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Syntheses and spectra of $(CO)_2(NO)Cr(\eta^5\text{-}C_5H_4\text{-}R)$ ($R = -C(O)-N_3$, $-N=C=O$, $-NH_2$, $-NH-C(O)-O\text{-}CH_2C_6H_5$ or $-NH-C(O)-NH-(\eta^5\text{-}C_5H_4)Cr(CO)_2(NO)$) and crystal structure of $(CO)_2(NO)Cr[(\eta^5\text{-}C_5H_4)-NH-C(O)-NH-(\eta^5\text{-}C_5H_4)]Cr(CO)_2(NO)$

Yu-Pin Wang [a,*], Tso-Shen Lin [a], Yuh-Huei Yang [a], Jen-Hai Liaw [a], Sue-Lein Wang [b], Fen-Ling Liao [b], Yuh-Jy Lu [c]

[a] *Department of Chemistry, Tunghai University, Taichung, Taiwan*
[b] *Department of Chemistry, National Tsing Hua University, Tsinchu, Taiwan*
[c] *National Center for High Performance Computing, Hsinchu, Taiwan*

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Abstract

(η^5-Isocyanatocyclopentadienyl)dicarbonylnitrosylchromium(**5**) (hereafter called isocyanatocynichrodene) was prepared from cynichrodenoic acid (**2**) via the Curtius rearrangement. Hydrolysis of **5** with 20% aqueous potassium hydroxide solution gave dicynichrodenylurea (**8**) with a 40% and aminocynichrodene (**6**) with a 30% yield. The structure of **8** was solved by an X-ray diffraction study: space group, $I4_1/a$; tetragonal; $a = 20.383(4)$ and $c = 18.001(4)$; $Z = 16$. Compound **8** adopts a transoid conformation at the organic imido bridge. The dihedral angle between the two planes of imido-substituted cyclopentadienyl rings is 38.9°. The nitrosyl group in each cynichrodenyl moiety is located at the site towards the corresponding imido nitrogen atom with twist angles of 8.3° and 9.7° respectively. The chemical shifts of H(2)–H(5) protons and C(2)–C(5) carbon atoms of a series of cynichrodene derivatives have been assigned using two-dimensional HetCOR NMR spectroscopy. The assigned chemical shifts of selected monosubstituted cynichrodene derivatives were compared with the NMR data of their analogues of ferrocene and benzene derivatives. For derivatives with electron-donating substituents, an analogy was observed between the shielding of C(2,5) and C(3,4) carbon atoms of cynichrodene derivatives and ferrocene derivatives and *ortho*- and *para*-carbon atoms of benzene derivatives. For derivatives bearing electron-withdrawing substituents, the opposite correlation on the assignments was observed between cynichrodene derivatives and the derivatives of ferrocene and benzene. The electron density distribution in the cyclopentadienyl ring is discussed on the basis of ^{13}C NMR data and that of **8** is compared with the ab-initio calculations.

Keywords: Chromium

1. Introduction

Since the advent of ferrocene in the early 1950s, the syntheses and characterization of the iron derivatives of cyclopentadiene have been extensively studied [1]. However, the number of Cp–chromium compounds being studied is relatively small [2]. In the case of cynichrodene (**1**), the electrophilic aromatic substitution reaction on the Cp ring had been studied thoroughly by Rausch et al. [3] and some Cp-substituted derivatives of **1** have been reported [2].

The Cp–chromium compounds may have properties distinct from their iron analogues. Earlier [4], we reported the unequivocal assignments of C(2,5) and C(3,4) on the Cp ring of the cynichrodene derivatives bearing electron-withdrawing substituent in ^{13}C NMR spectra. The opposite correlation on the assignments between ferrocene and cynichrodene (**1**) was a surprising finding. In the case of ferrocene, the 3,4-positions are more sensitive to the electron-withdrawing substituent while, in the case of cynichrodene, the 2,5-positions are more sensitive to the electron-withdrawing substituent by resonance. This finding has prompted us to study **5–8**, the derivatives of **1** bearing electron-donating substituents.

* Corresponding author.

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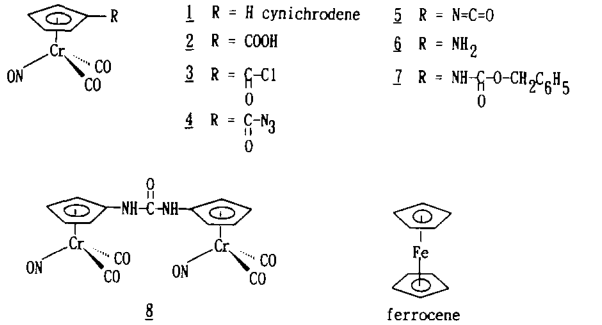


Further, while the chemistry of the dicarbonylcyclopentadienylnitrosyl complexes of chromium has become the subject of considerable study, the crystal structure and ^{13}C NMR of these complexes have not been examined thoroughly [2,5,6]. Herein we report thorough spectral studies on **1**–**8** and the crystal structure of $(CO)_2(NO)Cr[(\eta^5\text{-}C_5H_4)\text{–NH–C(O)–NH–}(\eta^5\text{-}C_5H_4)]Cr(CO)_2(NO)$ (**8**). Compound **8** appears to be the first reported X-ray structure of cynichrodene derivatives bearing a functionally electron-donating substituent. Spectral comparison between benzene, ferrocene and cynichrodene derivatives bearing corresponding substituents is also included.

2. Experimental details

All the syntheses were carried out under nitrogen by use of Schlenk techniques. Traces of oxygen in the nitrogen were removed with BASF catalyst and the deoxygenated nitrogen was dried over molecular sieves 3 Å 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. The silica gel was then stored under nitrogen until use. Cynichrodenoic acid (**2**) was prepared according to the literature procedure [2].

^1H and ^{13}C NMR were acquired on a Varian FT-NMR Unity-300 spectrometer. Chemical shifts were referenced to tetramethylsilane. IR spectra were recorded with a Perkin–Elmer Fourier transform IR 1725X spectrophotomer. Microanalyses were carried out by the Microanalytic Laboratory of the National Taiwan University.

2.1. Preparation of (η^5-azidocarbonylcyclopentadienyl)dicarbonylnitrosylchromium (cynichrodenoyl azide) (4)

Phosphorus pentachloride (0.93 g, 4.47 mmol) was added in two portions to a stirred solution of cynichrodenoic acid (**2**) (1.00 g, 4.05 mmol) in 50 ml of dry benzene. The solution was stirred for 1 h at room temperature, followed by filtration. The filtrate was concentrated under vacuum at 50°C to remove benzene and phosphorus oxychloride. Cynichrodenoyl chloride (**3**) was obtained as a dark-red residue. The residue was dissolved in 15 ml of tetrahydrofuran (THF) and treated all at once with sodium azide (0.40 g, 6.15 mmol). After stirring for 1 h at room temperature, 25 ml of ice–water was poured into the reaction mixture, and the stirring was continued for another 15 min. The reaction mixture was then extracted with three 25 ml portions of ether. The extracts were combined and dried with anhydrous magnesium sulphate. The solution was filtered and concentrated to a dark-brown residue under vacuum. The residue was extracted with hot hexane : pentane (2 : 1). The extract was concentrated to give a dark-red liquid. The liquid was dissolved in 50 ml of methylene chloride. 2 g of silica gel were added to the solution, and the solvent removed under vacuum. The residue was added to a dry-packed column (1.8 cm × 9 cm) of silica gel. Elution of the column with hexane : benzene (1 : 1) gave an orange band which upon removal of the solvent under vacuum gave cynichrodenoyl azide (**4**) (0.71 g (64%)). An analytical sample was obtained by molecular distillation at 45°C and 0.1 Torr.

Anal. Found: C, 35.55; H, 1.64; N, 20.43. $C_8H_4CrN_4O_4$ Calc.: C, 35.31; H, 1.48; N, 20.58%. IR (CH_2Cl_2): ν(intensity) 2180 (m), 2164 (vs), 2036 (vs), 1970 (vs), 1710 (vs), 1470 (s), 1380 (s), 1260 (s), 1185 (vs), 1120 (w), 1060 (s) 1044 (m), 998 (s), 898 (w), 832 (s), 670 (s) cm^{-1}. Mass spectrum: m/z 272 (M^+).

2.2. Preparation of cynichrodenyl isocyanate (5)

Cynichrodenoyl azide (**4**) (0.50 g, 1.84 mmol) was dissolved in 20 ml of benzene and the solution was refluxed for 3 h. The benzene solution was then filtered. After the filtration, the solvent was removed from the filtrate by evaporation under vacuum to give cynichrodenyl isocyanate (**5**) as a dark-brown oil (0.34 g (75%)). An analytical sample was obtained by molecular distillation at 60°C and 0.1 Torr.

Anal. Found: C, 39.40: H, 1.67; N, 11.61. $C_8H_4CrN_2O_4$ Calc.: C, 39.36; H, 1.65; N, 11.48%. IR ($CDCl_3$): ν (intensity): 2220 (vs), 2030 (vs), 1960 (vs), 1710 (vs), 1550 (m), 1490 (w), 1400 (w), 870 (s) cm^{-1}. Mass spectrum: m/z 244 (M^+).

2.3. Preparation of (η^5-aminocyclopentadienyl)dicarbonylnitrosylchromium (aminocynichrodene) (6)

Cynichrodenoyl azide (**4**) (generated in situ and used without isolation) was dissolved in 30 ml of benzene and the solution was refluxed for 3 h. The benzene solution was filtered and the solvent was then removed by evaporation under vacuum to give cynichrodenyl isocyanate (**5**) as a dark-brown oil. To the dark-brown oil, 30 ml of 20% aqueous potassium hydroxide solution was added and the mixture was refluxed for 1.5 h. The reaction mixture was then cooled and extracted with three 25 ml portions of ether and one 25 ml portion of tetrahydrofuran. The extracts were combined and dried with anhydrous magnesium sulphate. The solution was filtered and the concentrated to a brown residue. The residue was dissolved in 50 ml of methylene chloride. 2 g of silica gel were added to the solution, and the solvent was then removed under vacuum. The residue was added to a dry-packed column (1.8 cm × 9 cm) of silica gel. Elution of column with hexane : ether (3 : 1) gave a yellow–orange band which upon removal of the solvent under vacuum gave aminocynichrodene (**6**) (0.66 g (75%)). An analytical sample (melting point (m.p.), 61°C) was obtained by vacuum sublimation at 65°C and 0.1 Torr.

Anal. Found: C, 38.67; H, 2.98; N, 12.70. $C_7H_6CrN_2O_3$ Calc.: C, 38.54; H, 2.77; N, 12.84%. IR ($CDCl_3$): ν (intensity): 3420 (m), 2020 (vs), 1950 (vs), 1690 (vs), 1520 (s), 630 (s) cm^{-1}. Mass spectrum: m/z 218 (M^-).

2.4. Preparation of benzyl-N-cynichrodenyl carbamate (7)

A mixture of cynichrodenoyl azide (**4**) (1.00 g, 3.67 mmol) and benzyl alcohol (5 ml, 48.5 mmol) was heated with stirring at 100–120°C for 3 h. The unreacted benzyl alcohol was then evaporated under vacuum. The residue was dissolved in 30 ml of methylene chloride. 7 g of silica gel were added to the solution and the solvent was removed under vacuum. The residue was added to a dry-packed column (1.8 cm × 9 cm) of silica gel. Elution of the column with hexane : ether (2 : 1) gave an orange band which upon removal of the solvent under vacuum gave benzyl-*N*-cynichrodenyl carbamate (**7**) (0.9 g (73%); m.p., 125–127°C). An analytical sample was obtained by either sublimation at 140°C and 0.1 Torr or recrystallization using solvent expansion method from hexane:THF (2 : 1) at 0°C.

Anal. Found: C, 51.14; H, 3.56; N, 7.76. $C_{15}H_{12}CrN_2O_5$ Calc.: C, 51.14; H, 3.43; N, 7.95%. IR ($CDCl_3$): ν (intensity): 3400 (s), 2020 (vs), 1950 (vs), 1700 (vs), 1535 (s), 1400 (m), 1352 (m), 1232 (s), 1195 (s), 1072 (m), 1065 (m), 1035 (m), 1022 (m), 815 (m), 620 (m) cm^{-1}. Mass spectrum: m/z 324 ($(M-CO)^+$).

2.5. Preparation of dicynichrodenylurea (8)

The same procedure was followed as the preparation of aminocynichrodene except for using 10 ml of 20% aqueous potassium hydroxide solution instead of 30 ml for hydrolysis. When the column was eluted with hexane:ether (3 : 1), aminocynichrodene (**6**) (0.26 g (30%)) resulted. Further elution of the column with ether produced an orange band which upon removal of the solvent under vacuum gave dicynichrodenylurea (**8**) (0.37 g (40%)). An analytical sample (m.p., 178°C) was obtained by the solvent evaporation method from acetone.

Anal. Found: C, 39.07; H, 2.30; N, 12.10. $C_{15}H_{10}Cr_2N_4O_7$ Calc.: C, 38.96; H, 2.16; N, 12.12%. IR (KBr): ν (intensity): 3298 (m), 2009 (vs), 1914 (vs), 1678 (vs), 1573 1573 (s), 1493 (s), 1406 (m), 1258 (m), 831 (m), 637 (m) cm^{-1}. Mass spectrum: m/z 434 ($(M-CO)^+$).

2.6. X-ray diffraction analysis of 8

The intensity data were collected on a Nicolet R3m/V diffractomer with a graphite monochromator (Mo Kα radiation). θ–2θ 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.

The structure was solved by direct methods and was refined by full-matrix least-squares refinement based on F values. All the non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were positioned at calculated coordinates with a fixed isotropic thermal parameter ($U = 0.08$ Å^2). Neutral-atom scattering factors and corrections for anomalous dispersion were from [7]. All calculations were performed on a DEC microVAX II computer system using the SHELXTL-PLUS programs [8].

2.7. Ab initio molecular orbital calculation

The single point calculations of the ab-initio Hartree–Fock (3-21G*) method with the use of the geometry of X-ray experimental data were performed. Molecular orbital calculations were carried out by using the program SPARTAN [9] which also provided graphical display of molecular orbital pictures. The atomic charges [10] based on the fitting to the molecular electrostatic potential were adopted.

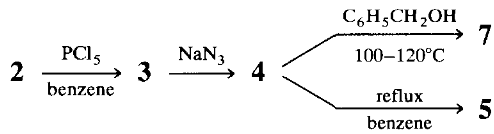
3. Results and discussion

By reacting with phosphorus pentachloride, cynichrodenoic acid (**2**) was transformed into the acid chloride **3** with a 94% yield [1]. Reaction of **3** with sodium azide

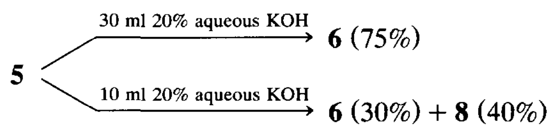
Table 1
Summary of crystal data and intensity collection of **8**

Empirical formula	$Cr_2C_{15}H_{10}N_4O_7$
Colour; habit	Yellow; rod
Crystal size (mm)	0.55 × 0.13 × 0.13
Space group	$I4_1/a$; tetragonal
Unit cell dimensions	
a (Å)	20.383(4)
c (Å)	18.001(4)
Number of reflections for indexing	13 (12.09° ≤ 2θ ≤ 27.22°)
Volume (Å^3)	7478(3)
Z	16
Formula weight	462.3
Density (calculated) (g cm^{-3})	1.642
Absorption coefficient (mm^{-1})	1.178
F(000)	3712
Diffractometer used	Siemens R3m/V
Radiation	Mo Kα (λ = 0.71073 Å)
Temperature (K)	297
Monochromator	Highly oriented graphite crystal
2θ range (°)	2.0–48.0
Scan type	θ–2θ
Scan speed (° min^{-1})	Variable; 3.26–14.65 (ω)
Scan range ω (°)	0.94 plus Kα separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Number of standard reflections	3 measured every 50 reflections
Index ranges	0 ≤ k ≤ 23 (h ≤ k), 0 ≤ l ≤ 17
Number of reflections collected	2497 (657 > 3.0σ(I))
Number of independent reflections	1782 (574 > 3.0σ((iI))
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
Number of parameters refined	253
Final R indices (observed data)	
R	0.0413
R_w	0.0355
Goodness of fit	1.42
Largest Δ/σ mean Δ/σ	0.010; 0.002
Largest difference peak (electrons Å^{-3})	0.23
Largest difference hole (electrons Å^{-3})	0.24

gave acid azide **4** with a 60% yield. Compound **4** lost nitrogen in two ways. Warming in benzyl alcohol resulted in the formation of the benzyl urethane (**7**) with a 73% yield; by refluxing in benzene, this resulted in the formation of the isocyanate **5** with a 75% yield:



When 2.0 mmol of the isocyanate **5** was subjected to the hydrolysis with 30 ml of 20% aqueous potassium hydroxide solution aminocynichrodene **6** was prepared with a 75% yield, while **8** was formed (40%) in addition to **6** (30%) when the same amount of **5** was hydrolysed in 10 ml of the 20% aqueous potassium hydroxide solution:



The nucleophilic substitution of **6** onto **5** results in the formation of **8**.

All compounds **3**–**8** exhibit two terminal carbonyl stretching bands, the symmetric mode occurring at 2009–2036 cm^{-1} and the asymmetric mode at 1914–1980 cm^{-1}. A nitrosyl stretching band is also observed at 1678–1720 cm^{-1} for all of the compounds. The following order of increasing wavenumber of CO (symmetric and asymmetric) and NO stretching was observed: **6** (2020, 1950; 1690 cm^{-1}) < **7** (2020, 1950; 1700 cm^{-1}) < **5** (2030, 1960; 1710 cm^{-1}) < **4** (2036, 1970; 1710 cm^{-1}) < **3** (2036, 1980; 1720 cm^{-1}). This trend is correlated well with the order of decreasing tendency of electron-releasing property of each substituent to the Cp ring. Other functional groups of these compounds show their characteristic absorbances.

The ^{1}H NMR spectra of **2**–**4** are consistent with their structures and similar to other metallocenyl systems (Table 2) [3,11].

Table 2
^{1}H NMR data of **1**–**8**

Compound	R	δ (ppm) (multiplicity, number of protons)		δ (ppm) (assignment)
		Cp(Cr) H(2,5)	Cp(Cr) H(3,4)	Others
1	H	5.07 (s,5)		
2	COOH	5.87 (t,2)	5.36 (t,2)	
3	C(O)Cl	5.91 (t,2)	5.23 (t,2)	
4	C(O)N_3	5.76 (t,2)	5.12 (t,2)	
5	N=C=O	5.10 (t,2)	4.92 (t,2)	
6	NH_2	4.59 (t,2)	4.79 (t,2)	3.21 (–NH_2)
7	NH–C(O)–O–$CH_2C_6H_5$	5.25 (t,2)	4.86 (t,2)	6.37 (–NH–), 5.16 (–CH_2–) 7.35 (–C_6H_5)
8	–NH–C(O)–NH–(C_5H_4)Cr(CO)$_2$(NO)	5.45 (t,4)	5.06 (t,4)	2.86, 8.19 (–NH–)

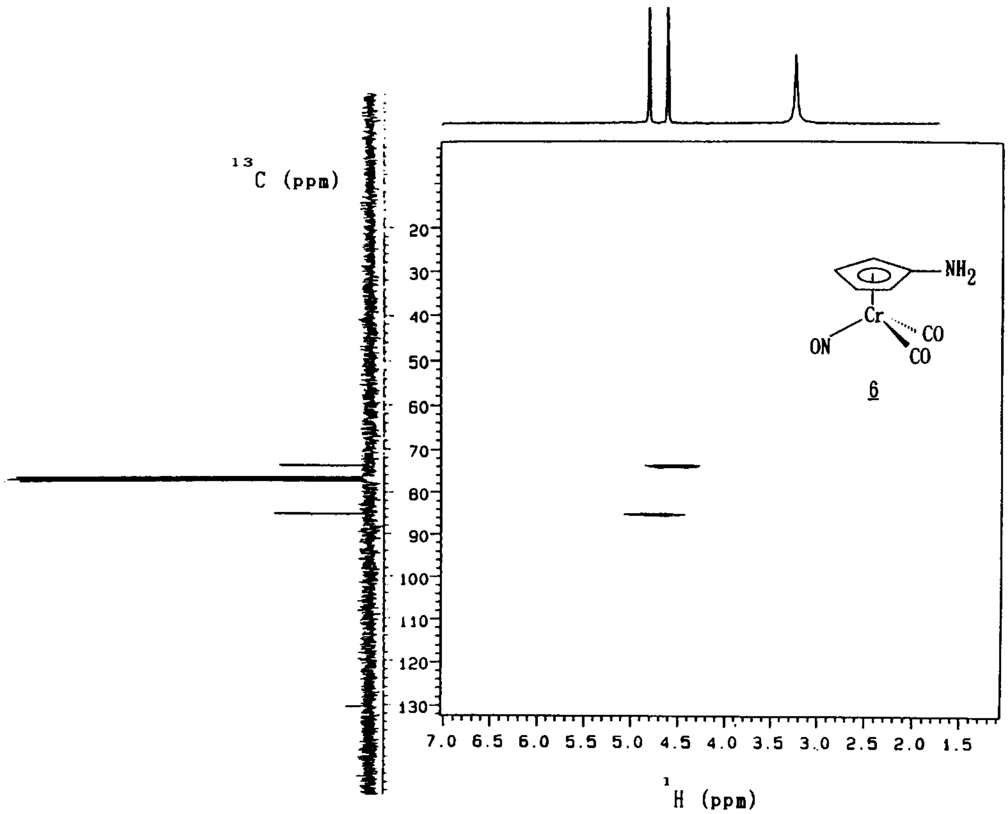


Fig. 1. 2D $^1H\{^{13}C\}$ HetCOR NMR spectrum of **6** in $CDCl_3$.

The ^1H NMR assignments for **5**–**8** were more difficult to make. Based on two-dimensional (2D) HetCOR spectra of **5**–**8** (Figs. 1 and 2 and Table 3) and the nuclear overhause effect spectrum of **6** (homodecoupling the amino protons), the ^1H NMR spectra of **5**–**8** were assigned (Table 2).

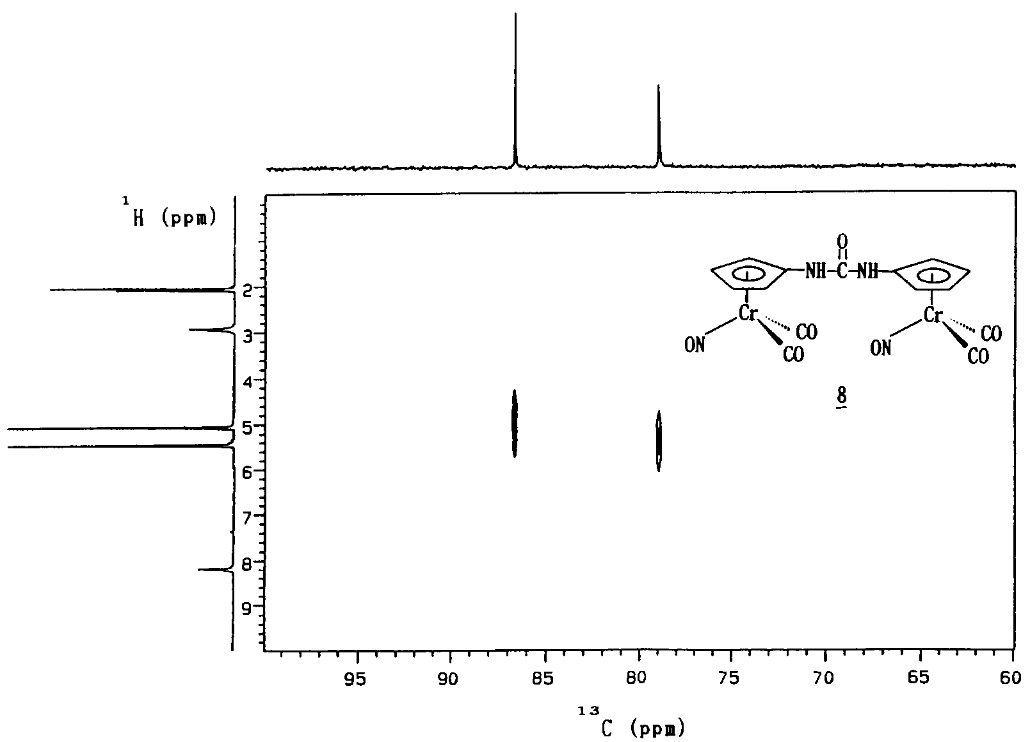


Fig. 2. 2D $^1H\{^{13}C\}$ HetCOR NMR spectrum of **8** in $(CD_3)_2CO$.

Table 3
The contracted 2D HetCOR spectra of **2–8**

Compound	R	^{1}H, Cp(Cr) [a]	2D HetCOR [b]	^{13}C, Cp(Cr) [a]
2	COOH	○ ∗	/	○ ∗
3	C(O)Cl	○ ∗	/	○ ∗
4	$C(O)N_3$	○ ∗	/	○ ∗
5	N=C=O	○ ∗	\	∗ ○
6	NH_2	∗ ○	/	∗ ○
7	$NH–C(O)–O–CH_2C_6H_5$	○ ∗	\	∗ ○
8	$NH–C(O)–NH–(C_5H_4)Cr(CO)_2(NO)$	○ ∗	\	∗ ○

[a] ○, (2,5); ∗, (3,4); the magnetic field increases towards the right.
[b] The magnetic fields of ^{1}H and ^{13}C NMR spectra increase towards the right and upper side respectively.

Table 4
^{1}H NMR chemical shifts of selected monosubstituted cynichrodene [a], ferrocene [b] and benzene [c] from tetramethylsilane and Δ [d]

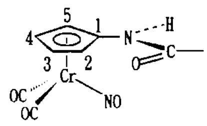
R	$(CO)_2(NO)Cr(C_5H_4–R)$			$(C_5H_5)Fe(C_5H_4–R)$			$C_6H_5–R$			
	δ (ppm)		Δ (ppm)	δ (ppm)		Δ (ppm)	δ (ppm)			Δ (ppm)
	H(2,5)	H(3,4)		H(2,5)	(3,4)		H(2)	H(3)	H(4)	
Electron-withdrawing substituents										
–CHO	$\underline{5.77}$	5.27	0.50	$\underline{4.70}$	4.47	0.23	$\underline{7.80}$	7.44	7.55	0.25
$–C(O)CH_3$	$\underline{5.72}$	5.16	0.56	$\underline{4.66}$	4.36	0.30	$\underline{7.91}$	7.38	7.48	0.43
Electron-donating substituents by resonance										
$–NH_2$	4.60	$\underline{4.81}$	−0.21	$\underline{3.83}$	3.70	0.13	6.57	7.09	$\underline{6.68}$	−0.09
–NH–C(O)–R′										
	$\underline{5.25}$	4.86	0.39	$\underline{4.36}$	3.84	0.52	$\underline{7.51}$	7.29	7.09	0.42
	$(R'=O–CH_2–C_6H_5)$			$(R'=O–CH_2–C_6H_5)$			$(R'=CH_3)$			

[a] From [2].
[b] From [11].
[c] From [12].
[d] $\Delta = \delta$ [H(2,5)] − δ [H(3,4)] for ferrocene and cynichrodene derivatives; $\Delta = \delta$ [H(2)] − δ [H(4)] for benzene derivatives. The lower-field chemical shift of each pair is underlined.

Table 5
^{13}C{H} NMR [a] of **1–8**

Compound	R	δ (ppm)					
		Cp(Cr) C(1)	Cp(Cr) C(2,5)	Cp(Cr) C(3,4)	Cr–*C*=O	C=O	Others
1	H	90.31 (C(1–5)) 237.10					
2	COOH	94.74	95.60	93.36	236.37	165.54	
3	C(O)Cl	93.96	95.35	92.12	231.27	161.99	
4	$C(O)N_3$	92.87	94.54	92.38	233.67	169.88	
5	N=C=O	85.93	84.42	86.91	236.00		132.67 (–N=*C*=O)
6	NH_2	130.54	73.89	85.13	237.90		
7	$NH–C(O)–O–CH_2C_6H_5$						67.57 ($–CH_2–$)
		118.72	78.07	85.79	236.95	153.00	128.67 (Ph, C(3,5))
							128.53 (Ph, C(4))
							128.24 (Ph., C(2,6))
							135.47 (Ph, C(1))
8	$–NH–C(O)–NH–(C_5H_4)Cr(CO)_2(NO)$						
		122.03	78.93	86.61	238.93	151.76	
			78.99				

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



Two interesting findings were observed. First, in the case of the aminocynichrodene **6**, the high field and low field chemical shifts are assigned to H(2,5) ($\delta = 4.59$ ppm) and H(3,4) ($\delta = 4.97$ ppm) respectively. The assignment is opposite to the assignment in its ferrocene analogue, aminoferrocene [11], while analogous to the assignment in its benzene analogue, aniline [12] (Table 4). The second is that the 2D HetCOR correlations of **5**, **7** and **8** are opposite to that of **6** (Table 3). Compound **6** exhibits positive slope, while **5**, **7** and **8** exhibit negative slopes. The strong diamagnetic anisotropic effect of the isocyanato or the imido carbonyl group on the ring protons might explain why the protons (2- and 5-positions) closer to it were deshielded from the lower field for **5**, **7** and **8**. Those results are in agreement with the corresponding benzene and ferrocene analogues (Table 4). Positive and relatively Δ values were observed for imido derivatives of cynichrodene, ferrocene and benzene (0.39, 0.52 and 0.42 ppm respectively) in comparison with those observed for the corresponding amino derivatives (−0.21, 0.13 and −0.09 ppm respectively) Δ is defined as equal to $\Delta\ \delta$ [H(2,5)] $-\delta$[H(3,4)] for cynichrodene and ferrocene derivatives, and equal to δ [H(2)] $-$ δ[H(4)] for benzene derivatives.

The assignments of ^{13}C NMR spectra of **4–8** (Table 5) were based on standard ^{13}C NMR correlations [13], 2D HetCOR, the DEPT technique and by comparison with other metallo-aromatic systems [14] (Table 5).

It is of interest to compare the ^{13}C NMR spectra of **2–8** with their unsubstituted parent compound **1**. For the carbon atoms on Cp(Cr) (C(3, 4) and C(2, 5)), the chemical shifts of **2–4** occur at a lower field than the chemical shifts of **1** at $\delta = 90.31$ ppm (Table 4), whereas the chemical shifts of **5–8** occur at a higher field than $\delta = 90.31$ ppm. This reflects the strong electron-with drawing effect of each substituent on **2–4** and the strong electron-donating effect of each substituent on **5–8**. It is worth pointing out from Table 5 that the chemical shifts of C(3, 4) occur at a higher field than the chemical shifts of C(2, 5) for **2–4**. On the contrary, the chemical shifts of C(3, 4) occur at a lower field than the chemical shifts of C(2, 5) for **5–8**.

Table 6 lists the ^{13}C chemical shifts for a representative group of substituted cynichrodene, ferrocene and benzene. Upon examination of this table the following conclusions may be drawn.

(a) In ferrocenes the 3,4-positions of the substituted cyclopentadienyl ring are more sensitive to electron-withdrawing substituents by resonance; the 2,5-positions are more sensitive to electron-donating groups by resonance [15].

(b) In benzenes the *para*-carbon (C(4)) atoms are more sensitive to electron-withdrawing substituents by resonance than are the *ortho*-carbon (C(2)) atoms; the *ortho*-carbon atoms are more sensitive to electron-donating groups by resonance than are the *para*-carbon atoms.

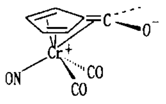
(c) In cynichrodenes the 2,5-positions of the substituted cyclopentadienyl ring are more sensitive to both electron-withdrawing and electron-donating substituents.

It is interesting to point out that the differences Δ in C(2, 5) and C(3, 4) shielding are relatively small and

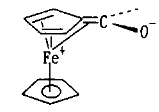
Table 6
^{13}C NMR chemical shifts of selected monosubstituted cynichrodene [a], ferrocene [b] and benzene [c] from tetramethylsilane and Δ [d]

R	$(CO)_2(NO)Cr(C_5H_4-R)$			$(C_5H_5)Fe(C_5H_4-R)$			C_6H_5-R			
	δ (ppm)		Δ (ppm)	δ (ppm)		Δ (ppm)	δ (ppm)			Δ (ppm)
	C(2, 5)	C(3, 4)		C(2, 5)	C(3, 4)		C(2)	C(3)	C(4)	
Electron-withdrawing substituents										
–COOH	95.6	93.4	2.2	70.6	72.0	−1.4	130.0	128.5	133.6	−3.6
–CHO	93.5	92.8	0.7	68.0	72.6	−4.6	129.8	129.1	134.0	−4.2
$-C(O)CH_3$	93.6	92.0	1.6	69.2	71.8	−2.6	128.6	128.5	132.7	−4.1
Electron-donating substituents by resonance										
$-NH_2$	73.9	85.1	−11.2	58.8	63.0	−4.2	115.3	129.4	118.7	−3.5
–NH–C(O)–R′	78.1	85.8	−7.7	64.7	69.0	−4.3	118.6	128.7	122.9	−4.3
	($R' = O-CH_2-C_6H_5$)	($R' = O-CH_2-C_6H_5$)		($R' = CH_3$)						

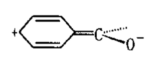
[a] From [5].
[b] From [13].
[c] From [10].
[d] $\Delta = \delta[C(2, 5)] - \delta[C(3, 4)]$ for ferrocene and cynichrodene derivatives; $\Delta = \delta[C(2)] - \delta[C(4)]$ for benzene derivatives. The lower-field chemical shift of each pair is underlined.



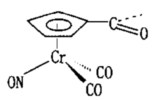
Ia



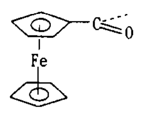
IIa



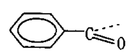
IIIa



I



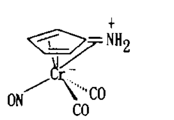
II



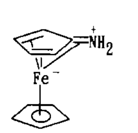
III

positive in cynichrodene derivatives (2.2, 0.7 and 1.6 ppm) bearing electron-withdrawing substituent in contrast with the negative values of Δ for the corresponding ferrocene derivative, (-1.4, -4.6 and -2.6) ppm and benzene derivatives (-3.6, -4.2 and -4.1 ppm). The smaller contribution of canonical form **Ia** than **IIa** and **IIIa** to each of the corresponding structures **I**, **II** and **III** may explain such behaviour. This is understandable in the destabilization of chromium cation because of the overall electron-withdrawing properties of CO and NO ligands. Therefore, in cynichrodenes bearing a electron-withdrawing substituent, the inductive effect that deshields the nearby carbon (C(2, 5)) atoms to a greater extent than to the more distant 3- and 4-positions may explain the observed data collected in Table 6.

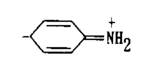
Conversely, relatively large negative differences Δ in C(2, 5) and C(3, 4) shielding were observed in cynichrodene derivatives (-11.2 and -7.7 ppm) bearing electron-donating substituent as compared with the values of Δ for their ferrocene analogues (-4.2 and -4.3 ppm) and benzene analogues (-3.5 and -4.3 ppm). The larger contribution of canonical form IVa than Va and VIa to each of the corresponding structures IV, V and VI may explain such behaviour.



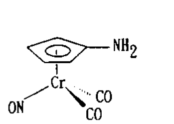
IVa



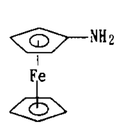
Va



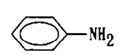
VIa



IV



V



VI

Table 7
Selected net atomic charges of **8**

C(11) 0.23	C(12) -0.31	C(13) -0.27	C(14) -0.22	C(15) -0.26
C(21) 0.31	C(22) -0.44	C(23) -0.04	C(24) -0.33	C(25) -0.24

An important advantage of the ^{13}C NMR method over ^{1}H NMR spectroscopy is the relatively lower sensitivity of ^{13}C chemical shifts to the effects of magnetically anisotropic groups and ring current [15]. In acylcynichrodenes, acylferrocenes, and acylbenzenes the circulating π electrons of the C=O bond deshield the ring protons closest to the substituents. Thus positive values of Δ are observed as listed in Table 4 for derivatives with electron-withdrawing substituents. The anisotropic effect apparently overwhelms the substituent effects for the ring protons in their chemical shifts. Therefore ^{13}C NMR spectra provide a clearer picture of the electron density distribution within a molecule than do proton NMR spectra. Thus, to obtain the unequivocal assignments of C(2, 5) and C(3, 4) on the Cp ring, the use of 2D HetCOR NMR spectroscopy is highly recommended, especially for metals coordinated with ligands bearing strong electron-withdrawing property.

The unequivocal assignments of ^{13}C chemical shifts for **8** were correlated well with the ab-initio calculations from the X-ray data of **8**. The average charges of C(2, 5) and C(3, 4) are -0.313 and -0.215 (Table 7) respectively.

The molecular structure of **8** is shown in Fig. 3. The atomic coordinates of the non-hydrogen atoms are listed in Table 8. Selected bond distances and angles are given in Table 9.

Compound **8** adopts a transoid conformation at the organic urea carbon atom. The coordination geometry about each of the Cr centres is approximately a distorted tetrahedron with two carbonyl groups, the Cp group and nitrosyl group as the four coordination sites. The nitrosyl groups of both of cynichrodenyl moieties are located at the side toward the exocyclic nitrogen atom of $Cp^{1}(Cr)$ and $Cp^{2}(Cr)$ with twist angles of 8.3° (Fig. 4(a)) and 9.7° (Fig. 4(b)) respectively. The twist angle is defined

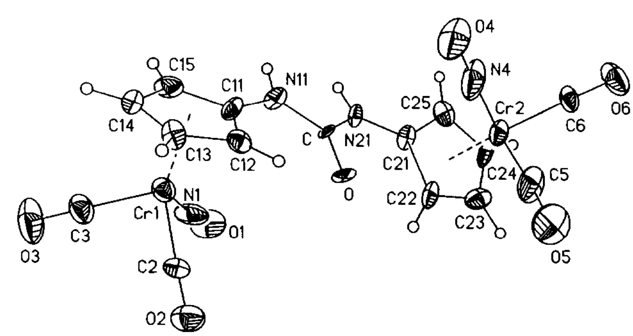


Fig. 3.

Table 8
Atomic coordinates and equivalent isotropic displacement coefficients

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq} [a] ($\times 10^{-3}$ Å^2)
Cr(1)	3777(2)	8749(2)	190(2)	62(2)
Cr(2)	975(2)	11242(2)	−201(2)	66(2)
O	2348(6)	10004(5)	247(7)	53(6)
O(1)	4163(9)	10067(7)	−294(9)	114(8)
O(2)	3937(7)	8986(7)	1798(8)	95(7)
O(3)	5118(6)	8216(8)	15(13)	162(10)
O(4)	753(12)	11166(15)	1442(13)	193(14)
O(5)	642(7)	9893(7)	−519(12)	151(11)
O(6)	−320(6)	11767	−460(11)	141(9)
N(1)	4016(9)	9541(9)	−63(10)	84(9)
N(11)	2592(6)	9416(8)	−783(8)	53(6)
N(21)	2207(6)	10447(8)	−898(8)	44(6)
N(4)	838(13)	11193(13)	789(18)	166(16)
C	2368(8)	9951(10)	−428(12)	33(8)
C(2)	3885(9)	8880(10)	1187(13)	53(8)
C(3)	4590(8)	8415(10)	98(15)	84(11)
C(5)	766(9)	10423(10)	−353(15)	106(13)
C(6)	187(8)	11562(8)	−360(15)	80(12)
C(11)	2822(10)	8843(11)	−421(13)	57(10)
C(12)	2705(9)	8622(10)	310(12)	53(9)
C(13)	3035(9)	8002(10)	372(13)	60(10)
C(14)	3360(9)	7879(9)	−288(15)	70(10)
C(15)	3238(9)	8388(11)	−787(13)	68(10)
C(21)	1956(10)	11038(10)	−721(13)	46(9)
C(22)	2030(8)	11365(13)	−9(15)	65(11)
C(23)	1730(11)	11971(14)	−96(16)	72(12)
C(24)	1454(11)	12036(11)	−765(17)	79(12)
C(25)	1597(9)	11465(12)	−1138(13)	65(9)

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

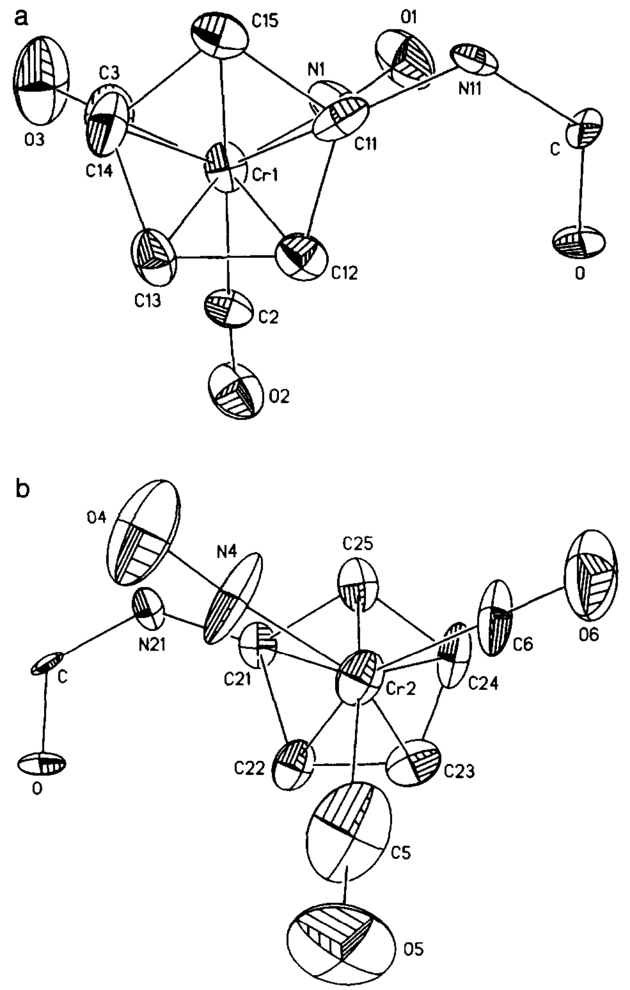


Fig. 4. Views of part of **8** along the normal of (a) the Cp(Cr(1)) ring and Cr(1), and (b) the Cp(Cr(2)) ring and Cr(2).

as the torsional angle between the nitrosyl nitrogen atom, the chromium atom, the Cp ring centre and the ring carbon atom bearing the exocyclic nitrogen atom.

In the cynichrodene moieties, the observed average bond lengths of Cr–C(ring) are 2.195(22) Å (Cp^1(Cr)), 2.177(25) Å (Cp^2(Cr)), in good agreement with those found in (η^5-C_5H_5)–Cr(CO)$_2$NO(**9**)(2.188(5) Å) [16], [(η^5-C_5H_5)Cr–(CO)$_3^-$]$_2$ (**10**) (2.20(1) Å) [17] and (η^5-C_5H_5)Cr(NO)$_2$Cl (**11**) (2.20(1) Å) [18]. The Cr–N lengths of 1.747(18) Å (Cr(1)–N(1)) and 1.807(33) Å (Cr(2)–N(4)) are longer than the values found in (CO)$_2$(NO)Cr(η^5-C_5H_4)C(O) (η^5-C_5H_4)Fe(C_5H_5) (**12**) (1.712(4) Å) [4] and in (η^5-C_5H_5)Cr(NO)$_2$(NCO) (**13**) (1.716(3) Å) [19]. The Cr–C (carbonyl) distances of 1.828(23) Å (Cr(1)–C(2)), 1.798(18) Å (Cr(1)–C(3)), 1.745(21) Å (Cr(2)–C(5)) and 1.758(17) Å (Cr(2)–C(6)) are shorter than the values found in [(η^5-C_5H_5)Cr-(CO)$_3$]$_2$ (1.861 Å) (**10**) [17] and (η^5-$C_{13}H_9$)Cr(CO)$_2$-(NO) (1.864 (6) Å) (**14**) [16]. The N=O bond lengths of 1.187(23) Å (N(1)–O(1)) and 1.189(40) Å (N(4)-O(4)) are longer than the C–O bond lengths of 1.126(27) Å (C(2)–O(2)), 1.160(22) Å (C(3)–O(3)), 1.149(25) Å (C(5)–O(5)) and 1.130(20) Å (C(6)–O(6)). This difference is expected as a result of the greater antibonding populations in the nitrosyl ligands than those in the carbonyl ligands. The Cr–N–O angles of 174.5(16)° (Cr(1)–N(1)–O(1)) and 179.3(27)° (Cr(2)–N(4)–O(4)), are consistent with the NO$^+$ formalism typical of linear M–NO linkage. The Cr–C–O angles of 177.0(18)° (Cr(1)–C(2)–C(2)), 177.2(19) (Cr(1)–C(3)–O(3)), 173.8(25)° (Cr(2)–C(5)–O(5)) and 179.8(25)° (Cr(2)–C(6)–O(6)) indicate the usual mode of bonding in the terminal metal carbonyl complexes. The Cr-centroid (Cp(Cr)) distances of 1.843 Å (Cr(1)–centroid (Cp^1(Cr)) and 1.840 Å (Cr(2)–centroid (Cp^2(Cr)) agree with the values of 1.844 Å in **9** [14] and 1.846 Å in **12** [4]. The average C–C distances in the ring (Cp(Cr)) are 1.409(33) Å (Cp^1(Cr)) and (1.382(40) Å (Cp^2(Cr)). The mean angles in the rings are 108°. Selected structural data of **8** and **10–14** are listed in Table 10.

The organic C–O bond length is 1.220(25) Å (C–O) and the angles at the carbonyl group are 113°, 123° and

124°. The exocyclic nitrogen atoms N(11) and N(21) are bent away from the corresponding Cr atom, with angles θ of -2.0 and $-2.1°$ respectively. The angle θ is defined as the angle between the exocyclic C–N bond and the corresponding Cp ring with positive angle towards metal and negative angles away from the metal. The carbonyl plane (N(11), C, O, N(21)) turns away from the ring planes Cp^1(Cr) and Cp^2(Cr) by 20.5° and 21.3° respectively. The dihedral angle between the two planes Cp^1 (Cr) and Cp^2(Cr) is 38.9°.

4. 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 list of

Table 9
Selected bond distances (Å) and angles (°) of **8**

Bond distances			
Cr(1)–C(11)	2.243(22)	Cr(1)–C(12)	2.212(18)
Cr(1)–C(13)	2.171(19)	Cr(1)–C(14)	2.147(21)
Cr(1)–C(15)	2.200(22)	Cr(2)–C(21)	2.245(21)
Cr(2)–C(22)	2.191(17)	Cr(2)–C(23)	2.146(25)
Cr(2)–C(24)	2.144(25)	Cr(2)–C(25)	2.517(22)
C(11)–C(12)	1.410(31)	Cr(11)–C(15)	1.419(30)
C(12)–C(13)	1.436(27)	C(13)–C(14)	1.384(33)
C(14)–C(15)	1.394(32)	C(21)–C(25)	1.362(31)
C(21)–C(22)	1.451(35)	C(22)–C(23)	1.387(36)
C(23)–C(24)	1.336(40)	C(24)–C(25)	1.375(34)
Cr(1)–N(1)	1.747(18)	Cr(1)–C(2)	1.828(23)
Cr(1)–C(3)	1.798(18)	Cr(2)–N(4)	1.807(33)
Cr(2)–C(5)	1.745(21)	Cr(2)–C(6)	1.758(17)
N(1)–O(1)	1.187(23)	C(2)–O(2)	1.126(27)
C(3)–O(3)	1.160(22)	N(4)–O(4)	1.189(40)
C(5)–O(5)	1.149(25)	C(6)–O(6)	1.130(20)
C(11)–(11)	1.418(26)	C(21)–N(21)	1.348(26)
C–N(11)	1.343(25)	C–N(21)	1.159(26)
C–O	1.220(25)	Cr(1) ··· centroid(Cp^1)	1.843
Cr(2) ··· centroid(Cp^2)	1.840	Cr(1) ··· N(11)	3.275
Cr(2) ··· N(21)	3.258		
H(C(12)) ··· O	2.525	H(C(22)) ··· O	2.488
C(12) ··· O	2.911	C(22) ··· O	2.887
C(12) ··· C	3.094	C(22) ··· C	3.058
C(15) ··· H(N(11))	2.630	C(25) ··· H(N(21))	2.661
H(C(15)) ··· H(N(11))	2.575	H(C(25)) ··· H(N(21))	2.719
H(N(11)) ··· H(N(21))	2.053		
Bond angles			
C(11)–C(12)–C(13)	105.9(18)	C(12)–C(13)–C(14)	108.5(19)
C(12)–C(11)–C(15)	109.0(19)	C(13)–C(14)–C(15)	109.4(18)
C(11)–C(15)–C(14)	107.1(20)	C(21)–C(22)–C(23)	105.3(21)
C(22)–C(21)–C(25)	104.4(19)	C(22)–C(23)–C(24)	112.0(24)
C(23)–C(24)–C(25)	105.5(22)	C(21)–C(25)–C(24)	112.6(22)
N(1)–Cr(1)–C(2)	95.0(9)	N(1)–Cr(1)–C(3)	93.9(9)
C(2)–Cr(1)–C(3)	92.0(10)	N(4)–Cr(2)–C(5)	93.7(12)
N(4)–Cr(2)–C(6)	92.3(12)	C(5)–Cr(2)–C(6)	96.1(8)
Cr(1)–N(1)–O(1)	174.5(16)	Cr(1)–C(2)–O(2)	177.0(18)
Cr(1)–C(3)–O(3)	177.2(19)	Cr(2)–N(4)–O(4)	179.2(27)
Cr(2)–C(5)–O(5)	173.8(25)	Cr(2)–C(6)–O(6)	179.8(25)
N(11)–C(11)–C(12)	129.5(19)	N(11)–C(11)–C(15)	121.5(19)
N(21)–C(21)–C(22)	125.5(20)	N(21)–C(21)–C(25)	130.1(22)
N(11)–C–O	123.8(18)	N(21)–C–O	123.1(18)
N(11)–C–N(21)	112.9(18)	C(11)–N(11)–C	124.2(17)
C(21)–N(21)–C	127.5(17)	Centroid(Cp^1)–Cr(1)–N(1)	123.7
Centroid(Cp^1)–Cr(1)–C(2)	120.5	Centroid(Cp^1)–Cr(1)–C(3)	124.5
Centroid(Cp^2)–Cr(2)–N(4)	121.1	Centroid(Cp^2)–Cr(2)–C(5)	120.1
Centroid(Cp^2)–Cr(2)–C(6)	127.1		

Table 10
Selected structural data of **8** and **10–14**

Compound	Bond length (Å)						
	Cr–C(ring)	Cr–NO	Cr–CO	N=O	C=O	Cr–N–O	Cr–C–O
8	2.195(22)	1.747(18)	1.798(18)	1.187(23)	1.126(27)	174.5(16)	177.0(18)
			1.828(23)		1.160(22)		177.2(19)
	2.177(25)	1.807(33)	1.745(21)	1.189(40)	1.130(20)	179.2(27)	173.8(25)
			1.758(17)		1.149(25)		179.8(25)
10	2.20(1)	–	1.861	–	1.143(3)	–	172.0(2)
							172.9(2)
							178.7(2)
11	2.20(1)	1.711	–	1.128(19)	–	166.4	–
				1.152(19)		170.8	
12	2.205(5)	1.712(4)	1.864(4)	1.178(5)	1.135(5)	179.4(3)	179.0(4)
			1.846(4)		1.135(5)		177.2(4)
13	2.200(4)	1.716(3)	–	1.157(3)	–	178.6(6)	–
14	2.233	1.687(7)	1.864(6)	1.169(9)	1.145(6)	178.9(7)	179.0(6)

8, $(CO)_2(NO)Cr[(\eta^5\text{-}C_5H_4)\text{-}NH\text{-}C(O)\text{-}NH\text{-}(\eta^5\text{-}C_5H_4)]Cr(CO)_2(NO)$; **10**, $[(\eta^5\text{-}C_5H_5)Cr\text{-}(CO)_3]_2$; **11**, $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$; **12**, $(CO)_2(NO)Cr(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$; **13**, $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NCO)$; **14**, $(\eta^5\text{-}C_{13}H_9)Cr(CO)_2NO$.

structure amplitudes (7 pages) have been deposited. Ordering information can be obtained from the authors.

Acknowledgments

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