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Friedel–Crafts cynichrodenoylation of $(\text{CO})_2(\text{NO})\text{Cr}(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ and X-ray structures of $(\text{CO})_2(\text{NO})\text{Cr}(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{O})(\eta^5\text{-C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$ and $(\text{CO})_2(\text{NO})\text{Cr}(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2(\eta^5\text{-}\{2\text{-C}(\text{O})\text{-}[(\eta^5\text{-C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})]\}\text{C}_5\text{H}_3)\text{-Fe}(\eta^5\text{-C}_5\text{H}_5)$

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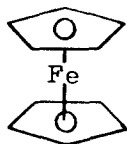
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Abstract

Friedel–Crafts cynichrodenoylation of $[\eta^5\text{-(ferrocenylmethyl)cyclopentadienyl}]_2\text{dicarbonylnitrosylchromium}$ (hereafter called cynichrodenylferrocenylmethane (**3**)) has afforded (1'-cynichrodenoylferrocenyl)cynichrodenylmethane (**5**), (3-cynichrodenoylferrocenyl)cynichrodenylmethane (**6**) and (2-cynichrodenoylferrocenyl)cynichrodenylmethane (**7**) in 32% total yield. The reactivities and orientations of the three Cp rings on **3** towards the Friedel–Crafts reaction are discussed. X-ray diffraction studies of **5** and **7** are reported; crystallographic data for **5** are as follows, space group $P2_1/c$, a 16.739(4), b 12.171(4), c 13.112(3) Å, β = 106.84(2)°, Z = 4; crystallographic data for **7** are as follows, space group $P2_1/n$, a 8.226(3), b 24.78(1), c 12.742(6) Å, β = 106.22(4)°, and Z = 4. The cynichrodenylmethyl and cynichrodenoyl moieties of **5** are in the 1,3'-configuration. Compound **7** adopts a *transoid* conformation at the organic carbonyl carbon and the dihedral angle between the two planes of methylene substituted cyclopentadienyl rings is 89.0°.

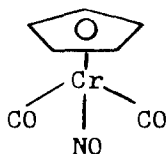
Introduction

The ways in which different substituents influence the process of electrophilic aromatic substitution in the ferrocene (**1**) series have been fully reviewed [1–5]. Introduction of an electron-donating substituent activates the molecule, whereas an electron-withdrawing substituent has the opposite effect. Such activation or deactivation has effects not only on the ring to which the substituent is attached but also, to a lesser extent, on the other Cp ring in the molecule.



ferrocene

1



cynichrodene

2

(η^5 -Cyclopentadienyl)dicarbonylnitrosylchromium (cynichrodene (2)) has also shown aromatic-type reactivity [6,7]. The following order of decreasing reactivity towards Friedel–Crafts acetylation has been established by Fischer et. al. [8]: ferrocene > anisole > ruthenocene > cymantrene > osmocene > cynichrodene \geq (η^5 -cyclopentadienyl)tetracarbonylvandium \approx benzene > (η^5 -cyclopentadienyl)tricarbonylrhenium. Since the compound cynichrodenylferrocenylmethane (3), which contains both cynichrodenyl and ferrocenyl groups, has now been prepared by the reduction of cynichrodenyl ferrocenyl ketone 4 with lithium aluminium hydride–aluminium chloride [9], it is of interest to study the Friedel–Crafts reaction on this compound.

Further, while the chemistry of dicarbonylcyclopentadienyl nitrosyl complexes of chromium has become the subject of considerable study, the crystal structure and ^{13}C NMR spectra of these complexes have not been examined thoroughly [7,10–15]. Here, we report the preparations and spectra of compounds 5–7 and the crystal structures of $(\text{CO})_2(\text{NO})\text{Cr}(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{O})(\eta^5\text{-C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})$ (5) and $(\text{CO})_2(\text{NO})\text{Cr}(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2(\eta^5\text{-}\{2\text{-C}(\text{O})\text{-}[(\eta^5\text{-C}_5\text{H}_4)\text{Cr}(\text{CO})_2(\text{NO})]\}\text{C}_5\text{H}_3)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ (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 deoxygenated nitrogen was dried with a 3Å molecular sieve and with P_2O_5 . Hexane, pentane, benzene and dichloromethane were dried over calcium hydride and freshly distilled under argon, also from calcium hydride. Diethyl ether was dried over sodium and redistilled under argon which had been exposed to sodium benzophenone. All other solvents were used as commercially obtained.

Column chromatography was carried out under nitrogen using Merck Kieselgel 60. Over 2 h, the silica gel was heated with a heat gun while being mixed in a rotary evaporator attached to a vacuum pump to remove water and oxygen. The silica gel was kept under nitrogen before use. Cynichrodenylferrocenylmethane (3) was prepared according to the literature procedure [9].

^1H and ^{13}C (300 and 400 MHz) NMR spectra were obtained with a Bruker AM-300-WB or AM-400 or a VXR-300 spectrometer. ^1H and ^{13}C were referenced to tetramethylsilane. Two-dimensional proton carbon-correlated (HetCOR) NMR experiments were performed in CDCl_3 solutions by using a VXR-5200 Host Computer System and pulse sequence program. Infrared spectra were recorded on a

Perkin–Elmer 682 spectrophotometer. Microanalyses were carried out in the Micro-analytic Laboratory at National Taiwan University.

Preparation of (1'-cynichrodenylferrocenyl)cynichrodenylmethane (5), (3-cynichrodenylferrocenyl)cynichrodenylmethane (6), and (2-cynichrodenylferrocenyl)cynichrodenylmethane (7)

Phosphorus pentachloride (0.26 g, 1.25 mmol) was added to a stirred suspension of cynichrodenyl carboxylic acid (0.31 g, 1.25 mmol) in 30 ml of methylene chloride. After stirring for about 20 min aluminium chloride (0.33 g, 2.50 mmol) was added and the reaction mixture was stirred for 2 h at room temperature. Excess AlCl_3 was filtered from the solution and the filtrate was added dropwise to a solution of **3** (0.50 g, 1.25 mmol) in 50 ml of methylene chloride at 0°C . After the addition was completed the reaction mixture was stirred at room temperature for 12 h. The reaction was then cooled to 0°C and slowly hydrolyzed with 50 ml of ice followed by 3 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 sulphate. The solution was filtered, and 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-packing column (1.8 cm \times 75 cm) of silica gel. Elution of the column with pentane–ether (6/1) gave one orange band which upon removal of solvent under vacuum gave **7** 0.022 g (3%). Elution of the column with pentane–ether (4:1) gave two orange bands which upon removal of solvent under vacuum gave **5** 0.168 g (21%) from the first layer, and **6** 0.063 g (8%) from the second layer. Melting points for **7**, **5** and **6** are 160°C (dec), $55\text{--}57^\circ\text{C}$, and $96\text{--}98^\circ\text{C}$, respectively. X-ray samples of **5** and **7** were obtained by the solvent expansion method from hexane/methylene chloride at 0°C .

Analytical and spectral data for **5**: Analysis: Found: C, 49.41; H, 2.95; N, 4.18. $\text{C}_{26}\text{H}_{18}\text{Cr}_2\text{FeN}_2\text{O}_7$ calcd.: C, 49.55; H, 2.88; N, 4.44%. Proton NMR (CDCl_3): δ (relative intensity, multiplicity, assignment): 3.21 (2H, s, CH_2); 4.18 (4H, s, $\text{Cp}^1(\text{Fe})$); 4.50 (2H, $\text{Cp}^2(\text{Fe})$, H(3,4)); 4.79 (2H, t, $\text{Cp}^2(\text{Fe})$, H(2,5)); 4.85 (2H, t, $\text{Cp}(\text{Cr})$, H(3,4)); 4.90 (2H, t, $\text{Cp}(\text{Cr})$, H(2,5)); 5.16 (2H, t, $\text{Cp}^2(\text{Cr})$, H(3,4)); 5.82 (2H, t, $\text{Cp}^2(\text{Cr})$, H(2,5)). Carbon-13 NMR (CDCl_3): δ (assignment): 27.57 (CH_2); 70.31 ($\text{Cp}^1(\text{Fe})$, C(2,5)); 70.71 ($\text{Cp}^1(\text{Fe})$, C(3,4)); 71.20 ($\text{Cp}^2(\text{Fe})$, C(2,5)); 73.18 ($\text{Cp}^2(\text{Fe})$, C(3,4)); 78.90 ($\text{Cp}^2(\text{Fe})$, C(1)); 88.03 ($\text{Cp}^1(\text{Fe})$, C(1)); 88.78 ($\text{Cp}(\text{Cr})$, C(3,4)); 90.24 ($\text{Cp}(\text{Cr})$, C(2,5)); 91.27 ($\text{Cp}^2(\text{Cr})$, C(3,4)); 94.07 ($\text{Cp}^2(\text{Cr})$, C(2,5)); 112.73 ($\text{Cp}(\text{Cr})$, C(1)); 102.9 ($\text{Cp}^2(\text{Cr})$, C(1)); 192.18 (C(O)); 234.70 ($\text{Cp}^2\text{C}\equiv\text{O}$); 237.21 (Cr $\text{C}\equiv\text{O}$). IR (CH_2Cl_2): 2014 (vs, b); 1946 (vs, b); 1698 (vs, b); 1625 (m) cm^{-1} . Mass spectrum: $m/e = 630$ (M^+).

Spectral data for **6**: Proton NMR (CDCl_3): δ (relative intensity, multiplicity, assignment): 3.31 (1H, d, J 15.4 Hz, CH_2); 3.37 (1H, d, J 15.4 Hz, CH_2); 4.19 (5H, s, $\text{Cp}^2(\text{Fe})$); 4.54 (1H, m, $\text{Cp}^1(\text{Fe})$, H(5)); 4.82 (2H, m, $\text{Cp}^1(\text{Fe})$, H(2,4)); 4.90 (2H, m, $\text{Cp}(\text{Cr})$, H(3,4)); 4.96 (2H, m, $\text{Cp}(\text{Cr})$, H(2,5)); 5.16 (2H, t, $\text{Cp}^2(\text{Cr})$, H(3,4)); 5.82 (2H, t, $\text{Cp}^2(\text{Cr})$, H(2,5)). Carbon-13 NMR (CDCl_3): δ (assignment): 28.52 (CH_2); 70.30 ($\text{Cp}^1(\text{Fe})$, C(2)); 70.67 ($\text{Cp}^1(\text{Fe})$, C(4)); 71.05 ($\text{Cp}^2(\text{Fe})$); 72.67 ($\text{Cp}^1(\text{Fe})$, C(5)); 78.05 ($\text{Cp}^1(\text{Fe})$, C(3)); 88.82, 89.08 ($\text{Cp}(\text{Cr})$, C(3,4)); 90.03, 90.15 ($\text{Cp}(\text{Cr})$, C(2,5)); 90.57 ($\text{Cp}^1(\text{Fe})$, C(1)); 91.15 ($\text{Cp}^2(\text{Cr})$, C(3,4)); 94.03 ($\text{Cp}^2(\text{Cr})$, C(2,5)); 102.69

(Cp²(Cr), C(1)); 112.06 (Cp(Cr), C(1)); 192.49 (C(O)); 234.70 (Cr²C≡O), 237.08 (CrC≡O). IR (CH₂Cl₂): 2020 (vs, b), 1945 (vs, b), 1703 (vs, b), 1631 (m) cm⁻¹. Mass spectrum: *m/e* = 630 (*M*⁺).

Analytical and spectra data for 7: Analysis: Found: C, 49.40; H, 3.02; N, 4.12. C₂₆H₁₈Cr₂FeN₂O₇ calcd.: C, 49.55; H, 2.88; N, 4.44%. Proton NMR (CDCl₃): δ (relative intensity, multiplicity, assignment): 3.35 (1H, d, *J* 15.1 Hz, CH₂), 4.08 (1H, d, *J* 15.1 Hz, CH₂); 4.19 (5H, s, Cp²(Fe)); 4.44, 4.54, 4.62, 4.75 (4H, m of each, Cp(Cr), H(2–5)); 4.85 (1H, m, Cp¹(Fe), H(5)); 4.90 (1H, m, Cp¹(Fe), H(4)); 5.08 (1H, m, Cp¹(Fe), H(3)); 5.16 (2H, m, Cp²(Cr), H(3,4)); 5.78, 5.82 (2H, m of each, Cp²(Cr), H(2,5)). Carbon-13 NMR (CDCl₃): 27.57 (CH₂); 70.32 (Cp¹(Fe), C(5)); 70.48 (Cp¹(Fe), C(3)); 71.05 (Cp²(Fe)); 73.79 (Cp¹(Fe), C(4)); 76.07 (Cp¹(Fe), C(2)); 87.53, 89.12 (Cp(Cr), C(3,4)); 90.85 (Cp¹(Fe), C(1)); 90.70, 90.94 (or 91.01) (Cp(Cr), C(2,5)); 91.01 (or 90.94), 91.48 (Cp²(Cr), C(3,4)); 93.67, 94.37 (Cp²(Cr), C(2,5)); 103.60 (Cp²(Cr), C(1)); 113.01 (Cp(Cr), C(1)); 193.91 (C(O)); 234.73 (Cr²C≡O); 237.47, 237.61 (CrC≡O). IR (CH₂Cl₂): 2019 (vs, b); 1949 (vs, b), 1699 (vs, b), 1631 (m) cm⁻¹. Mass spectrum: *m/e* = 630 (*M*⁺).

X-Ray diffraction analysis of 7

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

The structure was solved by direct methods using the SHELXTL PLUS program [16]. Full matrix least-squares refinement on F used anomalous-dispersion corrections for atoms with atomic numbers greater than 16. Neutral atom scattering form factors from the International Tables for X-ray Crystallography [17] were used. The non-hydrogen atoms were refined anisotropically and all hydrogen atoms were positioned at calculated coordinates and with fixed isotropic *U* of 0.08 Å². All calculations were performed on a MicroVAX II based Nicolet SHELXTL PLUS system.

Results and discussion

The technique of first preparing the Perrier-type complex [7] of cynichrodenoyl chloride (CO)₂(NO)Cr[(η⁵-C₅H₄)C(O)Cl] and aluminium chloride in the absence of 3, and then allowing this complex to react with 3, led to cynichrodenoylated derivatives 5, 6 and 7 (ratio of 66, 25 and 9%) in a combined yield of 32%.

All compounds 5–7 exhibit two carbonyl stretching bands, the symmetric mode occurring at 2014–2020 cm⁻¹ and the asymmetric mode at 1945–1949 cm⁻¹. A nitrosyl stretching band is also observed at 1698–1703 cm⁻¹ for all of the compounds. Delocalization of the π-electrons of the C=O group through both sides of the metallocenyl rings reduces the double bond character of the C–O bond, causing absorption at lower wavenumbers (longer wavelengths) than the normal absorption of the acetyl derivatives [14], i.e. in the range of 1625–1631 cm⁻¹. The broad absorptions of ν(CO) and ν(NO) in all compounds were observed. This is consistent with the fact that all compounds contain two kinds of cynichrodenyl groups: carbonyl and methylene substituted.

The ¹H NMR spectra of compounds 5–7 are consistent with their assigned structures and are similar to other metallocenyl systems [4,7,11]. In the case of 4, the

spectrum exhibits a singlet cyclopentadienyl resonance at δ 4.18 corresponding to the protons of $\text{Cp}^1(\text{Fe})$. A pair of triplets at δ 4.50 and 4.79 for the protons H(3,4) and H(2,5) of $\text{Cp}^2(\text{Fe})$, a pair of triplets at δ 4.85 and 4.90 corresponding to the

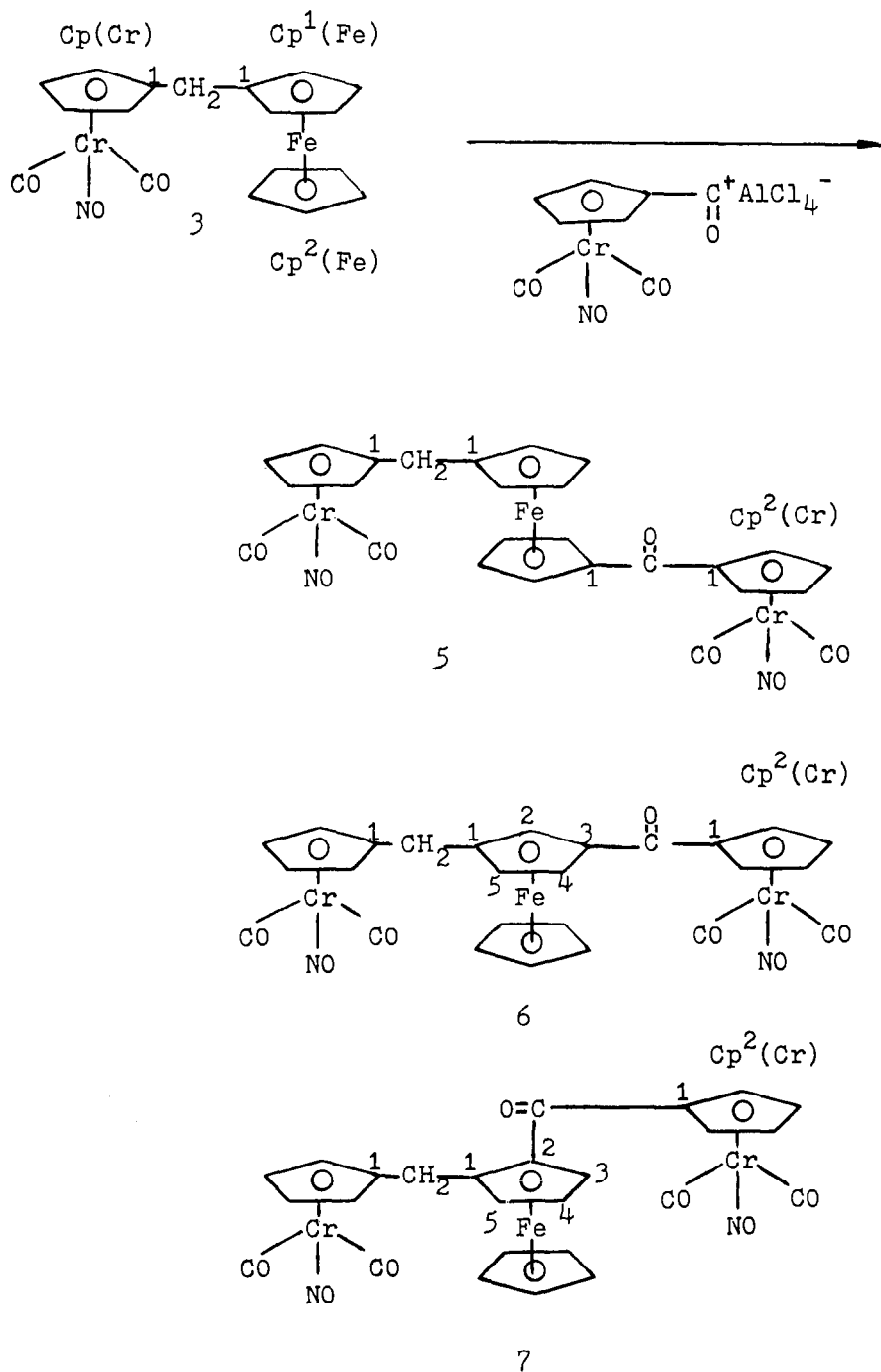


Table 1

Summary of crystal data and intensity collection

Empirical formula	$C_{26}H_{18}N_2O_7Cr_2Fe$
Colour; Habit	Red; Rod
Crystal size (mm)	0.26 mm × 0.23 mm × 0.50 mm
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 8.226(3) \text{ \AA}$ $b = 24.783(12) \text{ \AA}$ $c = 12.742(6) \text{ \AA}$ $\beta = 106.22(4)^\circ$
Volume	$2494(2) \text{ \AA}^3$
Z	4
Formula weight	630.3
Density (calc.)	1.678 Mg/m^3
Absorption coefficient	1.458 mm^{-1}
$F(000)$	1272
Diffractometer used	Nicolet $R3m/V$
Radiation	Mo- K_α ($\lambda = 0.71073 \text{ \AA}$)
Temperature	296 K
Monochromator	Highly oriented graphite crystal
2θ Range	$2.5\text{--}50.0^\circ$
Scan type	$2\theta - \theta$
Scan speed	Variable; $2.93\text{--}14.65^\circ/\text{min}$ in ω
Scan range (ω)	1.20° plus K_α -separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	3 measured every 50 reflections
Index ranges	$-9 \leq h \leq 9, -28 \leq k \leq 0, 0 \leq l \leq 14$
Reflections collected	4738 (2983 $I > 3.0\sigma(I)$)
Independent reflections	3931 (2457 $I > 3.0\sigma(I)$)
Extinction correction	N/A
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0009F^2$
Final R indices (obs. data)	$R = 0.0466, R_w = 0.0489$
Goodness-of-fit	1.42
Largest and mean Δ/σ	0.019, 0.000
Data-to-parameter ratio	7.1:1
Largest difference peak	0.87 e\AA^{-3}
Largest difference hole	-0.38 e\AA^{-3}

protons H(3,4) and H(2,5) of Cp(Cr), another pair of triplets at δ 5.16 and 5.82 corresponding to the protons H(3,4) and H(2,5) of Cp²(Cr), and a 2H singlet at δ 3.21 for methylene protons are observed. As expected Cp²(Fe) and Cp²(Cr) experienced a stronger carbonyl deshielding effect than the remote Cp¹(Fe) and Cp(Cr) rings. This assignment is consistent with the two-dimensional HetCOR NMR spectrum of **5** (Fig. 1).

Metallocenes substituted with at least two different groups on one ring are chiral compounds [18]. The Cp¹(Fe) of both **6** and **7**, having two different substituents (methylene and carbonyl) would be expected to show diastereotopic effect towards the neighbouring groups. It is natural that the diastereotopic protons should possess different physical and chemical properties in an analogous way to what would be

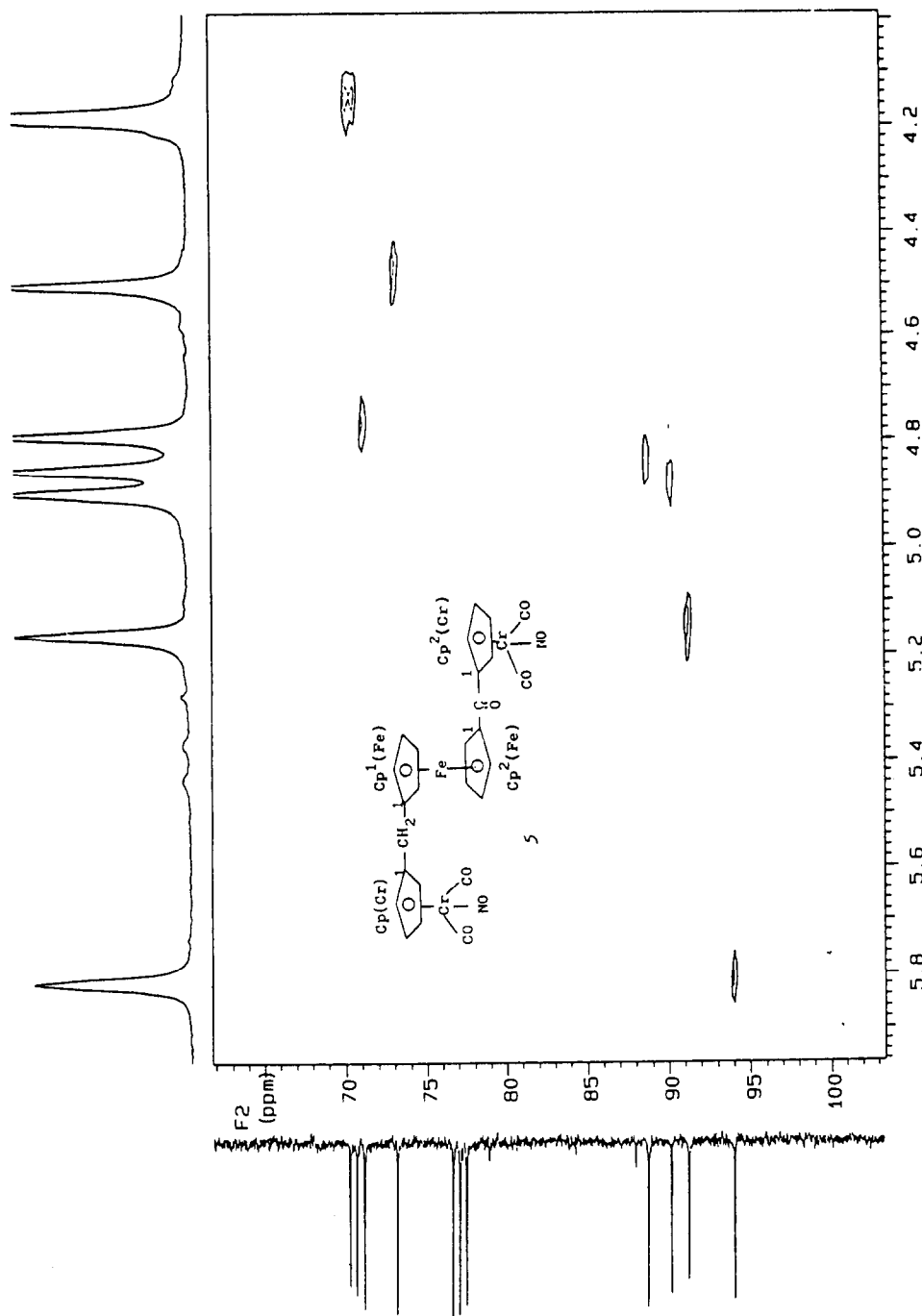


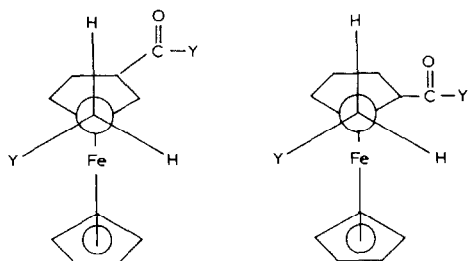
Fig. 1. Two-dimensional ^1H - ^{13}C HetCOR NMR spectrum of **5** in CDCl_3 .

seen with a pair of diastereomers and therefore one may expect different chemical shifts in the NMR spectrum for the protons of methylene as well as for the H(2,5) and H(3,4) ring protons of Cp(Cr). The ^1H NMR spectrum of **6** exhibits an AB pattern at δ 3.31 and 3.37 and coupling constant of 15 Hz corresponding to the two diastereotopic methylene protons, a singlet cyclopentadienyl resonance at δ 4.19 corresponding to the protons of $\text{Cp}^2(\text{Fe})$, two multiplets of relative intensity of 1 : 2 at δ 4.54 and 4.82 corresponding to H(5) and H(2,4) of $\text{Cp}^1(\text{Fe})$, two multiplets of relative intensity 1H at δ 4.89 and 4.91 corresponding to H(3k4) of Cp(Cr) and one multiplet of relative intensity 2H at δ 4.96 corresponding to H(2,5) of Cp(Cr), and two separately spaced triplets of relative intensity 2H at δ 5.16 and 5.82 corresponding to H(3,4) and H(2,5) of $\text{Cp}^2(\text{Cr})$ respectively. This assignment is analogous to reported in the literature [19].

The ^1H NMR spectrum of **7** exhibits an AX pattern at δ 3.35 and 4.08 with coupling constant of 15 Hz, corresponding to the two diastereotopic methylene protons. Chemical shift at δ 4.08 was assigned to H1a (Fig. 3). This assignment is made on the basis that H1a near the deshielding region of the induced magnetic field of $\text{Cp}^2(\text{Fe})$ would be expected to resonate at a lower field than the proton H1b in the more distant position. A singlet cyclopentadienyl resonance at δ 4.19 corresponds to protons of $\text{Cp}^2(\text{Fe})$, four multiplets of relative intensity 1H at δ 4.44, 4.54, 4.62 and 4.72 correspond to the protons of Cp(Cr), and three multiplets of relative intensity 1H at δ 4.85, 4.90 and 5.08 correspond to H(5), H(4) and H(3) of $\text{Cp}^1(\text{Fe})$, respectively. The assignment is made on the basis that the proton H(3) of $\text{Cp}^1(\text{Fe})$ nearest the electron-withdrawing carbonyl group would be expected to deshield to a greater extent than the protons H(4,5) in the more distant positions.

Analysis of steric relations for methylene protons of 1,2- and 1,3-disubstituted derivatives led to the conclusion that the 1,2-disubstituted **7** would be expected to exert a greater diastereotopic effect on the neighbouring groups than 1,3-disubstituted **6**. Correspondingly, larger diastereotopic shifts were observed for methylene protons H(2,5) and H(3,4) of Cp(Cr) in **7** than for those in **6**.

The assignments of ^{13}C NMR-spectra of compounds **5**–**7** are based on standard ^{13}C NMR correlations [20], off resonance decoupled spectra, DEPT technique, and comparison with other metallo-aromatic systems [13–15,21,22]. In the case of **5**, seven relatively less intense signals at δ 237.21, 234.70, 192.18, 112.73, 102.9, 88.03 and 78.90 correspond to terminal carbonyl carbons $\text{Cp}^1(\text{Cr})\text{C}\equiv\text{O}$, $\text{Cp}^2(\text{Cr})\text{C}\equiv\text{O}$, organic carbonyl carbon, C(1) of Cp(Cr), C(1) of $\text{Cp}^2(\text{Cr})$, C(1) of $\text{Cp}^1(\text{Fe})$ and C(1)



$\text{Y} = (\text{CO})_2(\text{NO})\text{Cr}(\text{C}_5\text{H}_4)$
6 (1,3-)

7 (1,2-)

of $\text{Cp}^2(\text{Fe})$, respectively, and none shows any short range coupling. Methylene carbon resonates at δ 27.57. The line assignments for C(2–5) of $\text{Cp}(\text{Cr})$, $\text{Cp}^2(\text{Cr})$, $\text{Cp}^1(\text{Fe})$ and $\text{Cp}^2(\text{Fe})$ are more difficult to make. Based on 2D HetCOR (Fig. 1), chemical shifts at δ 70.31 and 70.71 were assigned to C(2,5) and C(3,4) of $\text{Cp}^1(\text{Fe})$ ring, chemical shifts at δ 71.20 and 73.18 were assigned to C(2,5) and C(3,4) of $\text{Cp}^2(\text{Fe})$, chemical shifts at δ 88.78 and 90.24 were assigned to C(3,4) and C(2,5) of $\text{Cp}(\text{Cr})$ and chemical shifts at δ 91.27 and 94.07 were assigned to C(3,4) and C(2,5) of $\text{Cp}^2(\text{Cr})$. In the case of **7**, eight relatively less intense signals at δ 237.49, 237.61, 234.73, 193.91, 113.01, 103.61, 90.85, and 76.07 correspond to two diastereotopic terminal carbonyl carbons: $\text{Cp}(\text{Cr})\text{C}\equiv\text{O}$, $\text{Cp}^2(\text{Cr})\text{C}\equiv\text{O}$, organic carbonyl carbon, C(1) of $\text{Cp}(\text{Cr})$, C(1) of $\text{Cp}^2(\text{Cr})$, C(1) of $\text{Cp}^1(\text{Fe})$, and C(2) of $\text{Cp}^1(\text{Fe})$, respectively, and none shows any short range coupling. Methylene carbon resonates at δ 27.57. Carbons of $\text{Cp}^2(\text{Fe})$ resonate at δ 71.05. Chemical shifts at δ 87.53 and 89.12 were assigned to C(3,4) of $\text{Cp}(\text{Cr})$ ring, those at δ 90.70 and 91.01 (or 90.94) to C(2,5) or $\text{Cp}(\text{Cr})$ ring, those at 90.94 (or 91.01) and 91.48 were assigned to C(3,4) of $\text{Cp}^2(\text{Cr})$, those at 93.67 and 94.35 were assigned to C(2,5) of $\text{Cp}^2(\text{Cr})$, and finally the chemical shifts at δ 70.32, 70.48 and 73.79 were assigned to C(5), C(3) and C(4) of $\text{Cp}^1(\text{Fe})$, respectively. This assignment is analogous to that reported literature [22].

The assignments are made of high-field chemical shifts corresponding to C(2,5) and low-field chemical shifts corresponding to C(3,4) for substituents on a Cp ring of ferrocene derivatives, whereas, the opposite assignments for those of cynichro-dene derivatives are analogous to those reported in the literature [14,15].

The diastereotopic shifts for C(2,5) and C(3,4) of $\text{Cp}(\text{Cr})$ and $\text{Cp}^2(\text{Cr})$ and

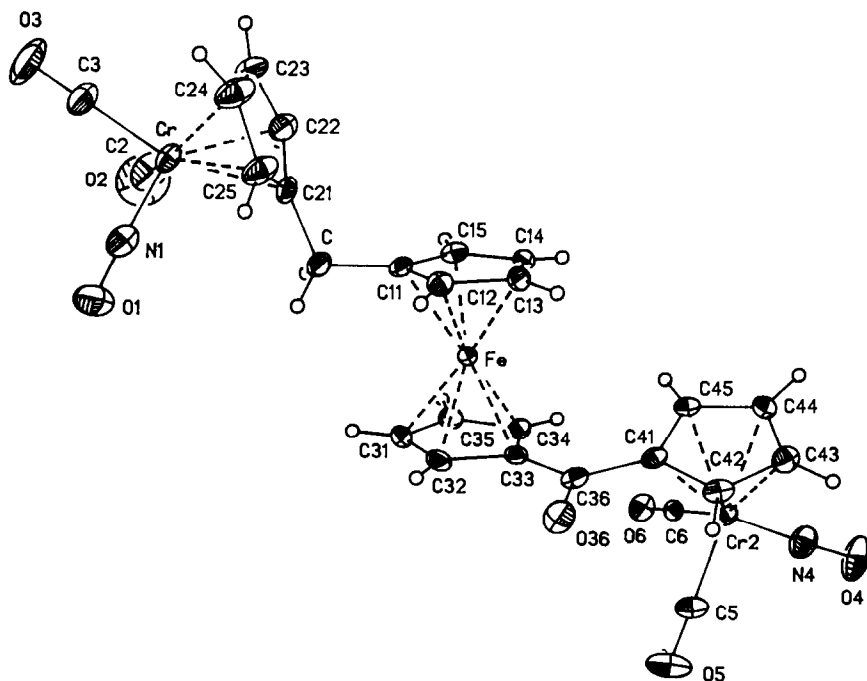


Fig. 2. Molecular configuration of **5**.

$\text{Cp}(\text{Cr})\text{C}\equiv\text{O}$ were observed to be greater for **7** than for **6**, which is parallel with the conclusions drawn from ^1H NMR spectra.

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

The molecular structure of **5** is shown in Fig. 2; its crystal structure has been reported previously [23]. The molecular structure of **7** is shown in Fig. 3. The atomic coordinates of the non-hydrogen atoms are listed in Table 2. Selected bond distances and angles are given in Table 3.

Compound **7** adopts a *transoid* conformation at the organic carbonyl carbon. The dihedral angle between the two planes of methylene substituted cyclopentadienyl rings, $\text{Cp}^1(\text{Cr})$ and $\text{Cp}^2(\text{Fe})$, is 89.0° , which is deviated from the corresponding angle $\text{C}(11) - \text{C}(1) - \text{C}(21)$ by 23.2° . The coordination geometry about each Cr centre approximates to a distorted tetrahedron with two carbonyl groups, the Cp group and nitrosyl group as the four coordination sites. The nitrosyl groups of the methylene and carbonyl substituted cyclopentadienyl moieties are located at the side toward the exocyclic carbon of $\text{Cp}(\text{Cr})$ and $\text{Cp}^2(\text{Cr})$ with a twist angle of 50.3 and 53.1° , respectively. The twist angle is defined as the torsional angle between the nitrogen atom, the chromium atom, the Cp ring centre and the ring carbon atom bearing exocyclic carbon.

In the cyclochromene moieties, the observed average bond lengths of $\text{Cr}-\text{C}(\text{ring})$: 2.195 ($\text{Cp}(\text{Cr})$), 2.200 Å ($\text{Cp}^2(\text{Cr})$) compare favourably with the $2.188(5)$ average found in $(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$ [24] and with the $2.20(1)$ Å average found in $[(\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ [25] and in $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{Cl}$ [26]. The $\text{Cr}-\text{N}$ bond lengths $1.791(8)$ ($\text{Cr}(1)-\text{N}(1)$) and $1.763(8)$ Å ($\text{Cr}(2)-\text{N}(4)$) are longer than the reported values, $1.712(4)$ Å in $(\text{CO})_2(\text{NO})\text{Cr}(\eta^5\text{-C}_5\text{H}_4)\text{C}(\text{O})(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)$ [15] and $1.72(1)$ Å in $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\text{NCO})$ [27]. The $\text{Cr}-\text{C}(\text{carbonyl})$ distance $1.801(9)$ ($\text{Cr}(1)-\text{C}(2)$), $1.809(7)$ ($\text{Cr}(1)-\text{C}(3)$), $1.823(7)$ ($\text{Cr}(2)-\text{C}(5)$), and $1.816(8)$ Å ($\text{Cr}(2)-\text{C}(6)$) are shorter than the reported values, $1.864(6)$ Å found in $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$ and 1.86 Å found in $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ [26]. The $\text{N}=\text{O}$ lengths of $1.151(10)$ ($\text{N}(1)-\text{O}(1)$), $1.155(10)$ ($\text{N}(4)-\text{O}(4)$) are longer than the $\text{C}\equiv\text{O}$ distances of $1.139(11)$ ($\text{C}(2)-\text{O}(2)$), $1.134(9)$ ($\text{C}(3)-\text{O}(3)$), $1.137(8)$ ($\text{C}(5)-\text{O}(5)$) in keeping with the greater antibonding population in the nitrosyl ligand. The $\text{Cr}-\text{N}-\text{O}$ angles of $178.9(6)^\circ$ ($\text{Cr}(1)-\text{N}(1)-\text{O}(1)$) and $178.4(6)$ ($\text{Cr}(2)-\text{N}(4)-\text{O}(4)$), are consistent with the NO^+

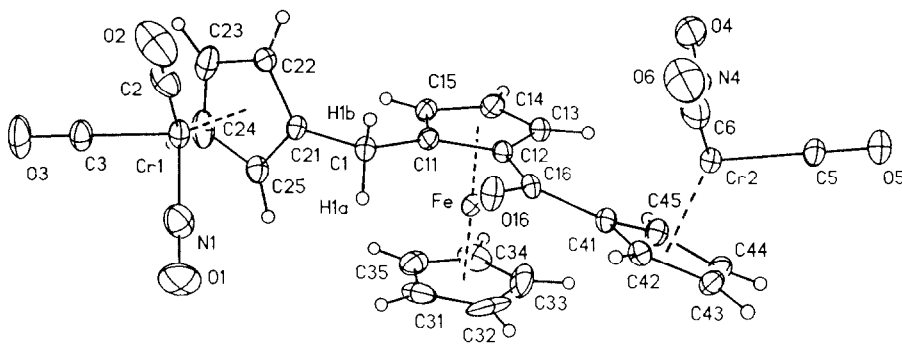


Fig. 3. Molecular configuration of **7**.

formalism, typical of linear M -NO linkage, while Cr-C-O angles of 179.5(8) (Cr(1)-C(2)-O(2)), 178.6(7) (Cr(1)-C(3)-O(3)), 179.7(5) (Cr(2)-C(5)-O(5)) and 177.4(8) $^\circ$ (Cr(2)-C(6)-O(6)) display the usual mode of bonding in the terminal metal carbonyl complexes. The Cr(1)-centroid (Cr(Cr)) and Cr(2)-centroid (Cp²(Cr)) distances are 1.843, 1.843 Å, which agree with the distances of 1.844 Å in (η^5 -C₅H₅)Cr(CO)₂NO and 1.846 Å in (CO)₂(NO)Cr(C₅H₄)C(O)(C₅H₄)Fe(C₅H₅) [15]. The average C-C distances in the rings are 1.40 (Cp(Cr)) and 1.41 Å (Cp²(Cr)). In both rings the mean angle is 108 $^\circ$.

The two cyclopentadienyl rings of the ferrocene moiety exhibit an average twist

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Fe	90(1)	8931(1)	4035(1)	41(1)
Cr(1)	5932(1)	9165(1)	8075(1)	50(1)
Cr(2)	2155(1)	8210(1)	442(1)	51(1)
O(1)	5723(9)	7988(3)	8312(6)	109(4)
O(2)	9396(8)	9130(3)	7860(6)	122(4)
O(3)	7157(9)	9349(3)	10447(4)	107(3)
O(4)	1968(11)	9382(3)	233(5)	128(4)
O(5)	1482(7)	7992(2)	-1926(4)	81(2)
O(6)	5873(7)	8135(3)	792(5)	125(4)
O(16)	4002(6)	8173(2)	3669(3)	63(2)
N(1)	5821(9)	8448(3)	8223(5)	77(3)
N(4)	2030(10)	8917(3)	300(5)	88(3)
C(1)	3968(7)	8924(3)	5438(4)	43(2)
C(2)	8055(10)	9141(3)	7945(6)	69(3)
C(3)	6669(10)	9283(3)	9532(6)	62(3)
C(5)	1745(8)	8076(3)	-1016(5)	54(3)
C(6)	4429(10)	8177(4)	649(5)	71(3)
C(11)	2615(7)	9115(3)	4489(5)	42(2)
C(12)	2093(7)	8890(2)	3398(5)	40(2)
C(13)	789(8)	9243(3)	2737(5)	49(2)
C(14)	521(8)	9664(3)	3409(5)	55(3)
C(15)	1636(8)	9592(3)	4468(5)	46(2)
C(16)	2715(7)	8382(3)	3082(4)	38(2)
C(21)	4152(7)	9277(3)	6434(5)	41(2)
C(22)	5191(8)	9733(3)	6700(5)	57(3)
C(23)	4901(12)	9970(3)	7635(6)	77(3)
C(24)	3701(10)	9670(4)	7947(6)	76(4)
C(25)	3227(8)	9240(3)	7208(5)	55(3)
C(31)	-305(11)	8399(4)	5129(9)	86(4)
C(32)	-857(15)	8186(3)	4073(12)	109(6)
C(33)	-2127(12)	8541(6)	3460(8)	101(5)
C(34)	-2323(10)	8927(4)	4167(9)	81(4)
C(35)	-1210(11)	8855(4)	5171(8)	76(4)
C(41)	1810(7)	8079(2)	2067(4)	40(2)
C(42)	2498(7)	7605(3)	1732(5)	44(2)
C(43)	1344(8)	7400(3)	792(5)	52(3)
C(44)	-86(8)	7737(3)	536(5)	54(3)
C(45)	190(8)	8151(3)	1313(5)	49(2)

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

Table 3

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

<i>Bond distances</i>			
Fe–C(11)	2.046(6)	Fe–C(12)	2.032(7)
Fe–C(13)	2.048(7)	Fe–C(14)	2.055(7)
Fe–C(15)	2.054(6)	Fe–C(31)	2.009(11)
Fe–C(32)	2.009(10)	Fe–C(33)	2.012(11)
Fe–C(34)	2.039(9)	Fe–C(35)	2.034(11)
Cr(1)–C(21)	2.210(5)	Cr(1)–C(22)	2.197(7)
Cr(1)–C(23)	2.180(8)	Cr(1)–C(24)	2.189(9)
Cr(1)–C(25)	2.199(6)	Cr(2)–C(41)	2.192(6)
Cr(2)–C(42)	2.184(6)	Cr(2)–C(43)	2.200(7)
Cr(2)–C(44)	2.216(7)	Cr(2)–C(45)	2.207(7)
C(11)–C(12)	1.447(8)	C(11)–C(15)	1.427(9)
C(12)–C(13)	1.455(8)	C(13)–C(14)	1.406(10)
C(14)–C(15)	1.415(8)	C(21)–C(22)	1.399(9)
C(21)–C(25)	1.407(10)	C(22)–C(23)	1.407(11)
C(23)–C(24)	1.380(13)	C(14)–C(25)	1.403(11)
C(31)–C(32)	1.398(17)	C(31)–C(35)	1.363(13)
C(32)–C(33)	1.422(15)	C(33)–C(34)	1.355(17)
C(34)–C(35)	1.361(12)	C(41)–C(32)	1.420(9)
C(41)–C(45)	1.420(7)	C(42)–C(43)	1.399(8)
C(43)–C(44)	1.405(9)	C(44)–C(45)	1.400(9)
Cr(1)–C(2)	1.800(9)	Cr(1)–C(3)	1.809(7)
Cr(1)–N(1)	1.791(8)	Cr(2)–C(5)	1.823(7)
Cr(2)–C(6)	1.816(8)	Cr(2)–N(4)	1.763(8)
C(2)–O(2)	1.139(11)	C(3)–O(3)	1.134(9)
C(5)–O(5)	1.137(8)	C(6)–O(6)	1.155(10)
N(4)–O(4)	1.155(10)	N(1)–O(1)	1.151(10)
C(1)–C(11)	1.474(7)	C(1)–C(21)	1.514(8)
C(12)–C(16)	1.459(9)	C(16)–C(41)	1.500(7)
C(16)–O(16)	1.227(7)	Cr(1)–cen.(Cp ² (Cr))	1.843
Cr(2)–cen.(Cp ² (Cr))	1.843	Cr(1)···C(1)	3.350
Cr(2)···C(16)	3.292		
	cen.(Cp ¹ (Fe))···cen.(Cp ² (Fe))	3.290	
Fe···C(1)	3.192	Fe···C(16)	3.072
Fe···C(Cp ¹ (Fe))	ave. 2.047	Fe···C(Cp ² (Fe))	ave. 2.021
Cr(1)···C(Cp(Cr))	ave. 2.195	Cr(2)···C(Cp ² (Cr))	ave. 2.200
<i>Bond angles</i>			
C(11)–C(12)–C(13)	107.3(5)	C(12)–C(13)–C(14)	108.0(5)
C(13)–C(14)–C(15)	108.5(5)	C(14)–C(15)–C(11)	109.5(5)
C(15)–C(11)–C(12)	106.6(5)	C(21)–C(22)–C(23)	107.8(7)
C(22)–C(23)–C(24)	108.8(7)	C(23)–C(24)–C(25)	107.6(7)
C(25)–C(21)–C(22)	107.2(6)	C(24)–C(25)–C(21)	108.5(7)
C(31)–C(32)–C(33)	106.7(9)	C(32)–C(33)–C(34)	106.1(9)
C(33)–C(34)–C(35)	111.0(8)	C(35)–C(31)–C(32)	108.5(8)
C(34)–C(35)–C(31)	107.7(9)	C(41)–C(42)–C(43)	109.0(5)
C(42)–C(43)–C(44)	107.9(6)	C(43)–C(44)–C(45)	108.2(5)
C(44)–C(45)–C(41)	108.8(6)	C(45)–C(41)–C(42)	106.1(5)
C(2)–Cr(1)–C(3)	92.5(4)	C(2)–Cr(1)–N(1)	93.2(4)
C(3)–Cr(1)–N(1)	93.7(3)	C(5)–Cr(2)–C(6)	91.7(3)
C(5)–Cr(2)–N(4)	95.1(3)	C(6)–Cr(2)–N(4)	95.0(4)
C(11)–C(1)–C(21)	112.2(5)	Cr(1)–N(1)–O(1)	178.9(6)
Cr(1)–C(2)–O(2)	179.5(8)	Cr(1)–C(3)–O(3)	178.6(7)
Cr(2)–N(4)–O(4)	178.4(6)	Cr(2)–C(5)–O(5)	179.7(5)
Cr(2)–C(6)–O(6)	177.4(8)	C(1)–C(11)–C(12)	128.3(6)

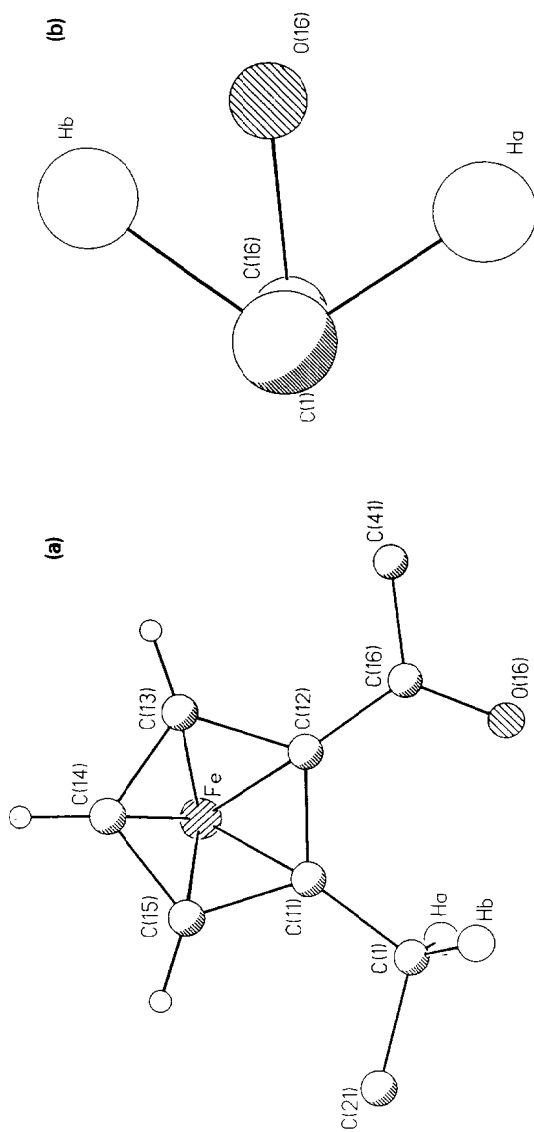


Fig. 4. (a) View of part of 7, along the normal of $\text{Cp}^1(\text{Fe})$ ring and $\text{Cp}^2(\text{Fe})$; (b) View of part of 7, along the axis through C and C(16).

Table 3 continued

<i>Bond angles</i>			
C(1)–C(11)–C(15)	125.0(5)	C(1)–C(21)–C(22)	125.5(6)
C(1)–C(21)–C(25)	127.0(6)	C(16)–C(12)–C(11)	124.3(5)
C(16)–C(12)–C(13)	128.2(5)	C(16)–C(41)–C(42)	122.0(5)
C(16)–C(41)–C(45)	131.8(6)	C(12)–C(16)–C(41)	122.8(5)
C(12)–C(16)–O(16)	120.4(5)	C(41)–C(16)–O(16)	116.8(5)
cen.–Cr(1)–C(2)	123.3	cen.–Cr(1)–C(3)	121.6
cen.–Cr(1)–N(1)	124.2	cen.–Cr(2)–C(5)	120.5
cen.–Cr(2)–C(6)	120.1	cen.–Cr(2)–N(4)	126.3

angle of 2.9° . The twist angle is defined by Palenik [28] as the torsional angle between a ring carbon, the two ring centres and the corresponding carbon on the opposite rings. It is apparent that compound **7** is close to the eclipsed configuration which is in good agreement with other ferrocenyl compounds [29,30]. There is 0.9° offset from parallelism between the two Cp rings of ferrocene moiety and those are separated by 3.29 \AA . The mean bond distances of the ferrocenyl moiety in compound **7** are very similar to those in related molecules [30]. The average Fe–C(ring) distances are 2.05 \AA ($\text{Cp}^1(\text{Fe})$), 2.02 \AA ($\text{Cp}^2(\text{Fe})$), the average C–C distances in rings are 1.43 \AA ($\text{Cp}^1(\text{Fe})$), 1.38 \AA ($\text{Cp}^2(\text{Fe})$), the exocyclic C–C bond measures $1.474(7) \text{ \AA}$ (C(1)–C(11), $1.459(9) \text{ \AA}$ (C(12)–C(16)), $1.514(8) \text{ \AA}$ (C(1)–C(21)), $1.500(7) \text{ \AA}$ (C(16)–C(41)) and the mean angle in the rings is 108° .

The organic C=O bond length is $1.230(7)$ and the angles at this carbonyl group ($117, 120, 123^\circ$) do not differ from normal values. The exocyclic carbons (C) are bent away from both metals, Cr and Fe, with θ angles of -3.67 and -2.77° , respectively. The θ angles for C(16) are -2.48 and $+3.45^\circ$. The θ angle is defined as the angle between the exocyclic C–C bond and the corresponding Cp ring, the angle towards the metal being defined as positive and that away from the metal,

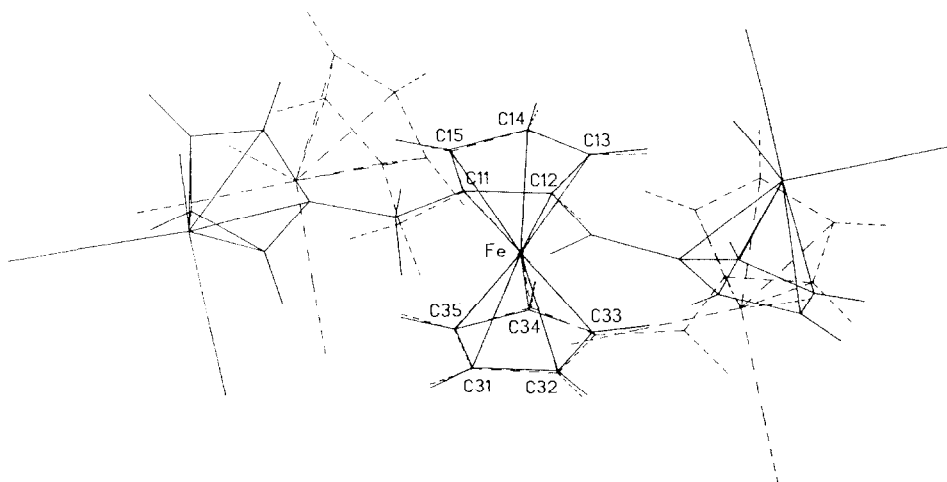


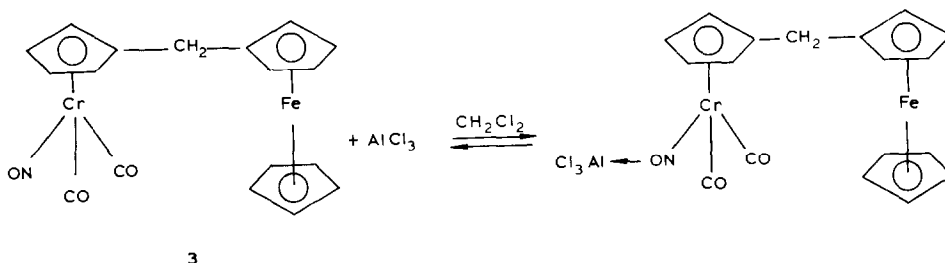
Fig. 5. Relative orientation of **5** and **7** solid line: **7**, dotted line: **5**.

negative. The carbonyl plane (C(12), C(16), O(16), C(41)) turns away from the corresponding ring planes $Cp^2(Fe)$ and $Cp^2(Cr)$ by 15.7 and 8.5°, respectively. These rotations are the result of intramolecular steric interference between atoms H(C(13)) and H(C(45)). This is supported by the enlargement of bond angles C(16)–C(41)–C(45) and C(16)–C(12)–C(13) to 131.6 and 128.5°, respectively.

The twist angles of the two diastereotopic hydrogen atoms H1a and H1b on methylene carbon (C(1)) are 62.4 and 48.6° (Fig. 4), respectively. The twist angle is defined as the torsional angle between the hydrogen atom (H1a or H1b), the methylene carbon (C(1)), the organic carbonyl carbon C(16), and the oxygen O(16). The relative orientation of **5** and **7** is shown in Fig. 5.

Mechanistic consideration

The deactivating nature of the cynichrodenyl group of **3** in Friedel-Crafts reactions might arise primarily from coordination of aluminium chloride, the Friedel-Crafts catalyst, with the NO ligand.



Rausch et al. [7] studied the interaction of aluminium chloride with **2**. They found that in the Friedel-Crafts reaction the complexation of aluminium chloride and the nitrosyl oxygen of **2** deactivates the Cp ring. Only in cases with a three-molar excess of aluminium chloride has coordination with CO been invoked. A related study by Lokshin et al. [31] concerning the interaction of aluminium chloride with the molybdenum and tungsten analogues of **2** was reported in 1976.

It is well known that the electrophilic substitution of a cyclopentadienyl ring bearing an alkyl-substituent occurs preferentially at the 3-position, to an extent which increases with increase in effective steric bulk of the substituent or the electrophile [5]. Accordingly, the preference for $Cp^2(Fe)$ -substitution to $Cp^1(Fe)$ and the preference for 3-position to 2-position of $Cp^1(Fe)$ might simply be the result of the steric hindrance to reaction at $Cp^1(Fe)$ and the 2-position of $Cp^1(Fe)$.

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Supplementary material available. A list of anisotropic temperature factors of nonhydrogen atoms and coordinates with isotropic temperature factors of hydrogen atoms as well as a list of structure amplitudes (15 pages) can be obtained from the authors.

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