

## Two atropisomers of tricarbonyl[ $\eta^6$ -7-chloro-3-(3-chloro-2-methylphenyl)-2,4,8-trimethyl-1,2,3,4-tetrahydro-2,4-dibora-1,3-diazanaphthalene]-chromium(0)

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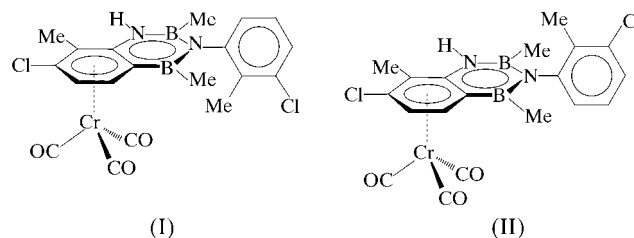
The structures of two atropisomers of the title compound,  $[\text{Cr}(\text{C}_{16}\text{H}_{18}\text{B}_2\text{Cl}_2\text{N}_2)(\text{CO})_3]$ , are reported. For both compounds, the  $\text{Cr}(\text{CO})_3$  moiety is bound to the  $\text{C}_6$  aromatic ring of the molecule; the existence of atropisomers resulting from the non-equivalence of both faces of the  $\text{C}_6$  aromatic ring is a consequence of the 3-chloro-2-methylphenyl ring being nearly perpendicular to the mean plane of the 2,4-dibora-1,3-diazanaphthalene ring. The orientation of the  $\text{Cr}(\text{CO})_3$  tripod relative to the  $\text{C}_6$  aromatic ring is such that it is nearly eclipsed in one isomer ( $2.4^\circ$  rotation from being eclipsed with C–N, C–Cl and C–H) and slightly twisted ( $16.2^\circ$ ) from an eclipsed conformation in the other.

### Comment

A large number of polycyclic arenetricarbonylchromium complexes have been reported to date (Bruce, 1982; Solladié-Cavallo, 1989; Blake *et al.*, 1995). These compounds have been extensively studied in part because the  $\text{Cr}(\text{CO})_3$  unit alters the reactivity of substituted arenes in ways that depend on the stereochemistry of the complexes. Complexes of a natural sesquiterpene series occur with high regio- and stereo-selectivity (El Firdoussi *et al.*, 1997; Abouhamza *et al.*, 1999). The present work follows related research by our group on organometallic compounds of aromatic terpene hydrocarbons (Ait Ali *et al.*, 2000). The title compounds are members of this series of complexes and the crystal structures of both isomers, (I) and (II), were determined to ascertain both the ligand arrangement around the metal centre and the stereochemistry.

Views of the molecules of (I) and (II) are shown in Figs. 1 and 2, respectively. A first comparison of these structures

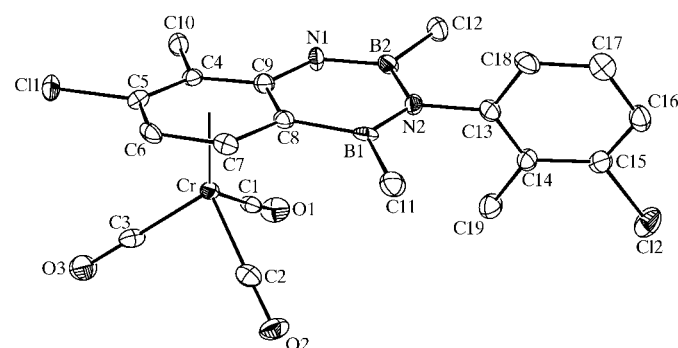
with the parent ligand, *i.e.* 7-chloro-3-(3-chloro-2-methylphenyl)-2,4,8-trimethyl-1,2,3,4-tetrahydro-2,4-dibora-1,3-diazanaphthalene, the structure of which was reported previously (Allaoud *et al.*, 1994), is of interest. Thus, the two expected atropisomers were indeed observed: compound (I), where the  $\text{Cr}(\text{CO})_3$  moiety together with the chlorine and methyl substituents on the phenyl ring are on the same side of the diboradiazanaphthalene mean plane (*cis* compound), and



compound (II), where they are on opposite sides of the same plane (*trans* compound). The angle measured between the planes of the diboradiazanaphthalene and phenyl-ring plane is  $77.22(5)^\circ$  for compound (I) and  $84.33(6)^\circ$  for compound (II); the corresponding value in the uncomplexed parent compound is  $84.2^\circ$ .

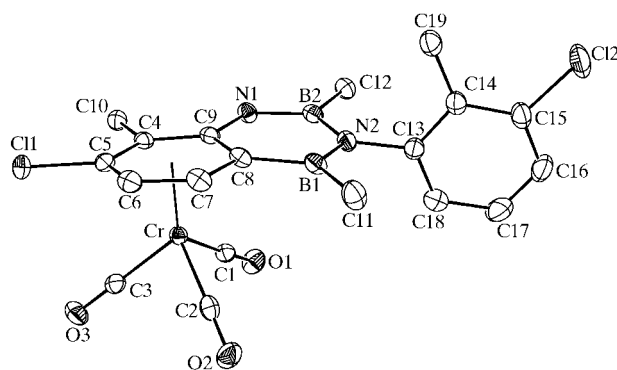
The presence of the  $\text{Cr}(\text{CO})_3$  group induces a systematic lengthening of the C–C bonds of the attached  $\text{C}_6$  aromatic ring compared with the parent ligand: mean increases of 0.026 and 0.024 Å are observed for compounds (I) and (II), respectively. For comparison, dimensions of the adjacent heteroatomic ring, composed of atoms C8/C9/N1/B2/N2/B1, only differ by +0.007 Å for (I) and +0.011 Å for (II) from those of the parent molecule. For both isomers, the Cr–C(ring) bond lengths fall in the range 2.178(2)–2.308(2) Å. For compound (I), the C1–Cr–Cg–C9, C2–Cr–Cg–C7 and C3–Cr–Cg–C5 torsion angles are 16.0, 17.0 and  $15.6^\circ$ , respectively (Cg is the centroid of the aromatic  $\text{C}_6$  ring), while for compound (II), the corresponding values ( $1.5$ ,  $1.8$  and  $3.9^\circ$ ) are indicative of a nearly eclipsed conformation, as already observed for disubstituted benzene containing electron-donating substituents (Mutterties *et al.*, 1982).

Few structural data are found where B–N heterocyclic arenes are bound to  $\text{Cr}(\text{CO})_3$  with the exception of the parent



**Figure 1**  
The molecular structure of (I) showing 50% probability displacement ellipsoids.

borazine ring. Thus, in the hexaethylborazine–Cr(CO)<sub>3</sub> complex, the B<sub>3</sub>N<sub>3</sub> borazine ring is puckered in a chair form such that all three Cr–N distances are shorter than the three Cr–B bonds (Huttner & Kreig, 1972). Every time a 6π-electron B–N heterocycle is fused to a benzene ring, the Cr(CO)<sub>3</sub> moiety prefers attachment to the benzene part of the molecule.



**Figure 2**  
The molecular structure of (II) showing 50% probability displacement ellipsoids.

## Experimental

All reactions were carried out under dry argon using Schlenk techniques. The reaction of Cr(CO)<sub>6</sub> (2.18 mmol) with the relevant ligand (1.51 mmol) produced a mixture of both isomers in 29% yield (Allaoud *et al.*, 1994) which was chromatographed on a silica column with a diethyl ether–hexane mixture (25/75) to yield a first fraction of pure compound (I) (m.p. 453–455 K) and a second fraction of compound (II) (m.p. 449–451 K). Each isomer was characterized by its <sup>1</sup>H and <sup>13</sup>C NMR spectrum; the assignment of the correct configuration was in complete agreement with those deduced from solvent effects in a previous study. Crystals were grown from a diethyl ether–hexane mixture (1:1).

## Compound (I)

### Crystal data

[Cr(C<sub>16</sub>H<sub>18</sub>B<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>)(CO)<sub>3</sub>]  
*M<sub>r</sub>* = 466.87  
 Triclinic, P1  
*a* = 6.750 (1) Å  
*b* = 10.839 (1) Å  
*c* = 14.858 (1) Å  
 α = 80.537 (2)°  
 β = 88.717 (1)°  
 γ = 73.409 (2)°  
*V* = 1027.3 (1) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.509 Mg m<sup>-3</sup>  
 Mo Kα radiation  
 Cell parameters from 12140 reflections  
 θ = 1.0–27.5°  
 μ = 0.84 mm<sup>-1</sup>  
*T* = 110 (2) K  
 Prism, yellow  
 0.20 × 0.10 × 0.07 mm

### Data collection

Nonius KappaCCD diffractometer  
 ω scans  
 12140 measured reflections  
 4611 independent reflections  
 1834 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.100  
 θ<sub>max</sub> = 27.5°  
*h* = 0 → 8  
*k* = -12 → 14  
*l* = -19 → 19

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.031  
*wR*(*F*<sup>2</sup>) = 0.076  
*S* = 0.82  
 3590 reflections  
 266 parameters

H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.01*P*)<sup>2</sup>]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.26 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.28 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °) for (I).

C<sub>g</sub> is the centroid of the C4–C9 ring.

Cr–C <sub>g</sub>	1.73	Cr–C7	2.178 (2)
Cr–C1	1.831 (1)	Cr–C8	2.252 (2)
Cr–C2	1.856 (2)	Cr–C9	2.308 (2)
Cr–C3	1.840 (2)	O1–C1	1.152 (2)
Cr–C4	2.261 (2)	O2–C2	1.145 (2)
Cr–C5	2.216 (2)	O3–C3	1.168 (3)
Cr–C6	2.218 (2)		
C <sub>g</sub> –Cr–C1	122.9	C1–Cr–C2	89.55 (8)
C <sub>g</sub> –Cr–C2	127.5	C1–Cr–C3	91.09 (9)
C <sub>g</sub> –Cr–C3	125.7	C2–Cr–C3	88.97 (9)

## Compound (II)

### Crystal data

[Cr(C<sub>16</sub>H<sub>18</sub>B<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>)(CO)<sub>3</sub>]  
*M<sub>r</sub>* = 466.87  
 Monoclinic, C2/c  
*a* = 25.666 (1) Å  
*b* = 7.0290 (3) Å  
*c* = 25.366 (1) Å  
 β = 112.907 (2)°  
*V* = 4215.3 (3) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.471 Mg m<sup>-3</sup>  
 Mo Kα radiation  
 Cell parameters from 19870 reflections  
 θ = 1.0–27.5°  
 μ = 0.82 mm<sup>-1</sup>  
*T* = 110 (2) K  
 Prism, yellow  
 0.20 × 0.15 × 0.05 mm

### Data collection

Nonius KappaCCD diffractometer  
 ω scans  
 19870 measured reflections  
 4824 independent reflections  
 4105 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.140  
 θ<sub>max</sub> = 27.5°  
*h* = 0 → 33  
*k* = 0 → 9  
*l* = -32 → 30

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.034  
*wR*(*F*<sup>2</sup>) = 0.087  
*S* = 1.05  
 4824 reflections  
 266 parameters  
 H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0306*P*)<sup>2</sup> + 8.1507*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.67 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.54 e Å<sup>-3</sup>

**Table 2**

Selected geometric parameters (Å, °) for (II).

C<sub>g</sub> is the centroid of the C4–C9 ring.

Cr–C <sub>g</sub>	1.74	Cr–C5	2.214 (2)
Cr–C1	1.833 (2)	Cr–C6	2.232 (2)
Cr–C2	1.853 (2)	Cr–C7	2.197 (2)
Cr–C3	1.841 (2)	Cr–C8	2.238 (2)
Cr–C4	2.272 (2)	Cr–C9	2.296 (2)
C <sub>g</sub> –Cr–C1	122.6	C1–Cr–C2	90.81 (8)
C <sub>g</sub> –Cr–C2	127.6	C1–Cr–C3	89.16 (8)
C <sub>g</sub> –Cr–C3	127.2	C2–Cr–C3	87.81 (8)

All H atoms were placed at idealized positions and were allowed to ride on their neighbouring atoms with isotropic displacement parameters [ $C-H = 0.93-0.96 \text{ \AA}$ ,  $N-H = 0.86 \text{ \AA}$  and  $U_{iso} = 1.3U_{eq}(C \text{ or } N)$ ].

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *DENZO* and *SCALE-PACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1625). Services for accessing these data are described at the back of the journal.

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