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Friedel–Crafts acylation of $(CO)_2(NO)Cr(\eta^5\text{-}C_5H_4)CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ and crystal structure of $(CO)_2(NO)Cr(\eta^5\text{-}C_5H_4)CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5H_4)Cr(CO)_2(NO)$

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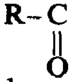
Abstract

Friedel–Crafts reaction of $[h^5$-(ferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (3) (hereafter called cynichrodenylferrocenylmethane) with various acyl chlorides $R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Cl$ (R = CH_3, C_6H_5, $(C_5H_4)Cr(CO)_2(NO)$, $(C_5H_4)Fe(C_5H_5)$) has afforded new metallocenyl ketones (1′-acylferrocenyl)cynichrodenylmethane (**5a**–**5d**) in 21–63% yield. The structure of [1′-(cynichrodenoyl)ferrocenyl]cynichrodenylmethane (**5c**) has been solved by an X-ray diffraction study: space group $P2_1/n$, a 16.739(4), b 12.171(4), c 13.112(3) Å, β 106.84(2)°, $Z = 4$. Compound **5c** adopts a transoid conformation at the organic carbonyl carbon and cisoid conformation at methylene carbon in which the cynichrodenyl moiety resides at the methylene site of ferrocenyl fragment. The cynichrodenylmethyl and cynichrodenoyl moieties are in the 1,3′-configuration.



$R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Cl$

Introduction

Substituent effects of electrophilic aromatic substitution in 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. 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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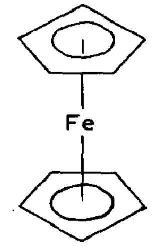
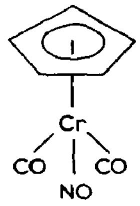


(ferrocene, 1)



(cynichrodene, 2)

(η^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 ≥ (η^5-cyclopentadienyl)tetracarbonylvanadium ≈ benzene > (η^5-cyclopentadienyl)tricarbonylrhenium. Since the compound cynichrodenylferrocenylmethane (3) containing both cynichrodenyl and ferrocenyl groups has been prepared by reduction of cynichrodenyl ferrocenyl ketone (4) with lithium aluminum hydride/aluminum chloride [9], 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 [7,10–15]. Herein, we report the preparations and spectra of compounds **5a**–**5d** and the crystal structure of $(CO)_2(NO)Cr(\eta^5\text{-}C_5H_4)CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5H_4)\text{-}Cr(CO)_2(NO)$ (**5c**).

Experimental

All operations were carried out under a nitrogen atmosphere by means of Schlenkware techniques. Trace oxygen in the nitrogen was removed by BASF catalyst and deoxygenated nitrogen was dried with molecular sieve 3Å and P_4O_{10}. 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 sodiumbenzophenone. All other solvents were used as commerically 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 use. Cynichrodenylferrocenylmethane (3) was prepared according to the literature procedure [9].

^{1}H and ^{13}C (300 and 400 MHz) NMR spectra were obtained on a Bruker AM-300-WB or AM-400 or a VXR-300 spectrometer. ^{1}H and ^{13}C NMR were referenced to tetramethylsilane. Two-dimensional 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 the Microanalytical Laboratory at National Taiwan University.

Preparation of (1′-benzoylferrocenyl)cynichrodenylmethane (5b)

Benzoyl chloride (0.18 g, 1.28 mmol) was stirred with aluminum chloride (0.34 g, 2.56 mmol) in 40 ml methylene chloride for 1 h at room temperature. The solution was filtered from excess $AlCl_3$ and the filtrate was added dropwise to a solution of **3** (0.5 g, 1.25 mmol) in 50 ml 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 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 three times 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 (2 g) was added, and the solvent removed under vacuum. The residue was added to a dry-packed column (2 × 45 cm) of silica gel. Elution of column with hexane/ether (10/1) gave an orange band which upon removal of solvent under vacuum gave **5b** (0.21 g, 33%) as a brownish red gummy solid.

^{1}H NMR ($CDCl_3$): δ (relative intensity, multiplicity, assignment): 3.14 (2H, s, CH_2); 4.12 (4H, s, Cp^1(Fe)); 4.52 (2H, t, Cp^2(Fe) H(3,4)); 4.84 (2H, t, Cp^2(Fe) H(2,5); 4H, m, Cp(Cr)); 7.44 (2H, m, Ph H(3,5)); 7.53 (1H, m, Ph H(4)); 7.85 (2H, m, Ph H(2,6)). ^{13}C NMR ($CDCl_3$): δ (assignment): 27.39 (CH_2); 70.00 (Cp^1(Fe), C(2,5)); 70.63 (Cp^1(Fe), C(3,4)); 72.20 (Cp^2(Fe), C(2,5)); 73.23 (Cp^2(Fe), C(3,4)); 78.64 (Cp^2(Fe), C(1)); 87.73 (Cp^1(Fe), C(1)); 88.61 (Cp(Cr), C(3,4)); 90.11 (Cp(Cr), C(2,5)); 112.67 (Cp(Cr),C(1)); 128.07 (Ph, C(2,6)); 128.30 (Ph, C(3,5)); 131.61 (Ph, C(4)); 139.72 (Ph, C(1)); 198.67 (C(O)): 237.25 (Cr–C≡O). IR (CH_2Cl_2): cm^{-1} (intensity): 2017 (vs), 1941 (vs), 1691 (vs), 1642 (s). Mass spectrum: $m/e = 505$ (M^+).

Preparation of (1′-acetylferrocenyl)cynichrodenylmethane (5a)

This compound was prepared by an analogous procedure to **5b** using acetyl chloride [14].

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%. ^{1}H 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)). ^{13}C 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 (CH_2Cl_2): cm^{-1} (intensity): 2020(vs), 1940(vs), 1690(vs), 1664(m,sh). Mass spectrum: $m/e = 443$ (M^+).

Preparation of (1′-cynichrodenoylferrocenyl)cynichrodenylmethane (5c)

To a stirred suspension of cynichrodenyl carboxylic acid [11] (0.31 g, 1.25 mmol) in 30 ml of methylene chloride, phosphorus pentachloride (0.26 g, 1.25 mmol) was added. After stirring about 20 min aluminum chloride (0.33 g, 2.50 mmol) was added and the reaction mixture was stirred for 2 h at room temperature. The solution was filtered from excess $AlCl_3$ 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 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 × 45 cm) of silica gel. Elution of column with pentane/ether (4/1) gave an orange band which upon removal of solvent under vacuum gave **5c** (0.17 g, 21%), m.p. 55–57 ° C. An X-ray sample was obtained by the solvent expansion method from hexane/methylene chloride at 0 ° C.

Analysis: Found: C, 49.41; H, 2.95; N, 4.18. $C_{26}H_{18}Cr_2FeN_2O_7$ calcd.: C, 49.55; H, 2.88; N, 4.44%. ^{1}H NMR ($CDCl_3$): δ(relative intensity, multiplicity, assignment): 3.21 (2H, s, CH_2); 4.18 (4H, s, Cp^1(Fe)); 4.50 (2H, Cp^2(Fe), H(3,4)); 4.79 (2H, t, Cp^2(Fe), H(2,5)); 4.85 (2H, t, Cp(Cr), H(3,4)); 4.90 (2H, t, Cp(Cr), H(2,5)); 5.16 (2H, t, Cp^2(Cr), H(3,4)); 5.82 (2H, t, Cp^2(Cr), H(2,5)). ^{13}C NMR ($CDCl_3$): δ(assignment): 27.57 (CH_2); 70.31 (Cp^1(Fe), C(2,5)); 70.71 (Cp^1(Fe), C(3,4)); 71.20 (Cp^2(Fe), C(2,5)); 73.18 (Cp^2(Fe), C(3,4)); 78.90 (Cp^2(Fe), C(1)); 88.03 (Cp^1(Fe), C(1)); 88.78 (Cp(Cr), C(3,4)); 90.24 (Cp(Cr), C(2,5)); 91.27 (Cp^2(Cr), C(3,4)); 94.07 (Cp^2(Cr), C(2,5)); 112.73 (Cp(Cr), C(1)); 102.9 (Cp^2(Cr), C(1)); 192.18 (C(O)); 234.70 (Cp^2–C$\equiv$O); 237.21 (Cr–C$\equiv$O). IR (CH_2Cl_2): cm^{-1} (intensity): 2014 (vs, b); 1946 (vs, b); 1698 (vs, b); 1625 (m). Mass spectrum: $m/e = 630$ (M^+).

Preparation of (1′-ferrocenoylferrocenyl)cynichrodenylmethane (5d)

To a stirred suspension of ferrocenylcarboxylic acid (0.30 g, 1.30 mmol) in 30 ml methylene chloride, phosphorus pentachloride (0.30 g, 1.44 mmol) was added. After stirring about 20 min aluminum chloride (0.51 g, 3.75 mmol) was added and the mixture was stirred for 2 h at room temperature. The solution was filtered from excess $AlCl_3$ and the filtrate was added dropwise to a solution of **3** (0.52 g, 1.30 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 mixture was then cooled to 0 ° C and slowly hydrolyzed with 50 ml 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 three times with water, once with a sodium bicarbonate solution, once again with water and dried with anhydrous magnesium sulfate. The solution was filtered, and the filtrate was 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 (2 × 45 cm) of silica gel. Elution of the column with hexane/ether (4/1) gave an orange band which upon removal of solvent under vacuum gave **5d** (0.20 g, 25%) as a brownish red solid, m.p. 135–137 ° C.

Analysis: Found: C, 56.68; H, 3.80; N, 2.60. $C_{29}H_{23}CrFe_2NO_4$ calcd.: C, 56.81; H, 3.78; N, 2.28%. ^{1}H NMR ($CDCl_3$): δ(relative intensity, multiplicity, assignment): 3.18 (2H, s, CH_2); 4.13 (4H, s, Cp^1(Fe)); 4.18 (5H, s, Cp^4(Fe)); 4.47 (2H, t, Cp^2(Fe), H(3,4)); 4.51 (2H, t, Cp^3(Fe), H(3,4)); 4.84 (2H, t, Cp(Cr), H(3,4)); 4.88 (2H, t, Cp(Cr), H(2,5)); 4.93 (2H, t, Cp^2(Fe), H(2,5)); 4.96 (2H, t, Cp^3(Fe), H(2,5)). ^{13}C

NMR ($CDCl_3$): δ (assignment): 27.52 (CH_2); 69.84 (Cp^1(Fe), C(2,5)); 69.98 (Cp^4(Fe)); 70.34 (Cp^1(Fe), C(3,4)); 70.51 (Cp^3(Fe), C(2,5)); 71.15 (Cp^2(Fe), C(2,5)); 71.53 (Cp^3(Fe), C(3,4)); 72.24 (Cp^2(Fe), C(3,4)); 80.44 (Cp^3(Fe), C(1)); 80.80 (Cp^2(Fe), C(1)); 87.52 (Cp^1(Fe), C(1)); 88.58 (Cp(Cr), C(3,4)); 90.11 (Cp(Cr), C(2,5)); 112.87 (Cp(Cr), C(1)); 198.98 (C(O)); 237.27 (Cr–C≡O). IR (CH_2Cl_2): cm^{-1} (intensity): 2017 (vs); 1941 (vs); 1691 (vs); 1615 (m). Mass spectrum: $m/e = 613$ (M^+).

X-ray diffraction analysis of 5c

The intensity data were collected on a Nicolet R3m/V diffractomer with a graphite monochromator (Mo-K_α radiation). $\theta/2\theta$ scan data were collected at room

Table 1

Summary of crystal data and intensity collection

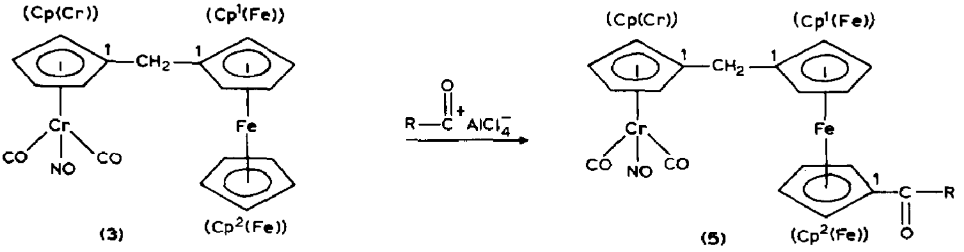
Empirical Formula		$C_{26}H_{18}N_2O_7Cr_2Fe$
Color; Habit		Orange to red; thin plate
Crystal size (mm^3)		$0.025 \times 0.50 \times 0.55$
Space group		Monoclinic, $P2_1/c$
Unit cell dimensions	(Å)	a 16.739(4)
	(Å)	b 12.171(4)
	(Å)	c 13.112(3)
	(°)	β 106.84(2)
Volume	(Å^3)	2554(1)
Formula units/cell		4
Formula weight	(AMU)	630.3
Density (calc.)	(g/cm^3)	1.64
Absorption coefficient	(cm^{-1})	13.93
F(000)	(e^-)	1272
Diffractometer used		Nicolet R3m/V
Radiation		Mo-K_α (λ 0.71073 Å)
Temperature	(°C)	23
Monochromator		Highly oriented graphite crystal
2θ Range	(°)	2.0 to 50.0
Scan type		$\theta/2\theta$
Scan speed	(°/min)	Variable; 3.26 to 14.65
Scan range	(°)	1.20 plus K_α-separation
Background measurement		Stationary crystal and stationary counter at beginning and end of scan, each for one-half of total scan time
Standard reflections		3 measured every 50 reflections
Index ranges		$-16 \leqslant h \leqslant 16$, $-15 \leqslant k \leqslant 0$, $0 \leqslant l \leqslant 20$
Reflections collected		4134 (2830 $I > 3.0\sigma(I)$)
Unique reflections		3411 (2526 $I > 2.5\sigma(I)$)
Extinction correction		$\chi = 0.00024(6)$, where $F^* = F\ [1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms		Riding model
Weighting scheme		$w^{-1} = \sigma^2(F) + 0.0013F^2$
Final residuals (obs. data)(%)		$R = 4.25$, $R_w = 4.50$
Goodness-of-Fit		1.20
Largest and mean Δ/σ		0.019, 0.006
Data-to-Parameter ratio		6.1/1
Largest difference peak	(e^-/Å^3)	0.31
Largest difference Hole	(e^-/Å^3)	−0.32

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.

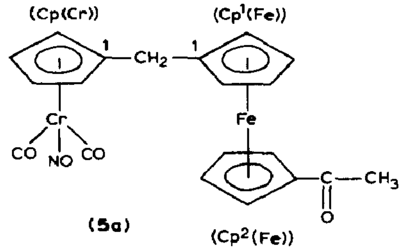
The structure was solved by direct methods using SHELXTL PLUS program [16]. Full matrix least-squares refinement on F used anomalous-dispersion corrections for atoms with atomic numbers greater than 16. Neutral atom scattering form factors from International Tables for X-ray Crystallography [17] was 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 Å^2. All calculations were performed on a MicroVAX II based Nicolet SHELXTL PLUS system.

Results and discussion

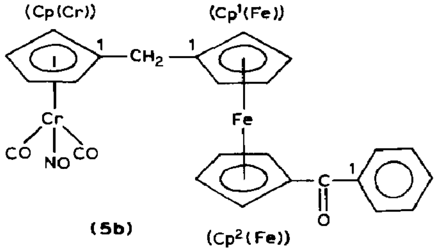
Preforming the Perrier-type complexes [7] of various acyl chloride $R{-}\underset{\underset{O}{\|}}{C}{-}Cl$ ($R = CH_3$, C_6H_5, $(C_5H_4)Cr(CO)_2(NO)$, $(C_5H_4)Fe(C_5H_5)$) and aluminum chloride in the absence of **3** and then allowing these complexes to react with **3**, respectively, led to the acylated derivatives **5a–5d** in 21–63% yield.



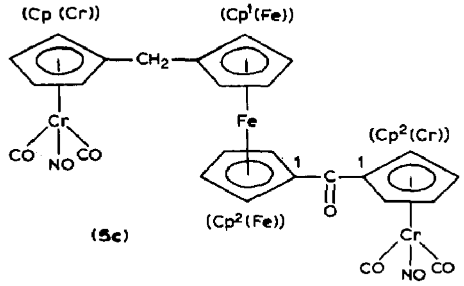
(3) (5)



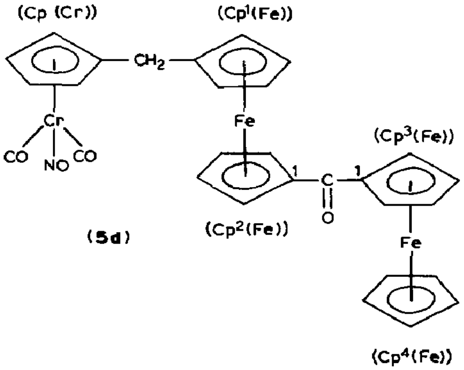
(5a)



(5b)



(5c)



(5d)

All compounds **5a**–**5d** exhibits two carbonyl stretching bands, the symmetric mode occurring at 2014–2020 cm^{-1} and the asymmetric mode at 1940–1946 cm^{-1}. A nitrosyl stretching band is also observed at 1690–1698 cm^{-1} for all of the compounds. The normal absorption of the acetyl group of **5a** is somewhat obscured by the NO stretching band and exhibits as a shoulder on the ν(NO) at 1664 cm^{-1}. In compounds **5b**–**5d** delocalization of the organic C=O group through both sides of the aromatic rings reduces the double bond character of the C to O bond, causing absorption at lower wavenumbers than that of **5a**. The following order of increasing wavenumber of C=O stretching: **5d** (1615 cm^{-1}) < **5c** (1625 cm^{-1}) < **5b** (1642 cm^{-1}) was observed. This trend is correlated well with the order of decreasing stability of the carbocations: $(C_5H_5)Fe(C_5H_4)C^+RR' > (CO)_2(NO)Cr(C_5H_4)C^+RR' > C_6H_5C^+RR'$ [18]. It suggests that the carbocation having greater capability of supplying electron density to the cationic center also has greater capability of delocalization of the carbonyl π-electrons. The broader absorption of ν(CO) and ν(NO) in **5c** compared to **5a**, **5b** and **5d** was observed. This is consistent with the fact that **5c** contains two kinds of cynichrodenyl groups: carbonyl and methylene substituted.

The ^1H NMR spectra of compounds **5a**–**5d** are consistent with their assigned structures and are similar to other metallocenyl systems [4,7,19,20]. In the case of **5c**, the spectrum exhibits a singlet cyclopentadienyl resonance at δ 4.18 corresponding to the protons of Cp^1(Fe). A pair of triplets at δ 4.50 and 4.79 for the protons H(3,4) and H(2,5) of Cp^2(Fe), a pair of triplets at δ 4.85 and 4.90 corresponding to the 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 Cp^2(Cr), and a 2H singlet at δ 3.21 for methylene protons are observed. As expected Cp^2(Fe) and Cp^2(Cr) experienced stronger carbonyl deshielding than the remote Cp^1(Fe) and Cp(Cr) rings. In the case of **5d**, the assignments for H(2–5) of Cp(Cr), H(2,5) of Cp^2(Fe) and H(2,5) of Cp^3(Fe) were difficult to make. Based on 2D-HETCOR (Fig. 1) chemical shifts at δ 4.84 and 4.88 were assigned to H(3,4) and H(2,5) of Cp(Cr) ring, at δ 4.93 and 4.96 were assigned to C(2,5) of Cp^2(Fe) and C(2,5) of Cp^3(Fe), respectively.

The assignments of ^{13}C NMR spectra of compounds **5a**–**5d** are based on standard ^{13}C NMR correlations [21], off resonance decoupled spectra, DEPT technique, and comparison with other metallo-aromatic systems [13–15,19,22,23]. In the case of **5c**, seven relatively less intense signals are observed at δ 237.21, 234.70, 192.18, 112.73, 102.9, 88.03 and 78.90 corresponding to terminal carbonyl carbons $Cp^1(Cr)\text{–}C{\equiv}O$, $Cp^2(Cr)\text{–}C{\equiv}O$, organic carbonyl carbon, C(1) of Cp(Cr), C(1) of Cp^2(Cr), C(1) of Cp^1(Fe) and C(1) of Cp^2(Fe), respectively, and all show no short range coupling. The methylene carbon resonates at δ 27.57. The assignments for C(2–5) of Cp(Cr), Cp^2(Cr), Cp^1(Fe) and Cp^2(Fe) are more difficult to make. Based on 2D HETCOR (Fig. 2), chemical shifts at δ70.31 and 70.71 were assigned to C(2,5) and C(3,4) of Cp^1(Fe) ring, chemical shifts at δ 71.20 and 73.18 were assigned to C(2,5) and C(3,4) of Cp^2(Fe), chemical shifts at δ 88.78 and 90.24 were assigned to C(3,4) and C(2,5) of Cp(Cr) and chemical shifts at δ 91.27 and 94.07 were assigned to C(3,4) and C(2,5) of Cp^2(Cr).

In the case of **5d**, the assignments for C(2–5) of Cp^1(Fe), Cp^2(Fe) and Cp^3(Fe) were difficult to make. Based on 2D-HETCOR (Fig. 1), chemical shifts at δ 69.84 and 70.34 were assigned to C(2,5) and C(3,4) of Cp^1(Fe), chemical shifts at δ 70.51 and 71.15 were assigned to C(2,5) of Cp^3(Fe) and Cp^2(Fe), and chemical shifts at δ

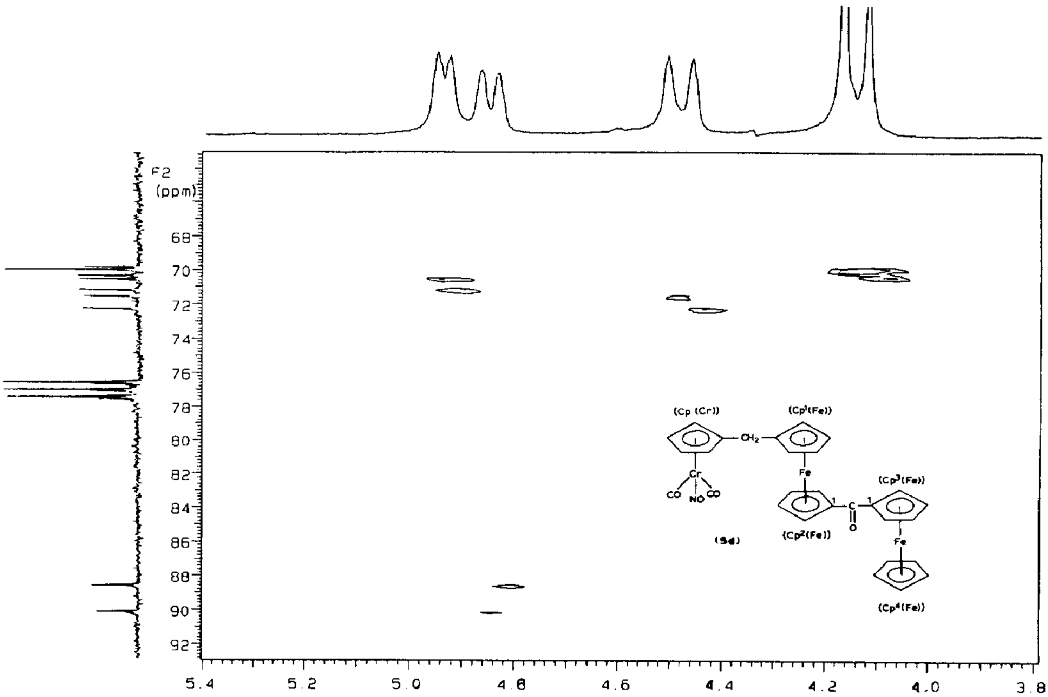


Fig. 1. Two-dimensional $^1H\{^{13}C\}$ HETCOR NMR spectrum of **5d** in $CDCl_3$.

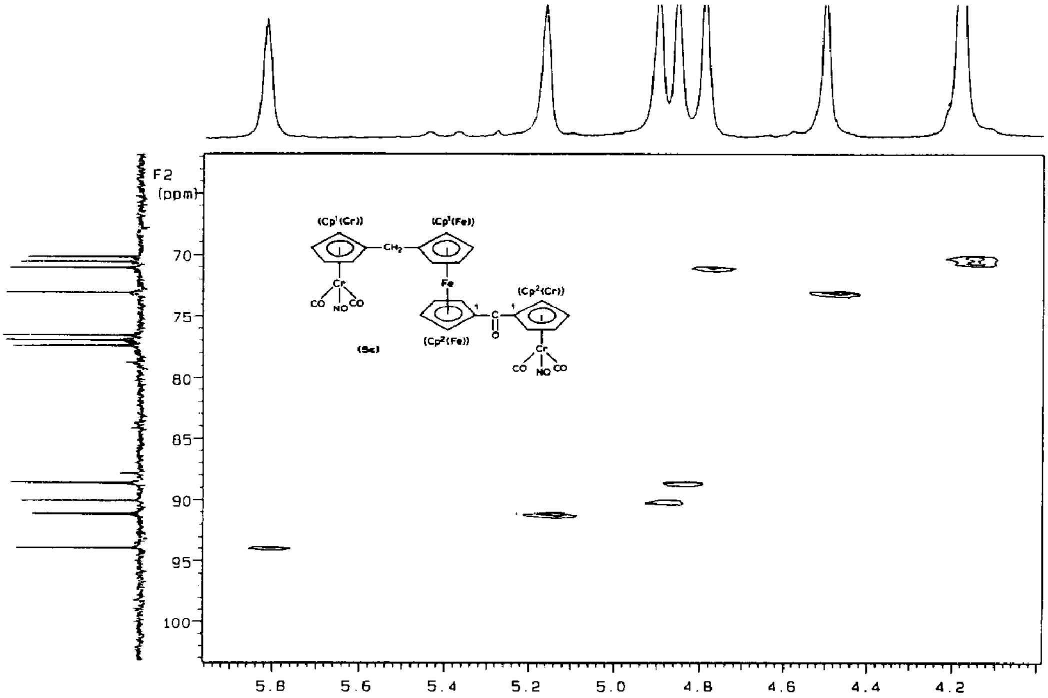


Fig. 2. Two-dimensional $^1H\{^{13}C\}$ HETCOR NMR spectrum of **5c** in $CDCl_3$.

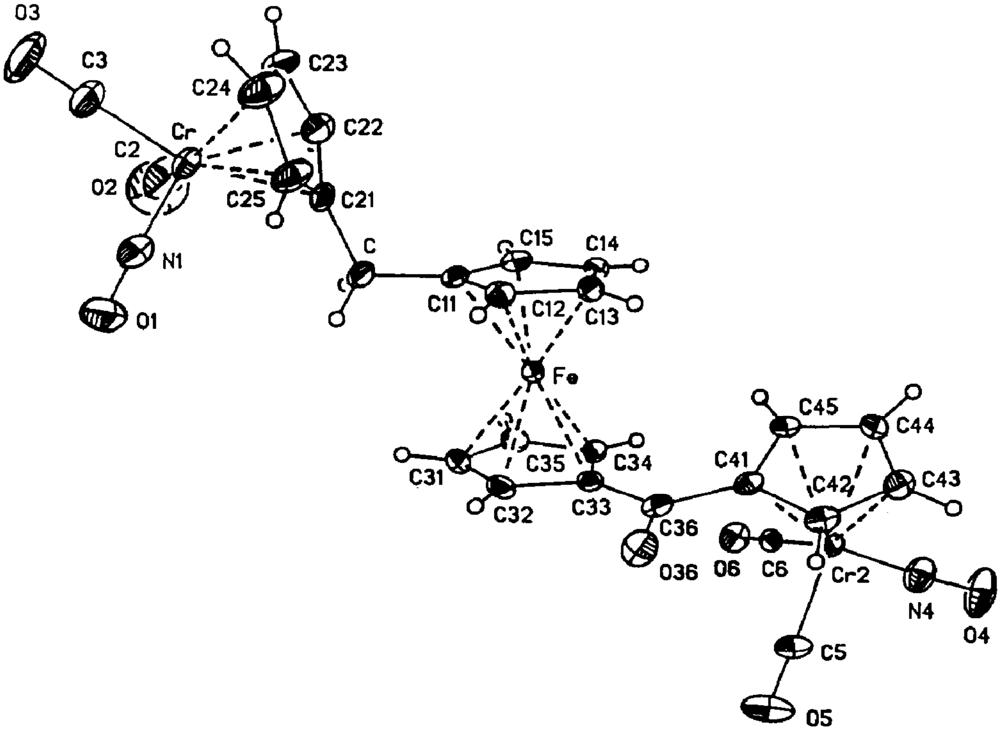


Fig. 3. Molecular configuration of **5c**.

71.53 and 72.24 were assigned to C(3,4) of Cp^3(Fe) and Cp^2(Fe). The assignment of lowfield chemical shifts to C(3,4) and the high chemical shifts to C(2,5) on Cp^1(Fe), Cp^2(Fe) and Cp^2(Fe) rings and the opposite assignments: the lowfield chemical shifts to C(2,5) and the highfield chemical shifts to C(3,4) on Cp(Cr) and Cp^2(Cr), are analogous to literature reports [14,15].

The mass spectra of **5a**–**5d** 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 **5c** is shown in Fig. 3. Selected bond distances and angles are given in Table 2. The atomic coordinates of non-hydrogen atoms are listed in Table 3.

Compound **5c** adopts a transoid conformation at the organic carbonyl carbon and cisoid conformation at the methylene carbon in which the cynichrodenyl moiety resides at the exo site of ferrocenyl fragment. The cynichrodenylmethyl and cynichrodenoyl moieties are in the 1,3′-configuration. The dihedral angle between Cp(Cr) and Cp^1(Fe) planes is 107.2° which deviates from the corresponding angle C(11)–C–C(21) by 3.6°. The coordination geometry about each of Cr centers 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 methylene-substituted cynichrodenyl moiety is located at the site toward the exocyclic carbon of the Cp(Cr) ring with a twist angle of 51.3°, while in the carbonyl-substituted cynichrodenyl fragment, the nitrosyl group is located at the site away the exocyclic carbon of Cp^2(Cr) ring with a twist angle of 174.5°. The twist angle is defined as the

Table 2

Selected bond distances (Å) and angles (°) of **5c**

Distances			
Fe–C(11)	2.040(5)	Fe–C(12)	2.034(6)
Fe–C(13)	2.051(7)	Fe–C(14)	2.033(7)
Fe–C(15)	2.037(5)	Fe–C(31)	2.034(7)
Fe–C(32)	2.040(6)	Fe–C(33)	2.035(4)
Fe–C(34)	2.031(5)	Fe–C(35)	2.045(6)
Cr–C(21)	2.185(5)	Cr–C(22)	2.217(9)
Cr–C(23)	2.191(9)	Cr–C(24)	2.175(9)
Cr–C(25)	2.184(8)	Cr(2)–C(41)	2.186(5)
Cr(2)–C(42)	2.194(6)	Cr(2)–C(43)	2.213(7)
Cr(2)–C(44)	2.221(6)	Cr(2)–C(45)	2.197(5)
C(11)–C(12)	1.422(9)	C(11)–C(15)	1.423(9)
C(12)–C(13)	1.416(9)	C(13)–C(14)	1.411(10)
C(14)–C(15)	1.403(9)	C(21)–C(22)	1.404(10)
C(21)–C(25)	1.404(11)	C(22)–C(23)	1.425(11)
C(23)–C(24)	1.372(15)	C(24)–C(25)	1.416(10)
C(31)–C(32)	1.401(10)	C(31)–C(35)	1.403(10)
C(32)–C(33)	1.434(8)	C(33)–C(34)	1.423(8)
C(34)–C(35)	1.414(9)	C(41)–C(42)	1.440(8)
C(41)–C(45)	1.426(8)	C(42)–C(43)	1.383(10)
C(43)–C(44)	1.419(9)	C(44)–C(45)	1.392(9)
Cr–C(2)	1.773(10)	Cr–C(3)	1.844(7)
Cr–N(1)	1.743(7)	Cr(2)–C(5)	1.849(6)
Cr(2)–C(6)	1.817(6)	Cr(2)–N(4)	1.738(5)
C(2)–O(2)	1.154(14)	C(3)–O(3)	1.141(10)
C(5)–O(5)	1.144(8)	C(6)–O(6)	1.157(7)
N(4)–O(4)	1.168(8)	N(1)–O(1)	1.173(11)
C–C(11)	1.499(9)	C–C(21)	1.512(8)
C(36)–C(33)	1.462(8)	C(36)–C(41)	1.475(8)
C(36)–O(36)	1.221(7)	Cr–cen.(Cp(Cr))	1.836
Cr(2)–cen.(Cp^2(Cr))	1.846	Cr ··· C	3.310
Cr(2) ··· C(36)	3.251		
cen.(Cp^1(Fe)) ··· cen.(Cp^2(Fe))	3.289		
Fe ··· C	3.175	Fe ··· C(36)	3.146
Fe ··· C(Cp^1(Fe)) ave	2.039	Fe ··· C(Cp^2(Fe)) ave.	2.037
Cr ··· C(Cp(Cr)) ave.	2.190	Cr(2) ··· C(Cp^2(Cr)) ave.	2.202
Angles			
C(11)–C(12)–C(13)	108.9(6)	C(12)–C(13)–C(14)	107.0(6)
C(13)–C(14)–C(15)	109.0(6)	C(14)–C(15)–C(11)	108.3(6)
C(15)–C(11)–C(12)	106.8(5)	C(21)–C(22)–C(23)	106.9(7)
C(22)–C(23)–C(24)	110.1(7)	C(23)–C(24)–C(25)	106.3(8)
C(25)–C(21)–C(22)	107.1(6)	C(24)–C(25)–C(21)	109.5(8)
C(31)–C(32)–C(33)	107.6(6)	C(32)–C(33)–C(34)	107.1(5)
C(33)–C(34)–C(35)	108.3(5)	C(35)–C(31)–C(32)	109.4(6)
C(34)–C(35)–C(31)	107.7(6)	C(41)–C(42)–C(43)	109.0(5)
C(42)–C(43)–C(44)	108.2(6)	C(43)–C(44)–C(45)	108.0(6)
C(44)–C(45)–C(41)	109.2(5)	C(45)–C(41)–C(42)	105.6(5)
C(2)–Cr–C(3)	95.1(4)	C(2)–Cr–N(1)	92.5(4)
C(3)–Cr–N(1)	93.2(3)	C(5)–Cr(2)–C(6)	92.7(3)
C(5)–Cr(2)–N(4)	95.6(3)	C(6)–Cr(2)–N(4)	93.5(3)
C(11)–C–C(21)	110.8(5)	Cr–N(1)–O(1)	177.5(6)
Cr–C(2)–O(2)	175.1(8)	Cr–C(3)–O(3)	178.9(8)
Cr(2)–N(4)–O(4)	177.1(6)	Cr(2)–C(5)–O(5)	177.1(5)

Table 2 (continued)

Angles			
Cr(2)–C(6)–O(6)	179.3(5)	C–C(11)–C(12)	125.9(6)
C–C(11)–C(15)	127.4(6)	C–C(21)–C(22)	127.5(7)
C–C(21)–C(25)	125.0(6)	C(36)–C(33)–C(32)	121.2(5)
C(36)–C(33)–C(34)	131.7(5)	C(36)–C(41)–C(42)	122.1(5)
C(36)–C(41)–C(45)	132.3(5)	C(33)–C(36)–C(41)	122.2(5)
C(41)–C(36)–O(36)	118.0(5)	C(33)–C(36)–O(36)	119.8(5)
cen.–Cr–C(2)	122.0	cen.–Cr–C(3)	121.5
cen.–Cr–N(1)	124.5	cen.–Cr(2)–C(5)	118.8
cen.–Cr(2)–C(6)	123.5	cen.–Cr(2)–N(4)	124.8

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

In the cynichrodene moieties, the observed average bond lengths of the Cr-C(ring): 2.190 (Cp(Cr)), 2.202 Å (Cp^2(Cr)) compare favorably with 2.188(5) Å average found in (η^5-C_5H_5)Cr$(CO)_2$(NO) [10], and with the 2.20(1) Å average found in [(η^5-C_5H_5)Cr$(CO)_3]_2$ [24] and in (η^5-C_5H_5)Cr$(NO)_2$Cl] [25]. The Cr–N lengths 1.743(7) (Cr–N(1)) and 1.738(5) Å (Cr(2)–N(4)) fall in the range of reported values, 1.712(4) in $(CO)_2$(NO)Cr(C_5H_4)C(O)(C_5H_4)Fe(C_5H_5) [15] and 1.72(1) Å in (η^5-C_5H_5)Cr$(NO)_2$(NCO) [26]. The Cr–C(carbonyl) distances 1.773 (Cr–C(2)), 1.844 (Cr–C(3)), 1.850 (Cr(2)–C(5)) and 1.817 Å (Cr(2)–C(6)) agree well with 1.864(6) Å found in (η^5-$C_{13}H_9$)Cr$(CO)_2$(NO) [10] and 1.864, 1.846 Å found in $(CO)_2$(NO)Cr-(C_5H_4)C(O)(C_5H_4)Fe(C_5H_5) [15]. The N≡O lengths of 1.173(11) (N(1)–O(1)), 1.168(8) Å (N(4)–O(4)) are longer than the C≡O distances of 1.154(14) (C(2)–O(2)), 1.141(10) (C(3)–O(3)), 1.144(8) (C(5)–O(5)) and 1.157(7) Å (C(6)–O(6)) in keeping with the greater antibonding population in the nitrosyl ligand. The Cr–N–O angles of 177.5(6) (Cr–N(1)–O(1)) and 177.1(6)° (Cr(2)–N(4)–O(4)) are consistent with the NO^+ formalism typical of linear M–NO linkage, while the Cr–C–O angle of 175.1(8) (Cr–C(2)–O(2)), 178.9(8) (Cr–C(3)–O(3)), 177.1(5) (Cr(2)–C(5)–O(5)) and 179.3(5)° (Cr(2)–C(6)–O(6)) indicate the usual mode of bonding in the terminal metal carbonyl complexes. The Cr–centroid (Cp(Cr)) and Cr(2)–centroid (Cp^2(Cr)) distances are 1.836 and 1.846 Å respectively, which agree with the 1.844 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) [10]. The average C–C distances in the rings are 1.404 (Cp(Cr)) and 1.412 (Cp^2(Cr)). The mean angles in both rings are 108°.

The two cyclopentadienyl rings of ferrocene moiety exhibit an average twist angle of 1.8°. The twist angle is defined by Palenik [27] as the torsional angle between a ring carbon, the two ring centers and the corresponding carbon on the opposite rings. It is apparent that compound **5c** is close to the eclipsed configuration which is in good agreement with other ferrocenyl compounds [28,29]. There is a 1.8° offset from parallelism between the two Cp rings of ferrocene moiety and those rings are separated by 3.29 Å. The mean bond distances of ferrocenyl moiety in compound **5c** are very similar to those in related molecules [29]. The average Fe–C(ring) distance is 2.04 Å, the average C–C distance in rigns is 1.415 Å, the exocyclic C–C bond measures 1.499(9) (C–C(11)), 1.462(8) (C(36)–C(33)), 1.512(8) (C–C(21)) and 1.475(8) Å (C(36)–C(41)) and the mean angle in the rings is 108°.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of **5c**

	x	y	z	U_{eq} [a]
Fe	1535(1)	847(1)	3762(1)	35(1)
Cr(1)	5045(1)	1628(1)	7389(1)	56(1)
Cr(2)	−1627(1)	524(1)	818(1)	42(1)
C(1)	3319(4)	1132(8)	5441(5)	62(3)
C(2)	5615(5)	585(8)	6965(7)	104(4)
C(3)	5931(5)	2107(7)	8496(6)	92(3)
C(5)	−1506(4)	1511(5)	−199(4)	55(2)
C(6)	−940(3)	−475(4)	477(4)	36(2)
C(11)	2407(3)	893(5)	5218(4)	46(2)
C(12)	1769(4)	1682(5)	5162(4)	46(2)
C(13)	993(4)	1133(6)	4954(4)	50(2)
C(14)	1151(4)	2(6)	4873(4)	55(3)
C(15)	2010(4)	−153(5)	5040(4)	48(2)
C(21)	3731(3)	1251(6)	6625(5)	54(2)
C(22)	4053(5)	412(7)	7364(6)	79(3)
C(23)	4329(5)	918(9)	8387(6)	86(4)
C(24)	4181(5)	2028(9)	8296(6)	92(4)
C(25)	3782(4)	2233(8)	7203(5)	80(3)
C(31)	2158(4)	1151(6)	2671(5)	56(3)
C(32)	1529(4)	1937(5)	2579(4)	51(2)
C(33)	749(3)	1364(4)	2350(4)	40(2)
C(34)	928(4)	225(5)	2307(4)	39(2)
C(35)	1799(4)	101(6)	2500(4)	48(2)
C(36)	−38(3)	1956(5)	2187(4)	45(2)
C(41)	−819(3)	1395(4)	2189(4)	39(2)
C(42)	−1616(4)	1939(5)	1859(4)	48(2)
C(43)	−2226(4)	1223(6)	1973(5)	55(3)
C(44)	−1835(4)	219(6)	2392(4)	51(2)
C(45)	−983(4)	325(5)	2524(4)	41(2)
N(1)	5237(4)	2580(6)	6495(5)	94(3)
N(4)	−2526(4)	−91(5)	13(4)	73(2)
O(1)	5343(5)	3204(6)	5865(5)	151(4)
O(2)	5934(6)	−134(8)	6661(8)	198(6)
O(3)	6476(4)	2420(7)	9178(6)	153(4)
O(4)	−3147(3)	−496(5)	−495(5)	116(3)
O(5)	−1408(4)	2146(4)	−794(4)	98(3)
O(6)	−496(3)	−1105(3)	263(3)	61(2)
O(36)	−63(3)	2947(3)	2035(4)	72(2)

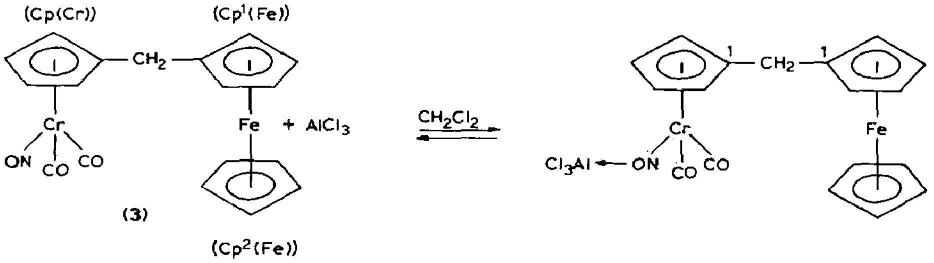
[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The organic C=O bond length is 1.221(7) Å and the angles at this carbonyl group (118, 120 and 122°) do not differ from normal values. The exocyclic carbon (C) is bent away from both metals, Cr and Fe, with θ angles of −0.06 and −0.62°, respectively. The θ angles for C(36) are −1.40 and −1.17°. The θ angle is defined as the angle between the exocyclic C–C bond and the corresponding Cp ring with positive angle toward metal and negative angles away the metal. The carbonyl plane (C(33), C(36), O(36), C(41)) turns away from the corresponding ring plane Cp^2(Fe) and Cp^2(Cr) by 14.9 and 11.7°, respectively. These rotations are the result of intramolecular steric interference between atoms H(C(34)) and H(C(45)). This is supported by the enlargement of bond angles C(36)–C(33)–C(34) and C(36)–C(41)–C(45) to 131.7(5) and 132.3(5)° respectively.

Mechanistic consideration

All three rings Cp(Cr), Cp^1(Fe) and Cp^2(Fe) of **3** are expected to undergo electrophilic aromatic substitution. The higher reactivity of Cp^2(Fe) than that of Cp(Cr) is understandable in that the overall electron withdrawing properties of CO and NO ligands destabilize the transition state for addition of electrophile to CpCr(CO)$_2$(NO) relative to those for reaction of Cp^2(Fe).

The ^{1}H NMR spectrum of **3** shows that the chemical shifts of protons on Cp^1(Fe) (δ 4.09, H(3,4); 4.11, H(2,5)) occur at a higher field than those of the corresponding protons of **1** (δ 4.18). This reflects the strong electron donating effect of the (CO)$_2$(NO)Cr(C$_5$H$_4$)CH$_2$ moiety. The effect should activate Cp^1(Fe) and, to a lesser extent, Cp^2(Fe). However, Cp^2(Fe) was observed to be more active, it might arise from the coordination of **3** with remaining aluminum chloride in the filtrate through the NO ligand. The coordination results in deactivating both Cp(Cr) and Cp^1(Fe) rings. A related study by Rausch et al. [7] concerning the interaction of **2** was reported in 1980. Another reason for the preference of Cp^2(Fe) ring over Cp(Cr) and Cp^1(Fe) toward Friedel-Crafts acylation might be the greater steric hindrance at the latter rings.



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 (10 pages) are deposited. Ordering information can be obtained from the authors.

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References

1 M. Cais, in E.E. Bergmann and B. Pullmann (Eds.), Aromaticity, Pseudo-aromaticity, Anti-aromaticity, Academic Press, New York, 1971.

2 G.G. Knox, I.G. Morrison, P.L. Pauson, P.L. Sandhy and W.E. Watts, J. Chem. Soc. C, (1967) 1853.

3 M. Rosenblum, Chemistry of the Iron Group Metallocenes. Wiley, New York, 1965.

4 D.W. Slocum and C.R. Ernst, Adv. Organomet. Chem., 10 (1972) 79.

5 W.E. Watts in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, Chapter 59.3, 8 (1982) 1017.

6 E.O. Fischer and K. Plesske, Chem. Ber., 94 (1961) 93.
7 M.D. Rausch, E.A. Mintz and D.W. Macomber, J. Org. Chem., 45 (1980) 689.
8 E.O. Fischer, M.V. Foerster, C.G. Kreiter and K.E. Schwarzhans, J. Organomet. Chem., 7 (1967) 113.
9 Y.-P. Wang, R.-S. Shyu, J.-M. Hwu and Y.-H. Li, Proc. Natl. Sci. Counc. ROC(A), 11(2) (1987) 110.
10 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.
11 D.W. Macomber and M.D. Rausch, Organometallics,, 2 (1983) 1523.
12 T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins and J. Trotter, Inorg. Chem., 18 (1979) 3548.
13 M.D. Rausch, D.J. Kowalski and E.A. Mintz, J. Organomet. Chem., 342 (1988) 201.
14 Y.-P. Wang, T.-S. Lin, R.-S. Shyu, J.-M. Hwu, Y. Wang and M.-C. Cheng, J. Organomet. Chem., 371 (1989) 57.
15 Y.-P. Wang, J.-M. Hwu and S.-L. Wang, J. Organomet. Chem., 371 (1989) 71.
16 G.M. Sheldrick, SHELXTL PLUS User Manual, Nicolet XRD Corporation, Madison, Wisconsin, 1986.
17 International Tables for X-ray Crystallography, Kynoch, Birmingham, England, Vol IV, 1974.
18 K. England and P.C. Reeves, J. Organomet. Chem., 319 (1987) 355.
19 M.I. Levenberg and J.H. Richards, J. Am. Chem. Soc., 86 (1964) 2634.
20 M.D. Rausch and A. Siegel, J. Organomet. Chem., 17 (1969) 117.
21 J.B. Stother (Ed.), Carbon-13-NMR Spectroscopy, Academic Press, New York, 1972.
22 B.E. Mann, Adv. Organomet. Chem., 12 (1974) 135.
23 G.H. Williams, D.D. Traficante and D. Seyferth, J. Organomet. Chem., 60 (1973) C53.
24 R.D. Adams, D.E. Collins and F.A. Cotton, J. Am. Chem. Soc., 96 (1974) 749.
25 O.L. Carter, A.T. Mcphail and G.A. Sim, J. Chem. Soc. A, (1966) 1095.
26 M.A. Bush and G.A. Sim., J. Chem. Soc. A., (1970) 605.
27 G.J. Palenik, Inorg. Chem., 9 (1970) 2424.
28 J. Trotter and A.C. Macdonald, Acta, Cryst., 21 (1966) 359.
29 A.P. Krukonis, J. Silverman, N.F. Yannoni, Acta. Cryst. B, 28 (1972) 987.