except for **4** and **8** where Ag–K_α radiation was used. The structures were solved by direct methods using the SHELXS-97 computer program [33] and refined on F^2 by full-matrix least-squares (SHELXL-97) [34]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. The Flack parameter of the acentric structure of **6** came to a value of 0.01(3). Due to the unusual space group C/c, we excluded all possible supergroups, like $C2/c$, $Fdd2$ and $R\bar{3}c$. The solutions in these supergroups as well as the transformation from C/c to these groups confirm the space group C/c for **6**. Complex **8** crystallises in thin platelets with a poor crystal quality (independent of the fact that several crystals from different reactions were used for X-ray diffraction). Unfortunately, for this compound high electron residue densities were found close to the atoms W1 (0.07 Å) and W2 (0.74 Å). Crystallographic data are given in Table 5.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, as supplementary publication no. CCDC-167059–167062 for the compounds **1**, **2**, **4** and **6**, and CCDC-168033 for complex **8**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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