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Synthesis, spectra and crystal structure of $(CO)_2(NO)Cr(\eta^5\text{-}C_5H_4)CH_2(\eta^5\text{-}C_5H_4)Fe[vinyl\text{-}(\eta^5\text{-}C_5H_4)]$

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Abstract

Friedel–Crafts acetylation of [η^5-(ferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (hereafter called cynichrodenylferrocenylmethane) (**3**) has afforded (1′-acetylferrocenyl)-cynichrodenylmethane (**5**) in 63% yield. Reduction of **5** with sodium borohydride gives 1-[1′-(cynichrodenylmethyl)ferrocenyl]ethanol (**6**). Dehydration of **6** produces [η^5-(1′-vinylferrocenyl)methyl]cyclopentadienyl]dicarbonylnitrosylchromium (**7**), a promising organometallic monomer, in 80% yield. The structure of **7** has been solved by an X-ray diffraction study: space group *Pbca*, *a* 10.966(2), *b* 12.595(1), *c* 26.137(3) Å, and $Z = 8$. The vinyl group and the exocyclic carbon are in the 1,3′-configuration with an average rotation of 7° of the corresponding Cp(Fe) rings from the eclipsed configuration.

Introduction

The synthesis of novel organometallic polymers and studies of their properties [1–6] have accelerated in recent years. Reports on the polymerization and copolymerization of organometallic carbonyl monomers are rare in contrast to their metallocene analogs. Furthermore, only a few organochromium monomers have been synthesized and polymerized. These include η^6-styrenetricarbonylchromium, η^6-(benzylacrylate)tricarbonylchromium [7], and η^6-(2-phenylethylacrylate)tricarbonylchromium [8].

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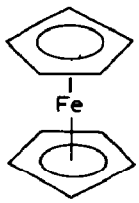
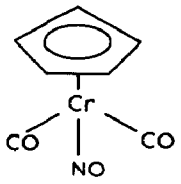


ferrocene

(1)



cynichrodene

(2)

Since the compound cynichrodenyl ferrocenyl methane (**3**) containing both cynichrodenyl and ferrocenyl groups has been prepared by reduction of cynichrodenyl ferrocenyl ketone (**4**) with lithium-aluminum hydride-aluminum chloride [9,10], it is of interest to prepare some vinyl-substituted derivatives of **3** as monomers for the synthesis of new organometallic polymers. Further, while the chemistry of 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 [11–15]. Herein, we reported the preparation and spectra of **5–7** and crystal structure of $(CO)_2(NO)(\eta^5\text{-}C_5H_4)CH_2(\eta^5\text{-}C_5H_4)Fe[vinyl\text{-}(\eta^5\text{-}C_5H_4)]$ (**7**).

Experimental

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

Column chromatography was carried out under nitrogen using Merck Kieselgel 60. The silica gel was heated with a heat gun while mixing in a rotary evaporator attached to a vacuum pump for 2 h to remove water and oxygen. The silica gel was kept under nitrogen before use. Cynichrodenylferrocenylmethane (**3**) was prepared according to the literature procedure [10].

^1H and ^{13}C (300 and 400 MHz) NMR spectra were obtained on a Bruker AM-300-WB or AM-400 spectrometer. ^1H and ^{13}C were referenced to tetramethylsilane. Infrared spectra were recorded on a Perkin–Elmer 682 spectrophotometer. Microanalyses were carried out in Microanalytic Laboratory at National Taiwan University.

Preparation of (1'-acetylferrocenyl)cinychrodenylmethane (5)

Acetyl chloride (0.5 ml, 6.8 mmol) was stirred with aluminum chloride (1.8 g, 13.5 mmol) in 60 ml methylene chloride for 2 h at room temperature to give a yellow solution of the corresponding acylium ion. The solution was filtered from excess $AlCl_3$. Subsequently, the filtrate was added dropwise to a solution of cynichrodenylferrocenylmethane (**3**) (2.7 g, 6.7 mmol) in 50 ml methylene chloride at 0 °C. After the addition was completed, the reaction mixture was allowed to stir at

room temperature for 12 h. The reaction was then cooled to 0°C and slowly hydrolyzed with 50 ml of ice followed by 2 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic portion was washed once with water, once with a 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 (20 g) was added, and the solvent removed under vacuum. The residue was added to a dry-packed column (1.8 cm × 10 cm) of silica gel. Elution of the column with hexane/ether (10/1) gave an orange band which upon removal of solvent under vacuum gave **5** 1.7 g (63%), m.p. 83–84°C. IR (CH_2Cl_2) 2020(vs), 1940(vs), 1690(vs), 1664(m,sh); mass spectrum, *m/e* 443 (M^+). Analysis: Found: C, 54.54; H, 4.05; N, 3.21. $C_{20}H_{17}CrFeNO_4$ calcd.: C, 54.20; H, 3.87; N, 3.16%.

Preparation of {[(1-α-hydroxyethyl)ferrocenyl]methylcyclopentadienyl}dicarbonylnitrosylchromium (1-[1′-(cynichrodenylmethyl)-ferrocenyl]ethanol) (6)

(1′-Acetylferrocenyl)cynichrodenylmethane (**5**) (1.8 g, 4.06 mmol) was dissolved in 100 ml of ethanol, sodium borohydride (0.7 g, 1.84 mmol) was added, and the mixture was refluxed for 30 min. To this solution was added 20 ml of 6*N* sodium hydroxide, and the reaction mixture continued to reflux for 15 min. The solution was concentrated by removing the solvent under aspirator vacuum. The residue was extracted with ether and then dried with anhydrous magnesium sulfate. The solution was filtered, concentrated to 50 ml under aspirator vacuum. Silica gel (2 g) was added 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/ether (6/1) gave an orange band which upon removal of the solvent gave **6** 1.71 g (95%). Melting point 52–53°C. IR (CH_2Cl_2): 3200–3600 (bs), 2032(vs), 1960(vs), 1715(vs); mass spectrum, *m/e* 445(M^+).

Analysis. Found: C, 54.04; H, 4.12; N, 2.99. $C_{20}H_{19}CrFeNO_4$ calcd.: C, 53.93; H, 4.30; N, 3.15%.

Preparation of [η^5-(1′-vinylferrocenyl)methylcyclopentadienyl]dicarbonylnitrosylchromium (7)

1-[1′-(Cynichrodenylmethyl)ferrocenyl]ethanol (**6**) (1 g, 2.24 mmol), anhydrous cupric sulfate (3 g, 18.73 mmol), and 5 mg of hydroquinone were dissolved in 100 ml of toluene. The mixture was refluxed for 45 min and then cooled to room temperature. After the filtration the solvent was removed under vacuum. The residue was extracted with ether and dried with anhydrous magnesium sulfate. The solution was filtered, concentrated to 50 ml 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 gave an orange band which upon removal of the solvent gave **7** 0.81 g (84%). An analytical sample was obtained by recrystallization from hexane/ether as red crystals: m.p. 56–57°C. An X-ray sample was obtained by solvent evaporation method from hexane/ether at 0°C. IR (CH_2Cl_2) 2030(vs), 1940(vs), 1690(vs); mass spectrum, *m/e* 427 (M^+).

Analysis. Found: C, 56.71; H, 3.96; N, 3.37. $C_{20}H_{17}CrFeNO_3$ calcd.: C, 56.23; H, 4.01; N, 3.28%.

X-ray diffraction analysis of 7

The X-ray diffraction intensity data were collected on a CAD4 diffractometer in the $\theta/2\theta$ scan fashion with a graphite monochromated Mo-K_α radiation. The other experimental detail is given in Table 1.

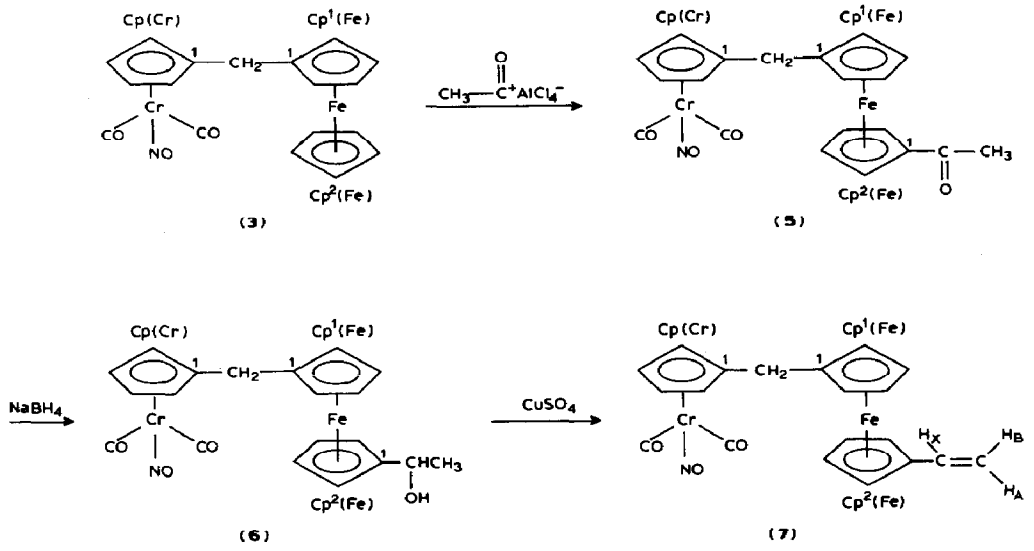
The structure was determined by heavy atom method. The full matrix least squares refinements were based on F. The atomic scattering factors, f_0, were taken from ref. 16a, the anomalous dispersion corrections were included based on ref. 16b. The secondary extinction corrections were applied. All the data processing were done on a PDP-11 and VAX 11/785 using NRCC programs [17].

Table 1

Summary of crystal data and intensity collection

Empirical formula	$C_{20}H_{17}NO_3CrFe$
Color	Orange
Crystal size (mm^3)	$0.3\times0.5\times0.6$ mm
Space group	orthorhombic, *Pbca*
Unit cell dimensions	*a* 10.966(2) Å
	b 12.595(1) Å
	c 26.137(3) Å
Volume	1032.73 Å^3
Formula units/cell	8
Formula weight	427 AMU
Density (calc.)	1.57 g/cm^3
Absorption coefficient	14.1 cm^{-1}
$F(000)$	1744 e$^-$
Diffractometer used	CAD4
Radiation	MO-K_α (λ 0.7107 Å)
Temperature	27 °C
Monochromator	Graphite crystal
2θ range	2 to 50 °
Scan type	$\theta/2\theta$
Scan speed	Variable; 20/20 to 20/3 deg/min
Scan range	$2(0.8+0.35\tan\theta)$
Background measurement	Stationary counts with 1/4 of total scan time at each side of the scan
Standard reflections	$\begin{Bmatrix} -5 & 0 & 4 \\ -5 & 0 & -4 \\ 0 & -8 & -3 \end{Bmatrix}$ for every 2 hour
Index ranges	$0 \le h \le 13, 0 \le k \le 15, 0 \le l \le 31$
Reflections collected	3641
Unique reflections	3163 (2074 $I > 2{,}5\sigma(I)$)
Final residuals	R 3.5%, R_w 2.6%
Goodness-of-fit	2.319
Largest and mean Δ/σ	0.166, 0.03
Data to parameter ratio	8.78/1
Largest difference peak	0.27 e$^-$/Å^3
Largest difference hole	-0.27 e$^-$/Å^3
No. of variables	236
S	2.32
g [a] (extinction coefficient)	9.0×10^{-5}

[a] $F_{obs}^{con} = F_{obs}(1 + g\beta F_c^2)^{-1/4}$



Results and discussion

Preforming the Perrier-type complex [14] of acetyl chloride and aluminum chloride in the absence of **3** and then subsequently allowing this complex to react with **3** led to the acetylated derivative **5** in 63% yield. Reduction of ketone **5** with sodium borohydride in 95% ethanol produced the corresponding secondary alcohol **6** in high yield. Dehydration of **6** in refluxing toluene using anhydrous cupric sulfate gave **7** in 80% yield based on **5**.

All compounds **5–7** exhibit two carbonyl stretching bands, the symmetric mode occurring at 2020–2032 cm^{-1} and the asymmetric mode at 1940–1960 cm^{-1}. A nitrosyl stretching band is also observed at 1690–1715 cm^{-1}. The normal absorption of the acetyl group of **5** is somewhat obscured by the NO stretching band and exhibited a shoulder on the ν(NO) at 1664 cm^{-1}.

The ^1H NMR spectrum of **5** exhibits a singlet cyclopentadienyl resonance at δ 4.13 corresponding to the protons of Cp^1(Fe), a pair of apparent triplets at δ 4.43 and 4.68 for the protons of Cp^2(Fe), another pair of apparent triplets at δ 4.84 and 4.88 corresponding to the protons of Cp(Cr), and a 2H singlet at δ 3.19 for methylene protons (Table 2). As expected, Cp^2(Fe) experienced a stronger carbonyl deshielding effect than the remote Cp(Cr) and Cp^1(Fe) rings.

The alcohol **6**, in which the hydroxyl substituted carbon is chiral, and thus expected to exhibit a A_2BB' pattern for the protons of Cp^2(Fe). It would consist of two closely spaced quartets of relative intensity 1H downfield and a triplet of relative intensity 2H upfield. The two downfield quartets can be assigned to the H(2,5) protons since the protons nearer to the alcohol would be expected to show the greater diastereotopic effect, whereas a proton at either the 3- and 4-position would show little or no diastereotopic effect. However, since the chemical shifts of Cp^1(Fe) and Cp^2(Fe) protons overlap, a multiplet of relative intensity of 8H at δ 4.09–4.16 was observed. Definite assignments could not be made.

Table 2

^{1}H NMR data [a]

Compound	Cp(Cr)		Cp^1(Fe)			Cp^2(Fe)		CH_2	Others
	H(2,5)	H(3,4)	H(2,5)	H(3,4)		H(2,5)	H(3,4)		
1			4.18 (s,5)			4.18 (s,5)			
2	5.07 (s,5)								
3	4.94 (t,2)	4.87 (t,2)	4.11 (t,2)	4.09 (t.2)		4.10 (s,5)		3.29 (s,2)	
4	5.82 (t,2)	5.15 (t,2)	4.83 (t,2)	4.54 (t,2)		4.23 (s,5)			
5	4.88 (t,2)	4.84 (t,2)	4.13 (s,4)			4.68 (t,2)	4.43 (t,2)	3.19 (s,2)	2.35 (s,3,CH_3)
6	4.91 (t,2)	4.87 (t,2)			4.09–4.14 (m,8)			3.19 (s,2)	1.42 (d,3,J 6.3, CH_3) 1.82 (d,1,J 3.6,OH) 4.53 (m,1,CH)
7	4.91 (t,2)	4.86 (t,2)	4.04 (s,4)			4.28 (t,2)	4.17 (t,2)	3.21 (s.2)	5.07 (dd,1,H_B) 5.32 (dd,1,H_A) 6.38 (dd,1,H_X) (J_{AB} 1.4, J_{AX} 17.5, J_{BX} 10.7)

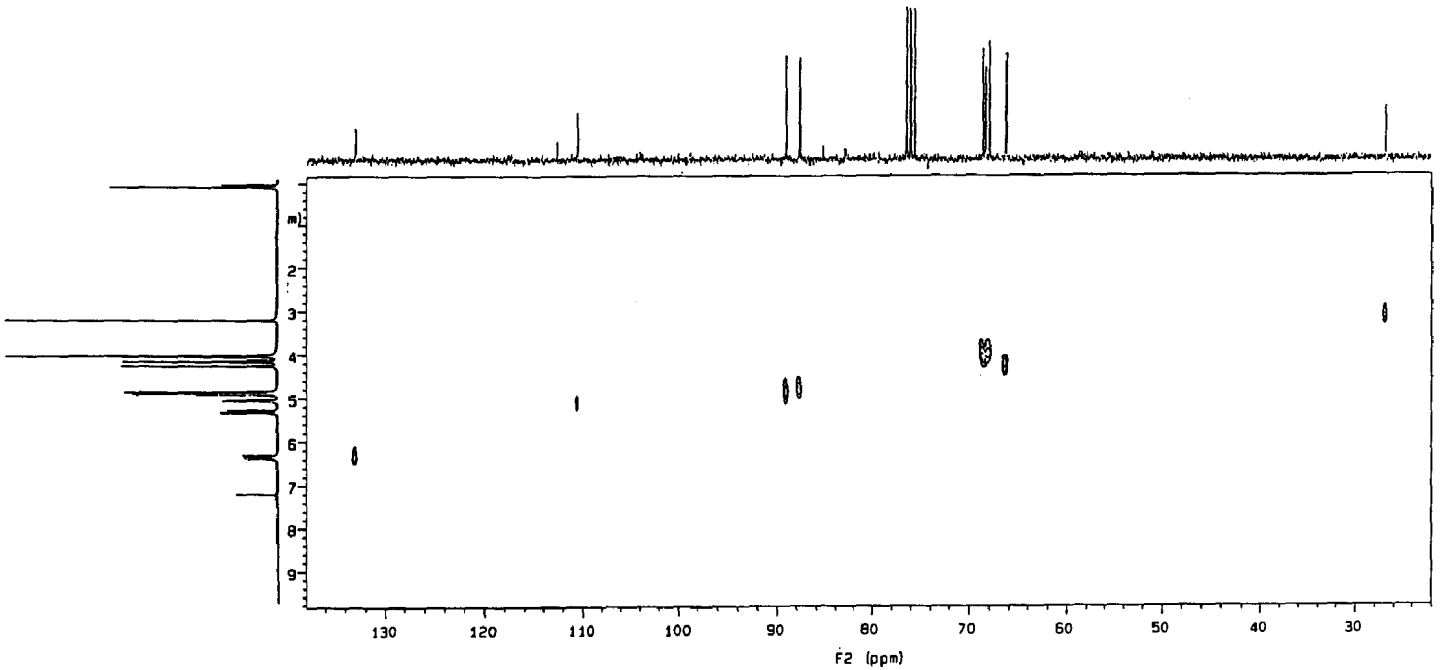
[a] The assignment in the substituted cynichrodene system parallel those in the ferrocene system and must be considered tentative until specific deuterium labeled derivatives in each system be prepared.

Table 3

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

Compound	Cp(Cr)			Cp^1(Fe)			Cp^2(Fe)			CH_2	Cr–C≡O	>C=O	Others
	C(1)	C(2,5)	(C(3,4)	C(1)	C(2,5)	C(3,4)	C(1)	C(2,5)	C(3,4)				
1					67.88 (C(1–5))			67.88 (C(1–5))					
2		90.31 (C(1–5))									237.10		
3	113.41	90.09	88.66	88.17	67.73	68.47		68.68 (C(1–5))		28.59	237.62		
4	103.03	93.89	91.06	78.39	70.43	72.25		70.24 (C(1–5)		–	234.76	192.52	
5	112.66	90.06	88.63	87.39	69.71	70.2	79.83	70.2	73.01	27.49	237.16	201.55	27.42 (CH_3)
6	113.20	89.98	88.68	86.38	68.06	68.8	94.86	66.71	68.8	28.33	237.32	–	23.84 (CH_3)
								66.74	68.9				65.50 (CH)
7	113.56	90.00	88.63	86.20	69.01	69.63	83.85	67.29	69.36	27.88	237.46	–	111.45 (CH_2)
													134.06 (CH)

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



(7)

Fig. 1. Two-dimensional ^{1}H-^{13}C HetCOR NMR spectrum of 7 in $CDCl_3$.

A study of the ^{1}H NMR spectrum of **7** demonstrated that a vinyl group exerts an electron-withdrawing effect. Downfield shifts of the Cp^2(Fe) protons relatively to the corresponding protons of **3** are observed. A typical ^{1}H NMR pattern of the vinylic system is also observed, namely an ABX pattern at δ 5.07, 5.32 and 6.38 for H^B, H^A and H^X with coupling constants of J_{AB} 1.4 Hz, J_{AX} 17.5 Hz, and J_{BX} 10.7 Hz. This assignment is made on the basis that H^A and H^B are not chemically equivalent. H^A (δ 5.32) is deshielded as compared with H^B, because of its relative proximity of the ring. H^X (δ 6.38) is strongly deshielded by the ring, and couples with H^A and H^B. The H^B proton couples with H^X and H^A.

The assignments of ^{13}C NMR spectra for compounds **5–7** (Table 3) are based on: standard ^{13}C NMR correlations [18]; 2D-HetCOR; DEPT technique and compared with other metallo-aromatic system [19,20]. In the case of **7**, four relatively less intense signals at δ 237.46, 111.56, 86.20 and 83.85 corresponding to terminal carbonyl carbon, C(1) of Cp(Cr), C(1) of Cp^1(Fe) and C(1) of Cp^2(Fe), all show no short range coupling. The line assignments for C(2–5) of Cp(Cr), Cp^1(Fe) and Cp^2(Fe) were more difficult to make. Based on 2D-HetCOR (Fig. 1) chemical shifts at δ 88.63 and 90.00 were assigned to C(3,4) and C(2,5) of Cp(Cr) ring and chemicals shifts at δ 69.01 and 69.63 were assigned to C(2,5) and C(3,4) of Cp^1(Fe), and at δ 67.29 and 69.36 were assigned to C(2,5) and C(3,4) of Cp^2(Fe), respectively. Chemical shifts at δ 27.88, 111.45, 134.06 were assigned to CH_2, $CH{=}CH_2$ and $CH{=}CH_2$ respectively.

The mass spectra of **5–7** all exhibit a parent peak and the expected chromium and iron isotopic pattern. Fragment peaks at $(M - CO)^+$, $(M - 2CO)^+$, and $(M - 2CO - NO)^+$ are also always observed.

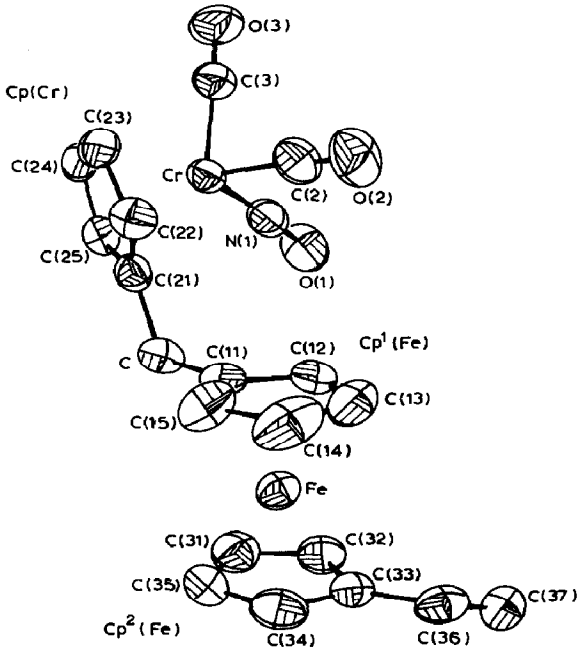


Fig. 2. Molecular configuration of **7**.

Table 4

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

Bond distances			
Fe–C(11)	2.037(4)	Fe–C(12)	2.032(5)
Fe–C(13)	2.036(5)	Fe–C(14)	2.034(5)
Fe–C(15)	2.040(5)	Fe–C(31)	2.033(4)
Fe–C(32)	2.036(4)	Fe–C(33)	2.041(4)
Fe–C(34)	2.029(5)	Fe–C(35)	2.032(5)
Cr–C(21)	2.212(5)	Cr–C(22)	2.203(5)
Cr–C(23)	2.185(4)	Cr–C(24)	2.188(5)
Cr–C(25)	2.194(4)	C(11)–C(12)	1.424(7)
C(11)–C(15)	1.415(7)	C(12)–C(13)	1.048(9)
C(13)–C(14)	1.391(11)	C(14)–C(15)	1.406(9)
C(21)–C(22)	1.403(6)	C(21)–C(25)	1.417(6)
C(22)–C(23)	1.411(7)	C(23)–C(24)	1.402(7)
C(24)–C(25)	1.409(7)	C(31)–C(32)	1.421(7)
C(31)–C(35)	1.390(7)	C(32)–C(33)	1.436(6)
C(33)–C(34)	1.412(7)	C(34)–C(35)	1.420(8)
Cr–N(1)	1.704(4)	Cr–C(2)	1.851(5)
Cr–C(3)	1.832(5)	N(1)–O(1)	1.183(5)
C(2)–O(2)	1.134(6)	C(3)–O(3)	1.146(6)
C–C(11)	1.488(6)	C–C(21)	1.507(6)
C(33)–C(36)	1.467(7)	C(36)–C(37)	1.296(8)
Bond angles			
C(11)–C(12)–C(13)	108.4(5)	C(12)–C(13)–C(14)	108.2(5)
C(13)–C(14)–C(15)	108.4(5)	C(11)–C(15)–C(14)	108.6(5)
C(12)–C(11)–C(15)	106.4(4)	C(21)–C(22)–C(23)	108.0(4)
C(22)–C(21)–C(25)	107.9(4)	C(22)–C(23)–C(24)	108.3(4)
C(23)–C(24)–C(25)	108.0(4)	C(21)–C(25)–C(24)	107.8(4)
C(32)–C(31)–C(35)	108.6(4)	C(31)–C(32)–C(33)	107.5(4)
C(32)–C(33)–C(34)	107.2(4)	C(33)–C(34)–C(35)	108.3(4)
C(31)–C(35)–C(34)	108.5(4)	N(1)–Cr–C(2)	92.97(20)
N(1)–Cr–C(3)	94.72(20)	C(2)–Cr–C(3)	94.67(22)
C(11)–C–C(21)	114.1(4)	Cr–N(1)–O(1)	177.9(3)
Cr–C(2)–O(2)	176.6(4)	Cr–C(3)–O(3)	176.4(5)
C–C(11)–C(12)	127.8(4)	C–C(11)–C(15)	125.7(4)
C(32)–C(33)–C(36)	126.5(4)	C(34)–C(33)–C(36)	126.3(4)
C(33)–C(36)–C(37)	126.5(4)	C–C(21)–C(22)	127.2(4)
C–C(21)–C(25)	124.8(4)	cen.–Cr–N(1)	127.3(2)
cen.–Cr–C(2)	120.1(2)	cen.–Cr–C(3)	119.3(2)

The molecular structure of **7** is shown in fig. 2. Selected bond distances and angles are given in Table 4. The atomic coordinates of the non-hydrogen atoms are listed in Table 5.

Compound **7** adopts a transoid conformation at methylene carbon and the cynichrodenyl moiety resides at *exo* site of ferrocenyl fragment. The dihedral angle between the Cp(Cr) and Cp^1(Fe) planes is 102.2° which deviates from the corresponding angle C(11)–C–C(21) by 11.9°. 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. The nitrosyl group of the cynichrodenyl moiety is located at the site toward the exocyclic carbon of the corresponding Cp(Cr) with a twist angle 43.4°. The twist angle is defined as the

Table 5

Atomic parameters x, y, z and B_{eq} of 7, e.s.d.s refer to the last digit printed

	x	y	z	B_{eq}
Fe	0.25530(6)	0.10693(5)	0.157609(21)	3.49(3)
Cr	0.23038(6)	0.26451(5)	0.91759(3)	3.26(3)
C	0.5400(4)	0.0723(4)	0.14286(16)	3.79(21)
N(1)	0.2137(4)	0.1901(3)	0.86359(14)	4.22(20)
O(1)	0.2012(4)	0.1414(3)	0.82527(11)	6.41(22)
C(2)	0.1169(5)	0.1853(4)	0.95353(19)	3.96(24)
O(2)	0.0433(3)	0.1377(3)	0.97362(14)	6.45(21)
C(3)	0.3621(5)	0.1898(4)	0.94131(19)	4.15(24)
O(3)	0.4483(4)	0.1461(3)	0.95444(15)	6.89(22)
C(11)	0.4213(4)	0.1117(4)	0.12275(15)	3.45(22)
C(12)	0.3715(5)	0.2157(4)	0.12723(19)	5.1(3)
C(13)	0.2593(6)	0.2181(5)	0.10110(22)	7.1(4)
C(14)	0.2387(6)	0.1181(6)	0.08027(18)	7.1(4)
C(15)	0.3381(5)	0.0524(5)	0.09284(18)	5.0(3)
C(21)	0.6449(4)	0.0842(4)	0.10607(17)	3.33(22)
C(22)	0.6384(4)	0.0928(4)	0.05262(18)	3.96(23)
C(23)	0.7586(5)	0.0970(4)	0.03349(16)	4.41(24)
C(24)	0.8393(4)	0.0908(4)	0.07499(20)	4.16(24)
C(25)	0.7696(4)	0.0837(3)	0.12015(16)	3.59(21)
C(31)	0.2847(4)	0.0505(4)	0.22941(17)	4.3(3)
C(32)	0.2237(4)	0.1499(4)	0.23153(15)	3.69(22)
C(33)	0.1107(4)	0.1387(4)	0.20432(16)	3.62(22)
C(34)	0.1053(5)	0.0333(4)	0.18609(19)	4.6(3)
C(35)	0.2128(5)	−0.0203(4)	0.20196(19)	4.8(3)
C(36)	0.0181(4)	0.2212(4)	0.19667(17)	4.3(3)
C(37)	0.0038(5)	0.3063(4)	0.22394(19)	5.3(3)

torsional angle between the nitrogen atom, the chromium atom, the Cp ring center and the ring carbon atom bearing exocyclic carbon.

In the cynichrodene moiety, the observed average bond lengths of Cr–C(ring) 2.196 Å, compare favorably with the 2.188(5) Å average found in (η^5-C_5H_5)Cr(CO)$_2$NO [11] and with the 2.20(1) Å average value in [(η^5-C_5H_5)Cr(CO)$_3$]$_2$ [21] and in (η^5-C_5H_5)Cr(NO)$_2$Cl [22]. The Cr–N length 1.704(4) Å, falls in the range of reported values, 1.687(7) Å in (η^5-$C_{13}H_9$)Cr(CO)$_2$NO [11] to 1.72(1) Å in (η^5-C_5H_5)Cr(NO)$_2$(NCO) [23]. The Cr–C(carbonyl) distance: 1.851(5) Å (Cr–C(2)); 1.832(5) (Cr–C(3)) agree well with the 1.864(6) found in (η^5-$C_{13}H_9$)Cr(CO)$_2$NO and 1.86 Å found in [(η^5-C_5H_5)Cr(CO)$_3$]$_2$ [21]. The N≡O length of 1.183(5) (N(1)–O(1)) is longer than the C≡O distances of 1.134(6) (C(2)–O(2)), 1.146(6) (C(3)–O(3)), in keeping with the greater antibonding population in the nitrosyl ligand. The Cr–N–O angle of 177.9(3) Å (Cr–N(1)–O(1)) is consistent with the NO^+ formalism typical of linear M–NO linkage, while the Cr–C–O angle of 176.6(4) (Cr–C(2)–O(2)), 176.4(5) (Cr–C(3)–O(3)) indicate the usual mode of bonding in the terminal metal carbonyl complexes. The Cr–centroid (Cp(Cr)) distance is 1.841(5), agrees with the 1.844 Å in (η^5-C_5H_5)Cr-(CO)$_2$NO and 1.884 Å in (η^5-$C_{13}H_9$)Cr(CO)$_2$NO [11]. The average C–C distance in the ring (Cp(Cr)) is 1.408 Å. The mean angle in the ring is 108°.

The two cyclopentadienyl rings of ferrocenyl moiety exhibit an average twist angle of 7°. The twist angle is defined by Palenik [24] as the torsional angle between

a ring carbon atom, the two ring centers and the corresponding carbon on the opposite ring. It is apparent that compound **7** is close to the eclipsed configuration, which is in good agreement with other ferrocenyl compounds [25,26]. There is 1.2° offset from parallelism between the two Cp rings of ferrocene moiety and those are separated by 3.29 Å. The mean bond distances of ferrocenyl moiety in compound **7** are very similar to those in related molecules [25]. The average Fe–C(ring) is 2.04 Å, the average C–C distances in the rings are C–C(Cp^1(Fe)) 1.41 Å, C–C(Cp^2(Fe)) 1.42 Å, The exocyclic C–C bond measures 1.488(6) (C–C(11)), 1.507(6) (C–C(21)) and the mean angle in the rings is 108°.

The exocyclic carbon (C) is bent away from both metals, Cr and Fe, with θ angles of −3.0° and −1.6° respectively. The θ angle is defined as the angle between the exocyclic C–C bond and Cp ring with positive angle toward metal. The θ angle between bond C(33)–C(36) and the ring plane of Cp^2(Fe) is −0.2°. The vinyl group and the exocyclic carbon are in the 1,3′-configuration and the vinyl plane (C(33)–C(36)–C(37)) turns away from the ring plane of Cp^2(Fe) by 21.0°. This rotation is the result of intramolecular steric interference between atoms H(C(32)) and H(C(37)). This is supported by the enlargement of bond angle (C(33)–C(36)–C(37)) to 126.5°.

Supplementary material available. List of anisotropic temperature factors of non-hydrogen atoms and the coordinates with isotropic temperature factors of hydrogen atoms as well as list of structure amplitudes (21 pages) are deposited. Ordering information can be obtained from the authors.

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References

1 C.U. Pittman, Jr., G.V. Marlin and T.D. Rounsefell, Macromol. 6 (1973) 1.
2 D.O. Cowan, J. Park, C.U. Pittman, Jr., Y. Sasaki, T.K. Mukherjee and N.A. Diamond, J. Am. Chem. Soc., 94 (1972) 5110.
3 C.E. Carraher, Jr., J.E. Sheats and C.U. Pittman, Jr. (Eds.), Organometallic Polymers, Academic Press, New York, 1978.
4 J.E. Sheats, C.E. Carraher, Jr., and C.U. Pittman, Jr. (Eds.), Metal-Containing Polymeric Systems, Plenum Press, New York, 1985.
5 M. Zeldin, K.J. Wynne, and H.R. Allcock (Eds.), Inorganic and Organometallic Polymers, ACS Symposium Series 360, American Chemical Society, Washington, DC, 1988.
6 C.U. Pittman, Jr., and M.D. Rausch, Pure & Appl. Chem., 58 (1986) 617.
7 C.U. Pittman, Jr., R.L. Voges and J. Elder, Macromol. 4 (1971) 302.
8 C.U. Pittman, Jr., and G.V. Marlin, J. Polymer Sci. A-1, 11 (1973) 2753.
9 C.U. Pittman, Jr., T.D. Rounsefell, E.A. Lewis, J.E. Sheats, B.H. Edwards, M.D. Rausch and E.A. Mintz, Macromol., 11 (1978) 560.
10 Yu-Pin Wang, R.-S. Shyu, J.-M. Hwu and Y.-H. Li, Proc, Natl. Sci. Counc. ROC (A), 11 (1987) 110.
11 J.L. Atwood, R. Shakir, J.T. Malito, M. Herberhold, W. Kremnitz, W.P.E. Bernhagen and H.G. Alt, J. Organomet. Chem., 165 (1979) 65.
12 T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins and J. Trotter, Inorg. Chem., 18 (1979) 3548.
13 D.W. Macomber and M.E. Rausch, Organometallics, 2 (1983) 1523.
14 M.D. Rausch, E.A. Mintz and D.W. Macomber, J. Org. Chem., 45 (1980) 689.
15 M.D. Rausch, D.J. Kowalski and E.A. Mintz, J. Organomet. Chem., 342 (1988) 201.

16 International Tables for X-ray Crystallography, Kynoch, Birmingham, England, 1974, (a) Vol IV. (b) Vol. III. (Present distributor D. Reidel, Dordrecht).
17 E.J. Gabe, Y. Lepage, P.S. White and F.L. Lee, Acta Cryst. A, 43 (1987) C294.
18 J.B. Stother, Ed. Carbon-13-NMR Spectroscopy, Academic Press, New York, 1972.
19 B.E. Mann, Adv. Organomet. Chem., 12 (1974) 135.
20 G.H. Williams, D.D. Traficante and D. Seyferth, J. Organomet. Chem., 60 (1973) C53.
21 R.D. Adams, D.E. Collins and F.A. Cotton, J. Am. Chem. Soc., 96 (1974) 749.
22 O.L. Carter, A.T. Mcphail and G.A. Sim, J. Chem. Soc. A, (1966) 1095.
23 M.A. Bush and G.A. Sim, J. Chem. Soc. A, (1970) 605.
24 G.J. Palenik, Inorg. Chem., 9 (1970) 2424.
25 A.P. Krukonis, J. Silverman, N.F. Yannoni, Acta Cryst. B, 28 (1972) 987.
26 J. Trotter and A. MacDonald, Acta Cryst., 21 (1966) 359.