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Key indicators

Single-crystal X-ray study
 $T = 296\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.012\text{ \AA}$
 R factor = 0.047
 wR factor = 0.161
Data-to-parameter ratio = 12.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**exo-(±)-Tricarbonyl(η^6 -1-hydroxy-1,2-dihydroace-
naphthylene)chromium(0)**

The crystal structure of the title compound, $[\text{Cr}(\text{C}_{12}\text{H}_{10}\text{O})(\text{CO})_3]$, contains two conformers in an asymmetric unit. The projection of the $\text{Cr}(\text{CO})_3$ unit on the arene ring is staggered in one conformer, whereas it is about midway between staggered and eclipsed in the other. In both conformers, the $\text{Cr}(\text{CO})_3$ unit is slightly displaced relative to the center of the arene ring. The hydroxyl groups are involved in hydrogen bonding between the conformers lying about glide planes, with $\text{O}\cdots\text{O}$ distances of 2.835 (8) and 2.771 (8) Å, resulting in chains along the a axis.

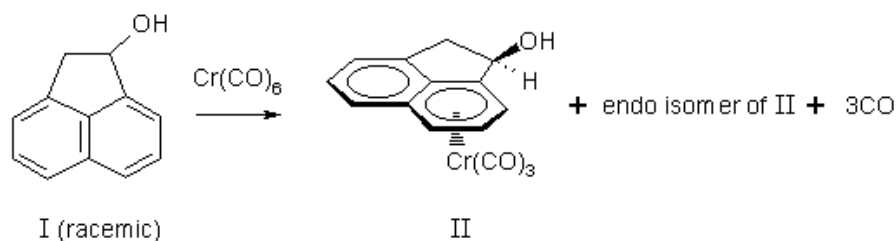
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Comment

Treatment of 1-hydroxy-1,2-dihydroacenaphthylene, (I), with $\text{Cr}(\text{CO})_6$ yields two $\text{Cr}(\text{CO})_3$ complexes, in addition to a number of other products (Simion, 1996). Based on ^1H NMR results, and on previous results from 1-indanol complexation (Jaouen & Dabard, 1971; Top *et al.*, 1979), it was thought that the two isomers involved *exo* and *endo* η^6 -coordination of $\text{Cr}(\text{CO})_3$ on the acenaphthylene ring nearest the OH group, and that initial complexation would occur with OH mediation to give the *endo* product. By means of OH ionization, and recombination *via* the *exo* face, one would obtain some of the *exo* isomer, (II). The structure of (II) was confirmed by a single-crystal X-ray diffraction study.



The asymmetric unit of (II) is composed of two independent conformers, *A* and *B* (Figs. 1 and 2). The two conformations are different, as is evident from a comparison of Figs. 1 and 2. This difference is mainly in the projection of the $\text{Cr}(\text{CO})_3$ fragment relative to the C atoms of the arene ring being complexed. In conformer *A*, the $\text{Cr}(\text{CO})_3$ unit is staggered, whereas in *B*, it is about midway between staggered and eclipsed. Several X-ray structures of naphthalene- $\text{Cr}(\text{CO})_3$ complexes have been included in the Cambridge Structural Database (Allen & Kennard, 1993). In naphthalene- $\text{Cr}(\text{CO})_3$ (Kunz & Nowacki, 1967), the $\text{Cr}(\text{CO})_3$ conformation resembles that of our *B* conformer.

The $\text{Cr}-\text{C}_{\text{CO}}$ distances lie in the range 1.822 (9)–1.847 (10) Å [mean 1.833 (9) Å], while the $\text{C}\equiv\text{O}$ distances lie

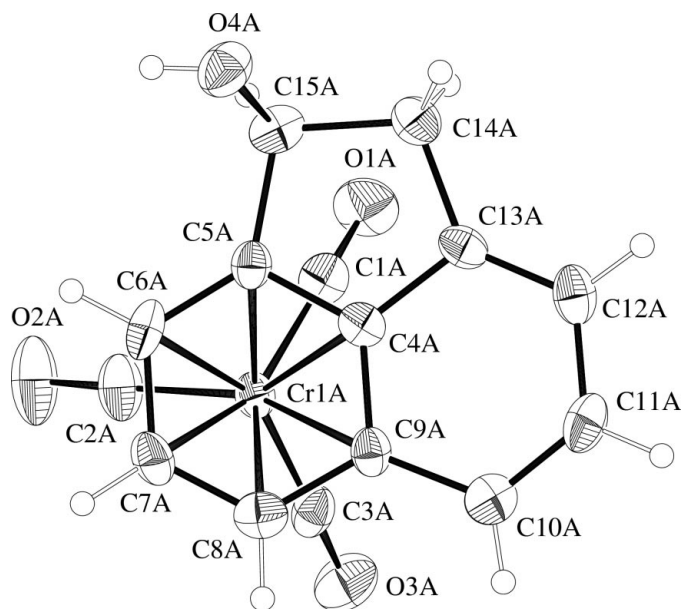


Figure 1
ORTEP (Johnson, 1976) drawing of conformer *A* of (II). Displacement ellipsoids have been plotted at the 30% probability level.

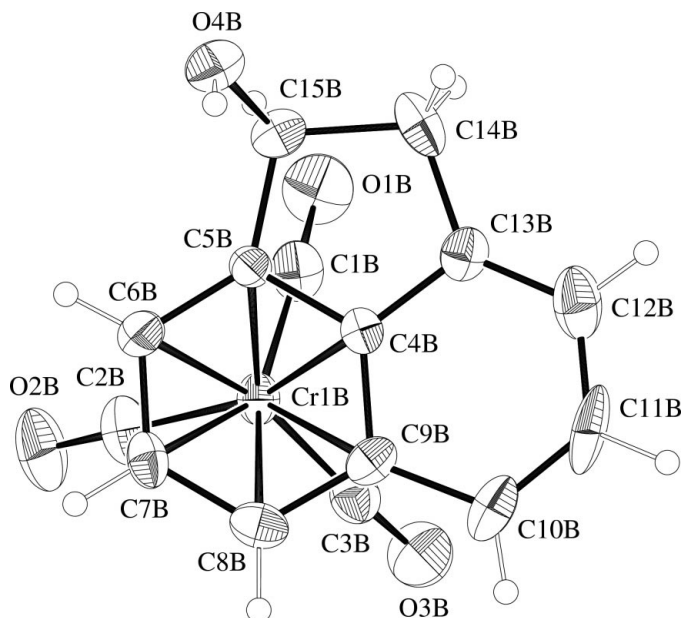


Figure 2
ORTEP (Johnson, 1976) drawing of conformer *B* of (II). Displacement ellipsoids have been plotted at the 30% probability level.

in the narrow range 1.141 (9)–1.153 (9) Å [mean 1.149 (4) Å]. These distances are in excellent agreement with the values reported for the corresponding distances in organometallic complexes (Orpen *et al.*, 1994). The Cr–C_{aromatic} distances span a wide range [2.189 (7)–2.318 (8) Å], with Cr–centroid distances of 1.744 (10) and 1.747 (10) Å for conformers *A* and *B*, respectively. In both naphthalene–Cr(CO)₃ and cyclopropanaphthalene–Cr(CO)₃ complexes (Müller *et al.*, 1989), one sees a slightly displaced Cr(CO)₃ relative to the center of

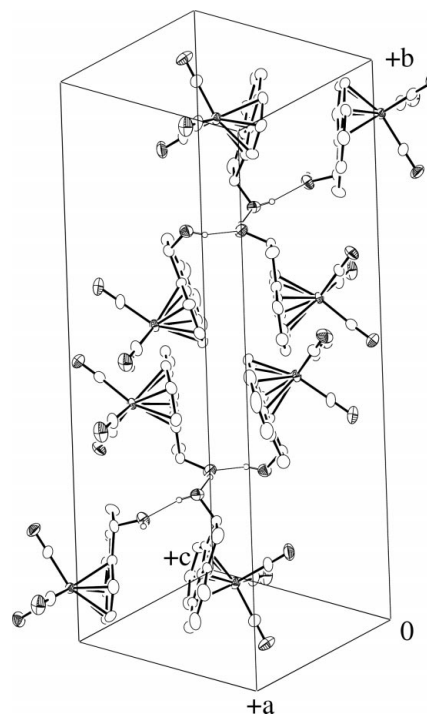


Figure 3
The unit-cell packing in (II) showing the hydrogen bonds.

the arene ring. In the former, the Cr–C_{bridgehead} carbon bonds are 2.306 and 2.337 Å *versus* an average of 2.200 Å for the four outside distances. Similar distances are observed in the cyclopropanaphthalene complex. One sees the same features in our *A* and *B* conformers. Thus, in *A*, the two central bonds average to 2.310 Å, *versus* 2.197 Å for the outside bonds (2.290 Å *versus* 2.221 Å for *B*). The remaining molecular dimensions in both the conformers are normal with mean bond lengths Csp³–Csp³ = 1.553 (1), Csp³–Csp² = 1.516 (10), C–C_{aromatic} = 1.40 (3) and Csp³–O = 1.423 (6) Å.

In both conformers, the acenaphthylene rings are essentially planar with the maximum deviation of any atom from the mean-planes being 0.061 (7) and 0.059 (7) Å, for atoms C6*A* and C6*B* in conformers *A* and *B*, respectively. The hydroxyl O atoms lie 1.187 (7) and 1.022 (8) Å from the acenaphthylene rings and the orientation of hydroxyl H atoms is different in the two molecules. The hydroxyl groups are involved in hydrogen bonding between the conformers lying about glide planes [O4*A*–H4*A*···O4*B* and O4*B*–H4*B*···O4*A*, with O···O distances of 2.835 (8) and 2.771 (8) Å, respectively], thus resulting in chains of structures along the *a* axis (Fig. 3); details are given in Table 2. The effect of hydrogen bonding is manifested in differences in bond angles around C15*A* and C15*B*, *e.g.* the O4–C15–C14 angles in conformers *A* and *B* are 109.4 (6) and 114.0 (7)°, respectively.

Experimental

A mixture of (±)-1-hydroxy-1,2-dihydroacenaphthylene, (I) (1.700 g, 10.0 mmol) and Cr(CO)₆ (1.10 g, 5.0 mmol) in 50 ml of 1:1 ⁿBu₂O/

heptane was thoroughly purged with argon and then refluxed for 72 h. After cooling to 293 K, the red solution was filtered (Celite) and the solvent removed *in vacuo*. Thin-layer chromatographic analysis (3:1 hexane/ethyl acetate) showed the presence of seven components. Flash chromatography (SiO₂ under N₂) provided 0.35 g (23% isolated yield) of a mixture of two Cr(CO)₃ complexes of the alcohol, and repeating the separation on this fraction produced a pure sample, 0.10 g, 6.5% yield, of the more polar (minor) isomer, (II) [m.p. 393 K (decomposition)]. The other (less polar and less stable) Cr(CO)₃ isomer was assigned the *endo* configuration.

Crystal data

[Cr(C₁₂H₁₀O)(CO)₃]
M_r = 306.23
 Monoclinic, *P*2₁/*a*
a = 10.0838 (16) Å
b = 25.963 (4) Å
c = 10.1696 (17) Å
 β = 95.641 (14)°
V = 2649.6 (7) Å³
Z = 8
D_x = 1.535 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 10.0–15.0°
 μ = 0.87 mm⁻¹
T = 296 (2) K
 Prism, deep red
 0.20 × 0.20 × 0.10 mm

Data collection

Rigaku AFC-6S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical
 via ψ -scan (3 reflections) (North *et al.*, 1968)
T_{min} = 0.84, *T_{max}* = 0.92
 4946 measured reflections
 4668 independent reflections
 1483 reflections with *I* > 2σ(*I*)
R_{int} = 0.087
 θ_{\max} = 25.0°
h = 0 → 12
k = 0 → 30
l = -12 → 12
 3 standard reflections
 every 200 reflections
 intensity decay: <0.2%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.047
wR (*F*²) = 0.161
S = 0.95
 4668 reflections
 363 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.049P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.40 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cr1A—C2A	1.824 (9)	Cr1A—C4A	2.285 (8)
Cr1A—C3A	1.833 (9)	Cr1A—C9A	2.334 (8)
Cr1A—C1A	1.834 (10)	O1A—C1A	1.141 (9)
Cr1A—C7A	2.189 (7)	O2A—C2A	1.152 (9)
Cr1A—C6A	2.192 (8)	O3A—C3A	1.149 (9)
Cr1A—C5A	2.198 (8)	O4A—C15A	1.429 (8)
Cr1A—C8A	2.209 (8)		
C2A—Cr1A—C3A	88.2 (4)	C3A—Cr1A—C1A	89.6 (4)
C2A—Cr1A—C1A	88.8 (4)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4A—H4A...O4B ⁱ	0.82	2.04	2.835 (8)	163
O4B—H4B...O4A	0.82	2.07	2.771 (8)	144

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z$.

The space group, *P*2₁/*a*, was uniquely determined from the systematic absences. The H atoms were located from difference maps and were included at geometrically idealized positions with O—H = 0.82 and C—H = 0.93–0.98 Å, in a riding mode with isotropic displacement parameters 1.2 (C atoms) and 1.5 (O atoms) times the thermal displacement parameters of the atoms to which they were attached. Two void areas of 26 Å³ each were indicated by the program *PLATON* (Spek, 1990) with no electron density in the difference map in those areas. The routine *SQUEEZE* was attempted but it could not eliminate the voids.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN*; software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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