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The first structurally characterized coordination compound containing direct Al–Cr bonding: $Cp^*Al–Cr(CO)_5$

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Abstract

In order to investigate the bonding of the carbene-like ligand AlCp* towards a transition metal, the compound $Cp^*AlCr(CO)_5$ has been prepared starting from $Cr(CO)_5COT$ and AlCp*. With the help of its crystal structure, some IR spectroscopic data and ab initio calculations, the Al–Cr bonding is discussed. The strong reducing ability of AlCp* leads to a shift in electron density towards the chromium atom and finally to the CO ligands. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The first preparation of AlCp* [1], which forms tetrameric units in the solid state, was the starting point for the formation of new species containing direct bonding between aluminium and transition metal atoms [2]. The reactivity of AlCp* is based on the easy formation of monomeric AlCp* species if the solution is heated above room temperature (r.t.) [3]. The resulting carbene-like AlCp* molecules can substitute other ligands by the formation of strong aluminium–transition-metal bonding. To date, only two examples have been obtained which contain AlCp* as a bridging ligand: $(AlCp^*)_2(NiCp)_2$ [4] and $(AlCp^*)_2(Co(CO)_3)_2$ [5]. However, by pursuing an alternative route, Fischer et al. have shown that $AlCp^*Fe(CO)_4$ as the first example of terminal bonded AlCp* could be obtained from the reaction of I_2AlCp^* with $K_2Fe(CO)_4$ [2b]. Furthermore, Roesky et al. and Jutzi et al. have demonstrated that there are classical routes available to obtain AlCp* as well as GaCp* [6,7]. Now the latter can be obtained in large amounts and therefore a series of reactions which end up with new Ga–M compounds (M = Fe, Ni, Cr...) have been performed.

In analogy to the results of Jutzi et al. [7] we are now able to prepare the second example containing AlCp* as a terminal ligand. However, we have shown recently for $AlCp^*Fe(CO)_4$ by means of DFT calculations [5] that the interpretation that an Al(I)Cp* ligand is stabilized by coordination to the unsaturated Fe center is not quite correct [2b], since there is large electron transfer from the Al atom to the transition-metal atom. Therefore, a more polar bonding scheme (RAl^{2+} $Fe(CO)_4^{2-}$) seems to be more appropriate for this kind of Al/Ga–M bonding [7].

2. Results and discussion

In order to study the structural details of AlCp* as a ligand in transition-metal compounds, we performed an improved crystal structure analysis of AlCp* at low temperature. The results obtained are significantly more accurate and much better for comparison with other data, which were collected at low temperature (200 K), e.g. of compounds containing AlCp* as a ligand. The most important structural parameters of AlCp* (**2**), in this reinvestigation, are the average Al–Al and Al–C_{cp} distances: 276.7 and 234.4 pm, respectively [8].

In order to synthesize a new Al–Cr compound AlCp*, prepared from AlBr [9] and Cp_2^*Mg [10], and $Cr(CO)_5C_8H_{14}$ (C_8H_{14} = *cis*-cyclooctene) [11] were al-

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lowed to react in a solution of toluene at about 60°C for 1 h. After slowly cooling down to $-22°C$, yellow-green crystals of $Cp^*AlCr(CO)_5$ (**1**) formed. The results of the crystal structure analysis are presented in Fig. 1 [12]. The most prominent structural feature is the Al–Cr distance of 237.6 pm, which is much larger than the distance in the only other example containing terminal bonded AlCp* to a transition metal: $Cp^*AlFe(CO)_4$ (223.1 pm) [2b]. That means there is a large variation in the Al–M distance which is also evident for compounds containing AlCp* as a bridging ligand:

$(AlCp^*)_2(NiCp)_2]$ [4]	d(Al–Ni)	(227 pm)
$(AlCp^*)_2(Co(CO)_3)_2$ [5]	d(Al–Co)	(237 pm)

The aluminium–transition-metal bonding is strong enough to allow vaporization of the compounds and to detect the molecule in the gas phase, e.g. by mass spectroscopy. The second important structural feature for **1**, which gives a hint of this polar bonding, is the short Al–C bond (217–218 pm). This shortening in comparison to monomeric AlCp* (239 pm) [13] of more than 20 pm is the result of a dramatic increase in the positive charge on the Al center, i.e., the strong reducing agent AlCp* has pumped electron density towards the transition metal with the result that the Al center may now be oxidized and a polar description like $R{-}Al^{2+}\cdots Cr^{2-}(CO)_5$ may be the basis for the high stability of such compounds. However, the most convincing experimental argument for this more polar description of bonding is the fact that for $(AlCp^*_2)^+$ as a compound containing unambiguously Al in the oxidation state +3, the Al–C distance of 215 pm [14] is as short as in **1** and especially as in $Cp^*AlFe(CO)_4$ (215 pm) [2b].

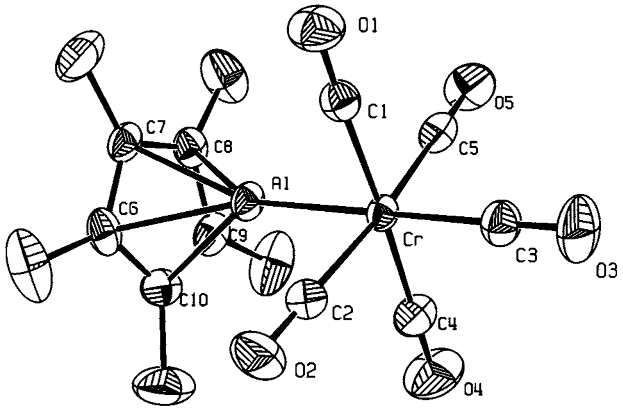

Fig. 1. Molecular structure of $(CO)_5CrAlCp^*$ (**1**) (50% probability of the thermal ellipsoids; hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°): Cr–Al 2.3761(6), Cr–C(2) 1.892(2), Cr–C(2) 1.882(2), Cr–C(3) 1.861(2), Cr–C(4) 1.888(2), Cr–C(1) 1.887(2), Al–C(6) 2.187(2), Al–C(7) 2.176(2), Al–C(8) 2.185(2), Al–C(9) 2.185(2), Al–C(10) 2.183(2), Al–Cr–C(3) 179.57(7), Al–Cr–C(1) 89.94(6).

In order to understand the bonding in **1** it may be interesting to present a comparison to similar GaCp*–transition-metal compounds which have been published recently [7]. In particular the following compounds, for which Ga–M and Ga–C distances are listed, should be discussed.

		d(Ga–M) (pm)	*d*(Ga–C) (pm)
$Cp^*GaFe(CO)_4$	terminal Cp*Ga	227.3(4)	222.6(2)
$Cp^*GaCr(CO)_5$	terminal Cp*Ga	240.5(7)	226.0(3)
$(Cp^*Ga)_2$ $(Co(CO)_3)_2$	bridging Cp*Ga	238.9(3)	228.7(3)

As expected, there is a shortening of the Ga–C distance observed in comparison with free GaCp* (236.9 pm) [15] as in the case of the AlCp* systems mentioned above. Obviously, this shortening is not as large as that for the monomeric AlCp* to the corresponding AlCp* complex, a fact which shows the larger polarity of the Al containing species. This trend is generally observed in Ga/Ga and Al/Al chemistry: for compounds containing nonpolar metal–metal bonding the Al–Al distance is larger than the Ga–Ga distance if similar ligands are present [16]:

	d(Al–Al) (pm)	*d*(Ga–Ga) (pm)
$[MC(SiMe_3)_3]_4$	274 [17]	269 [18]
$[M(Si^tBu_3)]_4$	260 [19]	257 [20]
$[MCH(SiMe_3)_2]_2$	266 [21]	254 [22]

In contrast the size of Al seems to be smaller than that of Ga if polar bonding is present.

	d(Al–X) (pm)	*d*(Ga–X) (pm)
$(MCl)_{gaseous}$ [23]	213	220
$(MI)_{gaseous}$ [23]	254	257

These data support the interpretation of a strong polarity between Al/Ga and the transition metal in the compounds discussed here, since the Ga–Cr distance in $Cp^*GaCr(CO)_5$ is larger than the Al–Cr distance in **1**.

In addition to the geometric data, the IR spectra, in particular the region of the CO stretching modes, should be discussed, since they also give a hint to the bonding behavior of AlCp* as a ligand. The IR spectrum of **1** in KBr pellet exhibits four absorptions in the CO region: 2039.0 (m), 1983.0 (m, sh), 1965.0 (m, sh), and 1909 cm^{-1} (vs). For the similar Ga species $GaCp^*Cr(CO)_5$ four absorptions are also mentioned: 2052, 1982, 1918 and 1902 cm^{-1} [7]. For this species the band at 1982 cm^{-1} has been tentatively assigned to the usually forbidden B_1 mode in a C_{4v} system. For comparison the IR absorptions in (TMEDA)ClAlCr-$(CO)_5$ should also be presented: 2016 (s), 1926 (vs), and 1876 cm^{-1} (vs). [2c].

If there is no coupling between the CO vibrations, which is an assumption of Cotton Craihanzel Force Field, the symmetry adopted force constants mainly determine the energy of the vibration, that means the equatorial A_1 vibration should be observed at higher wave numbers since the corresponding force constant contains the stretching and the following interaction constants $(f_{CO}+f^{(trans)}_{CO/CO}+2f^{(cis)}_{CO/CO})$. On the other hand, the second A_1 vibration is based only on the single stretching force constant $f^{(axial)}_{CO}$. That means, this vibration should be of the lowest energy if the ligand in the *trans*-position is mainly a σ donor, which weakens the opposite CO bond and consequently a lower force constant will result. Between these two A_1 vibrations the E mode should be observed, which normally has the largest intensity.

These qualitative predictions are supported by ab initio calculations [24]. On the basis of SCF calculations the following CO stretching modes have been obtained for $CpAlCr(CO)_5$: 2388 cm^{-1} (A_1) (27 km mol^{-1}), 2303 cm^{-1} (E) (200 km mol^{-1}), and 2301 cm^{-1} (A_1) (44 km mol^{-1}). The IR intensities are given in brackets. In order to understand these data some comments should be given: on the SCF level the frequencies are calculated as expected to be 10–15% higher than in reality. Furthermore, the displacement of the atoms during these vibrations shows that both A_1 modes are coupled to a certain degree. However, in the 2388 cm^{-1} mode four equatorial CO groups are mainly involved while the 2301 cm^{-1} mode may be assigned to a stretch of the axial CO ligand. In contrast to theory the measured spectra of all $Cr(CO)_5$ species under discussion give a hint to an A_1 absorption or shoulder at higher frequency than the E′ mode. These discrepancies show that there is a significant difference to normal bonding in $RCr(CO)_5$ species, for which the variation in σ and π bonding of the ligand R is essential for bonding of the CO units. However, for these species all CO frequencies are about 100 cm^{-1} blue shifted in comparison to the AlCp* and GaCp* chromiumcarbonyl compounds discussed here. This means that the amount of electron density being pumped from the AlCp* or the GaCp* ligands into the carbonyl entity is visualized by a dramatic red shift of all CO frequencies—which is just on the way to that of the 'isolated' carbonyl anions [5]—and consequently small changes of the CO frequencies caused e.g. by the *trans* effect of more covalent bonded ligands are superimposed and falsified.

However, since the calculated distances [25] are in line with the crystal structure data, further Raman and IR spectroscopic investigations should be performed in order to support our interpretation. Perhaps the measured weak absorptions or shoulders may be assigned to overtones or may be caused by Fermi resonances.

Furthermore, we plan the synthesis of similar AlCr compounds with differently substituted Cp ligands. The main interest of these planned experiments will cover the influence of the different Al containing ligands on bonding, especially on the Cr–Al bond. If a large number of these complexes were available further observations which are not plausible, so far, could be discussed: e.g. in the mass spectra the peaks with the highest intensity belong to the species Cp^*AlCr^+. In order to understand the high stability of these ionic species we want to perform gas phase measurements with the help of matrix IR techniques. If the abstraction of all CO ligands can also be induced by simple heating, these transition metal Al or Ga compounds seem to be suitable precursors for CVD experiments.

3. Experimental

3.1. General comments

All manipulations were carried out under an argon (glovebox, MBRAUN) or dinitrogen atmosphere. Toluene was dried (sodium), distilled and degassed prior to use.

3.2. Physical measurements

Mass spectra (EI, 70 eV) were run on a Finnigan MS 8230 instrument; NMR spectra were obtained using a Bruker AC250 spectrometer (^1H, 250, 133 MHz) and referenced to the residual protic impurities of the solvent ($\delta(C_6D_5H)$ 7.16 ppm). IR spectra were obtained using KBr pellets on a Bruker IFS 113v FT-IR spectrometer.

3.3. Synthesis of *Cp*AlCr(CO)₅* (**1**)

A mixture of $(Cp^*Al)_4$ (50 mg, 0.077 mmol) and $Cr(CO)_5C_8H_{14}$ (110 mg, 0.35 mmol) was dissolved in toluene (10 ml) and the solution heated to about 60°C for 1 h. The solution was stored at −22°C after it was cooled to r.t. and subsequently filtered. The yellow–green crystals formed after several days of standing. ^1H-NMR (C_6D_6, r.t.): $\delta = 1.60$ ppm; ^{27}Al-NMR: $\delta = -26.1$ ppm ($\omega_{1/2} = 3100$ Hz); MS (EI, 70 eV, 180°C, m/z (relative intensity)): 354.0 (16.5, M^+), 214.6 (100, $M^+ - 5CO$); IR (KBr; cm^{-1}): 2039.0 (m), 1983.0 (m, sh), 1965.0 (m, sh), and 1909 cm^{-1} (vs).

3.4. X-ray data collection and solution and refinement of structure

Crystals were selected under argon in perfluorinated polyethers. The oil coated crystals were manipulated onto a glass fiber and transferred to a cold nitrogen stream of the Stoe Stadi IV diffractometer (Mo–K$_\alpha$ radiation, $\lambda = 0.71069$ Å; graphite monochromated). The structures were solved by direct methods (SHELXS-90) [1a] and refined (SHELXL-93) [26b] by full-matrix least-squares on F^2 (hydrogen atoms: riding model, fixed isotropic U).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 111983 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Further details of the crystal structure analysis of compound **2** can be requested under the deposition number CSD 410502 from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen.

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