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Synthesis and Crystal Structure of Tricarbonyl(η^6-flavanone)chromium(0)

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Summary. The reaction of flavanone with $Cr(CO)_6$ gives two diastereomeric complexes **1** (*cis*) and **2** (*trans*) with the general formula $[Cr(CO)_3(C_{15}H_{12}O_2)]$. Due to the existence of an asymmetric carbon atom in the γ-pyrone ring, the two isomers are chiral. Both complexes were characterized by elemental microanalysis as well as by IR, NMR, UV, and mass spectroscopy. The X-ray analysis of **1** has shown that the $Cr(CO)_3$ tripod is complexed to the benzene ring in an eclipsed conformation. The phenyl group adopts a *cis* configuration with respect to the tricarbonylchromium moiety, and the γ-pyrone ring is oriented in a 1,2-diplanar conformation.

Keywords. Flavanones; Tricarbonylchromium complexes; X-ray analysis.

Darstellung und Kristallstruktur von Tricarbonyl(η^6-flavanon)chrom(0)

Zusammenfassung. Die Umsetzung von Flavanon mit $Cr(CO)_6$ ergibt zwei diastereomere Komplexe **1** und **2** der allgemeinen Formel $[Cr(CO)_3(C_{15}H_{12}O_2)]$. Wegen des asymmetrischen Kohlenstoffatoms im γ-Pyronring sind die beiden Isomeren chiral. Beide Komplexe wurden elementaranalytisch sowie IR-, NMR-, UV- und massenspektroskopisch charakterisiert. Die Röntgenstrukturanalyse von **1** zeigt, daß der $Cr(CO)_3$-Dreifuß bezüglich des Benzolrings ekliptisch orientiert ist. Die Phenylgruppe ist relativ zur Tricarbonylchromkomponente *cis*-konfiguriert, während der γ-Pyronring eine 1,2-diplanare Konformation einnimmt.

Introduction

Tricarbonyl(arene)chromium complexes have received much attention in organic synthesis as intermediates in regioselective reactions [1–3] and chiral auxiliaries [4, 5]. Owing to the altered reactivity of the arenes in chiral chromium tricarbonylarene complexes, the steric shielding exerted by the bulky metal fragment, and the ease of removal of the chromium moiety, there has been a rapid increase in the use of these complexes in asymmetric synthesis [3, 6, 7]. As part of

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our work on the synthesis of new bioactive flavanoids [8, 9] we are investigating the use of chromium complexes in flavanoid chemistry. In the present paper we describe the synthesis and structural investigation of a new chiral chromium-arene complex containing a flavanone molecule as arene ligand.

Results and Discussion

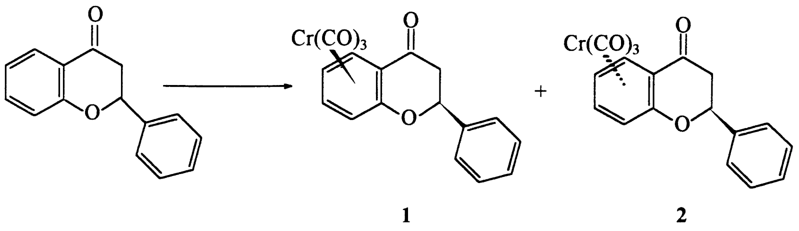
Preparation and spectroscopic characterization

The reaction of flavanone with $Cr(CO)_6$ results in the formation of two stereoisomeric complexes in a 1:1 ratio which can easily be separated by silica gel column chromatography.

The new chromium complexes were mainly identified by the typical upfield shifts of the aromatic protons of the complexed benzene ring (ring A) in the ^1H NMR spectra (1–2 ppm relative to the free aromatic ligand) [10]. In addition, the FT-IR spectra of **1** and **2** show two strong CO stretching bands in the region of 1980–1870 cm^{-1} which are characteristic of the $Cr(CO)_3$ group. The C=O absorption of the pyrone ring appears at ca. 1690 cm^{-1}. Both complexes gave acceptable C and H analyses, and their molecular weight (361) was in agreement with the molecular ion signal.

Molecular structure of **1**

Only compound **1** could be obtained in crystalline form; its molecular structure shows that the $Cr(CO)_3$ moiety is complexed to the benzene ring in an eclipsed conformation (Fig. 1). The benzene ring is essentially planar; the maximum deviation from the plane is 0.031(3) Å for C(7). The phenyl ring, which is also planar, adopts a *cis* configuration with respect to the tricarbonyl tripod. The angle between the phenyl ring and the plane of the benzene ring is 50.8(2)°. The C–C bond lengths, ranging from 1.394(4) to 1.428(3) Å for the benzene ring and from 1.369(6) to 1.384(4) Å for the phenyl ring, are fairly regular. The γ-pyrone ring exists in a 1,2-diplanar conformation where C(10), C(11), and O(4) are almost coplanar with the aromatic nucleus, whereas C(12) shows the largest deviation (0.482(3) Å) from the mean plane of the residual atoms. The bond lengths O(4)–C(4), O(4)–C(12), and O(5)–C(10) agree well with those found in other flavanone compounds [11].



1 **2**

Scheme 1

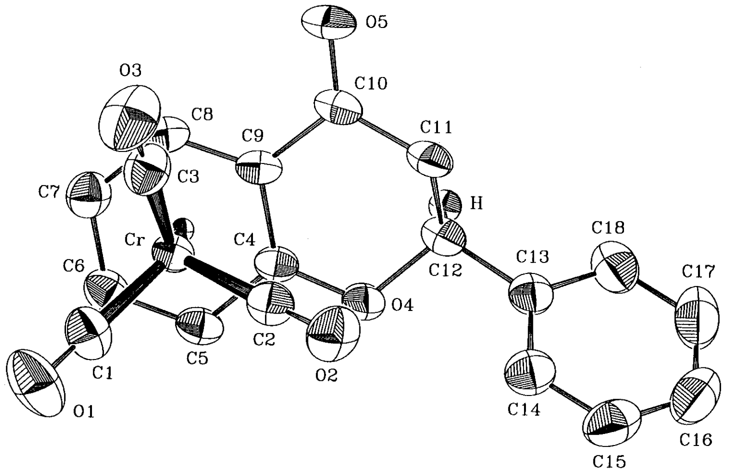


Fig. 1. Molecular structure and atom numbering scheme of $[Cr(CO)_3(C_{15}H_{12}O_2)]$ (**1**)

Concerning the geometry of the arene-$Cr(CO)_3$ system, the six individual Cr–C(arene) distances are different, the values ranging from 2.181(3) to 2.267(3) Å. The highest value observed for C(4) (bonded to the electronegative oxygen) suggests that this atom cannot π-interact with the chromium atom as effectively as the other five ring carbon atoms. The metal-arene(centroid) distance (1.719 Å) falls within the range of 1.67–1.74 Å reported for η^6-arene)$Cr(CO)_3$ complexes [12]. The remaining molecular parameters for the $Cr(CO)_3$ tripod are in accordance with previous results found in many organotricarbonylchromium complexes [13, 14].

Experimental

General methods and reactants

The reaction was carried out under an inert gas atmosphere and in the absence of light. Solvents were thoroughly dried before use. $Cr(CO)_6$ (Merck) and flavanone (Aldrich) were obtained commercially and used as received. Elemental analyses (C, H) were performed with a Perkin-Elmer 240C microanalyzer; they were in satisfactory agreement with the calculated values. Solid-state IR spectra were recorded in the 4000–500 cm^{-1} region using a Bruker IFS 113 v FT spectrometer. ^1H and ^{13}C NMR spectra were taken on a Varian Unity 400 spectrometer. The DCI-MS spectra were recorded on a Ridermag R10–10B quadrupole spectrometer with ammonia as the reagent gas. Electronic spectra were recorded on a Beckman DB-GT grating spectrophotometer.

Synthesis of tricarbonyl(η^6-flavanone)chromium(0)

A mixture of 1.0 g racemic flavanone (4.46 mmol) and 0.5 g $Cr(CO)_6$ (2.27 mmol) in 40 ml heptane and 0.1 ml AcOH was refluxed under nitrogen for 23 h in a light-covered *Strohmeier* apparatus [15]. The cooled solution was filtered, and the solvent was evaporated *in vacuo*. The crude product was separated by silica gel chromatography with heptane/ether (1:1). Two complexes were isolated as orange solids: complex **1** with $R_f = 0.20$ and complex **2** with $R_f = 0.32$. Total yield: 25%; m.p.(**1**): 152°C; m.p.(**2**): 143°C (both with decomposition).

Complex **1** (*racemic cis-complex*): ^{1}H NMR (400 MHz, δ, acetone-d$_6$): 2.79 (dd, 1H, CH$_2$), 3.22 (dd, 1H, CH$_2$), 5.33 (ddd, 1H$_{\text{arom A}}$), 5.50 (dd, 1H$_{\text{arom A}}$), 5.73 (dd, CH$_\phi$), 6.33 (ddd, 1H$_{\text{arom A}}$), 6.44 (dd, 1H$_{\text{arom A}}$), 7.45 (m, 3H$_{\text{arom B}}$), 7.57 (m, 2H$_{\text{arom B}}$) ppm; ^{13}C NMR (100 MHz, δ, acetone-d$_6$): 232.6, 188.8, 147.7, 139.1, 129.9, 129.7, 127.4, 98.9, 92.7, 87.1, 84.8, 81.6, 78.9, 43.5 ppm; IR (KBr): $\nu(\mathrm{Cr(CO)_3}) = 1978$ and 1873 cm^{-1}, $\nu(\mathrm{C{=}O}) = 1691$ cm^{-1}; UV (EtOH): $\lambda_{\max} = 267$ (A-ring), 319 (B-ring), 418 nm; MS (DCI): $m/z = 361$ (M$^+$).

Complex **2** (*racemic trans-complex*): ^{1}H NMR (400 MHz, δ, acetone-d$_6$): 2.98 (dd, 1H, CH$_2$), 3.22 (dd, 1H, CH$_2$), 5.44 (ddd, 1H$_{\text{arom A}}$), 5.62 (dd, 1H$_{\text{arom A}}$), 5.63 (dd, CH$_\phi$), 6.13 (ddd, 1H$_{\text{arom A}}$), 6.26 (dd, 1H$_{\text{arom A}}$), 7.44 (m, 3H$_{\text{arom B}}$), 7.56 (m, 2H$_{\text{arom B}}$) ppm; ^{13}C NMR (100 MHz, δ, acetone-d$_6$): 232.5, 191.2, 144.1, 138.9, 129.9, 129.6, 127.6, 98.2, 91.8, 87.9, 83.4, 83.3, 80.9, 43.3 ppm; IR (KBr): $\nu(\mathrm{Cr(CO)_3}) = 1964$ and 1877 cm^{-1}, $\nu(\mathrm{C{=}O}) = 1693$ cm^{-1}; UV (EtOH): $\lambda_{\max} = 262$ (A-ring), 319 (B-ring), 426 nm; MS (DCI): $m/z = 361$ (M$^+$).

Table 1. Summary of x-ray data

Empirical formula	$C_{18}H_{12}CrO_5$
Formula weight	360.28
Temperature (K)	298
Wavelength	CuK_α, 1.54180 Å
Space group	$P2_1/a$
a (Å)	14.245(2)
b (Å)	7.9737(9)
c (Å)	14.369(2)
β (°)	103.04(1)
V (Å^3)	1590.0(3)
Z	4
$D_{\text{calc}}/D_{\text{measd}}$ (g · cm^{-3})	1.505/1.48
Abs. coeff (μ, mm^{-1})	6.150
Max. abs. correction mode	1.16
Scan mode/speed (°/min)	$\theta-2\theta/3.0$
Scan range (°)	$2.4+\alpha_1\alpha_2$ separation
θ range (°)	3.16 to 65.05
Reflections collected	2805
Independent reflections	2690 (R(int) = 0.0489)
Range of h, k, l	$-16\rightarrow16$, $-9\rightarrow0$, $0\rightarrow16$
$F(000)$	736
$(\Delta\sigma)_{\max}$	0.084
W^a	$a = 0.0509$, $b = 0.8850$
$(\Delta\rho)_{\max}/(\Delta\rho)_{\min}$ (e/Å^3)	0.366 and −0.440
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2689/0/265
Goodness-of-fit on F^2	1.029
R indices (2067 refs $I > 2\sigma(I)$)^b	$R_1 = 0.0364$, $wR_2 = 0.0991$
R indices (all data)	$R_1 = 0.0513$, $wR_2 = 0.1122$

[a] $W = 1/(\sigma^2(F_o^2) + (aP)^2 + bP))$ and $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] R_1 based on F, wR_2 based on F^2

Table 2. Positional ($\times 10^4$) and equivalent thermal parameters ($\times 10^3$) of the non-H atoms; *esds* in parentheses; $U_{eq} = 1/3(U_{11}+U_{22}+U_{33})$

Atom	x	y	z	U_{eq}
Cr	1327(1)	2554(1)	3344(1)	38(1)
C(1)	2332(2)	1073(4)	3683(2)	58(1)
C(2)	1471(2)	2528(3)	2098(2)	46(1)
C(3)	2239(2)	4225(4)	3627(2)	56(1)
C(4)	−270(2)	2347(3)	2675(2)	36(1)
C(5)	40(2)	879(3)	3196(2)	43(1)
C(6)	519(2)	990(4)	4154(2)	47(1)
C(7)	683(2)	2553(4)	4620(2)	49(1)
C(8)	422(2)	4008(4)	4086(2)	46(1)
C(9)	−46(2)	3948(3)	3114(2)	38(1)
C(10)	−231(2)	5476(3)	2518(2)	43(1)
C(11)	−541(2)	5154(3)	1461(2)	44(1)
C(12)	−1199(2)	3625(3)	1255(2)	41(1)
C(13)	−1471(2)	3189(3)	214(2)	43(1)
C(14)	−900(3)	2151(4)	−201(2)	55(1)
C(15)	−1158(3)	1799(5)	−1163(3)	69(1)
C(16)	−1979(4)	2473(5)	−1719(3)	80(1)
C(17)	−2545(3)	3513(6)	−1317(3)	79(1)
C(18)	−2301(2)	3860(5)	−354(3)	60(1)
O(1)	2977(2)	163(4)	3890(2)	95(1)
O(2)	1530(2)	2536(3)	1316(2)	67(1)
O(3)	2824(2)	5244(4)	3811(2)	90(1)
O(4)	−728(1)	2154(2)	1757(1)	44(1)
O(5)	−125(2)	6868(2)	2868(2)	63(1)

X-ray crystallographic study

Suitable crystals of complex **1** were grown from a heptane solution. A crystal of **1** with approximate dimensions $0.10\times0.30\times0.40$ mm was mounted in air. Diffraction measurements were made on a $P2_1$ Nicolet diffractometer upgraded by Crystal Logic using Ni-filtered Cu radiation. Unit cell dimensions were determined and refined using the angular settings of 25 automatically centered reflections in the range of $24° < 2\theta < 54°$. Crystallographic data are given in Table 1. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. *Lorentz*, polarization, and ψ-scan absorption correction were applied using Crystal Logic software.

The structure was solved by direct methods using SHELXS-86 [16] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93 [17]. All hydrogen atoms were located by difference maps, and their positions were refined isotropically. All non-hydrogen atoms were refined anisotropically.

The positional parameters and the equivalent isotropic temperature factors for the non-hydrogen atoms are collected in Table 2. Hydrogen atomic coordinates and a list of structure factors can be obtained from the authors. A selection of bond distances and bond angles is given in Table 3.

Table 3. Selected bond lengths (Å) and angles (°) for $[Cr(CO)_3(C_{15}H_{12}O_2)]$ (**1**)

Cr–C(1)	1.835(3)	C(8)–C(9)	1.406(4)
Cr–C(2)	1.847(3)	C(9)–C(4)	1.428(3)
Cr–C(3)	1.841(3)	C(4)–O(4)	1.342(3)
Cr–C(4)	2.267(3)	O(4)–C(12)	1.458(3)
Cr–C(5)	2.239(3)	C(12)–C(11)	1.526(4)
Cr–C(6)	2.200(3)	C(11)–C(10)	1.505(4)
Cr–C(7)	2.228(3)	C(10–C(9)	1.478(4)
Cr–C(8)	2.181(3)	C(10)–O(5)	1.214(3)
Cr–C(9)	2.209(3)	C(12)–C(13)	1.499(4)
C(1)–O(1)	1.156(4)	C(13)–C(14)	1.386(5)
C(2)–O(2)	1.146(4)	C(14)–C(15)	1.376(5)
C(3)–O(3)	1.152(4)	C(15)–C(16)	1.369(6)
C(4)–C(5)	1.406(4)	C(16)–C(17)	1.371(7)
C(5)–C(6)	1.394(4)	C(17)–C(18)	1.378(5)
C(6)–C(7)	1.409(4)	C(18)–C(13)	1.384(4)
C(7)–C(8)	1.394(4)		
Cr–C(1)–O(1)	178.6(3)	O(4)–C(4)–C(9)	123.2(2)
Cr–C(2)–O(2)	177.7(3)	C(11)–C(12)–O(4)	110.6(2)
Cr–C(3)–O(3)	178.6(3)	C(12)–O(4)–C(4)	117.5(2)
C(1)–Cr–C(2)	89.96(13)		
C(2)–Cr–C(3)	89.72(13)		
C(3)–Cr–C(1)	86.4(2)		

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