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Friedel–Crafts acetylation of $(CO)_2(NO)Cr(h^5\text{-}C_5H_4)CH_2\text{-}(h^5\text{-}C_5H_4)Fe(h^5\text{-}C_5H_5)$ and X-ray structure of $(CO)_2(NO)Cr\text{-}(h^5\text{-}C_5H_4)CH_2[h^5\text{-(3-acetyl)}C_5H_3]Fe(h^5\text{-}C_5H_5)$

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Abstract

Friedel–Crafts acetylation of $[h^5$-(ferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (hereafter called cynichrodenylferrocenylmethane) (**3**) has afforded (1′-acetylferrocenyl)cynichrodenylmethane (**5**), (3-acetylferrocenyl)cynichrodenylmethane (**6**) and (2-acetylferrocenyl)cynichrodenylmethane (**7**) in 87% total yield. The relative reactivity and orientation of the three Cp rings on **3** toward the Friedel–Crafts reaction are discussed. The structure of **6** has been solved by an X-ray diffraction study: space group $P2_1/c$, a 22.445(4), b 7.129(2), c 11.467(4) Å, β 93.06(2)°, and $Z = 4$. The nitrosyl group is located at the site toward the exocyclic methylene carbon with a twist angle of 1.8°, and the two cyclopentadienyl rings of ferrocenyl moiety exhibit an average twist angle of 17°.

Introduction

Substituent effects of electrophilic aromatic substitution in ferrocene **1** series have been fully reviewed [1–5]. Introduction of an electron-donating substituent activated the molecule, whereas an electron-withdrawing substituent has the opposite effect. The activation or deactivation effects of a substituent is felt not only by the ring to which it is attached but also, to a lesser extent, by the other Cp ring in the molecule.

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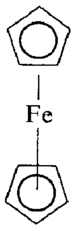
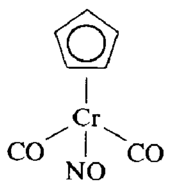


(ferrocene, **1**)



(cynichrodene, **2**)

(h^5-Cyclopentadienyl)dicarbonylnitrosylchromium (cynichrodene, **2**) has also shown aromatic-type reactivity [6,7]. The following order of decreasing reactivity toward Friedel–Crafts acetylation has been established by Fischer et al. [8] ferrocene > anisole > ruthenocene > cymantrene > osmocene > cynichrodene ≥ (h^5-cyclopentadienyl)tetracarbonylvanadium ≈ benzene > (h^5-cyclopentadienyl)tricarbonylrhenium. Since the compound cynichrodenylferrocenylmethane (**3**) containing both cynichrodenyl and ferrocenyl groups has been prepared by reduction of cynichrodenylferrocenyl ketone **4** with lithium aluminum hydride/aluminum chloride, it is of interest to study the Friedel–Crafts reaction on this compound.

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 [7,9–12]. Herein, we report the preparations and spectra of compounds **3** and **5**–**7** and the crystal structure of $(CO)_2(NO)Cr(h^5\text{-}C_5H_4)CH_2[h^5\text{-(3-acetyl)}C_5H_3]Fe(h^5\text{-}C_5H_5)$ (**6**).

Experimental

All operations were carried out under a nitrogen atmosphere by means of Schlenk technique. 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 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 Kiesel-gel 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 us. Cynichrodenylferrocenyl ketone **4** was prepared according to the literature procedure [13].

^{1}H and ^{13}C (300 and 400 MHz) NMR were obtained on a Bruker AM-300-WB or AM-400 or a VXR-300 spectrometer. ^{1}H and ^{13}C were referenced to tetramethylsilane. Two-dimensional proton J-correlated (COSY) and proton carbon-correlated (HetCOR) NMR experiments were performed in $CDCl_3$ solutions by using VXR-5200 Host Computer System and pulse sequence program. Infrared spectra were recorded on a Perkin–Elmer 682 spectrophotomer. Microanalyses were carried out in Microanalytic Laboratory at National Taiwan University.

Preparation of [h^5-(ferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (cynichrodenylferrocenylmethane) (3)

To a stirred suspension of lithium aluminum hydride (0.091 g, 2.3 mmol) in 3 ml of ethyl ether, aluminum chloride (0.31 g, 2.3 mmol) was added slowly. After the vigorous reaction had subsided, cynichrodenylferrocenyl ketone (0.5 g, 1.2 mmol) in 4 ml of ethyl ether was added dropwise so as to maintain a gentle reflux. The reaction mixture was then refluxed for 30 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 sulfate. The solvent was removed under aspirator vacuum and gave a residue, which was dissolved in 50 ml of methylene chloride, 20 g of silica gel added, and the solvent again removed under vacuum. The resulting residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane gave a yellow band which upon removal of the solvent under vacuum gave **3**, 0.20 g (41%). An analytical sample, m.p. 115 ° C, was obtained by vacuum sublimation at 100 ° C/0.1 torr.

Analysis: Found: C, 53.75; H, 4.04; N, 3.53. $C_{18}H_{15}CrFeNO_3$ calcd.: C, 53.89; H, 3.77; N, 3.49%. Proton NMR ($CDCl_3$), δ (relative intensity, multiplicity, assignment): 3.29 (2H, s, CH_2); 4.10 (5H, s, Cp^2(Fe) unsubstituted ring protons); 4.09 (2H, t, Cp^1(Fe) H(3,4)); 4.11 (2H, t, Cp^1(Fe) H(2,5)); 4.87 (2H, t, Cp(Cr) H(3,4)); 4.94 (2H, t, Cp(Cr) H(2,5)). Carbon-13 NMR ($CDCl_3$), δ (assignment): 28.59 (CH_2); 68.68 (Cp^2(Fe)); 67.73 (Cp^1(Fe), C(2,5)); 68.47 (Cp^1(Fe), C(3,4)); 88.17 (Cp^1(Fe), C(1)); 88.66 (Cp(Cr), C(3,4)); 90.09 (Cp(Cr), C(2,5)); 113.41 (Cp(Cr), C(1)); 237.62 ($Cr{-}C{\equiv}O$). IR spectrum ($CDCl_3$) (cm^{-1} (intensity)): 2035(vs), 1965(vs), 1717(vs), 1600(w), 1570(w), 1440(w), 1102(w), 1000(w), 865(w), 840(w). Mass spectrum: $m/e = 401$ (M^+).

Preparation of (1′-acetylferrocenyl)cynichrodenylmethane (5), (3-acetylferrocenyl) cynichrodenylmethane (6) and (2-acetylferrocenyl)cynichrodenylmethane (7)

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. Subsequently, a solution of **3** (2.7 g, 6.7 mmol) in 50 ml methylene chloride was added dropwise to the solution 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 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 × 100 cm) of silica gel. Elution of column with hexane/ether (10/1) gave three orange bands which upon removal of solvent under vacuum gave **7**, 0.08 g (3%) from the first band; **5**, 1.7 g (63%) from the second band; **6**, 0.6 g (21%) from the third band. Melting points for **5**, **6**, and **7** are 83–84, 108–109, and 100–101 ° C, respectively. An X-ray sample of **6** was obtained by the solvent expansion method from pentane/hexane/methylene chloride at 0 ° C.

Analytical and spectra data for 5. 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%. Proton NMR ($CDCl_3$): δ

(relative intensity, multiplicity, assignment); 2.35 (3H, s, CH_3): 3.19 (2H, s, CH_2); 4.13 (4H, s, Cp^1(Fe)); 4.43 (2H, t, Cp^2(Fe) H(3,4)); 4.68 (2H, t, Cp^2(Fe) H(2,5)); 4.84 (2H, t, Cp(Cr) H(3,4)); 4.88 (2H, t, Cp(Cr) H(2,5)). Carbon-13 NMR ($CDCl_3$), δ (assignment): 27.42 (CH_3): 27.49 (CH_2); 69.71 (Cp^1(Fe), C(2,5)); 70.2 (Cp^1(Fe), C(3,4)); 70.2 (Cp^2(Fe), C(2,5)); 73.01 (Cp^2(Fe), C(3,4)); 79.83 (Cp^2(Fe), C(1)); 87.39 (Cp^1(Fe), C(1)); 88.63 (Cp(Cr), C(3,4)); 90.06 (Cp(Cr), C(2,5)); 112.66 (Cp(Cr), C(1)); 201.55 (C=O); 237.16 (Cr–C≡O). IR spectrum (CH_2Cl_2) (cm^{-1} (intensity)): 2020(vs), 1940(vs), 1690(vs), 1664(m,sh). Mass spectrum: $m/e = 443$ (M^+).

Table 1

Summary of crystal data and intensity collection

Empirical formula	$C_{20}H_{17}NO_4CrFe$
Color	Orange
Crystal size (mm^3)	0.2×0.2×0.3 mm
Space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a 22.445(4) Å b 7.129(2) Å c 11.467(4) Å β 93.06(2)°
Volume	1832.18 A^3
Formula units/cell	4
Formula weight	443 AMU
Density (calc.)	1.607 g/cm^3
Absorption coefficient	14.0 cm^{-1}
$F(000)$	904 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; 20/13 to 20/3 deg/min
Scan range	$2(0.9+0.35 \tan\theta)$
Background measurement	Stationary counts with 1/4 of total scan time at each side of the scan
Standard reflections	$\left\{\begin{array}{l} 7\ -1\ \ 1 \\ -7\ \ 1\ -1 \text{ for every 2 h} \\ -7\ -1\ -1 \end{array}\right.$
Index ranges	$-26 \le h \le 26, 0 \le k \le 8, 0 \le l \le 13$
Reflections collected	3752
Unique reflections	3212 (1833 $I > 2.5\ \sigma(I)$)
Final residuals	R 4.8%, R_w 3.7%
Goodness-of-fit	2.13
Largest and mean Δ/δ	0.05, 0.00
Data-to-parameter ratio	7.48/1
Largest difference peak	0.45 $e^-/Å^3$
Largest difference hole	−0.45 $e^-/Å^3$
No. of variables	245
S	2.13
g (extinction coefficient) [a]a	1.7×10^{-5}

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

Analytical and spectral data for **6**. Analysis: Found: C, 54.54; H, 3.85; N, 3.20. $C_{20}H_{17}CrFeNO_4$ calcd.: C, 54.20; H, 3.87; N, 3.16%. Proton NMR ($CDCl_3$): δ (relative intensity, multiplicity, assignment): 2.35 (3H, s, CH_3); 3.28 (1H, d, J 15.7 Hz, CH_2), 3.34 (1H, d, J 15.7 Hz, CH_2); 4.14 (5H, s, Cp^2(Fe)); 4.46 (1H, m, Cp^1(Fe) H(5)); 4.71 (2H, m, Cp^1(Fe) H(2,4)); 4.87 (1H, m, Cp(Cr) H(3) or H(4)); 4.92 (1H, m, Cp(Cr) H(4) or H(3)); 4.93 (1H, m, Cp(Cr) H(2) or H(5)); 4.95 (1H, m, Cp(Cr) H(5) or H(2)). Carbon-13 NMR ($CDCl_3$), δ (assignment): 27.30 (CH_3); 28.52 (CH_2); 69.50 (Cp^1(Fe), C(2) or C(4)); 69.72 (Cp^1(Fe), C(4) or C(2)); 70.61 (Cp^2(Fe)); 72.70 (Cp^1(Fe), C(5)); 78.99 (Cp^1(Fe), C(3)); 88.69, 89.10 (Cp(Cr), C(3,4)); 89.99, 90.14 (Cp(Cr), C(2,5)); 90.61 (Cp^1(Fe), C(1)); 112.13 (Cp(Cr), C(1)); 201.95 (C=O); 237.07 (Cr–C≡O). IR spectrum (CH_2Cl_2), (cm^{-1} (intensity)): 2020(vs), 1940(vs), 1690(vs), 1662(m,sh). Mass spectrum: $m/e = 443$ (M^+).

Analytical and spectral data for **7**. Analysis: Found: C, 53.83; H, 3.66; N, 3.40. $C_{20}H_{17}CrFeNO_4$ calcd.: C, 54.20; H, 3.87; N, 3.16%. Proton NMR ($CDCl_3$): δ (relative intensity, multiplicity, assignment): 2.39 (3H, s, CH_3); 3.29 (1H, d, J 14.9 Hz, CH_2); 4.05 (1H, d, J 14.9 Hz, CH_2); 4.15 (5H, s, Cp^2(Fe)); 4.38, 4.48, 4.61, 4.74 (4H, m of each, Cp(Cr), H(2–5)); 4.87 (2H, m, Cp^1(Fe), H(4,5)); 5.14 (1H, m, Cp^1(Fe), H(3)). Carbon-13 NMR ($CDCl_3$), δ (assignment): 27.77 (CH_3); 28.36 (CH_2); 70.40 (Cp^1(Fe), C(5)); 70.53 (Cp^2(Fe)); 71.84 (Cp^1(Fe), C(3)); 74.08 (Cp^1(Fe), C(4)); 76.06 (Cp^1(Fe), C(2)); 87.48 (Cp^1(Fe), C(1)); 88.85, 88.93 (Cp(Cr), C(3,4)); 90.94, 91.01 (Cp(Cr), C(2,5)); 113.07 (Cp(Cr), C(1)); 203.15 (C=O); 237.58, 237.67 (Cr–C=O). IR spectrum (CH_2Cl_2), (cm^{-1} (intensity)); 2020(vs), 1940(vs), 1690(vs), 1665 (m, sh). Mass spectrum: $m/e = 443$ (M^+).

X-ray diffraction analysis of **6**

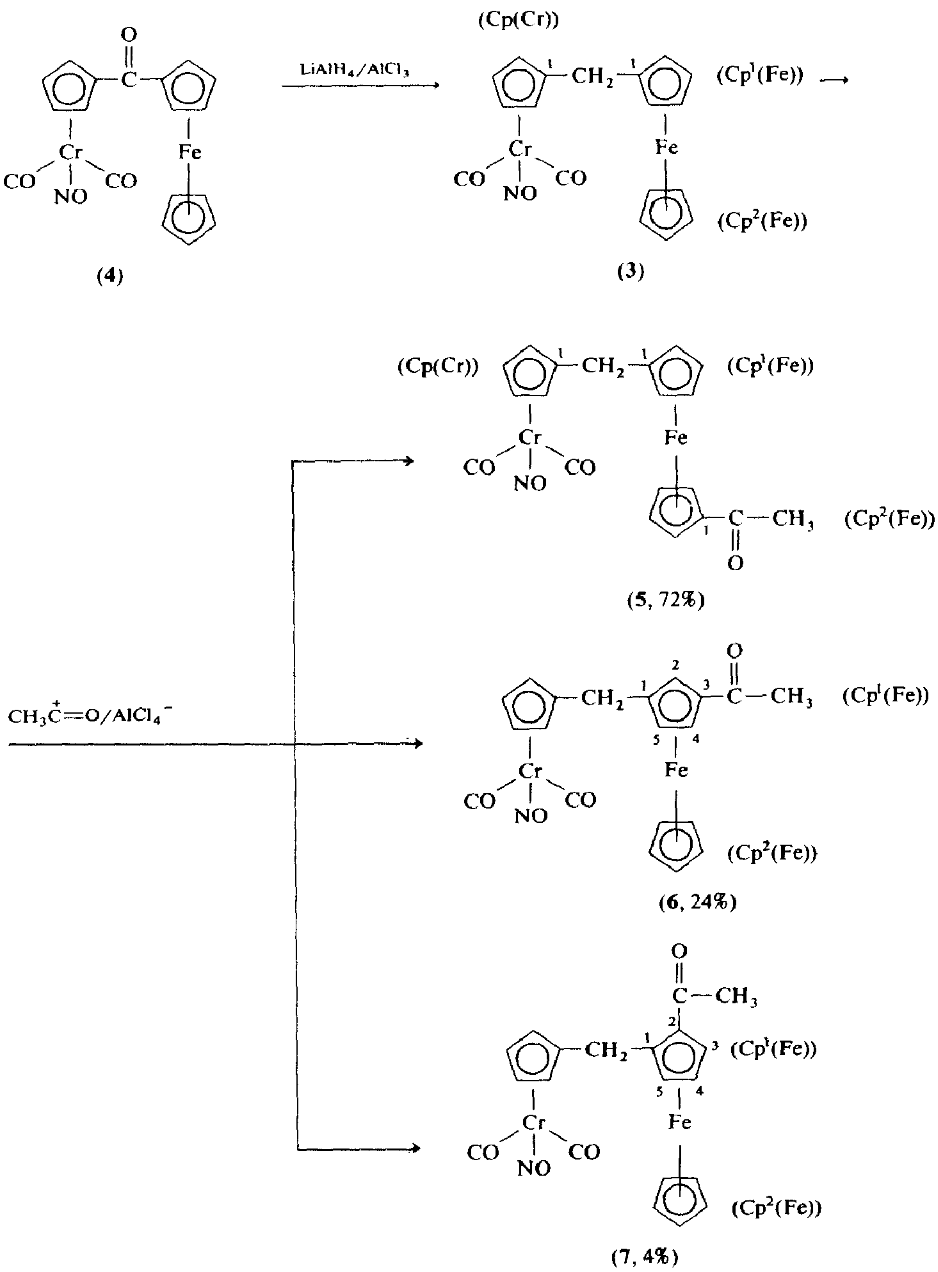
The X-ray diffraction intensity data were collected on a CAD4 diffractometer in $\theta/2\theta$ scan fashion with a graphite monochromated Mo-K_α radiation. The other experimental details are given in Table 1.

The structure was determined by the heavy atom method. The full matrix least squares refinements were based on F. The atomic scattering factors, f_0, were taken from ref. 14a; the anomalous dispersion corrections were included based on ref. 14b. The secondary extinction corrections were applied. All the data processing were done on a PDP-11 and VAX 11/785 using NRCC programs [15].

Results and discussion

Treatment of ketone **4** with 1/1 lithium aluminum hydride/aluminum chloride led to the product of hydrogenolysis **3**. Preforming the Perrier-type complex [7] 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 derivatives **5**, **6** and **7**, with a ratio of 72, 24 and 4%, in a combined yield of 87%.

All compounds **5**–**7** exhibit two carbonyl stretching bands, the symmetric mode occurring at 2020 cm^{-1} and the asymmetric mode at 1940 cm^{-1}. A nitrosyl stretching band is also observed at 1690 cm^{-1}. The normal absorptions of the acetyl groups of **5**–**7** are somewhat obscured by the NO stretching band and exhibited a shoulder on the ν(NO) at 1662–1665 cm^{-1}.



The infrared and ^1H NMR spectra of complex **3** are consistent with its assigned structure and are similar to other metallocenyl systems [4,7,17]. The ^1H NMR spectrum of **3** shows that the chemical shifts of protons on both $Cp^1(Fe)$ (δ 4.09, H(3,4); 4.11, H(2,5)) and Cp(Cr) (δ 4.87, H(3,4); 4.94, H(2,5)) occur at a higher field than those of the corresponding protons of **1** (δ 4.18) and **2** (δ 5.07). This reflects strong electron-releasing effects of both $(CO)_2(NO)Cr(C_5H_4)$-CH_2 and $(C_5H_5)Fe(C_5H_4)$-CH_2 groups.

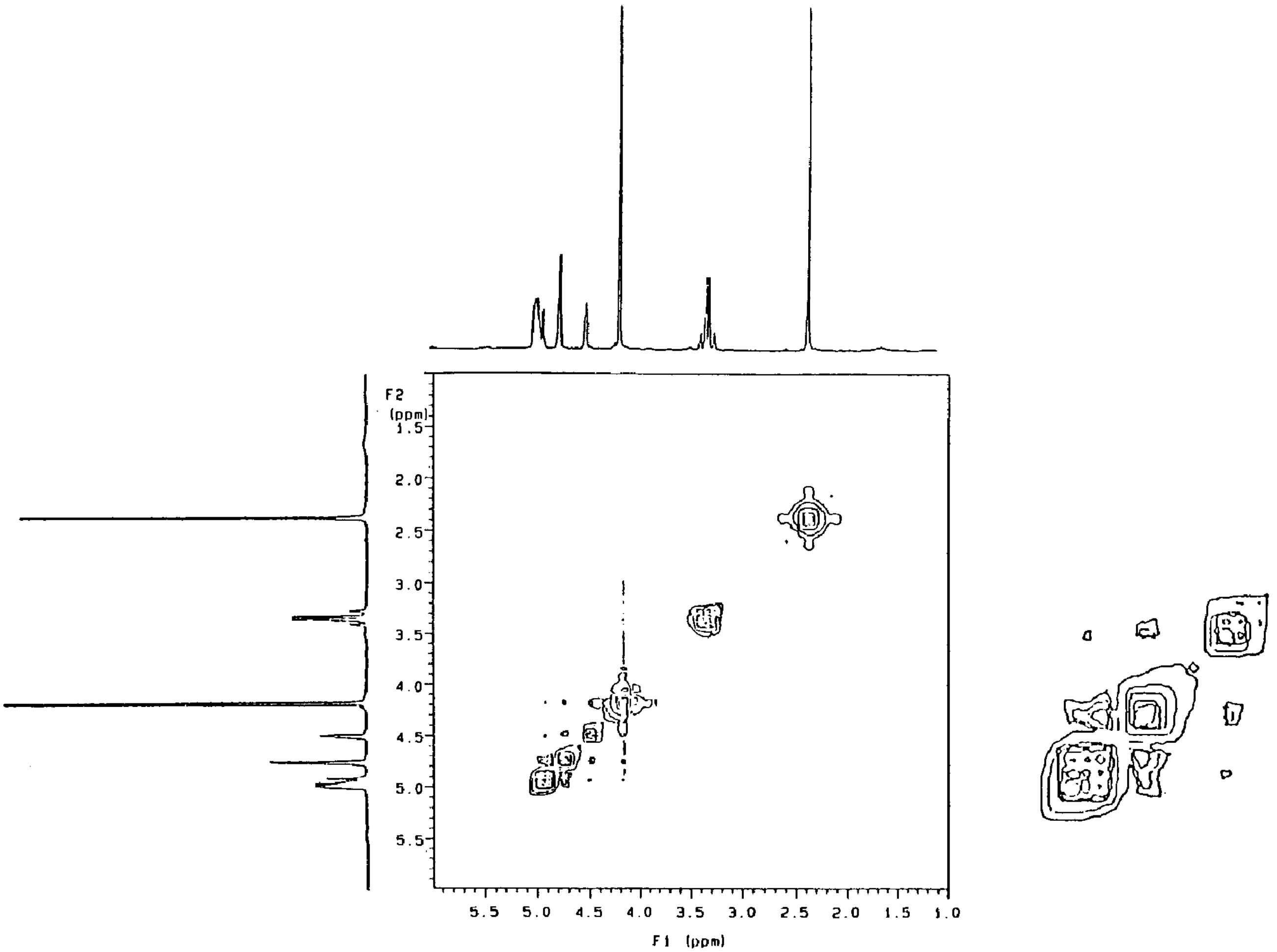
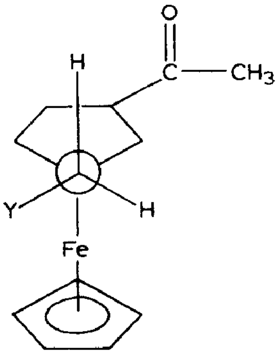


Fig. 1. Two-dimensional ^{1}H-COSY NMR spectrum of **6** in CDCl$_3$.

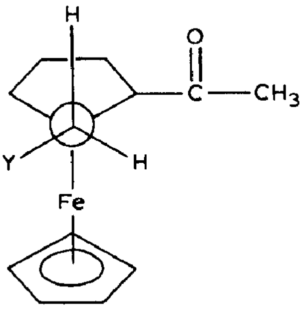
The ^1H NMR spectrum of **5** exhibits a singlet cyclopentadienyl resonance at δ 4.13 corresponding to the protons of $Cp^1(Fe)$, a pair of apparent triplets at δ 4.43 and 4.68 for the protons H(3,4) and H(2,5) of $Cp^2(Fe)$, another pair of apparent triplets at δ 4.84 and 4.88 corresponding to the protons H(3,4) and H(2,5) of Cp(Cr), a 3H singlet at δ 2.35 for acetyl protons, and a 2H singlet at δ 3.19 for methylene protons. As expected, $Cp^2(Fe)$ experienced a stronger carbonyl deshielding effect than the remote $Cp^1(Fe)$ ring.

Metallocenes substituted with at least two different groups on one ring are chiral compounds [16]. The $Cp^1(Fe)$ of both **6** and **7** having two different substituents, methylene and acetyl, would be expected to show diastereotopic effect to the neighboring groups. It is natural that the diastereotopic protons should possess different physical and chemical properties analogously to a pair of diastereomers and therefore one may expect different chemical shifts for the protons of methylene as well as H(2,5) and H(3,4) ring protons of Cp(Cr) in the NMR spectrum. The ^1H NMR spectrum of **6** exhibits an AB pattern at δ 3.18 and 3.34 and coupling constant of 16 Hz corresponding to the two diastereotopic methylene protons, a 3H singlet at δ 2.35 for the acetyl protons, a singlet cyclopentadienyl resonance at δ 4.14 corresponding to the protons of $Cp^2(Fe)$, two multiplets of relative intensity of 1/2 at δ 4.46 and 4.71 corresponding to H(5) and H(2,4) of $Cp^1(Fe)$, two multiplets of relative intensity of 1H at δ 4.87 and 4.92 corresponding to H(3,4) of Cp(Cr) and two closely spaced multiplets of relative intensity of 1H at δ 4.93 and 4.95 corresponding to H(2,5) of Cp(Cr). This assignment is made on the basis of two-dimensional COSY NMR spectrum of **6** (Fig. 1) and analogous to many other metallo-aromatic systems [4,7,10,17].

The ^1H NMR spectrum of **7** exhibits an AX pattern at δ 3.29 and 4.05 with a coupling constant of 15 Hz, corresponding to the two diastereotopic methylene protons, a 3H singlet at δ 2.39 for acetyl protons, a singlet cyclopentadienyl resonance at δ 4.15 corresponding to the protons of $Cp^2(Fe)$, four multiplets of relative intensity of 1H at δ 4.38, 4.48, 4.61 and 4.74 corresponding to the protons of Cp(Cr), and two multiplets of relative intensity of 2/1 at δ 4.87 and 5.14 corresponding to H(4,5) and H(3) of $Cp^1(Fe)$. This assignment is made on the basis



(6,1,3-)
(Y= $C_5H_4Cr(CO)_2NO$)



(7,1,2-)

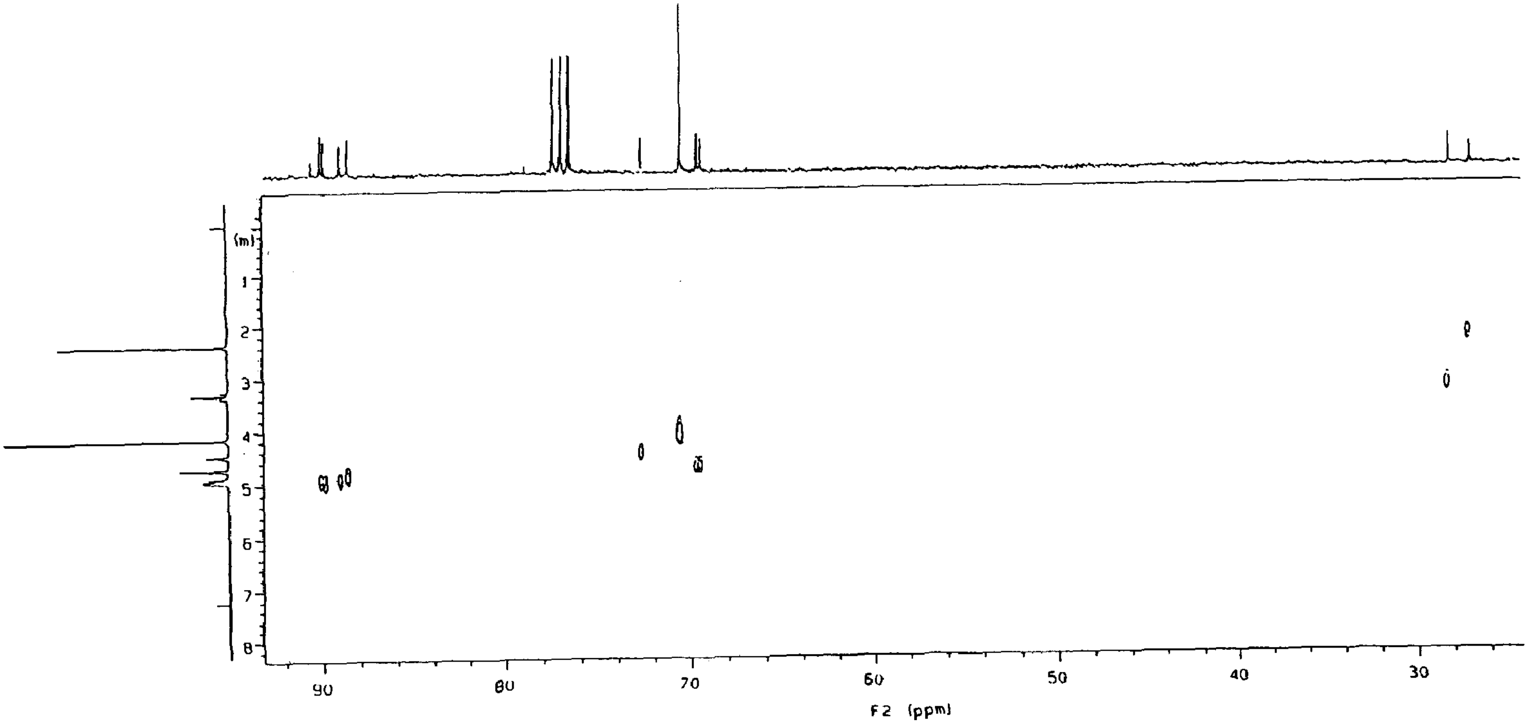


Fig. 2. Two-dimensional ^1H-^{13}C HetCOR NMR spectrum of **6** in $CDCl_3$.

that the proton H(3) of Cp^1(Fe) nearest the electron-withdrawing carbonyl group would be expected to be deshielded to a greater extent than the protons H(4,5) on 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 greater diastereotopic effect on the neighboring groups than 1,3-substituted **6**.

Correspondingly, a larger diastereotopic shifts for methylene protons, H(2,5) and H(3,4) of Cp(Cr) in **7** than those in **6** were observed.

The assignments of ^{13}C NMR spectra for **3** and **5**–**7** are based on standard ^{13}C NMR correlations [18], off resonance decoupled spectra, the DEPT technique, and comparison with other metallo-aromatic system [19]. In the case of **6**, five relatively less intense signals at δ 237.07, 201.95, 112.13, 90.61 and 78.99 corresponding to terminal carbonyl carbon, organic carbonyl carbon, C(1) of Cp(Cr), C(1) of Cp^1(Fe), and C(3) of Cp^1(Fe) respectively, are observed and all show no short range coupling. The carbon of Cp^2(Fe) resonate at δ 70.61. The line assignments for C(2–5) of Cp(Cr) and C(2,4,5) of Cp^1(Fe) were more difficult to make. Based on 2D-HetCOR (Fig. 2) chemical shifts at δ 88.69 and 89.10 were assigned to C(3,4) of the Cp(Cr) ring, at δ 89.99 and 90.14 were assigned to C(2,5) of the Cp(Cr) ring, and chemical shifts at δ 69.50, 69.72 were assigned to C(2,4) of Cp^1(Fe), and δ 72.70 was assigned to C(5) of Cp^1(Fe). Chemical shifts at δ 27.30 and 28.52 were assigned to CH_3 and CH_2.

The line assignments for C(2–5) of both Cp^1(Fe) and Cp(Cr) of compound **3** were also based on 2D-HetCOR (Fig. 3). From Fig. 3 it can clearly be seen that ^{13}C

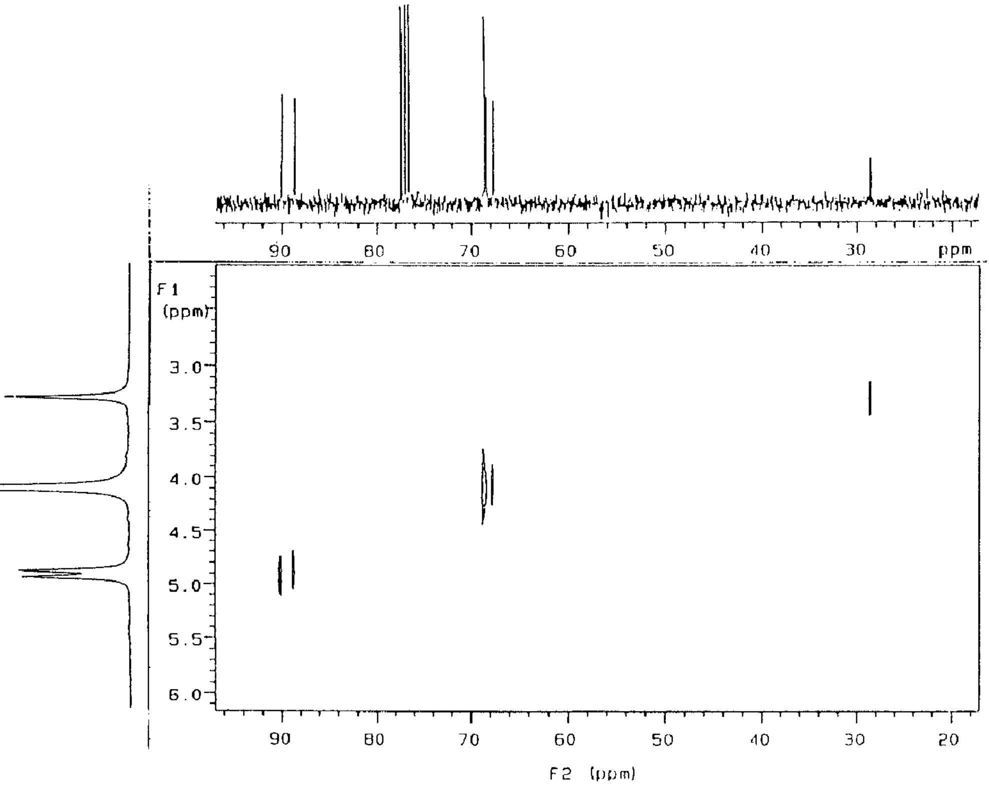


Fig. 3. Two-dimensional ^{1}H-^{13}C HetCOR NMR spectrum of **3** in CDCl$_3$.

resonances at δ 88.66 and 90.09 correlate with the ^{1}H resonances at δ 4.87 and 4.94 which have been assigned to H(3,4) and H(2,5) of Cp(Cr), and the ^{13}C resonances at δ 67.73 and 68.47 correlate with the ^{1}H resonances at δ 4.11 and 4.09 which have been assigned to H(2,5) and H(3,4) of Cp^1(Fe).

One surprising finding in the study of ^{13}C spectra of **3**, **4** [13] and **6** is that the highfield and lowfield chemical shifts are assigned to C(2,5) and C(3,4), respectively, for both electron-withdrawing and electron-releasing substituents on a Cp ring of ferrocene derivatives which is analogous to the literature report [19]. However, the opposite assignment in which the downfield shifts and upfield shifts are assigned to C(2,5) and C(3,4) respectively was made for those substituents on the Cp ring of cynichrodene derivatives.

The mass spectra of **3** and **5–7** all exhibit a parent peak and the expected chromium and iron isotopic pattern. Fragment peaks at $(M-\mathrm{CO})^+$, $(M-2\mathrm{CO})^+$, and $(M-2\mathrm{CO}-\mathrm{NO})^+$ are also always observed.

The molecular structure of **6** is shown in Fig. 4. Selected bond distances and angles are given in Table 2. The atomic coordinates of non-hydrogen atoms are listed in Table 3.

Compound **6** adopts a transoid conformation at the methylene carbon and the cynichrodenyl moiety resides at the *endo* site of the ferrocenyl fragment. The dihedral angle between the Cp(Cr) and Cp^1(Fe) plane is 121.6° which deviates from the corresponding angle C(11)–C–C(21) by 5.2°. 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 1.8°. The twist angle is defined as the torsional angle between the nitrogen atom, the chromium atom, the Cp ring center and the ring carbon bearing exocyclic carbon.

In the cynichrodene moiety, the observed average bond lengths of Cr–C(ring) 2.187 Å, compare favorably with the 2.188(5) average found in $(h^5\text{-}C_5H_5)Cr(CO)_2NO$ [9] and with the 2.20(1) Å average value in $[(h^5\text{-}C_5H_5)Cr(CO)_3]_2$ [20] and in $(h^5\text{-}C_5H_5)Cr(NO)_2Cl$ [21]. The Cr–N length 1.738(7) Å, agrees with the

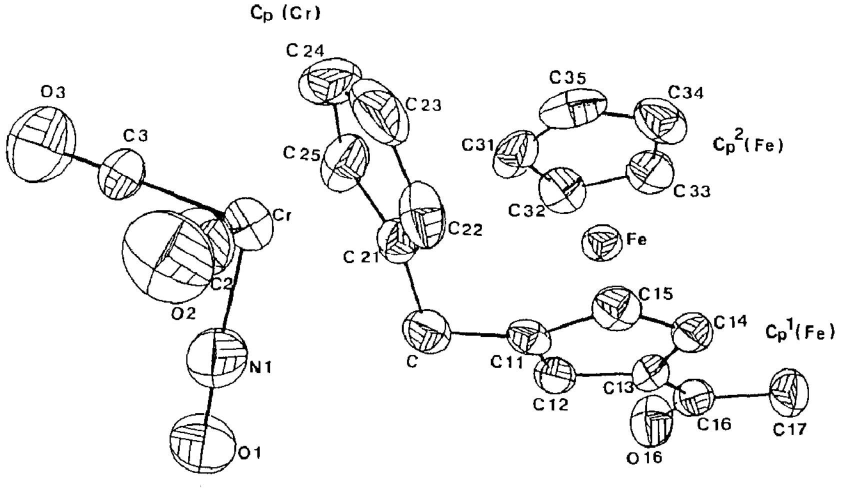


Fig. 4. Molecular configuration of **6**.

Table 2

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

Bond distances			
Fe–C(11)	2.047(7)	Fe–C(12)	2.016(7)
Fe–C(13)	2.025(6)	Fe–C(14)	2.037(6)
Fe–C(15)	2.042(7)	Fe–C(31)	2.017(7)
Fe–C(32)	2.037(7)	Fe–C(33)	2.052(7)
Fe–C(34)	2.042(7)	Fe–C(35)	2.043(7)
Cr–C(21)	2.216(6)	Cr–C(22)	2.177(7)
Cr–C(23)	2.172(8)	Cr–C(24)	2.180(8)
Cr–C(25)	2.188(8)	C(11)–C(12)	1.398(9)
C(11)–C(15)	1.413(9)	C(12)–C(13)	1.429(9)
C(13)–C(14)	1.409(9)	C(14)–C(15)	1.412(10)
C(21)–C(22)	1.420(9)	C(21)–C(25)	1.383(10)
C(22)–C(23)	1.388(11)	C(23)–C(24)	1.384(14)
C(24)–C(25)	1.401(12)	C(31)–C(32)	1.406(11)
C(31)–C(35)	1.385(11)	C(32)–C(33)	1.429(10)
C(33)–C(34)	1.402(11)	C(34)–C(35)	1.422(12)
Cr–N(1)	1.738(7)	Cr–C(2)	1.827(7)
Cr–C(3)	1.796(7)	N(1)–O(1)	1.171(8)
C(2)–O(2)	1.152(9)	C(3)–O(3)	1.139(9)
C–C(11)	1.485(9)	C–C(21)	1.475(9)
C(13)–C(16)	1.463(9)	C(16)–O(16)	1.229(8)
C(16)–C(17)	1.482(10)		
Bond angles			
C(11)–C(12)–C(13)	109.6(5)	C(12)–C(13)–C(14)	106.5(6)
C(12)–C(11)–C(15)	106.7(6)	C(13)–C(14)–C(15)	108.1(5)
C(11)–C(15)–C(14)	109.1(5)	C(21)–C(22)–C(23)	108.4(7)
C(22)–C(21)–C(25)	106.0(6)	C(22)–C(23)–C(24)	108.6(7)
C(23)–C(24)–C(25)	107.2(7)	C(21)–C(25)–C(24)	109.9(7)
C(32)–C(31)–C(35)	110.1(7)	C(31)–C(32)–C(33)	107.2(6)
C(32)–C(33)–C(34)	106.7(6)	C(33)–C(34)–C(35)	109.4(6)
C(31)–C(35)–C(34)	106.5(7)	N(1)–Cr–C(2)	93.2(3)
N(1)–Cr–C(3)	93.7(3)	C(2)–Cr–C(3)	92.1(4)
C(11)–C–C(21)	116.4(6)	Cr–N(1)–O(1)	176.5(6)
Cr–C(2)–O(2)	179.0(7)	Cr–C(3)–O(3)	177.9(7)
C–C(11)–C(12)	125.0(6)	C–C(11)–C(15)	128.2(6)
C–C(21)–C(22)	126.5(6)	C–C(21)–C(25)	127.5(6)
C(13)–C(16)–O(16)	120.6(6)	C(13)–C(16)–C(17)	118.3(6)
O(16)–C(16)–C(17)	121.1(6)	cen.–Cr–C(2)	120.7(2)
cen.–Cr–C(3)	125.0(3)	cen.–Cr–N(1)	123.6(2)
C(14)–C(13)–C(16)	128.1(6)	C(12)–C(13)–C(16)	125.3(6)

1.72(1) Å in (h^5-C_5H_5)Cr(NO)$_2$(NCO) [22], 1.704(4) Å in (CO)$_2$(NO)Cr(h^5-C_5H_5)CH_2(h^5-C_5H_4)Fe[vinyl-(h^5-C_5H_4)] [23] and 1.712(4) Å in (CO)$_2$(NO)Cr(h^5-C_5H_4)C(O)(h^5-C_5H_4)Fe(h^5-C_5H_5) [13]. The Cr–C(carbonyl) distances: 1.827(7) Å (Cr–C(2)); 1.796(7) Å (Cr–C(3)) agree with the 1.864(6) Å found in (h^5-$C_{13}H_9$)Cr(CO)$_2$NO, 1.86 Å found in [h^5-C_5H_5)Cr(CO)$_3$]$_2$ [20] and (CO)$_2$(NO)Cr(h^5-C_5H_4)C(O)(h^5-C_5H_4)Fe(h^5-C_5H_5), and 1.84 Å found in (CO)$_2$(NO)Cr(h^5-C_5H_4)CH_2(h^5-C_5H_4)Fe[vinyl-(h^5-C_5H_4)] [23]. The N≡O length of 1.171(8) Å (N(1)–O(1)) is longer than the C≡O distances of 1.152(9) Å (C(2)–O(2)), 1.139(9) Å (C(3)–O(3)), in keeping with the greater antibonding population in the nitrosyl ligand. The Cr–N–O angle of 176.5(6)° (Cr–N(1)–O(1))

Table 3

Atomic parameters x, y, z and B_{eq} of **6**, e.s.d.'s refer to the last digit printed.

	x	y	z	B_{eq} [a]
Fe	0.16075(5)	0.12813(15)	0.37826(9)	2.78(4)
Cr	0.39590(5)	0.50278(19)	0.36706(11)	3.59(6)
C	0.2526(3)	0.4432(10)	0.3024(6)	3.4(4)
N1	0.3701(3)	0.6622(10)	0.2614(6)	5.8(4)
O1	0.3499(3)	0.7691(10)	0.1926(5)	8.5(4)
C2	0.4340(3)	0.6836(11)	0.4558(6)	4.4(4)
O2	0.4573(3)	0.7989(8)	0.5119(5)	6.8(4)
C3	0.4623(3)	0.4491(11)	0.2931(6)	4.1(4)
O3	0.5049(3)	0.4206(9)	0.2464(6)	7.8(4)
C11	0.1935(3)	0.3895(9)	0.3447(5)	2.6(3)
C12	0.1427(3)	0.3499(10)	0.2731(5)	3.1(3)
C13	0.0935(3)	0.3126(9)	0.3437(5)	2.8(3)
C14	0.1151(3)	0.3316(9)	0.4607(5)	2.8(3)
C15	0.1763(3)	0.3782(10)	0.4612(5)	3.0(3)
C16	0.0339(3)	0.2556(10)	0.2998(6)	3.3(4)
O16	0.02245(21)	0.2365(8)	0.1944(4)	4.9(3)
C17	−0.0125(3)	0.2255(12)	0.3852(6)	4.4(4)
C21	0.3054(3)	0.3804(10)	0.3739(5)	2.9(3)
C22	0.3250(3)	0.4507(11)	0.4853(6)	4.0(4)
C23	0.3754(4)	0.3510(14)	0.5242(7)	6.2(5)
C24	0.3886(4)	0.2215(12)	0.4395(8)	6.6(6)
C25	0.3454(3)	0.2410(11)	0.3477(7)	4.5(4)
C31	0.2193(3)	−0.0597(10)	0.3196(7)	4.5(4)
C32	0.1613(4)	−0.1069(10)	0.2773(6)	4.3(4)
C33	0.1267(3)	−0.1391(11)	0.3765(7)	4.5(4)
C34	0.1650(4)	−0.1117(11)	0.4757(6)	4.9(5)
C35	0.2227(4)	−0.0620(11)	0.4405(7)	5.3(4)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

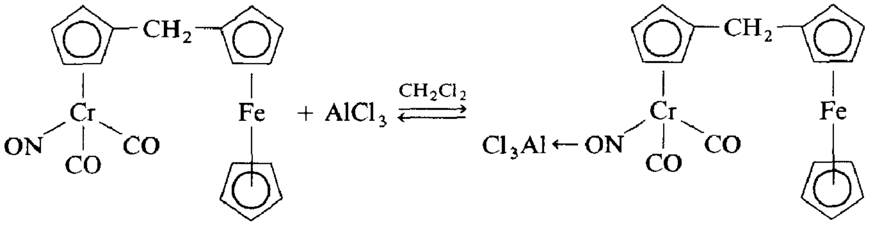
is consistent with the NO^+ formalism typical of the linear M–NO linkage, while the Cr–C–O angles of 179.0(7)° (Cr–C(2)–O(2)), 177.9(7)° (Cr–C(3)–O(3)) indicate the usual mode of bonding in the terminal metal carbonyl complexes. The Cr–centroid (Cp(Cr)) distance of 1.837(9) Å, agrees with the 1.844 Å in $(h^5\text{-}C_5H_5)Cr(CO)_2NO$ and 1.884 Å in $(h^5\text{-}C_{13}H_9)Cr(CO)_2NO$ [9]. The average C–C distance in the ring (Cr(Cr)) is 1.395 Å. The mean angle in the ring is 108°.

The two cyclopentadienyl rings of the ferrocenyl moiety exhibit an average twist angle of 17°. 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 the compound is somewhat between the staggered and the eclipsed configurations. There is a 2.2° offset from parallelism between the two Cp rings of the ferrocene moiety and the rings are separated by 3.29 Å. The mean bond distance of the ferrocenyl moiety in compound **6** is 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)) 1.412 Å, C–C (Cp^2(Fe)) 1.409 Å. The exocyclic C–C bond measures 1.485(9) Å (C–C(11)), 1.475(9) Å (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 −1.6° and −3.2°, respectively. The θ angle is defined as the angle between the exocyclic C–C bond and the Cp ring with positive angles toward the metal. The θ angle between bond C(13)–C(16) and the ring plane of Cp^1(Fe) is $-2.8°$. The acetyl plane (C(13)–C(16)–C(17)) turns away from the ring plane of Cp^1(Fe) by 20.1°. The bond lengths in the acetyl group are similar to the values expected for C=O, $C(sp^2)$–$O(sp^2)$, $C(sp^2)$–$C(sp^2)$ and $C(cp^2)$–$C(sp^3)$ bond lengths [26].

Mechanistic considerations

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



(3)

Rausch et al. [7] had studied the interaction of aluminum chloride with **2**. They found that in Friedel–Crafts reaction the complexation of aluminum chloride with the nitrosyl oxygen of **2** deactivates the Cp ring. Only in systems with a three molar excess of aluminum chloride has coordination with CO been invoked. A related study by Lokshin et al. [27] concerning the interaction of aluminum chloride with the molybdenum and tungsten analogues of **2** was reported in 1976.

Electrophilic substitution of a cyclopentadienyl ring bearing an alkyl substituent is well known to occur 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 2-position of Cp^1(Fe).

Supplementary material available

List of anisotropic temperature factors of nonhydrogen atoms and the coordinates with isotropic temperature factors of hydrogen atoms as well as list of structure amplitudes (23 pages) are deposited. Ordering information can be obtained from the authors.

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