



# Unequivocal assignments of C(2,5) and C(3,4) on the Cp ring of cynichrodene derivatives bearing an electron-donating substituent in $^{13}\text{C}$ NMR spectra and X-ray structures of $(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Ru}(\eta^5\text{-C}_5\text{H}_5)$ and $(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Ru}(\eta^5\text{-C}_5\text{H}_5)$

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## ABSTRACT

Friedel–Crafts acylation of ruthenocene with  $(\eta^5\text{-chloroformylcyclopentadienyl})\text{dicarbonylnitrosylchromium}$  **15** has afforded cynichrodene ruthenocenylic ketone **6** in 39% yield. Reduction of **6** and acetylcynichrodene **11** with lithium aluminum hydride/aluminum chloride leads to cynichrodene ruthenocenylic methane **8** and ethylcynichrodene **2** in 45% and 63% yield, respectively. Structures of compound **6** and **8** have been solved by X-ray diffraction studies. Both cisoid and transoid conformations at the organic carbonyl carbon were observed in **6**. The twist angle is  $177.2^\circ$ ,  $105.8^\circ$ ,  $72.3^\circ$ , and  $24.4^\circ$  for NO ligand of  $\text{Cp}(\text{CO})_2(\text{NO})$  moiety in **5**, transoid **6**, cisoid **6**, and **8**, respectively. Compared the HetCOR NMR data of **6–8** with those of their ferrocene analogues, the opposite correlation was observed on the chemical shift assignments of C(2)–C(5) of  $\text{Cp}(\text{Cr})$  in compound **5** and **6**, while the correlation in compound **7** and **8** is the same. The electron density distribution in the cyclopentadienyl ring is discussed on the basis of  $^{13}\text{C}$  NMR data and those of **5**, **8**, and **9** are compared with the calculations via density functional B3LYP correlation–exchange method.

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## 1. Introduction

Electronic effects of substituents can affect organometallic molecules in diverse ways [1]. Usually, loci near the substituent are most influenced, but often electron density is altered several bonds removed from the substituent. In metallocene and similar systems, the substituent may exert its effects homoannularly, interannularly, or via metal–ring interaction. Two distinct approaches to the elucidation of homoannular electronic effects within the transition metal–complexed aromatic ring have been utilized: (1) relative site reactivities and (2) NMR spectroscopy. Because of the relative availability of many ferrocene derivatives considerable attention has been devoted to this system. In several instances results for the ferrocene system have provided a basis for the analysis of electronic effects in related organometallic  $\pi$ -complexes [2]. However, from our earlier studies [3,4], two facts emerge quite clearly: electronic effects in metallocene systems do not parallel systematically with such effects in aromatic hydrocarbons and the electronic effects in the various metallocene systems may not parallel one another. For instance, the unequivocal assignments of C(2,5) and

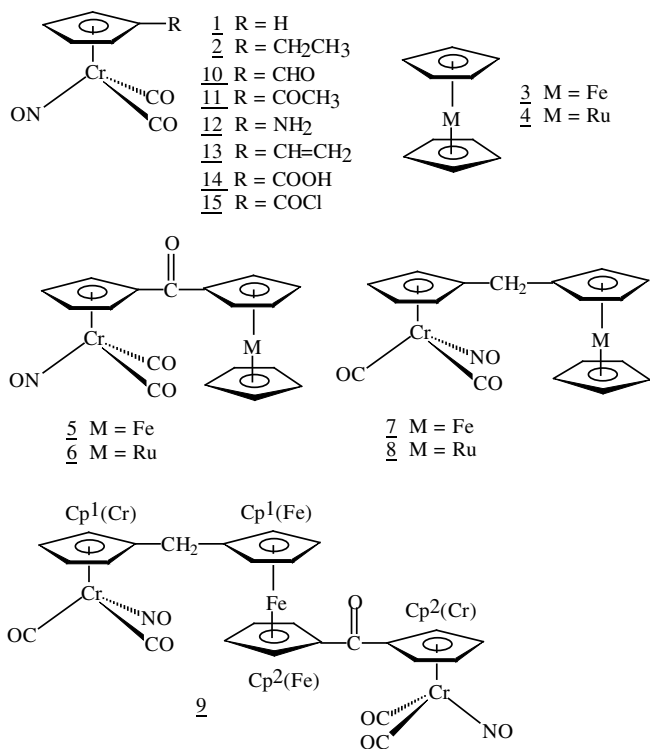
C(3,4) on the Cp ring of the (cyclopentadienyl)dicarbonylnitrosylchromium (hereafter called cynichrodene) derivatives bearing electron-withdrawing substituent in  $^{13}\text{C}$  NMR spectra were made and the opposite correlation on the assignments between ferrocene and cynichrodene was observed. The exact contributions of the various metal atoms, bearing diverse ligands, to the overall electron density distribution on the Cp ring in such molecules and the theory behind it are imponderable.

The opposite orientation between the NO ligand and the  $\pi$ -donor or the  $\pi$ -acceptor substituent on the Cp ring of monosubstituted cynichrodene derivatives was also discovered [5]. The nitrosyl group is located at the side toward the  $\pi$ -donor substituent, while trans oriented to the  $\pi$ -acceptor substituent [6]. The qualitative relationship of nonplanarity of Cp-exocyclic carbon to substituent  $\pi$ -donor and  $\pi$ -acceptor interactions have also been addressed. The  $\pi$ -donor substituents and the ipso-carbon atoms to which they are attached are bent away from the  $\text{Cr}(\text{CO})_2\text{NO}$  fragments while the  $\pi$ -acceptor substituents and the ipso-carbon atoms to which they are attached are approximately in the Cp plane or are bent slightly toward the  $\text{Cr}(\text{CO})_2\text{NO}$  fragments. The magnitudes and directions of these distortions of the Cp planarity appear to be due primarily to electronic effects [7]. In hopes of confirming those hypotheses and the validity of them to the

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inductively electron-donating substituents, compounds **5–9**, containing ferrocene or ruthenocene, were studied. The exploration of the ruthenocene derivatives came from the impetus that Rc is more effective than Fc at charge delocalization [8].

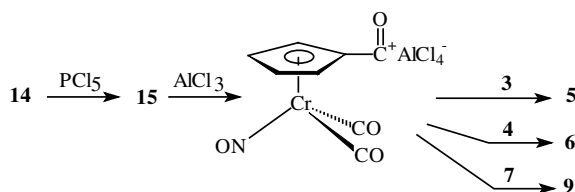
Herein, we report thorough spectral studies on **1–13**, and the crystal structures of  $(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{-Ru}(\eta^5\text{-C}_5\text{H}_5)$  **6** and  $(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{-Ru}(\eta^5\text{-C}_5\text{H}_5)$  **8**.



## 2. Results and discussion

### 2.1. Synthesis and characterization

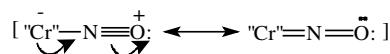
By reacting with phosphorus pentachloride, cynichrodenoic acid **14** [9] was transformed into the acid chloride **15** which in turn formed the Perrier-type complex [10] with aluminum chloride that subsequently reacted with **3**, **4**, or **7** to result in the corresponding ketone **5**, **6**, or **9** in 72, 39, and 21% yield, respectively [11,12].



Reduction of **5**, **6**, and **11** with 1/1 lithium aluminum hydride/aluminum chloride led to the hydrogenolysis products cynichrodenylferrocenylmethane **7**, cynichrodenylruthenocenylmethane **8** and ethylcynichrodenoic acid **2** in 41%, 45%, and 63% yield, respectively [13].

### **6** (**5**, **11**) $\xrightarrow{\text{LiAlH}_4/\text{AlCl}_3}$ **8** (**7**, **2**)

The IR data for complexes **1–2** and **5–9** in the CO and NO regions are listed in Table 1. All complexes exhibit two carbonyl stretching bands, the symmetric mode occurring at 2010–2030 cm<sup>-1</sup> and the asymmetric mode at 1937–1965 cm<sup>-1</sup>. A nitrosyl stretching band is also observed at 1685–1710 cm<sup>-1</sup>. It is interesting to note that lower CO and NO stretching frequencies for ruthenium complexes **6** and **8** were observed, compared to their corresponding iron analog **5** and **7**. The stronger electron-withdrawing ferrocenyl group than ruthenocenyl depletes greater extent of the electron density from Cr atom, decreasing the tendency of  $\pi$  back-bonding from Cr  $d\pi$ -orbitals to the  $\pi^*$  orbitals of NO groups, higher frequencies of NO result. Other functional groups of these compounds show their characteristic absorbances.



The <sup>1</sup>H and <sup>13</sup>C NMR spectra for complexes **1–9** are listed in Tables 2 and 3 [3,4,12]. It is of interest to compare the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2** and **5–8** with their unsubstituted parent compound **1**. For nuclei on Cp(Cr), the chemical shifts of **5** and **6** occur at a lower field than those chemical shifts of **1** at  $\delta$  5.07 and 90.31 ppm for <sup>1</sup>H and <sup>13</sup>C, respectively, whereas the chemical shifts of **2**, **7**, and **8** occur at a higher field. The depletion of electron density of Cp(Cr) by the strong electron-withdrawing carbonyl substituent explains the trend observed between **5**, **6**, and **1**. The higher field chemical shifts for **2** and **7**, **8**, and Cp<sup>1</sup>(Cr) of **9**, relative to their parent compound **1**, indicates that those substituents,  $-\text{CH}_2\text{CH}_3$ ,  $-\text{[CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Fe}[\eta^5\text{-}(\text{C}_5\text{H}_5)]$ ,  $-\text{[CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Ru}[\eta^5\text{-}(\text{C}_5\text{H}_5)]$ , and  $-\text{[CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Cr}(\text{CO})_2(\text{NO})$ , on the Cp(Cr) ring are inductively electron-donating groups.

The assignments of <sup>13</sup>C NMR spectra of **2** and **5–9** were based on standard <sup>13</sup>C NMR correlation [14–17], 2D HetCOR, the DEPT technique and by comparison with other metallo-aromatic systems [18,19]. Figs. 1–3 display the 2D <sup>1</sup>H{<sup>13</sup>C} HetCOR NMR spectrum of  $[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{CH}_3]\text{Cr}(\text{CO})_2(\text{NO})$  (**2**),  $(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Ru}[\eta^5\text{-}(\text{C}_5\text{H}_5)]$  (**6**), and  $(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Ru}[\eta^5\text{-}(\text{C}_5\text{H}_5)]$  **8**, respectively. It is interesting to note that 2D HetCOR correlations of **2** and **8** are the same. Both exhibit positive slope. Accordingly, alternative of assignments could be made: one is that both H(2,5) and C(2,5) were assigned lower field than H(3,4) and C(3,4). The other is that both H(2,5) and

**Table 1**  
IR spectra of **1**, **2** and **5–8**.

		$\nu(\text{CO})$	$\nu(\text{NO})$
<b>1</b>	$[\eta^5\text{-}(\text{C}_5\text{H}_5)]\text{Cr}(\text{CO})_2(\text{NO})^a$	2025	1955 1695
<b>2</b>	$(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{CH}_3]^b$	2010	1940 1685
<b>5</b>	$(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Fe}[\eta^5\text{-}(\text{C}_5\text{H}_5)]^c$	2030	1965 1710
<b>6</b>	$(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Ru}[\eta^5\text{-}(\text{C}_5\text{H}_5)]^c$	2020	1952 1701
<b>7</b>	$(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Fe}[\eta^5\text{-}(\text{C}_5\text{H}_5)]^d$	2020	1955 1700
<b>8</b>	$(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Ru}[\eta^5\text{-}(\text{C}_5\text{H}_5)]^d$	2020	1937 1692
<b>9</b>	$(\text{CO})_2(\text{NO})\text{Cr}[(\eta^5\text{-C}_5\text{H}_4)\text{-CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{-C}(\text{O})\text{-}(\eta^5\text{-C}_5\text{H}_4)]\text{Cr}(\text{CO})_2(\text{NO})^e$	2014 <sup>e</sup>	1946 <sup>e</sup> 1698 <sup>e</sup>

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>, from [6].

<sup>b</sup> Neat.

<sup>c</sup> In CH<sub>2</sub>Cl<sub>2</sub>.

<sup>d</sup> In CDCl<sub>3</sub>.

<sup>e</sup> Broad.

**Table 2**  
<sup>1</sup>H NMR data.

Compound	Cp(Cr)		Cp <sup>1</sup> (Fe or Ru)		Others
	H(2,5)	H(3,4)	H(2,5)	H(3,4)	
<b>1</b> [ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]Cr(CO) <sub>2</sub> (NO)	5.07 (s, 5)				
<b>2</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-CH <sub>2</sub> CH <sub>3</sub> ]	4.92 (t, 2)	4.98 (t, 2)			2.31 (-CH <sub>2</sub> ), 1.13 (-CH <sub>3</sub> )
<b>3</b> [ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]Fe[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	4.04 (s, 10)				
<b>4</b> [ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]Ru[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	4.56 (s, 10)				
<b>5</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-C(O)-( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Fe[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	5.82 (t, 2)	5.15 (t, 2)	4.83 (t, 2)	4.54 (t, 2)	4.23 (Cp <sup>2</sup> (Fe))
<b>6</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-C(O)-( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Ru[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	5.78 (t, 2)	5.14 (t, 2)	5.15 (t, 2)	4.82 (t, 2)	4.64 (Cp <sup>2</sup> (Ru))
<b>7</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-CH <sub>2</sub> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Fe[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	4.87 (t, 2)	4.94 (t, 2)	4.11 (t, 2)	4.09 (t, 2)	4.10 (Cp <sub>2</sub> (Fe)), 3.29 (-CH <sub>2</sub> -)
<b>8</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-CH <sub>2</sub> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Ru[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	4.92 (t, 2)	4.99 (t, 2)	4.55 (t, 2)	4.48 (t, 2)	4.51 (Cp <sub>2</sub> (Ru)), 3.16 (-CH <sub>2</sub> -)
<b>9</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-CH <sub>2</sub> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Fe[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-C(O)-( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Cr(CO) <sub>2</sub> (NO)	4.85 (t, 2)	4.90 (t, 2)	4.18 (s, 5)		3.21 (-CH <sub>2</sub> -)
	5.82 <sup>a</sup> (t, 2)	5.16 <sup>a</sup> (t, 2)	4.79 <sup>b</sup> (t, 2)	4.50 <sup>b</sup> (t, 2)	

<sup>a</sup> For Cp<sup>2</sup>(Cr).<sup>b</sup> For Cp<sup>2</sup>(Fe).**Table 3**  
<sup>13</sup>C{<sup>1</sup>H} NMR data.

Compound	Cp(Cr)			Cp <sup>1</sup> (Fe or Ru)			Cr(CO)	C=O	-CH <sub>2</sub> -	Others	
	C(1)	C(2,5)	C(3,4)	C(1)	C(2,5)	C(3,4)					
<b>1</b> [ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]Cr(CO) <sub>2</sub> (NO)	90.31 (C(1-5))						237.1				
<b>2</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-CH <sub>2</sub> CH <sub>3</sub> ]	116.16	88.62	89.11								
<b>3</b> [ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]Fe[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	67.88 (C(1-5))										
<b>4</b> [ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]Ru[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	69.97 (C(1-5))										
<b>5</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-C(O)-( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Fe[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	103.03	93.89	91.06	78.39	70.43	72.25	234.76	192.52		70.24 (Cp <sup>2</sup> (Fe))	
<b>6</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-C(O)-( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Ru[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	103.49	93.67	91.00	83.07	72.03	73.57	234.85	190.69		72.50 (Cp <sup>2</sup> (Ru))	
<b>7</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-CH <sub>2</sub> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Fe[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	113.41	88.66	90.09	86.17	68.47	67.73	237.62		28.59	68.68 (Cp <sup>2</sup> (Fe))	
<b>8</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-CH <sub>2</sub> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Ru[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )]	113.34	88.67	90.19	90.10	70.97	69.88	237.42		28.60	70.78 (Cp <sup>2</sup> (Ru))	
<b>9</b> (CO) <sub>2</sub> (NO)Cr[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-CH <sub>2</sub> -( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Fe[( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )-C(O)-( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Cr(CO) <sub>2</sub> (NO)	112.73	88.78	90.24	88.03	70.31	70.71	237.21	192.18	27.57		
	102.9 <sup>a</sup>	94.07 <sup>a</sup>	91.27 <sup>a</sup>	78.90 <sup>b</sup>	71.20 <sup>b</sup>	73.18 <sup>b</sup>	234.70 <sup>a</sup>				

<sup>a</sup> For Cp<sup>2</sup>(Cr).<sup>b</sup> For Cp<sup>2</sup>(Fe).

C(2,5) were assigned higher field than H(3,4) and C(3,4). Based on the previous finding [3] that in the cynichrodene the 2, 5-positions of the substituted cyclopentadienyl ring are more sensitive to electron-donating substituents, the unambiguous assignments for compounds **2** and **8** were made. In the case of **2**, C(2,5) and C(3,4) of Cp(Cr) resonates at  $\delta$  88.62 and 89.11 ppm, respectively, and for compound **8**,  $\delta$  88.67 and 90.19 ppm were assigned to C(2,5) and C(3,4), respectively.

Unfortunately, the X-ray structure of **2** was not obtained, the comparison between those of **8** and **9** were made instead. The unequivocal assignments of <sup>13</sup>C chemical shifts for **8** and **9** were correlated well with the ab initio calculations from the X-ray data of **8** and **9**. The average charges of C(2,5) and C(3,4) on Cp(Cr) are -0.2046 and -0.1870 for compound **8**, on Cp<sup>1</sup>(Cr) are -0.1980 and -0.1750 for compound **9** (Table 4). Conversely, the average charges of C(2,5) and C(3,4) on Cp(Cr) of compound **5** are -0.1367 and -0.1755, on Cp<sup>2</sup>(Cr) of **9** are -0.1504 and -0.1772. For derivatives bearing electron-donating substituents on the Cp ring, the electron density on C(2,5) are higher than those on C(3,4); while for derivatives bearing electron-withdrawing substituents, the electron density on C(2,5) are lower than those on C(3,4).

Given the unequivocal assignments for C(2,5) and C(3,4) and 2D HetCOR correlation spectra, the unequivocal assignments for H(2,5) and H(3,4) on Cp rings of compounds **2** and **7–9** were made. For compound **2**, H(2,5) and H(3,4) of Cp(Cr) resonates at  $\delta$  4.92 and 4.98 ppm, respectively, and in the case of **8**,  $\delta$  4.92 and 4.99 ppm were assigned to H(2,5) and H(3,4), respectively.

Two interesting findings were observed. First, from Table 5, the contracted 2D HetCOR spectra, all compounds, except **13**, exhibit positive slopes. However, the chemical shifts assignments are completely inverse. The chemical shifts of H(2,5) and C(2,5) occur at a lower field than the chemical shifts of H(3,4) and C(3,4) for **5**, **6**, **10**,

**11**, and Cp<sup>2</sup>(Cr) of **9**, however, the chemical shifts of H(2,5) and C(2,5) occur at a higher field than the chemical shifts of H(3,4) and C(3,4) for **2**, **7**, **8**, **12**, and Cp<sup>1</sup>(Cr) of **9**. It reveals that in cynichrodene the 2–5 positions of the substituted cyclopentadienyl ring are more sensitive to electron-donating substituents, regardless of whether it is through resonance or through inductive effect. The strong diamagnetic anisotropic effects of the vinyl group on the protons might explain why the protons (2- and 5-positions) closer to it were deshielded to the lower field for compound **13**. Second, from Table 6, the high field and low field chemical shifts of ethylcynichrodene **2** and **8** are assigned to H(2,5) ( $\delta$  = 4.92, 4.92) and H(3,4) ( $\delta$  = 4.98, 4.99), respectively. This is opposite to the assignment in its ferrocene analogue, ethylferrocene [2] and its benzene analogue, ethylbenzene [20,21].

Table 7 lists the <sup>13</sup>C chemical shifts for a representative group of substituted cynichrodene, ferrocene, and benzene. Upon examination of this table the following conclusions may be drawn [3,4].

In both cynichrodene and ferrocene the 2,5-positions of the substituted cyclopentadienyl ring are more sensitive to electron-donating substituents, either by resonance or by inductive effect. However, to the electron-withdrawing substituent the opposite correlation on the assignments between ferrocenes and cynichrodene was observed, in the case of ferrocene, the 3,4-positions are more sensitive, while in the case of cynichrodene the 2,5-positions are more sensitive.

A significant advantage of the <sup>13</sup>C NMR method over <sup>1</sup>H NMR spectroscopy is the relatively lower susceptibility of <sup>13</sup>C chemical shifts to the effects of magnetically anisotropic groups and ring current [1]. In acylcynichrodene, acylferrocene, and acylbenzene the circulating  $\pi$  electrons of the C=O bond deshield the ring protons closest to the substituents. Thus positive values of  $\Delta$  are

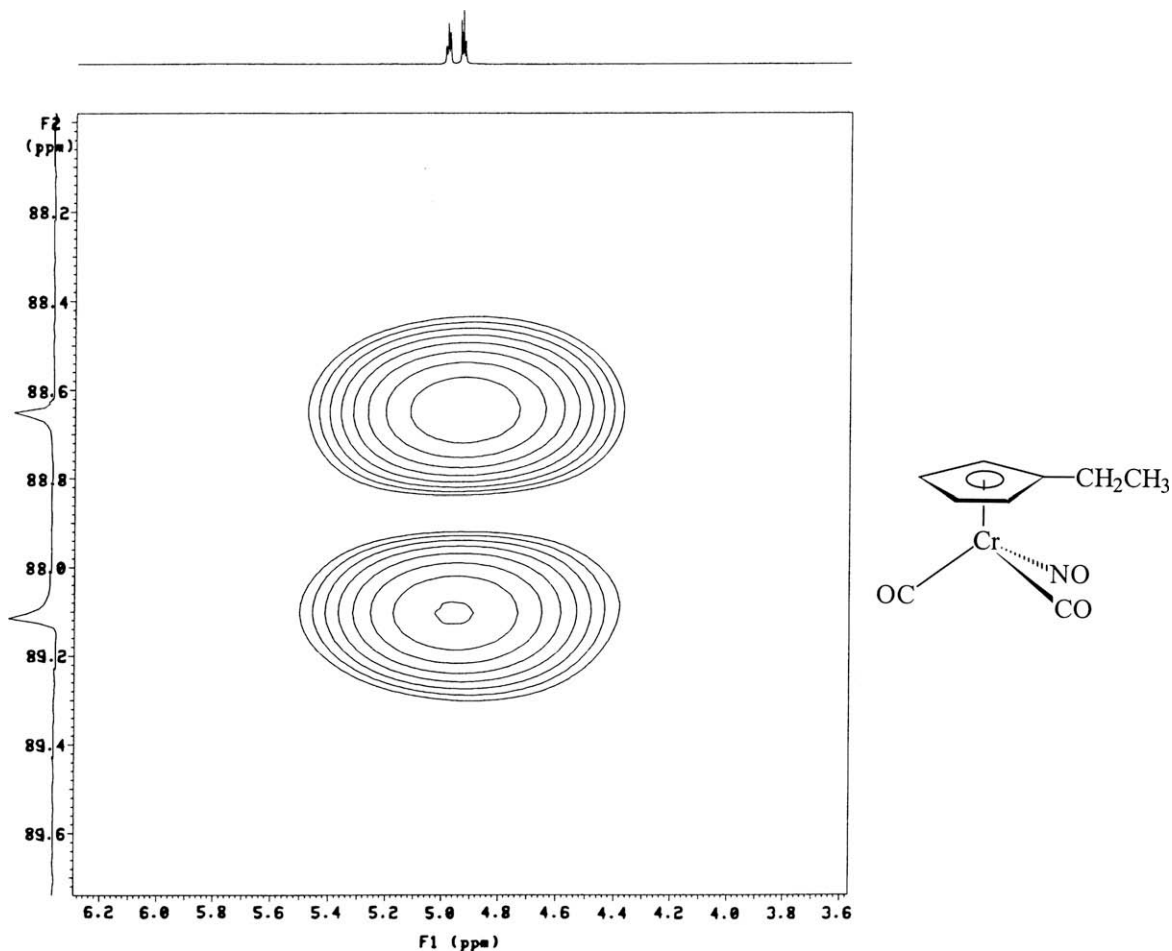


Fig. 1. 2D  $^1\text{H}\{^{13}\text{C}\}$ HetCOR NMR spectrum of **2** in  $\text{CDCl}_3$ .

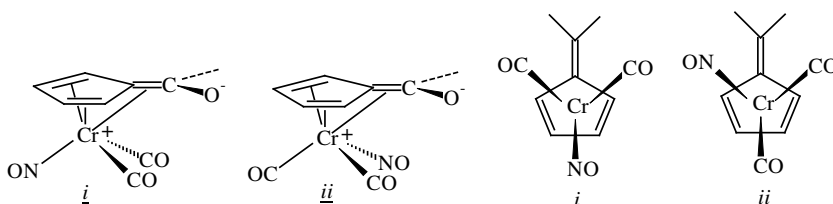
observed as listed in Table 6 for derivatives with electron-withdrawing substituents. The anisotropic effect apparently overwhelms the substituent effects for the ring protons in their chemical shifts. Therefore  $^{13}\text{C}$  NMR spectra (Table 7) provide a clearer picture of the electron density 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 very instructive.

The molecular structures of **5**, transoid **6**, cisoid **6**, and **8** are shown in Figs. 4–7, respectively. Selected bond distances and angles are given in Tables 8–10 for transoid **6**, cisoid **6**, and **8**.

Compound **5** adopts a transoid conformation at the organic carbonyl carbon. Both transoid and cisoid conformations were observed in **6**.

The transoid conformation is defined as a conformer in which the two metal atoms oriented themselves at the opposite sides of the Cp–C(O)–Cp plane. For the cisoid conformation, the two metal atoms were oriented at the same side of the plane. The coordination geometry about the Cr center is approximately a distorted tetrahedron with two carbonyl groups, the Cp group and nitrosyl group as the four coordination sites.

For  $\text{Cp}(\text{Cr}(\text{CO})_2(\text{NO}))$  moiety of **5**, several important features are observed [11]. The nitrosyl group is located at the site away from the exocyclic organic carbonyl carbon with a twist angle of  $177.2^\circ$  (Fig. 4). The twist angle is defined as the torsional angle between the nitrosyl nitrogen atom, the chromium atom, the Cp center and the ring carbon atom bearing the exo-



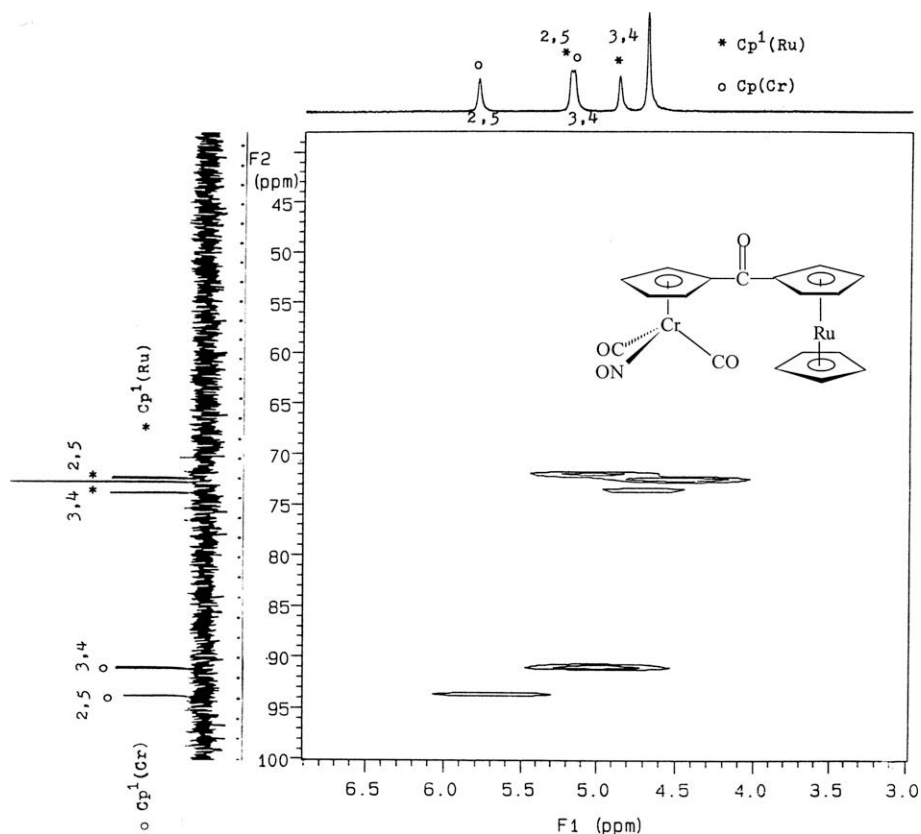
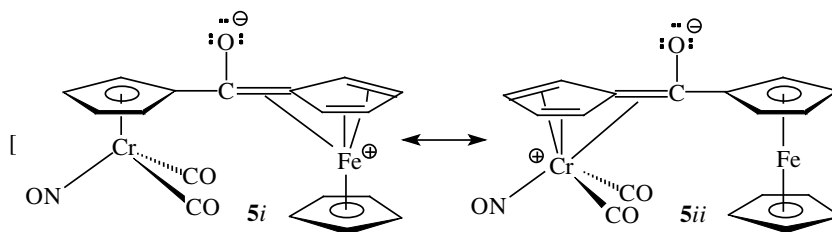


Fig. 2. 2D  $^1\text{H}\{^{13}\text{C}\}$ HetCOR NMR spectrum of **6** in  $\text{CDCl}_3$ .

cyclic carbon atom (C21). The preference for the symmetrical isomer *i* to the unsymmetrical isomer *ii* may be related to the ability of the exocyclic double bond to donate electron density to the chromium atom (reestablishing the favored 18-electron count) such that it is trans to the better  $\pi$ -accepting ligand, i.e.  $\text{NO}^+$  [14]. As a result, the twist angle of the nitrosyl nitrogen is  $177.2^\circ$  and exocyclic carbon of **5** is bent toward the chromium atom with a  $\theta$  angle of  $1.06^\circ$ . The  $\theta$  angle is defined as the angle between the exocyclic C–C bond (C21–C) and the corresponding Cp ring with a positive angle toward metal and a negative angle away from the metal. The relatively short bond length of Cr–N (1.712(4)) in **5** vs.

vs. 1.171(14), 1.167(15), and 1.174(12) in transoid **6**, cisoid **6**, and **8** (Table 11), consistently demonstrate that there is an electron flow from the exocyclic double bond to Cr atom which in turn  $\pi$ -back bonds to  $\pi^*$  orbitals of nitrosyl groups to give longer N–O bond lengths.

The exocyclic C–C bond of Cp(Cr) ring in **5** is 1.477(5) Å (C21–C), considerably shorter than those found in transoid **6** (1.529(13) Å) (C11–C4), cisoid **6** (1.506(14) Å) (C41–C8), **8** ((1.502(11) Å) (C11–C), and **9** (1.512(8) Å), but is comparable with that found in  $(\eta^5\text{-C}_5\text{H}_4\text{-CHO})\text{Cr}(\text{CO})_2(\text{NO})$  (1.470(8) Å)[5]. The contribution of canonical form **5ii** to compound **5** may account for the difference.



1.804(11), 1.842(12), and 1.757(9) in transoid **6**, cisoid **6**, and **8**, and a relatively longer N≡O bond length (1.178(5)) in **5**

It is interesting to find the difference between the two transoid structures of **5** and **6** (Table 11). Given that the exocyclic C–C

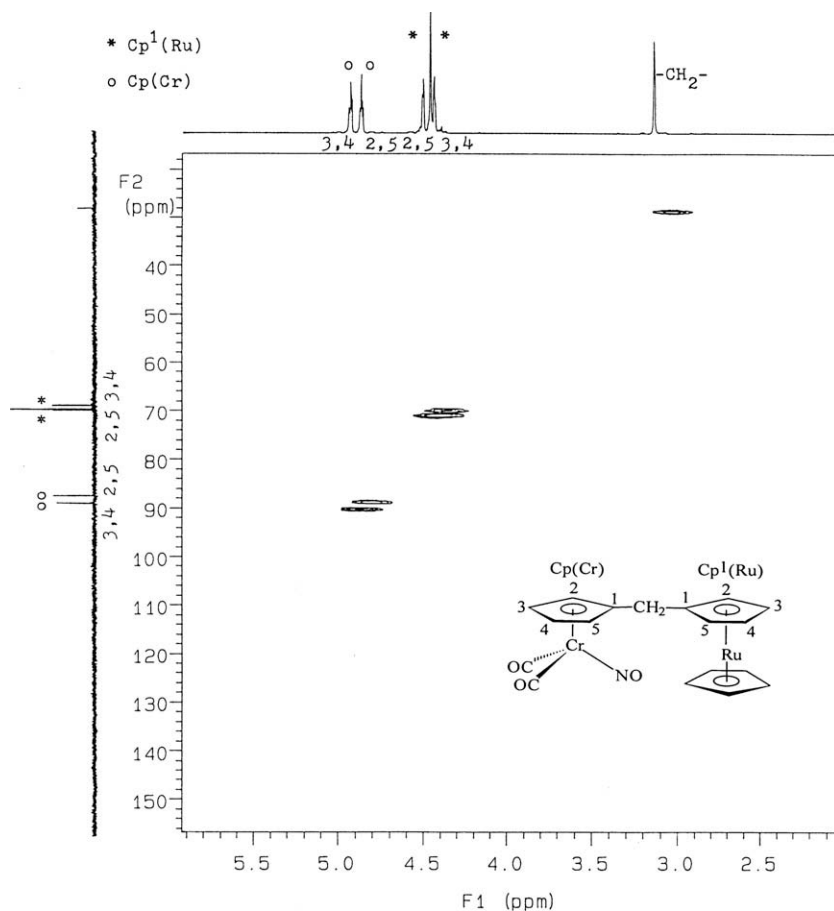
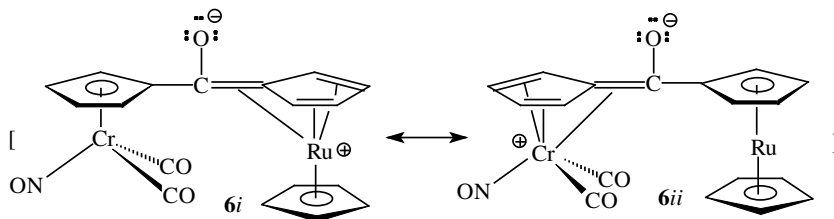


Fig. 3. 2D  $^1\text{H}(^{13}\text{C})\text{HetCOR}$  NMR spectrum of **8** in  $\text{CDCl}_3$ .

bond of Cp(Ru) and Cp(Cr) in **6** are 1.466(14) (C21–C4) and 1.529(13) Å (C11–C4), respectively, a predominant weight was assigned to canonical form **6i** and an insignificant weight to **6ii**. The outer valence electrons of ruthenium atom are much more shielded from the nucleus by the extra shell of electrons, d and f electrons, therefore much easier to be pushed around and more basic, than those of the iron atom. As a result, the ruthenocenyl

ishes the extent of resonance between the carbonyl and Cp(Cr) in **6**. This leads the longer exocyclic C–C bond length of Cp(Cr) (1.529(13) Å in **6** vs. 1.477(5) Å in **5**), a smaller  $\theta$  ( $-1.8^\circ$  in **6** vs.  $1.06^\circ$  in **5**), a larger dihedral angle between the carbonyl plane and the corresponding Cp(Cr) ( $8.98^\circ$  in **6** vs.  $1.58^\circ$  in **5**), and a larger deviation of twist angle ( $105.8^\circ$  in **6** vs.  $177.2^\circ$  in **5**) from  $180^\circ$ .



group is more effective than ferrocenyl group at charge delocalization [8]. Compared to the resonance exerted in **5**, the more effective resonance between the carbonyl and Cp(Ru) ring dimin-

The contribution of canonical form **6i** to **6** to some extent was revealed by the carbon–carbon bond lengths in the Cp<sup>1</sup>(Ru). The shorter bond lengths in Å of C(2)–C(3) (1.366(16)), C(3)–C(4)

**Table 4**

Selected net atomic charges of Cp(Cr)(CO)<sub>2</sub>(NO) moiety for **5**, **8** and **9** using the LANL2DZ basis set.

	C(1)	C(2)	C(3)	C(4)	C(5)
<b>5</b>	-0.14832	-0.12879	-0.18885	-0.16216	-0.14456
<b>8</b>	0.00746	-0.19335	-0.20279	-0.17123	-0.21581
<b>9</b> Cp <sup>1</sup> (Cr) (-CH <sub>2</sub> -)	-0.02443	-0.19296	-0.16276	-0.18724	-0.20304
Cp <sup>2</sup> (Cr) (-C(O)-)	-0.15024	-0.16731	-0.16771	-0.18665	-0.13355

(1.388(18)) and C(4)–C(5) (1.417(17)), and longer bond lengths of C(1)–C(2) (1.472(14)) and C(1)–C(5) (1.434(15)) were obtained. As well, the same trend was found in both Cp(Cr) and Cp<sup>1</sup>(Fe) of compound **5** [11], the shorter bond lengths in Å of C(2)–C(3) (1.404(6), 1.414(6)), C(3)–C(4) (1.411(7), 1.405(8)), and C(4)–C(5) (1.407(6), 1.407(7)), and longer bond lengths of C(1)–C(2) (1.435(5), 1.432(6)) and C(1)–C(5) (1.435(6), 1.433(6)), consistently demonstrating that both canonical forms, **5i** and **5ii**, have some extent of contribution to **5**.

### 3. Experimental details

All the syntheses were carried out under nitrogen by the use of Schlenk techniques. Traces of oxygen in the nitrogen were removed with BASF catalyst and deoxygenated nitrogen was dried over molecular sieves (3 Å) and P<sub>2</sub>O<sub>5</sub>. Hexane, pentane, benzene, and dichloromethane were dried over calcium hydride and freshly distilled under nitrogen. 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 1 h to remove water and oxygen. The silica gel was then stored under nitrogen until use. Compounds **11** and **14** were prepared according to the literature procedures [9]. Compounds **5** [11], **7** [13], and **9** [12], including the X-ray diffraction analyses data, had been reported previously in the literature.

**Table 5**

The contracted 2D HetCOR spectra of (CO)<sub>2</sub>(NO)Cr(C<sub>5</sub>H<sub>4</sub>-R).

R		<sup>1</sup> H, Cp(Cr) <sup>a</sup>	2D HetCOR <sup>b</sup>	<sup>13</sup> C, Cp(Cr) <sup>a</sup>
-CHO	<b>10</b>			
-C(O)CH <sub>3</sub>	<b>11</b>			
-NH <sub>2</sub>	<b>12</b>			
-CH=CH <sub>2</sub>	<b>13</b>			
-CH <sub>2</sub> CH <sub>3</sub>	<b>2</b>			
-C(O)Fc	<b>5</b>			
-C(O)Rc	<b>6</b>			
-[CH <sub>2</sub> (η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> )]Fe[η <sup>5</sup> -(C <sub>5</sub> H <sub>5</sub> )]	<b>7</b>			
-[CH <sub>2</sub> (η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> )]Ru[η <sup>5</sup> -(C <sub>5</sub> H <sub>5</sub> )]	<b>8</b>			
-[CH <sub>2</sub> -(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> )]Fe[(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> )-C(O)-(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> )]Cr(CO) <sub>2</sub> (NO)	<b>9</b> (Cp <sup>1</sup> (Cr))(-CH <sub>2</sub> -)			
	(Cp <sup>2</sup> (Cr))(-CO-)			

<sup>a</sup> 0, (2,5); \*, (3,4); the magnetic field increases toward the right.

<sup>b</sup> The magnetic fields of <sup>1</sup>H and <sup>13</sup>C NMR spectra increase toward the right and upper side, respectively.

**Table 6**  
<sup>1</sup>H NMR chemical shifts of selected monosubstituted cynichrodene,<sup>a</sup> ferrocene,<sup>b</sup> and benzene<sup>c</sup> from tetramethylsilane and  $\Delta$ .<sup>d</sup>

R	(CO) <sub>2</sub> (NO) <sub>2</sub> Cr(C <sub>5</sub> H <sub>4</sub> -R)			(C <sub>5</sub> H <sub>5</sub> )Fe(C <sub>5</sub> H <sub>4</sub> -R)			C <sub>6</sub> H <sub>5</sub> -R				
	$\delta$ (ppm)		$\Delta$ (ppm)	$\delta$ (ppm)		$\Delta$ (ppm)	$\delta$ (ppm)		$\Delta$ (ppm)		
	H(2,5)	H(3,4)		H(2,5)	H(3,4)		H(2)	H(3)		H(4)	
<i>Electron-withdrawing substituents by resonance</i>											
-CHO	<b>10</b>	5.77	5.27	0.50	4.70	4.47	0.23	7.80	7.44	7.55	0.25
-C(O)CH <sub>3</sub>	<b>11</b>	5.72	5.16	0.56	4.66	4.36	0.30	7.91	7.38	7.48	0.43
<i>Electron-donating substituents by resonance</i>											
-NH <sub>2</sub>	<b>12</b>	4.60	4.81	-0.21	3.83	3.70	0.13	6.57	7.09	6.68	-0.11
-CH=CH <sub>2</sub>	<b>13</b>	5.20	5.01	0.19	4.36	4.21	0.15	7.51	7.41	7.35	0.16
<i>Electron-donating substituents inductively</i>											
-CH <sub>2</sub> CH <sub>3</sub>	<b>2</b>	4.92	4.98	-0.06	3.83	3.82	0.01	7.16	7.18	7.13	0.03
-R'	<b>8</b>	4.92	4.99	-0.07	3.84	3.80	0.04	7.29	7.15	6.94	0.35
		(R' = [CH <sub>2</sub> ( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Ru[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )])			(R' = C(CH <sub>3</sub> ) <sub>3</sub> )			(R' = C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )			

<sup>a</sup> From [2].

<sup>b</sup> From [15].

<sup>c</sup> From [16,17].

<sup>d</sup>  $\Delta = \delta[\text{H}(2,5)] - \delta[\text{H}(3,4)]$  for ferrocene and cynichrodene derivatives;  $\Delta = \delta[\text{H}(2)] - \delta[\text{H}(4)]$  for benzene derivatives. The lower-field chemical shift of each pair is underlined.

**Table 7**  
<sup>13</sup>C NMR chemical shifts of selected monosubstituted cynichrodene,<sup>a</sup> ferrocene,<sup>b</sup> and benzene<sup>c</sup> from tetramethylsilane and  $\Delta$ .<sup>d</sup>

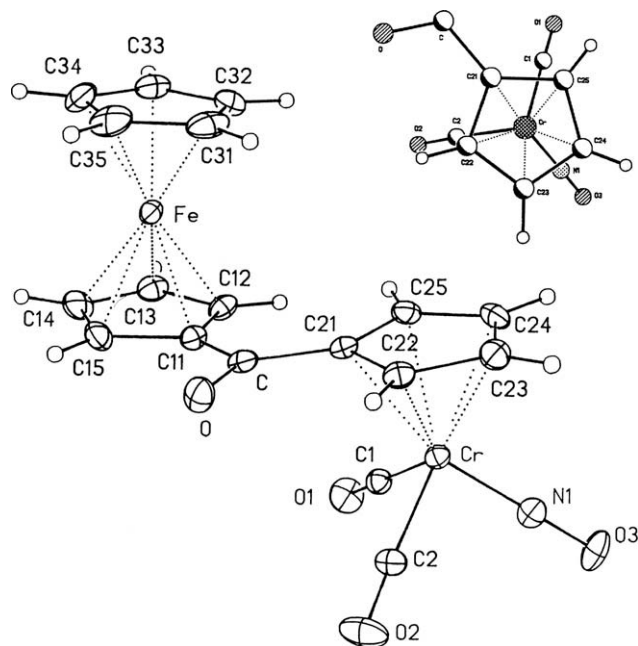
R	(CO) <sub>2</sub> (NO) <sub>2</sub> Cr(C <sub>5</sub> H <sub>4</sub> -R)			(C <sub>5</sub> H <sub>5</sub> )Fe(C <sub>5</sub> H <sub>4</sub> -R)			C <sub>6</sub> H <sub>5</sub> -R				
	$\delta$ (ppm)		$\Delta$ (ppm)	$\delta$ (ppm)		$\Delta$ (ppm)	$\delta$ (ppm)		$\Delta$ (ppm)		
	C(2,5)	C(3,4)		C(2,5)	C(3,4)		C(2)	C(3)		C(4)	
<i>Electron-withdrawing substituents by resonance</i>											
-CHO	<b>10</b>	93.5	92.8	0.7	68.0	72.6	-4.6	129.8	129.1	134.0	-4.2
-C(O)CH <sub>3</sub>	<b>11</b>	93.6	92.0	1.6	69.2	71.8	-2.6	128.6	128.5	132.7	-4.1
<i>Electron-donating substituents by resonance</i>											
-NH <sub>2</sub>	<b>12</b>	73.9	85.1	-11.2	58.8	63.0	-4.2	115.3	129.4	118.7	-3.4
-CH=CH <sub>2</sub>	<b>13</b>	88.1	89.7	-1.6	66.7	68.6	-1.9	126.1	128.3	127.6	-1.5
<i>Electron-donating substituents by inductive</i>											
-CH <sub>2</sub> CH <sub>3</sub>	<b>2</b>	88.6	89.1	-0.5	66.4	66.8	-0.4	127.8	128.5	125.9	1.9
-R'	<b>8</b>	88.7	88.7	0.0	66.4	64.7	1.7	127.8	127.8	128.4	-0.6
		(R' = [CH <sub>2</sub> ( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> )]Ru[ $\eta^5$ -(C <sub>5</sub> H <sub>5</sub> )])			(R' = C(CH <sub>3</sub> ) <sub>3</sub> )			(R' = C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )			

<sup>a</sup> From [2].

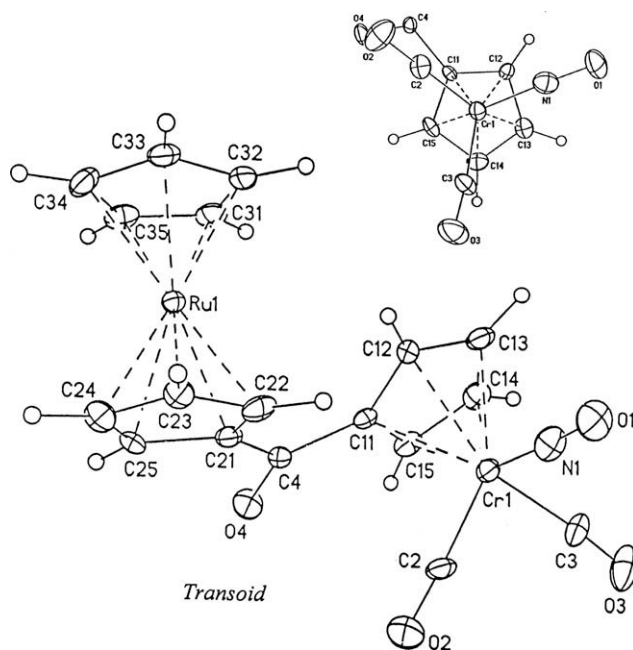
<sup>b</sup> From [3,13].

<sup>c</sup> From [16,17].

<sup>d</sup>  $\Delta = \delta[\text{C}(2,5)] - \delta[\text{C}(3,4)]$  for ferrocene and cynichrodene derivatives;  $\Delta = \delta[\text{C}(2)] - \delta[\text{C}(4)]$  for benzene derivatives. The lower-field chemical shift of each pair is underlined.



**Fig. 4.** Molecular configuration of **5** with the view along the normal of Cp(Cr) ring.



**Fig. 5.** Molecular configuration of transoid **6** with the view along the normal of Cp(Cr) ring.



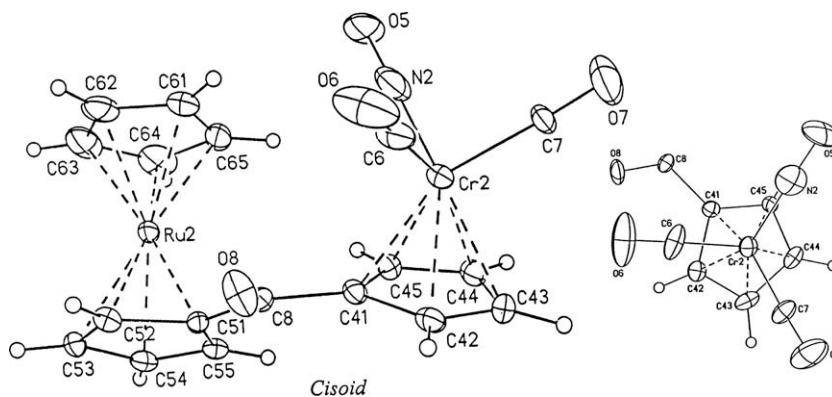


Fig. 6. Molecular configuration of cisoid **6** with the view along the normal of Cp(Cr) ring.

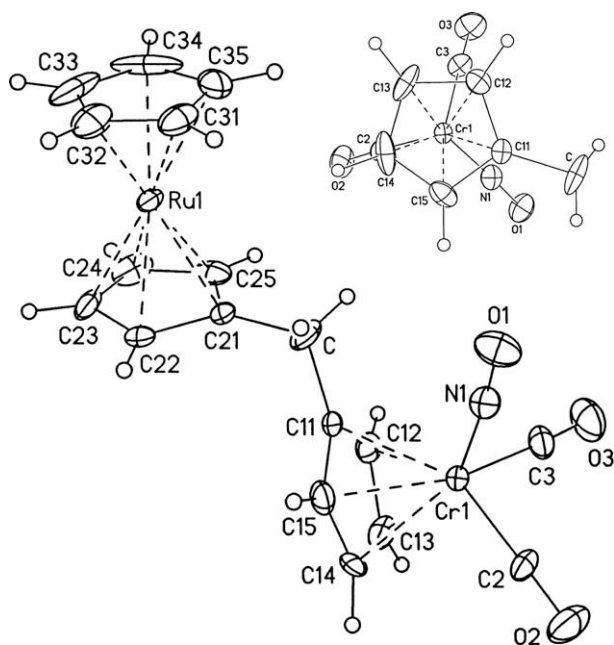


Fig. 7. Molecular configuration of **8** with the view along the normal of Cp(Cr) ring.

$^1\text{H}$  and  $^{13}\text{C}$  NMR were acquired on a Varian Unity-300 spectrometer. Chemical shifts were referenced to tetramethylsilane. IR spectra were recorded a Perkin-Elmer Fourier transform IR 1725X spectrophotometer. Microanalyses were carried out by the Microanalytic Laboratory of the National Chung Hsing University.

### 3.1. Preparation of dicarbonyl( $\eta^5$ -ethylcyclopentadienyl)-nitrosylchromium (**2**)

To a stirred suspension of lithium aluminum hydride (0.18 g, 4.6 mmol) in 30 ml of ethyl ether, aluminum chloride (0.62 g, 4.6 mmol) was added slowly. After the vigorous reaction had subsided, ( $\eta^5$ -acetylchopentadienyl)dicarbonylnitrosylchromium (**11**) (0.56 g, 2.3 mmol) in 20 ml of ethyl ether was added dropwise into so as to maintain gentle reflux. The reaction mixture was then stirred for 15 min, followed by the addition of 10 ml of ice water and 2 drops of concentrated hydrochloric acid. The solution was extracted with three 50 ml portions of dichloromethane. The combined extracts were washed three times with distilled water and dried with anhydrous magnesium sulfate. After filtration, the solution was concentrated under aspirator vacuum to 50 ml, 2 g

Table 8  
Selected bond length (Å) and selected bond angles ( $^\circ$ ) for transoid **6**.

C(11)–C(12)	1.392(13)	N(1)–Cr(1)–C(2)	94.7(5)
C(11)–C(15)	1.358(14)	N(1)–Cr(1)–C(3)	93.9(5)
C(12)–C(13)	1.424(15)	C(2)–Cr(1)–C(3)	91.7(5)
C(13)–C(14)	1.385(17)	C(11)–C(4)–C(21)	122.2(8)
C(14)–C(15)	1.405(16)	Cr(1)–N(1)–O(1)	177.1(10)
C(21)–C(22)	1.472(14)	Cr(1)–C(2)–O(2)	176.0(11)
C(21)–C(25)	1.434(15)	Cr(1)–C(3)–O(3)	175.4(10)
C(22)–C(23)	1.366(16)	C(4)–C(11)–C(12)	128.0(9)
C(23)–C(24)	1.388(18)	C(4)–C(11)–C(15)	121.8(8)
C(24)–C(25)	1.417(17)	C(4)–C(21)–C(22)	130.9(10)
C(31)–C(32)	1.380(16)	C(4)–C(21)–C(25)	124.5(9)
C(31)–C(35)	1.402(18)	C(11)–C(4)–O(4)	119.1(9)
C(32)–C(33)	1.484(16)	C(21)–C(4)–O(4)	118.6(9)
C(33)–C(34)	1.427(16)	Cp(cent.)–Cr(1)–N(1)	122.3
C(34)–C(35)	1.492(17)	Cp(cent.)–Cr(1)–C(2)	123.6
Cr(1)–N(1)	1.804(11)	Cp(cent.)–Cr(1)–C(3)	122.5
Cr(1)–C(2)	1.778(10)		
Cr(1)–C(3)	1.828(13)		
N(1)–O(1)	1.171(14)		
C(2)–O(2)	1.133(14)		
C(3)–O(3)	1.096(17)		
C(4)–C(11)	1.529(13)		
C(4)–C(21)	1.466(14)		
C(4)–O(4)	1.227(12)		
Cr(1)–cen.(Cp(Cr1))	1.844		
Cr(1)···C(4)	3.273		
Ru(1)···C(4)	3.327		
cen.(Cp <sup>1</sup> (Ru1))···cen.(Cp <sup>2</sup> (Ru1))	3.623		
H(C(12))···H(C(22))	2.381		
Cr(1)···C(Cp(Cr1)) ave.	2.192		
Ru(1)···C(Cp <sup>1</sup> (Ru1)) ave.	2.180		
Ru(1)···C(Cp <sup>2</sup> (Ru1)) ave.	2.180		
<i>Dihedral angles between planes</i>			
Cp(cent.), Cr(1), N(1) and C(11), Cp(cent.), Cr(1)		105.79	
Cp(cent.), Cr(1), C(2) and C(11), Cp(cent.), Cr(1)		16.72	
Cp(cent.), Cr(1), C(3) and C(11), Cp(cent.), Cr(1)		134.52	
Cp(Cr) and carbonyl plane(C11, C4, C21, O4)		8.98	
Cp <sup>1</sup> (Ru) and carbonyl plane(C11, C4, C21, O4)		25.70	
Cp(Cr) and Cp <sup>1</sup> (Ru)		32.91	
Cp <sup>1</sup> (Ru) and Cp <sup>2</sup> (Ru)		1.17	

of silica gel added, and the solvent again removed under vacuum. The resulting residue was added to dry-packed column (2 × 15 cm) of silica gel. Elution of the column with hexane gave a red band which upon removal of the solvent under vacuum gave dicarbonyl( $\eta^5$ -ethylcyclopentadienyl)nitrosylchromium (**2**) (0.33 g, 63%). An analytical sample was obtained by centrifugal TLC (Hexane/benzene = 1/1).

Anal. Calc. for  $\text{C}_9\text{H}_9\text{NO}_3\text{Cr}$ : C, 46.76; H, 3.92; N, 6.06. Found: C, 46.71; H, 3.91; N, 6.13%. Proton NMR( $\text{CDCl}_3$ ):  $\delta$  (relative intensity,

**Table 9**  
Selected bond length (Å) and selected bond angles (°) for cisoid **6**.

C(41)–C(42)	1.469(15)	N(2)–Cr(2)–C(6)	92.2(6)
C(41)–C(45)	1.405(14)	N(2)–Cr(2)–C(7)	91.4(5)
C(42)–C(43)	1.369(18)	C(6)–Cr(2)–C(7)	93.2(6)
C(43)–C(44)	1.479(17)	C(41)–C(8)–C(51)	120.3(9)
C(44)–C(45)	1.355(16)	Cr(2)–N(2)–O(5)	178.6(10)
C(51)–C(52)	1.420(14)	Cr(2)–C(6)–O(6)	179.0(14)
C(51)–C(55)	1.426(14)	Cr(2)–C(7)–O(7)	177.3(11)
C(52)–C(53)	1.390(16)	C(8)–C(41)–C(42)	122.2(9)
C(53)–C(54)	1.465(17)	C(8)–C(41)–C(45)	130.8(9)
C(54)–C(55)	1.382(15)	C(8)–C(51)–C(52)	124.4(9)
C(61)–C(62)	1.360(25)	C(8)–C(51)–C(55)	127.5(9)
C(61)–C(65)	1.416(22)	C(41)–C(8)–O(8)	118.1(9)
C(62)–C(63)	1.475(27)	C(51)–C(8)–O(8)	121.3(9)
C(63)–C(64)	1.434(27)	Cp(cen.)–Cr(2)–N(2)	124.9
C(64)–C(65)	1.425(22)	Cp(cen.)–Cr(2)–C(6)	121.6
Cr(2)–N(2)	1.842(12)	Cp(cen.)–Cr(2)–C(7)	124.4
Cr(2)–C(6)	1.818(13)		
Cr(2)–C(7)	1.792(12)		
N(2)–O(5)	1.167(15)		
C(6)–O(6)	1.139(17)		
C(7)–O(7)	1.095(17)		
C(8)–C(41)	1.506(14)		
C(8)–C(51)	1.468(14)		
C(8)–O(8)	1.226(13)		
Cr(2)–cen.(Cp(Cr2))	1.841		
Cr(2)···C(8)	3.309		
Ru(2)···C(8)	3.203		
cen.(Cp <sup>1</sup> (Ru2))···cen.(Cp <sup>2</sup> (Ru2))	3.625		
H(C45)···H(C55)	2.330		
Cr(2)···C(Cp(Cr2)) ave.	2.200		
Ru(2)···C(Cp <sup>1</sup> (Ru2)) ave.	2.177		
Ru(2)···C(Cp <sup>2</sup> (Ru2)) ave.	2.179		
<i>Dihedral angles between planes</i>			
Cp(cen.), Cr(2), N(2) and C(41), Cp(cen.), Cr(2)	72.31		
Cp(cen.), Cr(2), C(7) and C(41), Cp(cen.), Cr(2)	166.80		
Cp(Cr2) and carbonyl plane (C41, C8, C51, O8)	30.98		
Cp <sup>1</sup> (Ru2) and carbonyl plane (C41, C8, C51, O8)	11.81		
Cp(Cr2) and Cp <sup>1</sup> (Ru2)	38.50		
Cp <sup>1</sup> (Ru2) and Cp <sup>2</sup> (Ru2)	0.93		

multiplicity, assignment): 1.13 (3H, t,  $J = 7.5$  Hz,  $-\text{CH}_3$ ); 2.31 (2H, q,  $J = 7.5$  Hz,  $-\text{CH}_2-$ ); 4.92 (2H, t,  $J = 2.4$  Hz, Cp(Cr) H(2,5)); 4.98 (2H, t,  $J = 2.4$  Hz, Cp(Cr) H(3,4)). Carbon-13 NMR ( $\text{CDCl}_3$ ):  $\delta$  (assignment): 14.30 ( $-\text{CH}_3$ ); 21.11 ( $-\text{CH}_2-$ ); 88.62 (Cp(Cr), C(2,5)); 89.11 (Cp(Cr), C(3,4)); 116.16 (Cp(Cr), C(1)); 237.75 (Cr–C $\equiv$ O). IR(neat):  $\nu$  ( $\text{cm}^{-1}$ ) (intensity): 2010(s), 1940(s), 1685(s). Mass spectrum:  $m/z$  231(M)<sup>+</sup>.

### 3.2. Preparation of dicarbonylnitrosyl[ $\eta^5$ -(ruthenocenyl)-cyclopentadienyl]chromium (cynichrodenyl ruthenocenyl ketone) (**6**)

Cynichrodenoic acid (**14**) (0.5 g, 2.02 mmol) was stirred with phosphorus pentachloride (0.52 g, 2.5 mmol) in 50 ml of dry dichloromethane for 30 min at 0 °C. Subsequently, aluminum chloride (0.34 g, 2.5 mmol) was added and the mixture stirred for another 1 h. The solution was filtered from excess  $\text{AlCl}_3$  and the filtrate was added dropwise to a solution of ruthenocene (0.23 g, 0.99 mmol) in 25 ml dichloromethane. After the addition was completed, the reaction mixture was refluxed for 20 h. The reaction was then cooled to 0 °C and slowly hydrolyzed with 50 ml of ice followed by 5 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic portion was washed once with water, once with sodium bicarbonate solution, once again with water, and dried with anhydrous magnesium sulfate. The solution was filtered, concentrated to 50 ml under vacuum, silica gel (2 g) added, and the solvent removed under vacuum. The residue

**Table 10**  
Selected bond length (Å) and selected bond angles (°) for **8**.

C(11)–C(12)	1.413(16)	N(1)–Cr(1)–C(2)	94.3(5)
C(11)–C(15)	1.382(15)	N(1)–Cr(1)–C(3)	93.4(5)
C(12)–C(13)	1.406(14)	C(2)–Cr(1)–C(3)	92.4(5)
C(13)–C(14)	1.407(24)	C(11)–C(2)	112.4(8)
C(14)–C(15)	1.366(16)	Cr(1)–N(1)–O(1)	174.7(7)
C(21)–C(22)	1.436(12)	Cr(1)–C(2)–O(2)	177.8(11)
C(21)–C(25)	1.404(21)	Cr(1)–C(3)–O(3)	178.0(11)
C(22)–C(23)	1.400(17)	C–C(11)–C(12)	125.7(10)
C(23)–C(24)	1.369(20)	C–C(11)–C(15)	126.8(10)
C(24)–C(25)	1.392(18)	C–C(21)–C(22)	125.8(12)
C(31)–C(32)	1.310(20)	C–C(21)–C(25)	127.8(9)
C(31)–C(35)	1.324(26)	Cp(cen.)–Cr(1)–N(1)	123.6
C(32)–C(33)	1.355(32)	Cp(cen.)–Cr(1)–C(2)	123.7
C(33)–C(34)	1.374(28)	Cp(cen.)–Cr(1)–C(3)	121.3
C(34)–C(35)	1.464(28)		
Cr(1)–N(1)	1.757(9)		
Cr(1)–C(2)	1.775(12)		
Cr(1)–C(3)	1.838(11)		
N(1)–O(1)	1.174(12)		
C(2)–O(2)	1.162(15)		
C(3)–O(3)	1.127(15)		
C–C(11)	1.502(11)		
C–C(21)	1.511(14)		
Cr(1)–Cp(cen.)	1.830		
Cr(1)···C	3.287		
Ru(1)···C	3.284		
cen.(Cp <sup>1</sup> (Ru(1)))···cen.(Cp <sup>2</sup> (Ru(1)))	3.620		
Cr(1)···C(Cp(Cr)) ave	2.181		
Ru(1)···C(Cp <sup>1</sup> (Ru)) ave	2.158		
Ru(1)···C(Cp <sup>2</sup> (Ru)) ave	2.160		
<i>Dihedral angles between planes</i>			
Cp(cen.), Cr(1), N(1) and C(11), Cp(cen.), Cr(1)	24.44		
Cp(cen.), Cr(1), C(2) and C(11), Cp(cen.), Cr(1)	147.96		
Cp(cen.), Cr(1), C(3) and C(11), Cp(cen.), Cr(1)	95.20		
Cp(Cr) and Cp <sup>1</sup> (Ru)	108.49		
Cp <sup>1</sup> (Ru) and Cp <sup>2</sup> (Ru)	0.85		

was added to a dry-packed column (2 × 15 cm) of silica gel. Elution of column with benzene gave a dark red band which upon removal of the solvent under vacuum gave cynichrodenyl ruthenocenyl ketone (**6**) (0.18 g 39%). An analytical sample (red yellow crystal), m.p. 147–150 °C, was obtained by solvent expansion method from dichloromethane: pentane (1:1) at 0 °C for 48 h.

Anal. Calc. for  $\text{C}_{18}\text{H}_{13}\text{NO}_4\text{CrRu}$ : C, 46.96; H, 2.83; N, 3.04. Found: C, 46.65; H, 2.84; N, 3.09%. Proton NMR( $\text{CDCl}_3$ ):  $\delta$  (relative intensity, multiplicity, assignment): 4.64 (5H, s, Cp<sup>2</sup>(Ru)); 4.82 (2H, s, Cp<sup>1</sup>(Ru) H(3,4)); 5.14 (2H, s, Cp(Cr) H(3,4)); 5.15 (2H, s, Cp<sup>1</sup>(Ru) H(2,5)); 5.78 (2H, s, Cp(Cr) H(2,5)). Carbon-13 NMR ( $\text{CDCl}_3$ ):  $\delta$  (assignment): 72.03 (Cp<sup>1</sup>(Ru), C(2,5)); 72.50 (Cp<sup>2</sup>(Ru)); 73.57 (Cp<sup>1</sup>(Ru), C(3,4)); 83.07 (Cp<sup>1</sup>(Ru), C(1)); 91.00 (Cp(Cr), C(3,4)); 93.67 (Cp(Cr), C(2,5)); 103.49 (Cp(Cr), C(1)); 190.69 (C(O)); 234.85 (Cr–C $\equiv$ O). IR( $\text{CH}_2\text{Cl}_2$ ):  $\nu$  ( $\text{cm}^{-1}$ ) (intensity): 2020(s), 1952(s), 1701(s), 1636 (m), 1472(w), 1293(w), 804(w), 668(m). Mass spectrum:  $m/z$  432 (M–CO)<sup>+</sup>.

### 3.3. Preparation of dicarbonylnitrosyl[ $\eta^5$ -(ruthenocenylylmethyl)-cyclopentadienyl]chromium (cynichrodenylruthenocenylylmethane) (**8**)

To a stirred suspension of lithium aluminum hydride (0.06 g, 1.52 mmol) in 3 ml of ethyl ether, aluminum chloride (0.2 g, 1.5 mmol) was added slowly. After the vigorous reaction had subsided, cynichrodenyl ruthenocenyl ketone (**6**) (0.3 g, 0.65 mmol) in 4 ml of ethyl ether was added dropwise so as to maintain a gentle reflux. The reaction mixture was then refluxed for 45 min, followed by the addition of 10 ml of ice water and 2 drops of concentrated hydrochloric acid. The ether layer was separated, washed twice with water, and dried with magnesium

**Table 11**  
Selected structural data of **5**, **6** and **8**.<sup>a</sup>

Compound	Bond length (Å)		$\omega\text{Cr}^b$ (°)	$\theta\text{Cr}^c$ (°)	$\theta\text{M}$ (°) (M = Fe or Ru)	Cr–C (exocyclic)	Cr–NO	Cr–CO	N≡O	C≡O	Cr–N–O	Cr–C–O
	C(Cp(Cr))– C(exocyclic)	C(Cp(M))– C(exocyclic) (M = Fe or Ru)										
<b>5</b> (transoid)	1.477(5) (C21–C)	1.470(5) (C11–C)	177.2	1.06	5.09	3.223	1.712(4)	1.846(4)	1.178(5)	1.135(5)	179.4(3)	177.2(4)
<b>6</b> (transoid)	1.529(13) (C11–C4)	1.466(14) (C21–C4)	105.8	–1.8	0.42	3.272	1.804(11)	1.865(4)	1.171(14)	1.096(17)	177.1(10)	176.0(11)
								1.778(10)	1.133(14)	1.139(17)	175.4(10)	179.0(14)
<b>6</b> (cisoid)	1.506(14) (C41–C8)	1.468(14) (C51–C8)	72.3	–2.25	–0.24	3.309	1.842(12)	1.792(12)	1.167(15)	1.095(17)	178.6(10)	179.0(14)
								1.818(13)	1.139(17)	1.139(17)	177.3(11)	179.0(14)
<b>8</b>	1.502(11) (C11–C)	1.511(14) (C21–C)	24.4	–0.69	–1.65	3.287	1.757(9)	1.775(12)	1.174(12)	1.127(15)	174.7(7)	177.8(11)
								1.838(11)	1.162(15)	1.162(15)	178.0(11)	178.0(11)

<sup>a</sup> **5** (CO)<sub>2</sub>(NO)Cr[(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)-C(O)-(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)]Fe[η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>]; **6** (CO)<sub>2</sub>(NO)Cr[(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)-C(O)-(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)]Ru[η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>]; **8** (CO)<sub>2</sub>(NO)Cr[(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)-CH<sub>2</sub>-(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)]Ru[η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>].

<sup>b</sup>  $\omega\text{Cr}$ (°): the twist angle is defined as the torsional angle between the nitrosyl nitrogen atom, the chromium atom, the Cp center and the ring carbon atom bearing the exocyclic carbon atom.

<sup>c</sup>  $\theta\text{Cr}$ (°): the  $\theta$  angle is defined as the angle between the exocyclic C–C bond and the corresponding Cp ring with a positive angle toward metal and a negative angle away from the metal.

**Table 12**  
Selected crystal data and refinement parameters for **6**.

Empirical formula	C <sub>18</sub> H <sub>13</sub> CrNO <sub>4</sub> Ru
Formula weight (g/mol)	920.7
Temperature (K)	296
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Unit cell dimensions	
<i>a</i> (Å)	20.617(5)
<i>b</i> (Å)	12.378(2)
<i>c</i> (Å)	13.062(3)
$\beta$ (°)	96.60(2)
Volume (Å <sup>3</sup> )	3311.3(12)
<i>Z</i>	8
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.847
Absorption coefficient (mm <sup>-1</sup> )	1.591
<i>F</i> (000)	1824
Crystal size (mm)	0.44 × 0.18 × 0.16
Diffractometer used	Siemens R3m/V
Monochromator	Highly oriented graphite crystal
2 $\theta$ range (°)	2.5–50.0
Scan type	$\theta/2\theta$
Scan speed °/min in $\omega$	Variable; 2.93–14.65
Scan range $\omega$	1.00° plus K $\alpha$ -separation
Background measurement	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
Index ranges	–24 ≤ <i>h</i> ≤ 24, 0 ≤ <i>k</i> ≤ 14, 0 ≤ <i>l</i> ≤ 15
Reflections collected	6453 (4173 > 3 $\sigma$ ( <i>I</i> ))
Independent reflections	5880 (3908 > 3 $\sigma$ ( <i>I</i> ))
Extinction correction	$\chi_e = 0.00003(4)$ , where $F = F[1 + 0.002\chi_e^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0024F^2$
Final <i>R</i> indices (obs. data) (%)	<i>R</i> = 4.59, <i>R</i> <sub>w</sub> = 5.11
Goodness-of-fit	1.45
Largest and mean $\Delta/\sigma$	0.002, 0.000
Data-to-parameter ratio	8.6:1
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.71 and –0.96

sulfate. The solvent was removed under aspirator vacuum and gave a residue, which was dissolved in 50 ml of dichloromethane, 2 g of silica gel added, and the solvent again removed under vacuum. The resulting residue was added to dry-packed column (2 × 15 cm) of silica gel. Elution of the column with hexane gave a yellow band which upon removal of the solvent under vacuum gave cynichrodenylruthenocenylnmethane (**8**) (0.13 g, 45%). An

**Table 13**  
Selected crystal data and refinement parameters for **8**.

Empirical formula	C <sub>18</sub> H <sub>15</sub> CrNO <sub>3</sub> Ru
Formula weight (g/mol)	446.4
Temperature (K)	296
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pna2 <sub>1</sub>
Unit cell dimensions	
<i>a</i> (Å)	25.513(7)
<i>b</i> (Å)	11.032(3)
<i>c</i> (Å)	6.040(1)
Volume (Å <sup>3</sup> )	1700.1(7)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.744
Absorption coefficient (mm <sup>-1</sup> )	1.510
<i>F</i> (000)	888
Crystal size (mm)	0.10 × 0.12 × 0.58
Diffractometer used	Siemens R3m/V
Monochromator	Highly oriented graphite crystal
2 $\theta$ range (°)	2.5–50.0
Scan type	$\theta/2\theta$
Scan speed °/min in $\omega$	Variable; 2.44–14.65
Scan range ( $\omega$ )	1.00° plus K $\alpha$ -separation
Background measurement	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
Index ranges	0 ≤ <i>h</i> ≤ 30, 0 ≤ <i>k</i> ≤ 13, –7 ≤ <i>l</i> ≤ 0
Reflections collected	1799 (1162 > 3 $\sigma$ ( <i>I</i> ))
Independent reflections	1663 (1139 > 3 $\sigma$ ( <i>I</i> ))
Extinction correction	$\chi_e = 0.00016(4)$ , where $F = F[1 + 0.002\chi_e^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
Final <i>R</i> indices (obs. data) (%)	<i>R</i> = 3.22, <i>R</i> <sub>w</sub> = 3.01
Goodness-of-fit	1.22
Largest and mean $\Delta/\sigma$	0.006, 0.001
Data-to-parameter ratio	5.2:1
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.35 and –0.37

analytical sample, m.p. 126 °C, was obtained by solvent expansion method from dichloromethane: pentane (1:1) at 0 °C for 48 h.

Anal. Calc. for C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub>CrRu: C, 48.43; H, 3.36; N, 3.14. Found: C, 48.42; H, 3.35; N, 3.18%. Proton NMR(CDCl<sub>3</sub>):  $\delta$  (relative intensity, multiplicity, assignment): 3.16 (2H, s, CH<sub>2</sub>); 4.48 (2H, t, *J* = 1.5 Hz, Cp<sup>1</sup>(Ru) H(3,4)); 4.51 (5H, s, Cp<sup>2</sup>(Ru)); 4.55 (2H, t,

$J = 1.5$  Hz, Cp<sup>1</sup>(Ru) H(2,5)); 4.92 (2H, t,  $J = 2.1$  Hz, Cp(Cr) H(2,5)); 4.99 (2H, t,  $J = 2.1$  Hz, Cp(Cr) H(3,4)). Carbon-13 NMR (CDCl<sub>3</sub>):  $\delta$  (assignment): 28.60 (CH<sub>2</sub>); 69.88 (Cp<sup>1</sup>(Ru), C(3,4)); 70.78 (Cp<sup>2</sup>(Ru)); 70.97 (Cp<sup>1</sup>(Ru), C(2,5)); 88.67 (Cp(Cr), C(2,5)); 90.10 (Cp<sup>1</sup>(Ru), C(1)); 90.19 (Cp(Cr), C(3,4)); 113.34 (Cp(Cr), C(1)); 237.42 (Cr–C≡O). IR(CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  (cm<sup>-1</sup>) (intensity): 2021(s), 1937(s), 1692(s), 1264(m), 806(m). Mass spectrum:  $m/z$  446 (M)<sup>+</sup>.

### 3.4. X-ray diffraction analyses of **6** and **8**

The intensity data were collected on a Siemens R3m/V diffractometer using  $\omega$  scan for compounds **6** and **8**.  $\theta$ – $2\theta$  scan data were collected at room temperature (24 °C). The data were corrected for absorption, Lorentz and polarization effects. The absorption correction is according to the empirical psi rotation. In a single crystal of **6**, an asymmetric unit contain both transoid and cisoid forms. The details of crystal data and intensity collection are summarized in Tables 12 and 13 for compound **6** and **8**, respectively.

The structures were solved by direct methods and were refined by full matrix least squares refinement based on  $F$  values. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms were positioned at calculated coordinate with a fixed isotropic thermal parameter ( $U = U(\text{attached atom}) + 0.01 \text{ \AA}^2$ ). Atomic scattering factors and corrections for anomalous dispersion were from *International Tables for X-ray Crystallography* [22]. All calculations were performed on a PC computer using SHELX software package [23].

### 3.5. Computational method

Calculations based on DFT are carried out using B3LYP hybrid method involving three-parameter Becke exchange functional [24] and a Lee–Yang–Parr correlation functional [25]. All calculations are performed using the GAUSSIAN-03 program [26]. The geometries for **5**, **8** and **9** are taken from the crystallographic data. The atomic charges have been analyzed using the natural population analysis (NPA) which yields reliable atomic charges and natural bond orbital (NBO) calculations [27]. An important feature of the NBO method is that the presence of diffuse functions in the basis sets does not affect the results.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.041.

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