

C31	-0.0708 (4)	-0.4209 (4)	-0.2522 (4)	0.0520 (12)
C32	-0.1756 (6)	-0.4133 (5)	-0.2574 (6)	0.085 (2)
C33	-0.2432 (7)	-0.4835 (6)	-0.2875 (8)	0.105 (3)
C34	-0.2055 (7)	-0.5601 (6)	-0.3153 (7)	0.093 (3)
C35	-0.1002 (7)	-0.5666 (5)	-0.3109 (6)	0.090 (2)
C36	-0.0339 (5)	-0.4990 (5)	-0.2788 (5)	0.073 (2)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Sn1—C13	2.118 (6)	C14—C15	1.394 (13)
Sn1—C1	2.120 (6)	C15—C16	1.31 (2)
Sn1—C7	2.134 (6)	C16—C17	1.35 (2)
Sn1—O1	2.336 (4)	C17—C18	1.424 (15)
Sn1—Br1	2.6186 (11)	C19—C24	1.393 (12)
P1—O1	1.493 (4)	C19—C20	1.416 (10)
P1—C31	1.789 (6)	C20—C21	1.349 (11)
P1—C19	1.794 (6)	C21—C22	1.39 (2)
P1—C25	1.807 (6)	C22—C23	1.36 (2)
C1—C6	1.362 (10)	C23—C24	1.402 (13)
C1—C2	1.384 (9)	C25—C26	1.379 (9)
C2—C3	1.351 (11)	C25—C30	1.399 (10)
C3—C4	1.293 (14)	C26—C27	1.380 (11)
C4—C5	1.34 (2)	C27—C28	1.368 (14)
C5—C6	1.430 (13)	C28—C29	1.366 (14)
C7—C12	1.375 (10)	C29—C30	1.348 (11)
C7—C8	1.379 (10)	C31—C32	1.367 (9)
C8—C9	1.404 (12)	C31—C36	1.392 (9)
C9—C10	1.38 (2)	C32—C33	1.387 (11)
C10—C11	1.34 (2)	C33—C34	1.386 (13)
C11—C12	1.393 (11)	C34—C35	1.375 (12)
C13—C18	1.359 (10)	C35—C36	1.355 (10)
C13—C14	1.378 (10)		
C13—Sn1—C1	118.5 (2)	C18—C13—C14	119.3 (7)
C13—Sn1—C7	120.5 (2)	C18—C13—Sn1	120.8 (5)
C1—Sn1—C7	118.9 (2)	C14—C13—Sn1	119.8 (5)
C13—Sn1—O1	85.0 (2)	C13—C14—C15	119.8 (9)
C1—Sn1—O1	85.5 (2)	C16—C15—C14	120.2 (10)
C7—Sn1—O1	85.0 (2)	C15—C16—C17	122.7 (9)
C13—Sn1—Br1	94.1 (2)	C16—C17—C18	118.4 (10)
C1—Sn1—Br1	95.7 (2)	C13—C18—C17	119.6 (10)
C7—Sn1—Br1	94.7 (2)	C24—C19—C20	120.3 (7)
O1—Sn1—Br1	178.73 (11)	C24—C19—P1	121.1 (5)
O1—P1—C31	111.3 (3)	C20—C19—P1	118.6 (6)
O1—P1—C19	109.8 (3)	C21—C20—C19	118.9 (9)
C31—P1—C19	107.6 (3)	C20—C21—C22	120.8 (9)
O1—P1—C25	113.0 (3)	C23—C22—C21	121.6 (8)
C31—P1—C25	108.1 (3)	C22—C23—C24	119.0 (10)
C19—P1—C25	106.8 (3)	C19—C24—C23	119.4 (9)
P1—O1—Sn1	166.5 (3)	C26—C25—C30	118.5 (6)
C6—C1—C2	116.2 (6)	C26—C25—P1	122.0 (5)
C6—C1—Sn1	122.4 (5)	C30—C25—P1	119.5 (5)
C2—C1—Sn1	121.3 (5)	C27—C26—C25	119.9 (8)
C3—C2—C1	121.4 (8)	C28—C27—C26	119.7 (9)
C4—C3—C2	123.4 (9)	C29—C28—C27	121.3 (8)
C3—C4—C5	118.8 (9)	C30—C29—C28	119.2 (9)
C4—C5—C6	120.3 (9)	C29—C30—C25	121.4 (8)
C1—C6—C5	119.9 (8)	C32—C31—C36	119.2 (6)
C12—C7—C8	118.6 (6)	C32—C31—P1	116.5 (5)
C12—C7—Sn1	121.9 (5)	C36—C31—P1	124.3 (4)
C8—C7—Sn1	119.4 (5)	C31—C32—C33	119.9 (7)
C7—C8—C9	119.4 (9)	C34—C33—C32	120.2 (7)
C10—C9—C8	120.5 (10)	C35—C34—C33	119.4 (7)
C11—C10—C9	120.2 (8)	C36—C35—C34	120.2 (7)
C10—C11—C12	119.7 (9)	C35—C36—C31	121.1 (6)
C7—C12—C11	121.5 (8)		

H atoms were allowed to ride on their parent C atoms with  $U(\text{H}) = 1.5U_{\text{eq}}$  of the parent atom.

Data collection: *CAD-4 VAX/PC* (Enraf-Nonius, 1988). Cell refinement: *CAD-4 VAX/PC*. Data reduction: *Xtal3.0* (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## *exo*- $\pi$ -(Benzonorbornadiene)tricarbonylchromium

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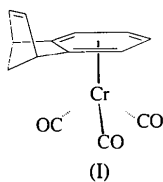
## Abstract

The title compound, tricarbonyl[(4a,5,6,7,8,8a- $\eta$ )-1,4-dihydro-1,4-methanonaphthalene]chromium,  $[\text{Cr}(\text{C}_{11}\text{H}_{10})\text{(CO)}_3]$ , is a complex of chromium(0) in which the arene ring of the organic ligand is hexahapto-coordinated to the Cr atom. Three terminal carbonyl ligands form the triangular base of the molecule. The mode of coordination of the  $\text{Cr}(\text{CO})_3$  moiety to the ligand is such

that the free double bond of the benzonorbornadiene is oriented away from the Cr atom. The chromium–carbonyl tripod is rotated slightly from a perfectly staggered arrangement with respect to the arene ring and, hence, the molecule does not possess a plane of symmetry.

### Comment

A large number of arenetricarbonylchromium compounds have been reported (Bruce, 1982). These compounds have been greatly studied, in part, because the Cr(CO)<sub>3</sub> unit alters the reactivity of substituted arenes in ways that depend on the stereochemistry of the complex (Bly & Maier, 1978). The prototype complex benzenetricarbonylchromium has a highly regular structure in which the Cr–CO bonds are staggered between the Cr–C bonds of the benzene ligand (Bailey & Dahl, 1965; Rees & Coppens, 1972). Complexes of substituted arenes are known in both staggered and eclipsed configurations, with the specific arrangement appearing to depend on the nature of the arene (Silverthorn, 1975). The structure of the most closely related compound to that reported here, *exo*- $\pi$ -(2-acetoxynorbornadiene)tricarbonylchromium, has a staggered arrangement of the carbonyl ligands and an approximate plane of symmetry bisecting the Cr coordination sphere (Taylor, Griffith & Amma, 1976). The authors attribute the staggering of the carbonyl ligands to steric repulsions between the ligands and the bridgehead methylene group. The title benzonorbornadiene complex, (I) (Fig. 1), displays a similar structure in which the Cr atom is slightly displaced from the center of the arene ring, away from the norbornyl group. This is indicated by the shorter distances from the Cr atom to atoms C(9) and C(10) in comparison with those to C(2) and C(3) (Table 2).



The three carbonyl ligands form an almost regular triangular base for the complex. The two carbonyls adjacent to the norbornyl moiety are spread slightly apart so that the C(13)—Cr—C(14) angle is a few degrees larger than the angle that either C atom makes with C(12). The carbonyl tripod is not perfectly staggered between the benzene C atoms, but is rotated towards atoms C(9), C(2) and C(11). This displacement is evident in the bond angles between the carbonyl C atoms and those of the benzene ring, for example, C(13)—Cr—C(11) of 90.0 (3) and C(13)—Cr—C(3) of 93.9 (4). As a result, the molecule lacks a plane of symmetry that would otherwise bisect the benzonorbornadiene ligand,

the Cr atom and one of the carbonyl ligands. A study of the *exo* and *endo* isomers of tricarbonyl(2-methyl-1-indanol)chromium found the tripod ideally staggered in the *endo* isomer and twisted in a very similar manner to the present compound in the *exo* isomer (Gentric, Le Borgne & Grandjean, 1978).

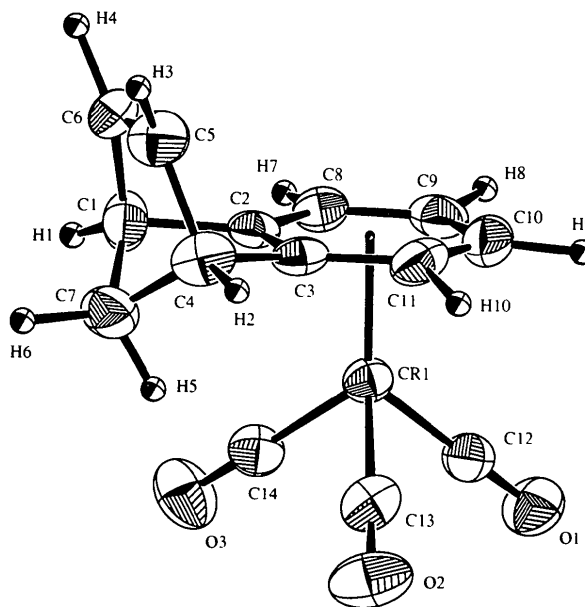


Fig. 1. ORTEP diagram (Johnson, 1976) of the title compound showing the atomic labeling scheme. The displacement ellipsoids of the non-H atoms are shown at the 35% probability level.

The title compound was synthesized as part of a study of (alkenylarene)chromium compounds. Our original goal was to prepare the benzonorbornadiene complex with the free double bond directed towards the Cr atom in order to effect the coordination of the alkene *via* photolytic CO dissociation. The stereochemistry of the coordination of substituted indanes to chromium has been found to be highly dependent on reaction conditions, including solvent and temperature, with the ratio of *exo* and *endo* isomers varying widely for a given ligand (Gracey, Jackson, McMullen & Thompson, 1969). Our studies would seem to indicate the same is true of norbornylarenes.

### Experimental

The benzonorbornadiene ligand was synthesized by the reaction of anthranilic acid, cyclopentadiene and *tert*-butyl nitrite in acetone and methylene chloride. The chromium complex was prepared by the reaction of hexacarbonylchromium (previously refluxed in acetonitrile) and the benzonorbornadiene ligand in refluxing glyme (1,2-dimethoxyethane). The product was isolated on a silica column with hexane and was recrystallized from a mixture of ether and pentane.

*Crystal data*[Cr(C<sub>11</sub>H<sub>10</sub>)(CO)<sub>3</sub>]M<sub>r</sub> = 278.23

Orthorhombic

Pna2<sub>1</sub>

a = 15.225 (4) Å

b = 8.652 (3) Å

c = 9.306 (2) Å

V = 1225 (1) Å<sup>3</sup>

Z = 4

D<sub>x</sub> = 1.507 Mg m<sup>-3</sup>

Mo Kα radiation

λ = 0.7107 Å

Cell parameters from 17 reflections

θ = 9.2–13.3°

μ = 0.905 mm<sup>-1</sup>

T = 296.2 K

Plate

0.35 × 0.10 × 0.05 mm

Yellow

*Data collection*

Rigaku AFC-6S diffractometer

ω/2θ scans

Absorption correction:  
none

1281 measured reflections

1281 independent reflections

755 observed reflections

[I &gt; 3σ(I)]

θ<sub>max</sub> = 24.99°

h = 0 → 18

k = 0 → 11

l = 0 → 10

3 standard reflections

monitored every 150

reflections

intensity decay: 0.1%

*Refinement*

Refinement on F

R = 0.0328

wR = 0.0287

S = 1.579

755 reflections

162 parameters

H atom parameters obtained  
from difference map and  
not refinedWeighting scheme based  
on measured e.s.d.'s(Δ/σ)<sub>max</sub> = 0.0011Δρ<sub>max</sub> = 0.19 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.29 e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables  
for X-ray Crystallography*  
(1974, Vol. IV, Table  
2.2B)

Cr(1)—C(10)	2.214 (9)	C(3)—C(4)	1.50 (1)
Cr(1)—C(11)	2.246 (7)	C(3)—C(11)	1.422 (9)
Cr(1)—C(12)	1.814 (7)	C(4)—C(5)	1.50 (1)
Cr(1)—C(13)	1.851 (9)	C(4)—C(7)	1.57 (1)
Cr(1)—C(14)	1.828 (7)	C(5)—C(6)	1.33 (1)
O(1)—C(12)	1.170 (7)	C(8)—C(9)	1.406 (10)
O(2)—C(13)	1.143 (10)	C(9)—C(10)	1.37 (1)
O(3)—C(14)	1.148 (8)	C(10)—C(11)	1.42 (1)
C(1)—C(2)	1.533 (10)		
C(2)—Cr(1)—C(14)	88.6 (3)	C(2)—C(3)—C(11)	118.3 (8)
C(3)—Cr(1)—C(13)	93.9 (4)	C(4)—C(3)—C(11)	134.3 (7)
C(8)—Cr(1)—C(14)	91.1 (3)	C(3)—C(4)—C(5)	105.6 (7)
C(9)—Cr(1)—C(12)	90.1 (4)	C(3)—C(4)—C(7)	99.2 (6)
C(10)—Cr(1)—C(12)	94.4 (3)	C(5)—C(4)—C(7)	98.1 (7)
C(11)—Cr(1)—C(13)	90.0 (3)	C(4)—C(5)—C(6)	108.5 (7)
C(12)—Cr(1)—C(13)	88.2 (4)	C(1)—C(6)—C(5)	106.7 (8)
C(12)—Cr(1)—C(14)	87.4 (4)	C(1)—C(7)—C(4)	93.2 (6)
C(13)—Cr(1)—C(14)	90.0 (4)	C(2)—C(8)—C(9)	117.6 (7)
C(2)—C(1)—C(6)	103.5 (7)	C(8)—C(9)—C(10)	122.4 (8)
C(2)—C(1)—C(7)	100.6 (7)	C(9)—C(10)—C(11)	120.2 (8)
C(6)—C(1)—C(7)	99.2 (7)	C(3)—C(11)—C(10)	119.1 (7)
C(1)—C(2)—C(3)	105.0 (7)	Cr(1)—C(12)—O(1)	179.3 (7)
C(1)—C(2)—C(8)	132.6 (8)	Cr(1)—C(13)—O(2)	178.6 (9)
C(3)—C(2)—C(8)	122.3 (7)	Cr(1)—C(14)—O(3)	179.5 (8)
C(2)—C(3)—C(4)	106.9 (6)		

When the opposite enantiomer was refined under identical conditions, slightly poorer agreement indices were obtained: for observed data,  $R = 0.0337$ ,  $wR = 0.0296$  and  $S = 1.621$ .

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1991). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: FG1100). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cr(1)	0.83227 (6)	0.2955 (1)	0.4033	0.0457 (3)
O(1)	0.7313 (3)	0.5867 (5)	0.4504 (6)	0.076 (2)
O(2)	0.8863 (4)	0.4172 (7)	0.1154 (7)	0.094 (2)
O(3)	0.6707 (4)	0.1644 (7)	0.2711 (7)	0.086 (2)
C(1)	0.8557 (4)	-0.1010 (7)	0.408 (2)	0.063 (2)
C(2)	0.8666 (4)	0.0580 (8)	0.4784 (8)	0.046 (2)
C(3)	0.9427 (4)	0.1220 (7)	0.414 (1)	0.048 (2)
C(4)	0.9782 (5)	0.002 (1)	0.3128 (10)	0.066 (3)
C(5)	1.0058 (5)	-0.1311 (8)	0.406 (2)	0.068 (2)
C(6)	0.9343 (5)	-0.1930 (8)	0.4649 (9)	0.067 (3)
C(7)	0.8891 (6)	-0.067 (1)	0.2567 (9)	0.073 (3)
C(8)	0.8215 (5)	0.1322 (8)	0.5888 (8)	0.050 (2)
C(9)	0.8540 (6)	0.276 (1)	0.6359 (9)	0.063 (3)
C(10)	0.9275 (6)	0.3422 (9)	0.578 (1)	0.073 (3)
C(11)	0.9738 (4)	0.2667 (9)	0.4656 (10)	0.063 (3)
C(12)	0.7712 (4)	0.4730 (8)	0.431 (1)	0.055 (2)
C(13)	0.8664 (6)	0.372 (1)	0.226 (1)	0.062 (3)
C(14)	0.7329 (5)	0.2155 (9)	0.3221 (8)	0.057 (2)

Table 2. Selected geometric parameters (Å, °)

Cr(1)—C(2)	2.233 (7)	C(1)—C(6)	1.533 (10)
Cr(1)—C(3)	2.256 (6)	C(1)—C(7)	1.53 (1)
Cr(1)—C(8)	2.237 (7)	C(2)—C(3)	1.417 (9)
Cr(1)—C(9)	2.196 (8)	C(2)—C(8)	1.392 (9)

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