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Reactivity of InCp* Towards Transition Metal Carbonyl Clusters: Synthesis and Structural Characterization of the $Rh_6(CO)_{16-x}(InCp^*)_x$ Mixed-Metal Cluster Compounds, $x = 1–2$

Elena V. Grachova*[a] and Gerald Linti[b]

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With $[Rh_6(CO)_{15}(InCp^*)]$, the first example of a transition metal carbonyl cluster with a coordinated InCp* (Cp* = C_5Me_5) fragment in the ligand environment is reported. This cluster with direct Rh–In bonds forms in the reaction of the hexanuclear carbonyl rhodium cluster $Rh_6(CO)_{15}(NCMe)$ with InCp* under mild conditions. This is characterized by means of IR and NMR spectroscopy and crystal structure analysis.

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Introduction

Creation of new materials primarily requires chemists to create new compounds with novel and unusual properties. In most cases, unusual properties are the result of the unusual composition and structure of a new compound and the combination of incompatible elements, as for example direct bonds between d- and s,p metals.

Compounds ECp* (E = group 13 metal) are used in organometallic chemistry of transition metals as "building blocks" owing to their capacity to substitute carbonyl ligands and to coordinate directly to a transition metal atom.[1,2] This enables the design of small carbonyl cluster compounds containing direct bonds between transition and non-transition metals.

Recently, we reported the synthesis and structural characterization of a series of mixed-metal rhodium and ruthenium carbonyl cluster complexes containing GaCp* fragments in the coordination environment.[3–5] Extension of these studies to InCp* complexes is directed not only to the creation of novel compounds, but to understand regular trends for the interaction of low nuclear carbonyl cluster compounds with ECp* complexes as well. This understanding is necessary to know how to create the mixed-metal carbonyl cluster compounds with a predetermined, specified relation of transition metal to group 13 metal.

Results and Discussion

Reactivity of InCp* towards transition metals has been studied and various mixed-metal complexes with InCp* as a ligand were synthesized.[6–11]

We found that the reaction of the labile $[Rh_6(CO)_{15}(NCMe)]$ cluster with a slight excess of InCp* in dry toluene results in the formation of monosubstituted $[Rh_6(\mu_3\text{-}CO)_3(\mu_3\text{-}InCp^*)(CO)_{12}]$ (**1**) and disubstituted $[Rh_6(\mu_3\text{-}CO)_2(\mu_3\text{-}InCp^*)_2(CO)_{12}]$ (**2**) cluster complexes. This is similar to the analogous reaction of the starting cluster with GaCp*.[3,4] The very curious fact is that treatment of the parent $Rh_6(CO)_{16}$ cluster with any amount of InCp* gives no substituted derivatives, which is in contrast to the behaviour of GaCp*. This fact demonstrates the lower coordination ability of In^I derivatives relative to Ga^I organyls.

Clusters **1** and **2** are air-sensitive and are destroyed on silica gel. Single crystals of **1** were obtained and its structure was determined by X-ray analysis. Compound **1** crystallizes

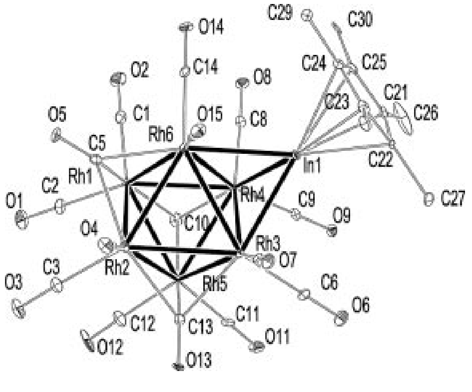

Figure 1. ORTEP view of $Rh_6(CO)_{15}(InCp^*)$ (**1**).

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[a] Department of Chemistry, St. Petersburg State University, Universitetskii pr. 26, 198504 St. Petersburg, Russia
Fax: +7-812-428-6939
E-mail: bird231102@mail.ru
[b] Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

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Table 1. Selected structural parameters for **1**.

		d(Rh–Rh), In-capped triangle [Å]			
Rh3–Rh6	2.8467(9)	Rh3–Rh4	2.8549(9)	Rh4–Rh6	2.8648(9)
		d(Rh–Rh), triangles remote to In [Å]			
Rh1–Rh4	2.7372(10)	Rh1–Rh5	2.7530(9)	Rh4–Rh5	2.7494(9)
Rh1–Rh6	2.7464(9)	Rh1–Rh2	2.7532(10)	Rh2–Rh6	2.7373(9)
Rh2–Rh5	2.7457(9)	Rh3–Rh5	2.7361(9)	Rh2–Rh3	2.7583(10)
		d(In–Rh) [Å]			
In1–Rh6	2.7072(10)	In1–Rh4	2.7075(9)	In1–Rh3	2.7196(9)
		d(In–C) [Å]			
In1–C22	2.346(15)	In1–C21	2.442(8)	In1–C24	2.532(12)
In1–C23	2.461(7)	In1–C25	2.504(16)		
		d(μ_3-CO–Rh) [Å]			
Rh6–C5	2.136(8)	Rh1–C5	2.187(8)	Rh2–C5	2.217(8)
Rh4–C10	2.134(8)	Rh5–C10	2.178(8)	Rh1–C10	2.197(8)
Rh3–C13	2.146(8)	Rh2–C13	2.186(8)	Rh5–C13	2.220(7)
($Cp^*_{centroid}$–In) distance [Å]: 2.153		($In–Rh_{triangle}$) distance [Å]: 2.153		($Cp^*_{centroid}$–In–$Rh_{triangle}$) angles [°]: 170.27	

together with one molecule of diethyl ether in the monoclinic crystal system and with the space group $P2_1/n$. An ORTEP view of **1** is shown in Figure 1, selected structural parameters are given in Table 1.

The cluster of **1**, provided that InCp* is a two-electron donor, has 7 skeletal electron pairs that fit the *closo* octahedral rhodium cluster skeleton that is surrounded by 16 ligands as in the parent $Rh_6(CO)_{16}$ cluster. The molecular structure of **1** demonstrates the substitution of one μ_3-CO in the $Rh_6(CO)_{16}$ molecule for an InCp* fragment. As a result, the coordination environment of **1** consists of 12 terminal CO, 3 face-bridging CO and an InCp* fragment, which is coordinated to the metal core in a μ_3 mode.

The InCp* ligand in **1** occupies a nearly symmetrical position over a rhodium triangle. The In–Rh distances fall in the range from 2.7072(10) to 2.7196(9) Å. This fits well with the result found in the only known cluster compound with μ_3-InCp* fragments in the ligand sphere, $[Pd_3(PPh_3)_3(\mu_2\text{-}InCp^*)(\mu_3\text{-}InCp^*)_2]$.[10]

The $Cp^*_{centroid}$–In–$Rh_{triangle}$ vector in **1** deviates from linearity (170.27°). This distortion is reflected in the InCp* ligand itself, which is coordinated in a pseudo η^3 manner [In–C_{Cp^*} contacts, 2.532(12), 2.346(15) Å]. Because there is some rotational disorder in the Cp* ring, which was treated as split positions of the carbon atoms in a 0.67:0.33 ratio, the results must not be overinterpreted. A similar situation was found before in the solid state for the $Rh_6(CO)_{16-x}(\mu_3\text{-}GaCp^*)_x$ clusters.[3,4] This outward move from the ideal symmetrical position can be formally described as a $\eta^5 \rightarrow \eta^3$ haptotropic shift in the C_5 rings of the ECp* fragment, but from our point of view, this phenomenon is essentially caused by steric distortions because of molecule packing in the crystal cell.

The insertion of InCp* in the coordination environment of the carbonyl cluster results in substantial distortions of the parent rhodium octahedron. These distortions are located in the vicinity of the substitution site. Thus, the mean Rh–Rh distance value in the rhodium triangle connected to In in **1** is 2.856(9) Å, whereas the mean Rh–Rh contact for the other metals in the cluster core is 2.746(8) Å (Table 1). Elongation of the Rh–Rh bonds of the indium-capped rhodium triangle looks very similar to the structural effect of weak π-acceptors, which was mentioned earlier for the terminally substituted $Rh_6(CO)_{16}$ derivatives.[12] We found the same effect for the $Rh_6(CO)_{16-x}(\mu_3\text{-}GaCp^*)_x$ and the $Ru_6C(CO)_{14}(GaCp^*)_3$ clusters, too. This phenomenon provides support to describe the InCp* complex as σ-donor and π-acceptor ligand toward transition metals.[13] However, InCp* is a weaker σ-donor than GaCp*, which is reflected in the lower stability of the $Rh_6(CO)_{16-x}(\mu_3\text{-}InCp^*)_x$ substituted cluster derivatives relative to $Rh_6(CO)_{16-x}(\mu_3\text{-}GaCp^*)_x$. Quantum chemical calculations on Pt–GaCp* and Pt–InCp* complexes hint to an analogous interpretation.[8]

The bonding of the face-bridging carbonyl ligands in **1** shows distortion from the highly symmetric coordination mode found in the parent $Rh_6(CO)_{16}$ cluster. This was observed earlier in $Rh_6(CO)_{15}(PR_3)$ compounds.[12] The structural effect of InCp* substitution in this case consists in a shift of all three bridging CO ligands from the idealized position over the centre of the rhodium triangles toward the Rh atoms bonded to In. Thus, one can observe a major contraction of the Rh–μ_3-C bonds on the In–Rh–μ_3-C line and light elongation of the Rh–μ_3-C distances on the μ_3-C–Rh–μ_3-C line, with the average value of the six bond lengths being 2.197(17) Å. That is a little bit longer than the average of 2.186 Å in $Rh_6(CO)_{16}$ (see Table 1).

The structure of **1** as determined in the solid state is evidently maintained in solution. The ^1H NMR spectrum of **1** displays a singlet signal at $\delta = 2.31$ ppm, which is typical for symmetrical coordination of the Cp* moiety. This resonance is low-field shifted relative to the corresponding signals of terminally bonded InCp* fragments. This deshielding is typical for the bridging InCp* coordination.[6–11]

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The IR spectrum (in CH_2Cl_2) of **1** shows peaks in the carbonyl region at 2092 (w), 2075 (sh), 2055 (s) and 2012 (sh) cm^{-1}, which correspond to the terminal CO groups, and the middle broad peaks at 1789 and 1778 cm^{-1}, which correspond to the bridging carbonyl ligands. The relative positions and intensities of the peaks in the IR spectrum of **1** agree with the spectroscopic results obtained for the $Rh_6(CO)_{15}(\mu_3\text{-GaCp*})$ cluster.[3]

We have not yet obtained crystals of **2** that are suitable for X-ray analysis, but its structure was characterized on the basis of spectroscopic data. The FD mass spectrum of **2** displays the signal of the $Rh_6(CO)_{14}(InCp*)_2$ molecular ion. The observed isotopic distribution pattern fits completely to the calculated one.

The IR spectrum of **2** in the CO region (CH_2Cl_2 solution) consists of peaks at 2083 (m), 2049 (s), 2029 (m) and 2010 (w) cm^{-1}, which correspond to the terminal CO groups, and the middle broad peak at 1777 cm^{-1}, which correspond to the bridging carbonyl ligands. The relative positions and intensities of the signals in the IR spectrum of **2** agree with the spectroscopic results obtained for the $Rh_6(CO)_{14}(\mu_3\text{-GaCp*})_2$ cluster, which consists of peaks at 2088 (m), 2052 (s), 2032 (m), 2008 (w) and 1774 (m br.) cm^{-1} ($CHCl_3$ solution). This corroborates that these two cluster compounds comprise identical CO environments. A room temperature ^1H NMR spectrum of **2** shows only one signal, a singlet for the methyl groups at $\delta = 2.29$ ppm. This is 0.02 ppm shifted upfield relative to the spectrum of **1**; likewise, this was found for the pair of $Rh_6(CO)_{16-x}(GaCp*)_x$, $x = 1–2$ clusters. These spectroscopic data clearly point to substitution of two bridging CO groups in the $Rh_6(CO)_{16}$ cluster environment. Thus, the structure of **2** can be described as a Rh_6 octahedron surrounded by 2 face-bridging InCp* fragments, 2 face-bridging CO ligands and 12 terminal carbonyl groups.

Conclusions

InCp*, similar to GaCp*, is capable of occupying the μ_3-bridging positions of a transition metal core in carbonyl clusters. This results in the formation of cluster compounds with direct bonds between the transition metal and the In atom. The results described above will be used to create mixed-metal cluster compounds with direct bonds between transition and group 13 metals.

Experimental Section

General Comments: All operations were carried out under an atmosphere of dry argon with the use of standard Schlenk techniques. All solvents were distilled under an inert atmosphere over appropriate drying agents prior to use. The starting $Rh_6(CO)_{15}(NCMe)$[14] cluster and the InCp*[15] complex were synthesized according to literature procedures. The purity control of InCp* was carried out by ^1H NMR spectroscopy. Infrared spectra were recorded with a Perkin–Elmer 16PC FTIR spectrometer. ^1H NMR spectra were measured with a Bruker ARX200 instrument. The chemical shifts were referenced to residual solvent resonances. Microanalysis was carried out in the Microanalytical Laboratory, University of Heidelberg. FAB and FD mass spectra were obtained with a JEOL JMS-700 instrument, Institute of Organic Chemistry, University of Heidelberg.

Synthesis of 1 and 2: The chromatographically pure $Rh_6(CO)_{15}(NCMe)$ cluster (68 mg, 0.063 mmol) was dissolved in dry toluene (20 mL), and solid InCp* (30 mg, 0.120 mmol) was added under high stirring. The reaction mixture was kept at room temp. under an atmosphere of argon overnight, wrapped in aluminium foil for light protection. The solvent was then removed in vacuo leaving some brown material. The residue was washed with *n*-hexane (5 mL) and dried in vacuo again. The reaction mixture was extracted with CH_2Cl_2 (2 × 5 mL) to yield a red–brown solution with a brown oily precipitate. The solution was diluted with *n*-hexane (5 mL) and filtered through a glass filter giving a dark maroon transparent solution. The solvents were removed in vacuo leaving a dry crystalline material. It was extracted with pentane (2 × 10 mL) by using an ultrasonic bath (2 min) and then passed through a cellulose column (3 × 2 cm) to give a transparent red–brown solution. Removal of the solvent gave brown crystals of $Rh_6(CO)_{15}(InCp*)$ (**1**); 19 mg were isolated. The residue of the pentane extraction was dissolved in CH_2Cl_2 (3 mL), diluted with pentane (5 mL) and passed through a cellulose column giving a transparent brown solution. Removal of the solvents gave a brown crystalline precipitate of $Rh_6(CO)_{14}(InCp*)_2$ (**2**), 23 mg.

1: ^1H NMR (200 MHz, $CDCl_3$, ambient temperature): $\delta = 2.31$ (s, CH_3). IR (CH_2Cl_2, ν_{CO}): $\tilde{\nu} = 2092$ (10), 2075 (sh), 2055 (100), 2012 (sh), 1789 (19), 1778 (21) cm^{-1}. IR (n-hexane, ν_{CO}): $\tilde{\nu} = 2098$ (16), 2075 (33), 2064 (100), 2045 (45), 2029 (7), 2010 (6), 1820 (18), 1804 (43) cm^{-1}. MS (FD+): $m/z = 1092$ $[M - 7CO]^+$ $C_{18}H_{15}InO_8Rh_6$. MS (FAB+): $m/z = 1148$ $[M - 5CO]^+$ $C_{20}H_{15}In_1O_{10}Rh_6$, 1064 $[M - 8CO]^+$ $C_{17}H_{15}InO_7Rh_6$, 1008 $[M - 10CO]^+$ $C_{15}H_{15}InO_5Rh_6$, 952 $[M - 12CO]^+$ $C_{13}H_{15}InO_3Rh_6$, 924 $[M - 13CO]^+$ $C_{12}H_{15}InO_2Rh_6$. $C_{25}H_{15}InO_{15}Rh_6$ (1287.63): calcd. C 23.32, H 1.17; found C 23.82, H 1.88. Single crystals of **1** suitable for X-ray studies were grown from saturated pentane solution under an argon atmosphere at –25 °C.

2: ^1H NMR (200 MHz, $CDCl_3$, ambient temperature): $\delta = 2.29$ (s, CH_3). IR (CH_2Cl_2, ν_{CO}): $\tilde{\nu} = 2083$ (17), 2049 (100), 2029 (22), 2010 (9), 1777 (12) cm^{-1}. MS (FD+): $m/z = 1509$ $[M]^+$ $C_{34}H_{30}In_2O_{14}Rh_6$.

X-ray Crystal Structure Determination: Intensity data were collected at 100 K with a Bruker AXS Smart CCD diffractometer (Mo-K_α radiation, $\lambda = 0.71073$ Å) and corrected for absorption and other effects. The structure was solved by direct methods and refined by full-matrix least-squares based on F^2. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were inserted in calculated positions. Calculations were performed by using the SHELXTL package.[16] $C_{29}H_{15}InO_{16}Rh_6$ (1361.8 $g\,mol^{-1}$), monoclinic, space group $P2_1/n$, $a = 12.146(2)$ Å, $b = 22.427(4)$ Å, $c = 14.402(2)$, $\beta = 100.081(3)°$, $V = 3862(1)$ Å^3, $Z = 4$, $\phi_{calcd.} = 2.342$ $g\,cm^{-3}$, $\mu = 3.152$ mm^{-1}, $F(000) = 2584$, crystal dimensions 0.08 × 0.06 × 0.06 mm^3, 2θ range for data collection 2–56°, absorption corrections: ellipsoidal, min/max transmission: 0.714/0.808, 39084 collected reflections, 9620 unique, 4940 observed $[I > 2\sigma(I)]$, 508 parameters, GOOF 0.793, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0155P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, $R_1 = 0.044$, $wR_2 = 0.066$ $[I > 2\sigma(I)]$, $R_1 = 0.114$, $wR_2 = 0.076$ (all data, 0.129 for unit weights), residual electron density 1.42 $e\,Å^{-3}$.

CCDC-634755 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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