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Bromido(η^5-carboxycyclopentadienyl)dinitrosylchromium(0) and (η^5-benzoylcyclopentadienyl)bromidodinitrosylchromium(0)

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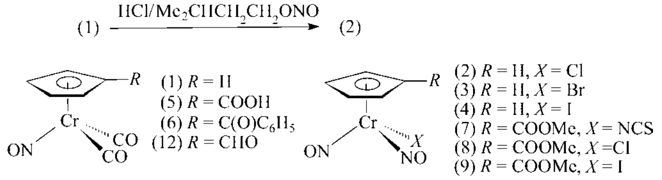
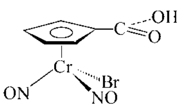
In the structures of each of the title compounds, [CrBr($C_6H_5O_2$)($NO)_2$], (I), and [CrBr($C_{12}H_9O$)($NO)_2$], (II), one of the nitrosyl groups is located at a site away from the exocyclic carbonyl C atom of the cyclopentadienyl (Cp) ring, with twist angles of 174.5 (3) and 172.5 (1)°. The observed orientation is surprising, since the NO group is expected to be situated *trans* to an electron-rich C atom in the ring. The organic carbonyl plane is turned away from the Cp ring plane by 5.6 (8) and 15.2 (3)°in (I) and (II), respectively. The exocyclic C—C bond in (I) is bent out of the Cp ring plane towards the Cr atom by 2.8 (3)°, but is coplanar with the Cp ring in (II); the angle is 0.1 (1)°.

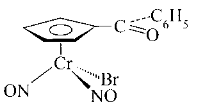
Comment

Although CpCr(NO)$_2$(Br) was first reported in 1956 (Piper & Wilkinson, 1956), the difficulties encountered in making it undergo electrophilic aromatic substitution reactions such as Friedel–Crafts acylation have blocked the way to the synthesis of its Cp derivatives (Rausch *et al.*, 1980). A novel method of replacing two carbonyl groups with a nitrosyl and a chloro ligand using hydrogen chloride/isoamyl nitrite has been reported by Wang & Hwu (1990) to convert (1) to (2) (see the first scheme below). The analogous bromide compounds, *viz.* (η^5-C_5H_4COOH)Cr(NO)$_2$Br, (I), and (η^5-$C_5H_4COC_6H_5$)Cr(NO)$_2$Br, (II), were prepared using hydrogen bromide/isoamyl nitrite from (5) and (6), respectively (Wang *et al.*, 2007).





(I)



(II)

Wang *et al.* (1995, 1999) reported the qualitative relationship of the nonplanarity of the Cp–exocyclic carbon system to the substituent π-donor and π-acceptor interactions. The π-donor substituents and the *ipso*-C atoms to which they are attached are bent away from the Cr(CO)$_2$NO fragments, while the π-acceptor substituents and the *ipso*-C atoms to which they are attached lie approximately in the Cp plane or are bent slightly toward the Cr(CO)$_2$NO fragments. The magnitudes and directions of these distortions from planarity appear to be due primarily to electronic effects. In the hope of confirming these hypotheses, the title compounds, (I) and (II), were studied. The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are given in Tables 1 and 2.

The coordination geometry about the Cr center in each case is approximately a distorted tetrahedron, with two nitrosyl groups, the Cp group and a Br atom as the four coordination sites. It is worth pointing out that for both structures one of the nitrosyl groups is located at a site away from the exocyclic C atom, *i.e.* atom Br1 is located at a site close to the exocyclic C atom.

The twist angle, defined as the torsion angle between nitrosyl atom N2, the Cr1 atom, the centroid (*Cg*) of the Cp center and the ring C atom bearing the exocyclic C atom, is

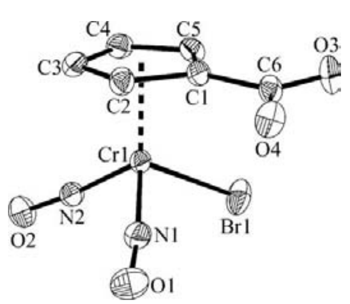


Figure 1
The molecular configuration of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

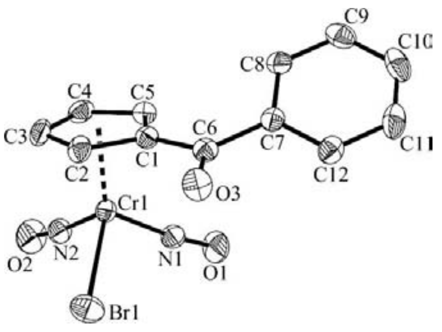


Figure 2
The molecular configuration of (II). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

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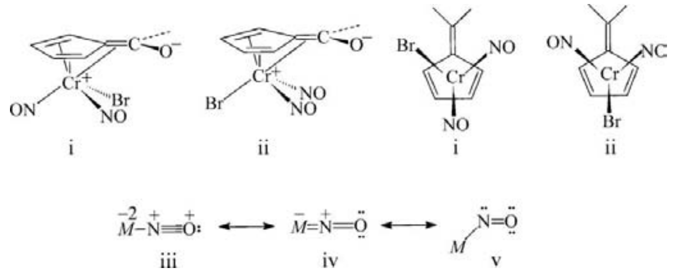
174.5 (3)° for (I) and 172.5 (1)° for (II). The preference for isomer i (see the scheme below) over the symmetrical isomer ii may be related to the ability of the exocyclic double bond to donate electron density to the Cr atom if it is in a position *trans* to the better π-accepting ligand, *i.e.* NO^+. As a result, the exocyclic C1—C6 bond in (I) is bent out of the Cp ring plane towards atom Cr1 by θ = 2.8 (3)°, although in (II) θ is only 0.1 (1)°. The θ angle is defined as the angle between the exocyclic C—C bond (C1—C6) and the corresponding Cp ring, with a positive angle toward the metal and a negative angle away from the metal.



The fact that the electron-withdrawing carbonyl group on the Cp ring orients itself *trans* to the stronger electron-withdrawing NO group rather than a weaker electron-withdrawing ligand is surprising (Rogers *et al.*, 1988). It is interesting to discover that the contribution of the canonical form i to (I) or (II) to some extent is revealed by the C—C bond lengths in the cyclopentadienyl ring. Comparatively, shorter bond lengths for C2—C3 and C4—C5, and longer bond lengths for C1—C2, C3—C4 and C1—C5 are observed in both (I) and (II).

In view of the shortness of the Cr1—NO distances in (I) and (II) (*ca* 1.71 Å) compared with the Cr—NCS distance of 1.983 (3) Å in compound (7) (Wang *et al.*, 2007), appreciable d_π back-donation from the Cr atom to the π^* orbitals of the nitrosyl group is demonstrated. It appears that canonical form iv rather than iii makes a greater contribution to the chromium–nitrosyl bonding. The lesser contribution of v with respect to that of iv is reflected by the Cr1—N—O angles of *ca* 171°. These values are similar to those found in (8) [171.2 (5) and 172.1 (4)°] and (9) [176.0 (5) and 174.3 (4)°] (Wang *et al.*, 1991).

The two Cr1–(Cp centroid) distances agree with the values of 1.844 Å in (1) and 1.884 Å in $(\eta^5\text{-}C_{13}H_9)Cr(CO)_2(NO)$ (Atwood *et al.*, 1979). The average Cr1···C(ring) distances of 2.209 (4) and 2.215 (4) Å are close to the value in (2) (2.20 Å). The average C—C distances in the Cp rings are 1.409 (6) and 1.403 (6) Å for (I) and (II), respectively. In the case of (I), the exocyclic C1—C6 bond is considerably shorter than those found in [η^5-(1-vinylferrocenyl)methylcyclopentadienyl]dicarbonylnitrosylchromium [1.507 (6) Å; Wang *et al.*, 1989] and (1-cynichrodenoylferrocenyl)cynichrodenylmethane [1.512 (8) Å; Wang *et al.*, 1990], but is comparable to that found in (12) [1.470 (8) Å; Rogers *et al.*, 1988]. Again, the contribution of canonical form i to compound (I) may account for the difference.

It is interesting to note the difference between the structures of (I) and (II). The resonance between the carbonyl and phenyl ring diminishes the extent of the contribution of i to (II). This entails a longer exocyclic C—C bond, a smaller θ [0.1 (1) *versus* 2.8 (3)°], and a larger dihedral angle between the carbonyl plane and the corresponding Cp plane. The results indicate that the resonance between the carbonyl and phenyl groups overwhelms the resonance between the carbonyl and Cp groups. It is conceivable that the two electron-withdrawing nitrosyl groups and the bromide ion on the Cr atom deplete the electron density on the Cp ring. The π electrons on the Cp ring are less able to resonate with the carbonyl ligand. In the case of (II), the carbonyl plane (C1/C6/O3/C7) is turned away from those of the Cp and phenyl rings by 15.2 (3) and 24.5 (1)°, respectively. This rotation might be the result of intramolecular steric interference between atoms H5 and H8. This is supported by the enlargement of the C5—C1—C6 and C8—C7—C6 angles to 131.8 (4) and 123.2 (4)°, respectively. As a result of the steric interference, the dihedral angle between the Cp and phenyl ring planes is quite large [35.3 (1)°].

Experimental

Hydrogen bromide was bubbled through a solution of dicarbonyl(η^5-carboxycyclopentadienyl)nitrosylchromium (cynichrodenoic acid), (5) (2.49 g, 9.56 mmol), in 2-propanol (30 ml) for 5 min. After cooling to 273–283 K with stirring for 20 min (an orange–red solution resulted), isoamyl nitrite (2.6 ml, 19.12 mmol) was added slowly. Carbon monoxide evolved and the colour of the solution subsequently changed to dark green. The reaction mixture was stirred for 1 h. After concentration of the solution to a volume of 10 ml, dichloromethane (30 ml) was added and a large quantity of dark-green solid precipitated out. The solid was recovered through frit filtration and washed several times with distilled water. Compound (I) (yield 2.24 g, 74%) was obtained after vacuum drying (Wang *et al.*, 2007). An X-ray sample (granular black–brown crystals) was prepared by recrystallization using the solvent expansion method from hexane–tetrahydrofuran (5:2) at 273 K for 48 h. The same procedure was followed for the preparation of (II) (in 90% yield), starting from (η^5-benzoylcyclopentadienyl)dicarbonylnitrosylchromium (benzoylcynichrodene), (6) (1.23 g, 4.00 mmol).

Compound (I)

Crystal data

$[CrBr(C_6H_5O_2)(NO)_2]$
M_r = 301.03
Monoclinic, $P2_1/c$
a = 7.6395 (19) Å
b = 10.591 (2) Å
c = 12.122 (2) Å
β = 105.40 (2)°
V = 945.6 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.42 mm^{-1}
T = 293 (2) K
0.50 × 0.40 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.141, T_{max} = 0.236 (expected range = 0.118–0.196)
2378 measured reflections
2168 independent reflections
1408 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.100$
$S = 0.99$
2168 reflections
131 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.61$ e Å^{-3}

Compound (II)

Crystal data

$[CrBr(C_{12}H_9O)(NO)_2]$
$M_r = 361.12$
Monoclinic, $P2_1/c$
$a = 12.1936$ (13) Å
$b = 6.5027$ (9) Å
$c = 16.305$ (2) Å
$\beta = 95.731$ (10)°
$V = 1286.4$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 4.00$ mm^{-1}
$T = 293$ (2) K
0.55 × 0.45 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.220$, $T_{\max} = 0.333$ (expected range = 0.199–0.301)
3233 measured reflections
2952 independent reflections
1881 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.130$
$S = 1.09$
2952 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.61$ e Å^{-3}

The position of the hydroxy H atom in (I) was refined together with an isotropic displacement parameter. All other H atoms in (I) and (II) were placed in geometrically calculated positions and refined using a riding model, with C—H = 0.93 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(parent atom).

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1994); cell refinement: *CAD-4 Software*; data reduction: *DATRD2* in *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3052). Services for accessing these data are described at the back of the journal.

Table 1
Geometric parameters (Å, °) for (I).

Cg is the centroid of the cyclopentadienyl ring.

Cr1—N1	1.710 (4)	C1—C2	1.426 (5)
Cr1—N2	1.706 (3)	C1—C6	1.462 (5)
Cr1—Br1	2.4551 (8)	C2—C3	1.390 (6)
C6—O4	1.258 (5)	C3—C4	1.422 (6)
C6—O3	1.272 (5)	C4—C5	1.390 (6)
Cr1···C6	3.201 (5)	N1—O1	1.158 (4)
Cr1···*Cg*	1.856	N2—O2	1.158 (4)
O1···Br1	4.177 (6)	C1—C5	1.409 (5)
O2···Br1	4.161 (5)		
N1—Cr1—N2	92.92 (16)	C1—C5—Cr1	70.0 (2)
N1—Cr1—Br1	100.03 (12)	O4—C6—O3	124.2 (4)
N2—Cr1—Br1	99.69 (12)	O4—C6—C1	119.1 (3)
O1—N1—Cr1	171.6 (3)	O3—C6—C1	116.7 (4)
O2—N2—Cr1	172.0 (3)	*Cg*···Cr1—N1	121.8
C5—C1—C6	126.3 (4)	*Cg*···Cr1—N2	121.2
C2—C1—C6	126.8 (4)	*Cg*···Cr1—Br1	116.2
C6—C1—Cr1	120.3 (3)		

Dihedral angles between planes	
Cp and carbonyl plane C1/C6/O3/O4	5.6 (8)
Cr1/Cp/N1 and Cr1/Cp/C1	58.0 (6)
Cr1/Cp/N2 and Cr1/Cp/C1	174.5 (3)
Cr1/Cp/Br1 and C1r/Cp/C1	64.2 (7)

Table 2
Geometric parameters(Å, °) for (II).

Cg is the centroid of the cyclopentadienyl ring.

Cr1—N1	1.721 (3)	C3—C4	1.401 (7)
Cr1—N2	1.708 (3)	C4—C5	1.389 (5)
Cr1—Br1	2.4394 (8)	C6—O3	1.221 (5)
Cr1—C1	2.236 (4)	C6—C7	1.497 (5)
N1—O1	1.140 (4)	N2—O2	1.154 (4)
C1—C2	1.405 (5)	Cr1···C6	3.306 (1)
C1—C5	1.430 (6)	Cr1···*Cg*	1.867
C1—C6	1.489 (5)	O1···Br1	4.068 (7)
C2—C3	1.388 (6)	O2···Br1	4.124 (6)
N1—Cr1—N2	92.50 (17)	O3—C6—C7	120.1 (4)
N1—Cr1—Br1	97.21 (12)	C1—C6—C7	120.6 (3)
N2—Cr1—Br1	98.63 (13)	C6—C7—C8	123.2 (4)
O1—N1—Cr	172.6 (4)	C6—C7—C12	117.2 (4)
O2—N2—Cr1	171.3 (4)	*Cg*—Cr1—N1	123.8
C2—C1—C6	122.2 (4)	*Cg*—Cr1—N2	120.2
C5—C1—C6	131.8 (4)	*Cg*—Cr1—Br1	118.4
O3—C6—C1	119.2 (4)		

Dihedral angles between planes	
Cp and carbonyl plane C1/C6/O3/C7	15.2 (3)
Benzene and carbonyl plane C1/C6/O3/C7	24.5 (1)
Cp and benzene	35.3 (1)
Cr1/Cp/N1 and Cr1/Cp/C1	55.7 (1)
Cr1/Cp/N2 and Cr1/Cp/C1	172.5 (1)
Cr1/Cp/Br1 and Cr1/Cp/C1	66.5 (9)

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