Journal of Organometallic Chemistry, 419 (1991) 325–335
Elsevier Sequoia S.A., Lausanne
JOM 22002

Syntheses and spectra of $[\eta^5\text{-}(C_5H_4COOCH_3)]Cr(NO)_2L$ (L = Cl, I, CH_3) and crystal structures of $[\eta^5\text{-}(C_5H_4COOCH_3)]Cr(NO)_2L$ (L = Cl, I)

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(Received January 18th, 1991)

Abstract

Chlorination/nitrosylation of $[\eta^5$-(carbomethoxy)cyclopentadienyl]dicarbonylnitroslychromium **5** with hydrogen chloride/isoamyl nitrite gives chloro$[\eta^5$-(carbomethoxy)cyclopentadienyl]dinitrosylchromium **6** in 78% yield. Compound **6** was converted to $[\eta^5$-(carbomethoxy)cyclopentadienyl iododinitrosylchromium **7** with potassium iodide in 85% yield. Compound **7** in turn was methylated with Grignard reagent to give **8** in 45% yield. The structures of **6** and **7** have been solved by X-ray diffraction studies. Both **6** and **7** crystallize in the monoclinic space group $P2_1/n$. Lattice constants of **6** are *a* 6.932(2), *b* 18.239(5), *c* 8.117(2) Å, β 93.48(2)° and $Z = 4$. Lattice constants of **7** are *a* 7.229(2), *b* 8.177(3), *c* 19.201(7) Å, β 99.38(3)° and $Z = 4$. The organic carbonyl plane (C(1), C(11), O(3), O(4)) deviates from the coplanarity of the corresponding ring plane Cp(Cr) by 1.4 and 0.3° in compounds **6** and **7**, respectively.

In **6** the chlorine atom is located at the site twoard the exocyclic carbon of the Cp(Cr) ring with a twist angle of 72.2°, while in **7**, the iodine atom has a twist angle of 68.9°.

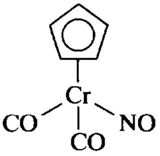
Introduction

Since the advent of ferrocene in the early 1950s, the syntheses and characterizations of metallocenes have been extensively, especially for the iron compounds. However the number of chromium metallocenes being studied is relatively small. The number of isolated and well characterized alkylchromium complexes is even more limited.

The chromium metallocenes may have properties distinct from their iron analogues. Recently, we have reported [1] the unequivocal assignment of C(2,5) and C(3,4) of cynichrodene **1** derivatives bearing electron-withdrawing groups. The highfield and lowfield chemical shifts are assigned to C(3,4) and C(2,5), respectively, which is opposite to the assignments for the ferrocene derivatives. This surprising finding has prompted us to study the derivatives of **2**, **3** and **4**.

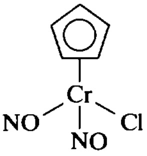
Compounds **2**, **3** and **4** were first reported in 1956 [2], 1956 [3] and 1955 [4], respectively. A novel method of replacing dicarbonyl with (NO)Cl ligand with hydrogen chloride/isoamylnitrite has been revealed by us to convert **1** to **2** [5]. The difficulties encountered for compounds **2–4** to undergo electrophilic aromatic substitution reactions such as Friedel–Crafts acylation have blocked the way to the synthesis of their respective derivatives. The availability of [η^5-(carbomethoxy)cyclopentadienyl]dicarbonylnitrosylchromium **5** [6] makes the syntheses of carbomethoxy derivatives **6**, **7** and **8** accessible.

Two main approaches have been utilized in the investigation of the substituent effects on the electronic-density distribution of the substituted ring in Cp-metal compounds [7]. The first is the chemical method concerned with the relative reactivity of the 2,5- and 3,4-positions in the substituted Cp ring, e.g. in acylation and metallation reactions. The second is the spectroscopic approach based on the measurements of relative shielding of the C(2,5) and C(3,4) carbons by the ^{13}C NMR method. Here, we report the preparations and spectra of compounds **6–8** and the crystal structures of **6** and **7**.



(1)

cynichrodene



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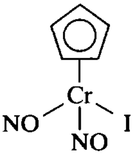

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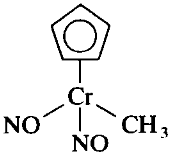

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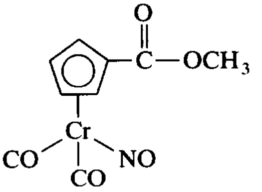

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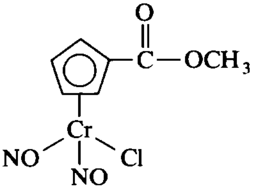

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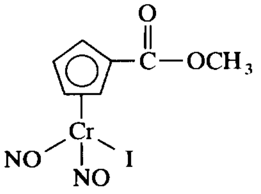

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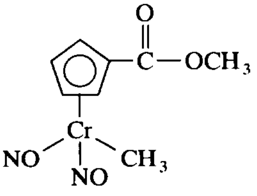

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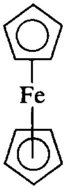


(9)

Experimental

All operations were carried out under nitrogen using Schlenk techniques. Traces of oxygen in the nitrogen were removed with BASF catalyst and the deoxygenated nitrogen was dried over molecular sieves 3A and P_2O_5. Hexane, pentane, benzene and dichloromethane were dried over calcium hydride and freshly distilled under nitrogen from calcium hydride. Diethyl ether was dried over sodium and redistilled under nitrogen from sodium-benzophenone ketyl. All the other solvents were used as commercially obtained.

Column chromatography was carried out under nitrogen with Merck Kiesel-gel 60. The silica gel was heated with a heat gun during mixing in a rotary evaporator attached to a vacuum pump for 2 h to remove water and oxygen, and was kept under nitrogen. [(η^5-Carboxmethoxy)cyclopentadienyl)]dicarbonylnitrosylchromium **5** was prepared according to the literature procedure [6].

^{1}H and ^{13}C NMR were recorded on a Varian VXR-300 spectrometer. Chemical shifts were referenced to tetramethylsilane. Infrared spectra were recorded with a Perkin-Elmer 682 spectrophotometer. Microanalyses were carried out by the Microanalytic Laboratory of the National Taiwan University.

Preparation of (η^5-cyclopentadienyl)methyldinitrosylchromium 4

To a stirred solution of **3** (0.7 g, 2.3 mmol) in 80 ml of diethyl ether, a solution of methyl magnesium iodide (0.4 g, 2.4 mmol) in diethyl ether was syringed in slowly. After stirring for 15 min at room temperature, 4 g of silica gel was added and the solvent was removed under vacuum. The residue was added to a dry-packed column (1.8 × 9 cm) of silica gel. Elution of the column with diethyl ether/hexane (4:1) gave a green band which upon removal of solvent under vacuum gave **4**, 0.25 g (57%) as a dark green solid. IR spectrum (KBr): 2970w, 2900w, 1780vs, 1675b, vs, 1270m, 1140w, 1105m, 1030m, 830s cm^{-1} (intensity). Mass spectrum: $m/e = 192$ (M^+). The data are consistent with published data for the compound [8].

Preparation of (η^5-carbomethoxycyclopentadienyl)chlorodinitrosylchromium 6

Through a solution of **5** (2.57 g, 9.86 mmol) in 20 ml of isopropanol, was bubbled hydrogen chloride for 5 min. After cooling to 0–10 ° C, isoamyl nitrite (2.0 ml, 14.88 mmol) was added slowly and the reaction mixture was stirred for 30 min. The solvent was removed. The residue was extracted with 70 ml of methylene chloride. The extracts were washed several times with distilled water and dried with magnesium sulfate. After filtration 5 g of silica gel was added and the solvent was removed under vacuum. The residue was added to a dry-packed column (1.8 × 9 cm) of silica gel. Elution of the column with diethyl ether/hexane (1:2) gave a brownish-green band which upon removal of solvent under vacuum gave **6**, 2.08 g (78%). An analytical sample, m.p. 46–47 ° C, was obtained by solvent expansion from methylene chloride/pentane (3:8) at 0 ° C.

Anal. Found: C, 31.30; H, 2.70; N, 9.99. $C_7H_7ClN_2O_4Cr$ calc.: C, 31.05; H, 2.59; N, 10.35%. IR spectrum (KBr): 1829s, 1750s, 1732s, 1716s, 1300m, 1165m cm^{-1} (intensity) Mass spectrum: $m/e = 270$ (M^+).

Preparation of (η^5-carbomethoxycyclopentadienyl)iododinitrosylchromium 7

To a stirred solution of (η^5-carbomethoxycyclopentadienyl)chlorodinitrosylchromium **6** (1.27 g, 4.7 mmol) in 70 ml of methanol, potassium iodide (1.0 g, 6.02 mmol) was added. The reaction mixture was stirred for 15 min at 45 ° C. The solvent was then removed under vacuum. The residue was extracted with 70 ml methylene chloride. The extracts were washed four times with distilled water and dried with magnesium sulfate. After filtration 5 g of silica gel was added and the solvent was removed under vacuum. The residue was added to a dry-packed column (1.8 × 9 cm) of silica gel. Elution of the column with diethyl ether/hexane (1:2) gave a dark brown band which upon removal of the solvent under vacuum gave **7**, 1.45 g (85%) as a dark brown solid. An analytical sample, m.p. 66–67 °C, was obtained by solvent expansion from methylene chloride/pentane (4:9) at 0 °C.

Anal. Found: C, 23.47; H, 1.85; N, 7.45. $C_7H_7IN_2O_4Cr$ calc.: C, 23.23; H, 1.93; N, 7.74%. IR spectrum (KBr): 1821vs, 1749vs, 1729vs, 1715vs, 1300s, 1160s cm^{-1} (intensity). Mass spectrum: $m/e = 362$ (M^+).

Preparation of (η^5-carbomethoxycyclopentadienyl)methyldinitrosylchromium 8

To a stirred solution of (η^5-carbomethoxycyclopentadienyl)iododinitrosylchromium **7** (0.5 g, 1.38 mmol) in 30 ml of methylene chloride, a solution of methyl magnesium iodide (0.40 g, 2.37 mmol) in diethyl ether was syringed in slowly. After filtration, 4 g of silica gel was added and the solvent was removed under vacuum. The residue was added to a dry-packed column (1.8 × 9 cm) of silica gel. Elution of the column with diethyl ether/pentane (1:4) gave a dark green band which upon removal of solvent under vacuum gave **8**, 0.155 g (45%) as a dark green liquid. An analytical sample was obtained by vacuum distillation at 66 °C/0.1 Torr.

Anal. Found: C, 38.80; H, 4.23; N, 10.98. $C_8H_{10}N_2O_4Cr$ calc.: C, 38.42; H, 4.00; N, 11.20%. IR spectrum (KBr): 1779vs, 1723vs, 1669b, vs, 1295s, 1155s cm^{-1} (intensity). Mass spectrum: $m/q = 250$ (M^+).

X-Ray diffraction analyses of 6 and 7

The intensity data were collected on a Nicolet R3m/V diffractomer with a graphite monochromator (Mo-K_α radiation). $\theta/2\theta$ scan data were collected at room temperature (24 °C). The data were corrected for Lorentz and polarization effects. The details of crystal data and intensity collection are summarized in Table 1 for compounds **6** and **7**, respectively.

Structures were solved by direct methods using the SHELXTL PLUS program [9]. Full matrix least-squares refinement on F used anomalous-dispersion corrections for atoms with atomic numbers greater than 16. Neutral atom scattering form factors from *International Tables for X-ray Crystallography* [10] were used. The non-hydrogen atoms were refined anisotropically and all hydrogen atoms were positioned at calculated coordinates and with fixed isotropic U of 0.08 Å^2. All calculations were performed on a MicroVAX II based Nicolet SHELXTL PLUS system.

Results and discussion

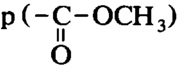
Chlorination/nitrosylation of **5** with hydrogen chloride/isoamyl nitrite in isopropanol, a novel method of replacing dicarbonyl with (NO)Cl ligand [5], produced **6** in 78% yield. Treatment of **6** with potassium iodide led to iodo product **7** in 85% yield. Alkylation of **7** with methyl magnesium iodide gave **8** in 44% yield.

$$\mathbf{5} \xrightarrow[\text{isopropanol}]{HCl/(CH_3)_2CHCH_2CH_2ONO} \mathbf{6} \xrightarrow{KI} \mathbf{7} \xrightarrow{CH_3MgI} \mathbf{8}$$

Table 1

Summary of crystal data and intensity collection of **6** and **7**

	6	**7**
Formula	$C_7H_7N_2O_4ClCr$	$C_7H_7N_2O_4CrI$
Color; habit	Black; chunk	Black, chunk
Crystal size (mm)	0.3×0.2×0.1	0.2×0.2×0.2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions	$a = 6.932(2)$ Å $b = 18.239(5)$ Å, $\beta = 93.48(2)°$ $c = 8.117(2)$ Å	$a = 7.229(2)$ Å $b = 8.177(3)$ Å, $\beta = 99.38(3)°$ $c = 19.201(7)$ Å
Volume	1024.4(5) $Å^3$	1119.8(6) $Å^3$
Z	4	4
Formula weight	270.6	362.0
Density (calc.)	1.755 g/cm^3	2.147 g/cm^3
Absorption coefficient	1.347 mm^{-1}	3.721 mm^{-1}
$F(000)$	544	688
Diffractometer used	Nicolet R3m/V	Nicolet R3m/V
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)	Mo-K_α ($\lambda = 0.71073$ Å)
Temperature (K)	297	298
Monochromator	Highly roiented graphite crystal	Highly oriented graphite crystal
2θ range	2.5–50.0°	2.5–50.0°
Scan type	2θ-θ	$\theta/2\theta$
Scan speed	Variable, 2.93–14.65°/min in ω	Variable, 2.93–14.65°/min in ω
Scan range (ω)	0.96° plus K_α-separation	1.00° plus K_α-separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	3 measured every 50 reflections	3 measured every 50 reflections
Index ranges	$0 \leqslant h \leqslant 8, 0 \leqslant k \leqslant 21, -9 \leqslant l \leqslant 9$	$0 \leqslant h \leqslant 8, -9 \leqslant k \leqslant 0, -22 \leqslant l \leqslant 22$
Reflections collected	2169 ($1229 > 3\sigma(I)$)	2299 ($1873 > 3\sigma(I)$)
Independent reflections	1814 ($1216 > 3\sigma(I)$)	1972 ($1767 > 3\sigma(I)$)
Extinction correction	$\chi = 0.0005(3)$, where $F^* = F[1+0.002\chi F^2/\sin(2\theta)]^{-1/4}$	$\chi = 0.0026(4)$, where $F^* = F[1+0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	Riding model, fixed isotropic U	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$	$w^{-1} = \sigma^2(F) + 0.0077F^2$
Final R indices (obs. data)	$R = 4.01\%$, $R_w = 4.77\%$	$R = 4.02\%$, $R_w = 4.94\%$
Goodness-of-fit	1.10	0.80
Largest and mean Δ/σ	0.077, 0.001	0.002, 0.001
Data-to-parameter ratio	8.0:1	12.7:1
Largest difference peak	0.30 $eÅ^{-3}$	1.06 $eÅ^{-3}$
Largest difference hole	−0.33 $eÅ^{-3}$	0.98 $eÅ^{-3}$

The infrared and ^1H NMR spectra of compounds **5**–**8** are consistent with their assigned structures and are similar to other metallocenyl systems [3,5,8,1–13]. In infrared spectra, the normal absorption of the organic carbonyl group  $(-\underset{\underset{O}{\|}}{C}-OCH_3)$ of **5**–**8** is obscured by the NO stretching band.

In ^1H NMR spectra, all compounds **5**–**8** exhibit a pair of apparent triplets. The downfield triplet can be assigned to H(2,5) protons of the Cp. This assignment is

Table 2

^1H NMR data [a]

Compound	Cp(Cr)		-OCH$_3$	Cr-CH$_3$
	H(2,5)	H(3,4)		
1	5.07 (s, 5)			
2	5.73 (s, 5)			
3	5.78 (s, 5)			
4	5.40 (s, 5)			0.57
5	5.76 (t, 2)	5.11 (6, 2)	3.80 (s, 3)	
6	6.25 (t, 2)	5.78 (t, 2)	3.89 (s, 3)	
7	6.29 (t, 2)	5.82 (t, 2)	3.85 (s, 3)	
8	5.93 (6, 2)	5.44 (t, 2)	3.79 (s, 3)	0.63

[a] The assignment in each Cp-substituted system parallels those in the ferrocene system and must be considered tentative until specific deuterium labeled derivatives in each system can be prepared.

made on the basis that the carbonyl group would exert stronger magnetic anisotropy effect to the ring protons closer to it. As expected, H(2,5) would be deshielded to a greater extent than the protons on the more remote 3- and 4-positions.

It is of interest to compare the ^1H NMR spectra of **5–8** with their corresponding unsubstituted parent compounds **1–4**. The chemical shifts of protons on Cp(Cr) (H(3,4) and H(2,5)) of **5–8** occur at much lower fields than those of the corresponding protons of **1–4** (Table 2). This reflects the strong electron-withdrawing effect of the organic carbonyl groups.

The assignments of ^{13}C NMR spectra of compounds **1–8** (Table 3) are based on standard ^{13}C NMR correlations [14], 2D-HetCOR, DEPT technique and comparison with other metallo-aromatic systems [13]. In the case of **6**, two relatively less intense signals were observed at δ 161.87 and 103.14 corresponding to the organic carbonyl carbon and C(1) of Cp(Cr), respectively. The methoxy carbon resonates at δ 52.79. The line assignments for C(2–5) of Cp(Cr) were more difficult to make. Based on 2D-HetCOR, chemical shifts at δ 104.14 and 106.05 were assigned to C(3,4) and C(2,5) of Cp(Cr), respectively. Similarly, in the case of **7**, chemical shifts of δ 102.30 and 104.30 were assigned to C(3,4) and C(2,5) of Cp(Cr); and in the

Table 3

$^{13}C\{^1H\}$ NMR [a]

Compound	Cp(Cr)			Cr–C≡O	$>C=O$	-OCH$_3$	Cr-CH$_3$
	C(1)	C(2,5)	C(3,4)				
1	90.31 (C(1–5))			237.10			
2	103.02 (C(1–5))						
3	101.32 (C(1–5))						
4	99.26 (C(1–5))						−1.22
5	92.94	94.12	91.74	234.67	165.07	52.16	
6	103.14	106.05	104.14		161.87	52.79	
7	101.96	104.30	102.30		162.10	52.72	
8	101.78	102.83	99.48		163.65	52.08	0.85

[a] Chemical shifts are reported in ppm with respect to internal Me_4Si.

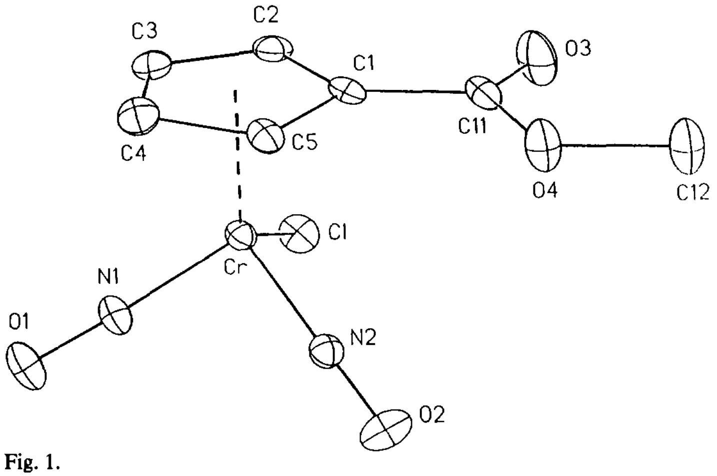


Fig. 1.

case of **8**, chemical shifts of δ 99.48 and 102.83 were assigned to C(3,4) and C(2,5) of Cp(Cr), respectively.

One surprising finding in the study of ^{13}C spectra of **5**–**8** is that the highfield and lowfield chemical shifts are assigned to C(3,4) and C(2,5) respectively for electron-withdrawing carbomethoxy substituent on Cp ring of **5**–**8** which is opposite to the assignment of ferrocene derivatives [1,5,13] in which the downfield shifts and upfield shifts are assigned to C(3,4) and C(2,5), respectively.

The molecular structures of **6** and **7** are shown in Figs. 1 and 2 respectively. Selected bond distances and angles are given in Tables 4 and 5. The atomic coordinates of non-hydrogen atoms are listed in Tables 6 and 7, respectively.

The coordination geometry about the Cr center in each case is approximately a distorted tetrahedron with two nitrosyl groups, the Cp group and halogen as the four coordination sites. In the case of **6** the chlorine atom is located at the site

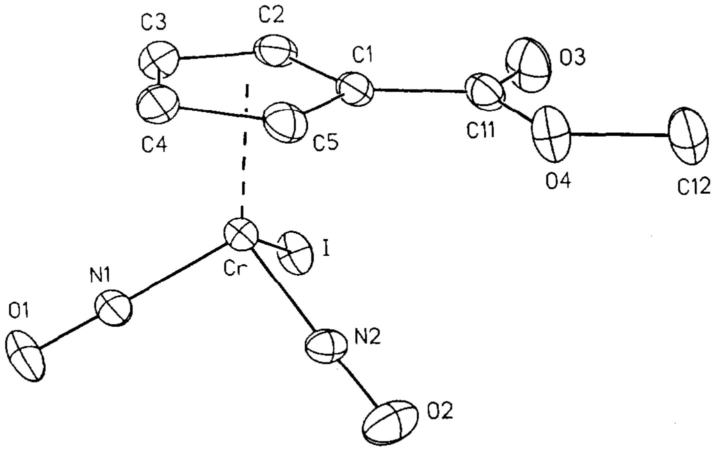


Fig. 2.

Table 4

Selected bond distances (Å) and angles (°) of **6**

Distances			
Cr–C(1)	2.213(5)	Cr–C(2)	2.251(5)
Cr–C(3)	2.218(6)	Cr–C(4)	2.198(6)
Cr–C(5)	2.196(5)	C(1)–C(2)	1.409(8)
C(2)–C(3)	1.391(9)	C(3)–C(4)	1.407(9)
C(4)–C(5)	1.401(8)	C(1)–C(5)	1.442(8)
Cr–Cl	2.317(2)	Cr–N(1)	1.705(5)
Cr–N(2)	1.712(5)	N(1)–O(1)	1.160(7)
N(2)–O(2)	1.163(6)	C(1)–C(11)	1.465(8)
C(11)–O(3)	1.204(7)	C(11)–O(4)	1.327(7)
C(12)–O(4)	1.439(8)	Cr–cen.(Cp(Cr))	1.870
Cr ··· C(11)	3.246	Cr ··· C(Cp(Cr)) ave.	2.215
O(3) ··· C(2)	2.982	O(3) ··· H(C(2))	2.883
O(4) ··· C(5)	2.831	O(4) ··· H(C(5))	2.683
Angles			
C(1)–C(2)–C(3)	108.4(5)	C(2)–C(3)–C(4)	108.7(5)
C(3)–C(4)–C(5)	108.5(5)	C(5)–C(1)–C(2)	107.3(5)
Cl–Cr–N(1)	99.4(2)	Cl–Cr–N(2)	99.0(2)
N(1)–Cr–N(2)	93.5(2)	Cr–N(1)–O(1)	171.2(5)
Cr–N(2)–O(2)	172.1(4)	C(11)–C(1)–C(2)	125.9(5)
C(11)–C(1)–C(5)	126.8(5)	C(1)–C(11)–O(3)	124.8(5)
C(1)–C(11)–O(4)	112.2(5)	C(11)–O(4)–C(12)	118.1(5)
cen.–Cr–Cl	116.7	cen.–Cr–N(1)	121.3
cen.–Cr–N(2)	121.9		

Table 5

Selected bond distances (Å) and angles (°) of **7**

Distances			
Cr–C(1)	2.205(5)	Cr–C(2)	2.244(5)
Cr–C(3)	2.227(5)	Cr–C(4)	2.203(5)
Cr–C(5)	2.195(5)	C(1)–C(2)	1.400(7)
C(2)–C(3)	1.413(9)	C(3)–C(4)	1.395(8)
C(4)–C(5)	1.399(8)	C(1)–C(5)	1.420(8)
Cr–I	2.657(1)	Cr–N(1)	1.718(5)
Cr–N(2)	1.705(4)	N(1)–O(1)	1.169(8)
N(2)–O(2)	1.162(6)	C(1)–C(11)	1.466(8)
C(11)–O(3)	1.207(9)	C(11)–O(4)	1.331(7)
C(12)–O(4)	1.444(9)	Cr–cen.(Cp(Cr))	1.865
Cr ··· C(11)	3.247	Cr ··· C(Cp(Cr)) ave.	2.215
O(3) ··· C(2)	2.978	O(3) ··· H(C(2))	2.857
O(4) ··· C(5)	2.834	O(4) ··· H(C(5))	2.673
Angles			
C(1)–C(2)–C(3)	107.8(5)	C(2)–C(3)–C(4)	108.6(5)
C(3)–C(4)–C(5)	107.8(5)	C(5)–C(1)–C(2)	107.5(5)
I–Cr–N(1)	94.8(2)	I–Cr–N(2)	95.2(1)
N(1)–Cr–N(2)	96.2(2)	Cr–N(1)–O(1)	176.0(5)
Cr–N(2)–O(2)	174.3(4)	C(11)–C(1)–C(2)	125.0(5)
C(11)–C(1)–C(5)	127.5(5)	C(1)–C(11)–O(3)	125.7(5)
C(1)–C(11)–O(4)	112.2(5)	C(11)–O(4)–C(12)	118.5(5)
cen.–Cr–I	118.0	cen.–Cr–N(1)	122.9
cen.–Cr–N(2)	123.0		

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) of **6**

	x	y	z	U_{eq} [a]
I	7133(1)	2081	3367(1)	59(1)
Cr	3337(2)	2072(1)	2393(1)	38(1)
O(2)	1937(10)	58(8)	3652(5)	84(3)
O(1)	1800(9)	4213(6)	3444(4)	65(2)
N(2)	2591(9)	873(6)	3172(5)	46(2)
N(1)	2547(10)	3355(7)	3073(5)	51(2)
C(4)	3765(23)	2902(14)	851(7)	98(6)
C(5)	1827(23)	2898(14)	869(7)	99(6)
C(3)	4264(23)	1639(25)	883(8)	148(9)
C(1)	1224(21)	1695(23)	954(9)	132(8)
C(2)	2717(44)	900(10)	967(10)	173(13)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

toward the exocyclic carbon of the Cp(Cr) ring with a twist angle of 72.2 °, while in the case of **7**, the iodine atom with a twist angle of 68.9 °. The twist angle is defined as the torsional angle between the halogen atom, the chromium atom, the Cp ring center and the ring carbon atom bearing exocyclic carbon.

The observed average bond lengths of the Cr–C(ring)$_6$ 2.215 Å for both compounds **6** and **7**, compare favorably with the 2.218 Å average found in [Cl(NO)$_2$Cr(η^5-C$_5$H$_4$)]C(CO)[(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)] [15] and the 2.20(1) Å average found in (η^5-C$_5$H$_5$)Cr(NO)$_2$Cl [16] and [(η^5-C$_5$H$_5$)Cr(CO)$_3$]$_2$ [17]. The Cr–N lengths of 1.705(5) (Cr–N(1)) and 1.712(5) (Cr–N(2)) and 1.718(5) (Cr–N(1)) and 1.705(4) Å (Cr–N(2)) of **6** and **7**, respectively, are considerably shorter than the predicted values [16] and there must be appreciable electron donation from the metal dπ-orbitals to the π^* orbitals of the nitrosyl groups. The Cr–N lengths agree well with the reported values 1.714(4) and 1.718(3) Å in [Cl(CO)$_2$Cr(η^5-

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) of **7**

	x	y	z	U_{eq} [a]
I	281(1)	2242(1)	2136(1)	58(1)
Cr	−3250(1)	2497(1)	1492(1)	37(1)
O(1)	−4905(8)	2689(7)	2759(3)	73(2)
O(2)	−3186(7)	5932(5)	1206(2)	75(2)
O(3)	−285(7)	1993(7)	−63(3)	83(2)
O(4)	−2704(6)	3636(6)	−416(2)	66(1)
N(1)	−4172(8)	2618(5)	2260(3)	46(1)
N(2)	−3158(6)	4553(5)	1354(2)	47(1)
C(5)	−4983(9)	2085(7)	458(3)	52(2)
C(1)	−3105(7)	1651(6)	412(3)	44(1)
C(2)	−2625(8)	315(6)	861(3)	54(2)
C(3)	−4180(9)	−41(7)	1195(3)	59(2)
C(4)	−5622(7)	1049(7)	947(3)	56(2)
C(11)	−1877(9)	2399(6)	−36(3)	51(2)
C(12)	−1707(10)	4431(10)	−915(3)	76(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$C_5H_4)]C(O)$ $[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ [15], 1.711 Å in $(\eta^5\text{-}C_5H_5)(NO)_2Cl$ [16], 1.712(4) Å in $(CO)_2(NO)Cr(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ [1] and 1.72(1) Å in $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NCO)$ [18]. The N≡O lengths of 1.160(7) (N(1)–O(1)) and 1.163(6) (N(2)–O(2)); and 1.169(8) (N(1)–O(1)) and 1.162(6) Å (N(2)–O(2)) of **6** and **7**, respectively, are comparable with 1.142(6) and 1.160(5) Å found in $[Cl(NO)_2Cr(\eta^5\text{-}C_5H_4)]C(O)[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ [15]. The Cr–N–O angles of 171.2(5) (Cr–N(1)–O(1)) and 172.1(4) (Cr–N(2)–O(2)) and 176.0(5) (Cr–N(1)–O(1)) and 174.3(4) Å of **6** and **7**, respectively, are not significantly different from those of 169° in $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ [16] and $[(\eta^5\text{-}C_5H_5)Cr(NO)NMe_2]_2$ [19], 170° in $[(\eta^5\text{-}C_5H_5)Cr(NO)SPh]_2$ [20] and 171° in $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NCO)$ [18]. The Cr-centroid [Cp(Cr)] distance is 1.857, 1.870 and 1.865 Å of **3**, **6** and **7** agrees with 1.859 Å in $[Cl(NO)_2Cr(\eta^5\text{-}C_5H_4)]C(O)[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ and 1.844 Å in $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$ [21]. The average C–C distance in the Cp ring is 1.320, 1.410 and 1.405 Å for **3**, **6** and **7**, respectively. The mean angle in each ring is 108°.

The organic C=O bond lengths of **6** and **7** are 1.204(7) C(11)–O(3)) 1.207(9) Å (C(11)–O(3)), respectively, and the angles at carbonyl groups (124.8(5), 112.2(5) and 118.1(5)) and (125.7(5), 112.2(5) and 118.6(5)) do not differ from normal values. The exocyclic carbons C(11) of **6** and **7** are bent towards the chromium atom with θ angles of 0.70 and 0.02°, respectively. The θ angle is defined as the angle between the exocyclic C–C bond (C(1)–C(11)) and the corresponding Cp ring with a positive angle toward metal and a negative angle away from the metal. The carbonyl plane (C(1), C(11), O(3), O(4)) turns away from the corresponding ring plane Cp(Cr) by 1.4 and 0.3°, respectively, for compounds **6** and **7**.

Supplementary material available. A list of anisotropic temperature factors of non-hydrogen atoms and the coordinates with isotropic temperature factors of hydrogen atoms as well as a list of structure amplitudes (7 and 8 pages for compounds **6** and **7**, respectively) are available. Ordering information can be obtained from the authors.

Acknowledgements

The authors are grateful to the National Science Council of the Republic of China for grants in support of this research program.

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