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Notes

Pentamethylcyclopentadienylindium (Cp*In) as Terminal Ligand in the Chemistry of Chromium

Peter Jutzi,* Beate Neumann, Guido Reumann, Lars Oliver Schebaum, and Hans-Georg Stammler

Fakultät für Chemie, Universität Bielefeld, Bielefeld, Germany

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*Summary: The reaction of Cp*In with the $Cr(CO)_5$-transfer agent $Cr(CO)_5(C_8H_{14})$ (C_8H_{14} = cis-cyclooctene) results in the formation of $Cr(Cp^*In)(CO)_5$ (**1**), in which Cp*In acts as an electron pair donor. Compound **1** was characterized by spectroscopic data and by an X-ray analysis. The structure of **1** is compared with the analogous gallium compound $Cr(Cp^*Ga)(CO)_5$ (**2**).*

Introduction

There is great interest in the organometallic chemistry of monovalent group 13 elements.[1−3] Due to the presence of a metal-centered lone pair, the monomeric species of this type can act as Lewis bases in transition metal chemistry. The ligand potential of monomeric Cp*Al[4] and of Cp*Ga[5] has been demonstrated by the synthesis of several complexes with terminal and bridging Cp*M units. Only recently has the synthesis of the first complex containing a Cp*B unit been reported.[6] From this point of view it is of interest to extend this series to the element indium and to see whether Cp*In can act as donor ligand in a similar fashion. To the best of our knowledge, a transition metal complex with a Cp*In ligand thus far is unknown. We report here the synthesis of the first compound of this type and compare its structure with that of the known gallium analogue.

Results and Discussion

Heating a toluene solution of $Cr(CO)_5(C_8H_{14})$ (C_8H_{14} = *cis*-cyclooctene) and Cp*In at reflux led to the formation of $Cr(Cp^*In)(CO)_5$ (**1**) (eq 1). The reaction could be followed by a color change from initially light yellow to orange.

$$\mathrm{Cp^*In} + \mathrm{Cr(CO)_5(C_8H_{14})} \xrightarrow[-\,\mathrm{C_8H_{14}}]{n\text{-hexane}} \underset{\mathbf{1}}{\mathrm{Cr(Cp^*In)(CO)_5}}$$

$$(\mathrm{C_8H_{14}} = cis\text{-cyclooctene})$$

After removing all volatile components in vacuo, **1** was obtained as a yellow, very air-sensitive powder, which melts with decomposition at 150 °C. The compound readily dissolves in aprotic organic solvents such as *n*-hexane and toluene. Crystals suitable for an X-ray structure analysis were obtained from toluene solution. 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.

In **1**, the chromium atom is surrounded by five CO ligands and one Cp*In ligand in an octahedral geometry. Within the Cp*In fragment, the η^5-bonding mode of the Cp* ring is maintained, although small deviations from ideal η^5-bonding are observed. Interestingly, the $Cp^*_{centroid}$−In−Cr vector deviates significantly from linearity (157.7°). Compared to Cp*In in the solid state[7] or in the gas phase,[7] the $Cp^*_{centroid}$−In distance in **1** is shortened by approximately 6%. A reduced distance corresponds to an indium atom in a comparatively higher oxidation state and indicates mainly σ-donor quality of the Cp*In fragment. This effect can also be confirmed by bonding parameters within the $Cr(CO)_5$ unit. Thus, the axial CO ligand is affected by the trans-orientated Cp*In ligand in such a way that a significantly shorter $Cr-C(CO_{trans})$ distance is observed (1.861(4) Å) in comparison to the corresponding $Cr-C(CO_{equatorial})$ distances (average value 1.904(4) Å).

The solid-state structure of **1** explains the deviation of the $Cp^*_{centroid}$−In−Cr vector from linearity. Repulsive intermolecular interactions between the Cp* methyl groups and surrounding $CO_{equatorial}$ ligands are the main reason for the observed deviation. For illustration, the unit cell of compound **1** is shown in Figure 2.

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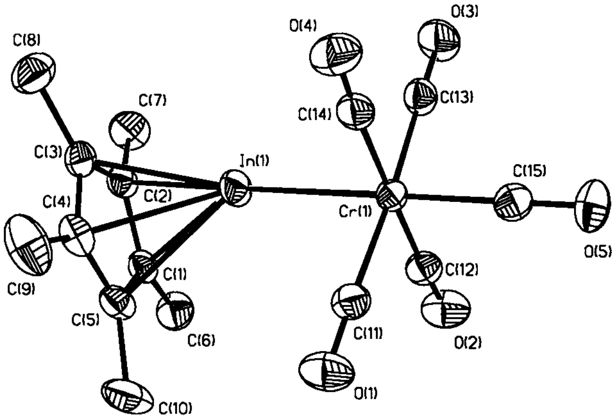

Figure 1. Molecular structure of Cr(Cp*In)(CO)$_5$ (**1**), thermal ellipsoids at 50% probability.

Table 1. Crystallographic Data for Cr(Cp*In)(CO)$_5$ (1)

empirical formula	$C_{15}H_{15}CrInO_5$
fw	442.10
cryst color, habit	yellow, irregular
cryst size, mm^3	0.50 × 0.30 × 0.20
temp, K	173(2)
wavelength	Mo Kα 0.71073 Å (graphite monochromator)
space group	$P\bar{1}$
unit cell dimens	$a = 9.110(3)$ Å
	$b = 9.789(4)$ Å
	$c = 10.298(3)$ Å
	$\alpha = 103.36(3)°$
	$\beta = 90.41(3)°$
	$\gamma = 104.44(3)°$
V, Å^3	863.2(5)
Z	2
density (calcd), Mg/m^3	1.701
θ range for data collection	2.21−30.00°
no. of reflns collected	5321
no. of ind reflns	5026 ($R_{\mathrm{Int}} = 0.0343$)
abs corr	empirical from ψ-scans
final R_F [$I > 2\sigma(I)$]	0.0426 [4090]
wR_{F2} (all data)	0.1067
no. of params	204
largest diff peak and hole, e Å^{-3}	1.050 and −1.479
diffractometer used	Siemens P2(l) 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

In(1)−C(1)	2.500(3)	Cr(1)−C(11)	1.901(4)
In(1)−C(2)	2.406(3)	Cr(1)−C(12)	1.899(4)
In(1)−C(3)	2.435(3)	Cr(1)−C(13)	1.909(4)
In(1)−C(4)	2.524(4)	Cr(1)−C(14)	1.908(4)
In(1)−C(5)	2.561(4)	Cr(1)−C(15)	1.861(4)
In(1)−Cr(1)	2.5854(13)	O(1)−C(11)	1.146(4)
		O(2)−C(12)	1.149(5)
		O(3)−C(13)	1.146(5)
		O(4)−C(14)	1.143(5)
		O(5)−C(15)	1.146(4)
C(14)−Cr(1)−C(12)	179.23(15)	C(15)−Cr(1)−In(1)	179.31(12)
C(11)−Cr(1)−C(13)	176.00(15)		

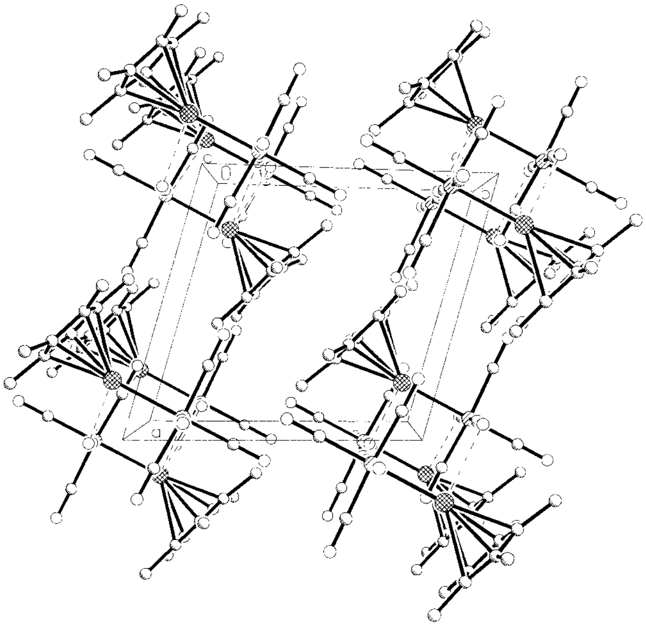

Figure 2. Drawing of the unit cell of **1**.

The asymmetry within the Cp*InCr moiety in the solid state of **1** is not maintained in solution. The presence of a fluxional Cp* fragment is demonstrated by the observation of only one resonance for the five methyl groups and one for the five ring carbon atoms in the ^{13}C NMR spectrum, even at low temperature (−80 °C). In addition, two signals for the equatorial and axial CO ligands are detected. In the IR spectrum of **1** four CO stretching vibrations are observed. Three vibrations are to be expected on the basis of a local C_{4v} symmetry. The usually IR-forbidden B$_1$ mode at 1977 cm^{-1} is present due to the symmetry reduction caused by the C_5 symmetry of the Cp* ring.

It is interesting to compare structural parameters of **1** with those of the gallium analogue Cr(Cp*Ga)(CO)$_5$, **2**. In Table 3 important structural data of both compounds are given.

1 and **2** both crystallize in the $P\bar{1}$ space group and are isostructural from the crystallographic point of view. According to the different covalent radii of Ga (1.26 Å)[8] and In (1.44 Å),[8] the Cp*$_{\mathrm{centroid}}$−M and M−Cr distances as well as the cone angles θ are different but reflect comparable bonding situations. Interestingly, significant differences concerning the Cp*$_{\mathrm{centroid}}$−M−Cr vectors are observed. This is a consequence of different intermolecular van der Waals contacts between the M−CO$_{\mathrm{equatorial}}$ groups and the Cp* units. Concerning the Cr(CO)$_5$ moiety, comparable bonding parameters are observed for **1** and **2**, indicating similar donor properties of Cp*In and Cp*Ga. Thus, a complex chemistry similar to that of Cp*Ga is expected for Cp*In. The comparatively weaker Cp*−In interaction might favor reactions with Cp* as leaving group.

Experimental Section

General Comments. All manipulations were carried out under a purified argon atmosphere using standard vacuum techniques. The solvents were commercially available, purified by conventional means, and distilled immediately prior to use. Cp*In[7] and Cr(CO)$_5$(C$_8$H$_{14}$)[9] were prepared according to the literature. 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

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Table 3. Selected Bond Lengths (Å), Angles (deg), and IR Data (cm^{-1}) for Compounds 1 and 2

	$Cp^*_{centroid}-M$	M−Cr	θ	$Cp^*_{centroid}-M-Cr$	$Cr-(CO)_{ax}$	$Cr-(CO)_{eq}$	$\nu(CO)$			
$Cr(Cp^*In)(CO)_5$, **1**	2.168(4)	2.5854(13)	102	157.7	1.861(4)	1.904(4)	2050	1977	1919	1894
$Cr(Cp^*Ga)(CO)_5$, **2**	1.910(4)	2.4046(7)	112	167.5	1.858(4)	1.899(4)	2052	1982	1918	1902

500.1 MHz; $^{13}C\{^1H\}$ 125.8 MHz). Chemical shifts are reported in ppm and are referenced to the solvent as internal standard. IR data were collected using a Bruker Vektor 22-FT spectrometer. The samples were measured as KBr pellets.

Preparation of $Cr(Cp^*In)(CO)_5$ (1). A mixture of $Cr(CO)_5(C_8H_{14})$ (60 mg; 0.20 mmol) and Cp*In (50 mg; 0.20 mmol) was dissolved in toluene (2 mL). While the reaction mixture was heated at reflux for 1 min, the color changed from yellow to orange. After the mixture was cooled to room temperature, all volatile components were removed *in vacuo* to yield 75 mg of $Cr(Cp^*In)(CO)_5$ (**1**) (0.17 mmol, 85%). Mp: 150 °C (dec). ^1H NMR: δ 1.73 (s, 15 H, Cp* methyl). ^{13}C NMR: δ 9.53 (Cp* methyl), 116.52 (Cp* ring), 219.13 ($CO_{equatorial}$), 225.31 (CO_{axial}). IR (cm^{-1}, KBr): 2986 (w), 2923 (w), 2851 (w), 2050 (s, ν_{CO}, $A_1(2)$), 1977 (s, sh, ν_{CO}, B_1), 1919 (vs, ν_{CO}, $A_1(1)$), 1894 (vs, ν_{CO}, E), 1388 (w), 1261 (w), 659 (s), 649 (s). Anal. Calcd for $C_{15}H_{15}O_5CrIn$ ($M = 442.10$ g mol^{-1}): C, 40.75; H, 3.41. Found: C, 40.55; H, 3.34.

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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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