

## Synthesis and 2D NMR spectra of $\alpha$ -cynichrodenyl- $\alpha$ -ferrocenylmethylium tetrafluoroborate

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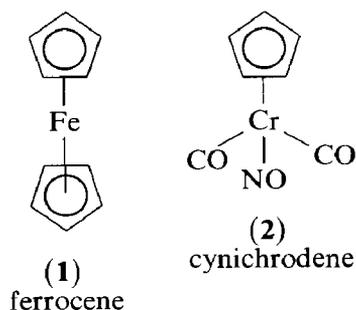
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### Abstract

Reduction of  $[\eta^5\text{-(ferrocenyl)cyclopentadienyl}]_2\text{dicarbonylnitrosylchromium}$  (hereafter called cynichrodenylferrocenylketone) (**1**) with sodium borohydride gives cynichrodenylferrocenyl carbinol (**5**), whereas reduction with lithium aluminum hydride/alluminum chloride leads to cynichrodenylferrocenylmethane (**6**). Protonation of **5** with fluoroboric acid produces  $\alpha$ -cynichrodenyl- $\alpha$ -ferrocenylmethylium tetrafluoroborate (**4**), a new dimetalloccenyl-stabilized carbonium ion. The diastereotopism of  $^1\text{H}$  and  $^{13}\text{C}$  nuclei was observed in both of **4** and **5**. The chemical shifts of H(2–5) protons and C(2–5) carbons in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra respectively have been assigned using two dimensional NMR spectroscopy.

### Introduction

The great stability of  $\alpha$ -metalloccenylcarbonium ions have been the subject of considerable study. The vast majority of these studies have been completed for ferrocene analogs [1,2]; however, to a lesser extent investigations have been devoted to carbonium ions adjacent to ruthenocene [3,4], osmocene [3,4], cymantrene [2,5], ( $\eta^6\text{-benzene}$ )tricarboxylchromium [6], ( $\eta^4\text{-cyclobutadiene}$ )tricarboxyliron [7] and ( $\eta^5\text{-cyclopentadienyl}$ )dicarbonylnitrosylchromium [8,9].



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The availability of cynichrodenylferrocenylketone **3** from the Friedel–Crafts acylation of cynichrodenoylchloride with ferrocene [10] makes of interest the synthesis of a new dimetalloacenyl-stabilized carbonium ion:  $\alpha$ -cynichrodenyl- $\alpha$ -ferrocenylmethylium tetrafluoroborate **4** by reaction of cynichrodenylferrocenylcarbinol **5** with fluoroboric acid in acetic anhydride/ether. Further, while the chemistry of the well-known dicarbonylcyclopentadienylnitrosyl complexes of chromium has become the subject of considerable study, the  $^{13}\text{C}$  NMR of these complexes have not been examined thoroughly [8,11,12]. Herein, we report the preparation and thorough spectral studies of **4–6**. **4** appeared to be the first isolated cynichrodenyl carbonium ion [8,9].

## Experimental

All operations were carried out under a nitrogen atmosphere by means of Schlenk techniques. Trace oxygen in the nitrogen was removed by BASF catalyst and the deoxygenated nitrogen was dried with molecular sieve 3A and  $\text{P}_2\text{O}_5$ . Hexane, 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 Kieselgel 60. The silica gel was heated with a heat gun while mixing in a rotary evaporator attached to a vacuum pump for 2 h to remove water and oxygen. The silica gel was kept under nitrogen before use. Ferrocenoylcyclopentadienyldicarbonylnitrosylchromium **3** was prepared according to the literature procedure [10].

### *Preparation of 1-hydroxyl-1-ferrocenylmethyl-( $\eta^5$ -cyclopentadienyl)dicarbonylnitrosylchromium (5)*

Ferrocenoylcyclopentadienyldicarbonylnitrosylchromium (0.5 g, 1.21 mmol) was dissolved in 20 ml of ethanol. Sodium borohydride (0.16 g, 4.26 mmol) dissolved in 1 ml of water was added and the mixture was refluxed for 30 min. After this period, 5 ml of 6*N* sodium hydroxide was added and the mixture heated for 15 min at 70°C. The ethanol was removed under vacuum and the product extracted with ethyl ether. The ether was washed with water and dried over magnesium sulfate, filtered, and the solvent removed under vacuum leaving a residue. The latter was then dissolved in 50 ml of methylene chloride, 20 g of silica gel was added, and the solvent removed under vacuum. The residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with benzene gave a yellow band which upon removal of the solvent under vacuum gave 1-hydroxy-1-ferrocenylmethyl( $\eta^5$ -cyclopentadienyl)dicarbonylnitrosylchromium 0.45 g (90%). An analytical sample, m.p. 111°C, was obtained by vacuum sublimation at 100°C/0.1 torr.

Analysis: Found: C, 51.65; H, 3.72; N, 3.42.  $\text{C}_{18}\text{H}_{15}\text{CrFeNO}_4$  calcd.: C, 51.82; H, 3.62; N, 3.36%. Proton NMR ( $\text{CDCl}_3$ ):  $\delta$  (relative intensity, multiplicity, assignment): 2.29 (1H, d (*J* 2.8 Hz), OH); 4.20 (2H, m,  $\text{Cp}^1(\text{Fe})$  H(3,4)); 4.21 (5H, s,  $\text{Cp}^2(\text{Fe})$  unsubstituted ring protons); 4.27 (2H, m,  $\text{Cp}^1(\text{Fe})$  H(2,5)); 4.89 (2H, m,  $\text{Cp}(\text{Cr})$  H(3,4)); 5.07, 5.08 (2H, m,  $\text{Cp}(\text{Cr})$  H(2,5)); 5.19 (1H, d (*J* 2.8 Hz), CH(OH)). Carbon-13 NMR ( $\text{CDCl}_3$ ):  $\delta$  (assignment): 65.09, 67.51 ( $\text{Cp}^1(\text{Fe})$ , C(2,5));

66.41 (CH(OH)); 68.25,68.29 (Cp<sup>1</sup>(Fe), C(3,4)); 68.49 (Cp<sup>2</sup>(Fe)); 88.28, 88.53 (Cp(Cr), C(3,4)); 89.78 (Cp(Cr), C(2,5)); 92.83 (Cp<sup>1</sup>(Fe), C(1)); 115.58 (Cp(Cr),C(1)); 236.98 (Cr–C≡O). IR Spectrum, (CDCl<sub>3</sub>): cm<sup>-1</sup>(intensity): 3550m, 3380m, 3120m, 2040vs, 1969vs, 1700vs, 1575w, 1420w, 1350w, 1260w, 1220w, 1110w, 1050m, 1020m, 1005m, 825s, 640s. Mass spectrum:  $m/e = 417 (M^+)$ .

*Preparation of [(η<sup>5</sup>-ferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (6)*

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, ferrocenoylcyclopentadienyldicarbonylnitrosylchromium (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 dichloromethane, 20 g of silica gel added, and the solvent again removed under vacuum. The resulting residue was added to 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 [(η<sup>5</sup>-ferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium, 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<sub>18</sub>H<sub>15</sub>CrFeNO<sub>3</sub> calcd.: C, 53.89; H, 3.77; N, 3.49%. Proton NMR (CDCl<sub>3</sub>): δ (relative intensity, multiplicity, assignment): 3.29 (2H, s, CH<sub>2</sub>); 4.09 (2H, t, Cp<sup>1</sup>(Fe) H(3,4)); 4.10 (5H, s, Cp<sup>2</sup>(Fe) unsubstituted ring protons); 4.11 (2H, t, Cp<sup>1</sup>(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<sub>3</sub>): δ (assignment): 28.59 (CH<sub>2</sub>); 67.73 (Cp<sup>1</sup>(Fe), C(2,5)); 68.47 (Cp<sup>1</sup>(Fe), C(3,4)); 68.68 (Cp<sup>2</sup>(Fe)); 86.17 (Cp<sup>1</sup>(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≡O). IR Spectrum, (CDCl<sub>3</sub>): cm<sup>-1</sup>(intensity); 2035vs, 1965vs, 1717vs, 1600w, 1570w, 1440w, 1102w, 1000w, 865w, 840w. Mass spectrum:  $m/e = 401 (M^+)$ .

*Preparation of α-cynichrodenyl-α-ferrocenylmethylum tetrafluoroborate (4)*

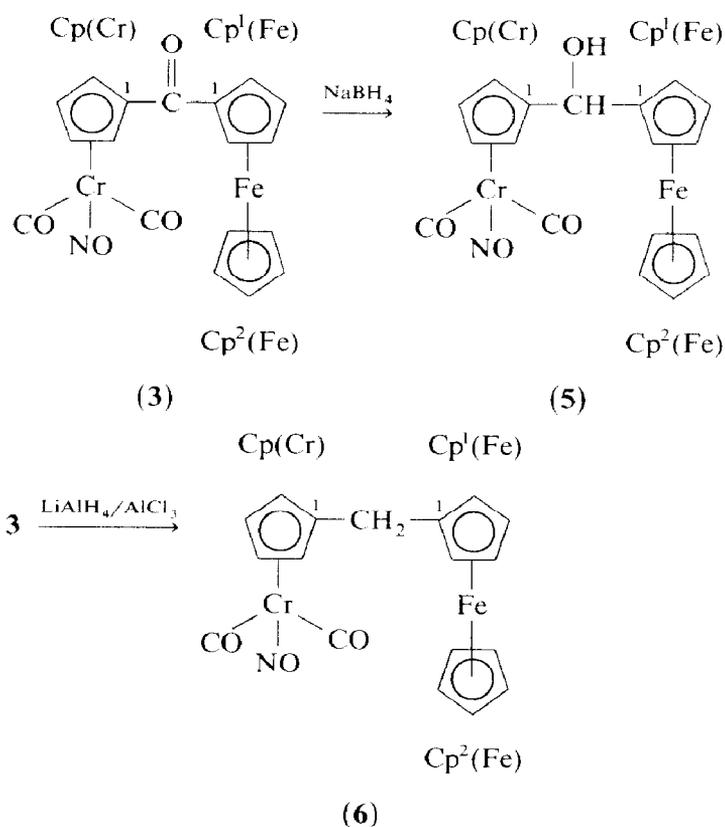
To a solution of 1-hydroxy-1-ferrocenylmethyl(η<sup>5</sup>-cyclopentadienyl)dicarbonylnitrosylchromium (0.42 g, 1.0 mmol) in 5 ml of acetic anhydride was added 1 ml of a solution of fluoroboric acid in acetic acid/anhydride (prepared by dissolving 1.5 ml of 48% aqueous fluoroboric acid solution in 4 ml of acetic anhydride). After stirring for 10 min, dry ethyl ether (20 ml) was added. A brown-black precipitate formed and was filtered, washed with dry ether several times, and dried in vacuum to give the carbonium ion fluoroborate salt, 0.43 g (88%). An analytical sample was obtained as a brown-red solid by recrystallization from acetone/ether/hexane.

Analysis: Found: C, 44.38; H, 3.18; N, 2.77. C<sub>18</sub>H<sub>14</sub>BCrFeF<sub>4</sub>NO<sub>3</sub> calcd.: C, 44.40; H, 2.90; N, 2.88%. Proton NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ (relative intensity, multiplicity, assignment): 4.86 (1H, s, Cp<sup>1</sup>(Fe) H(5)); 5.11 (5H, s, Cp<sup>2</sup>(Fe) unsubstituted ring protons); 5.61 (1H, s, Cp(Cr) H(4)); 5.70 (1H, s, Cp<sup>1</sup>(Fe) H(2)); 5.74 (1H, s, Cp(Cr) H(3)); 5.98 (1H, s, Cp(Cr)H(2)); 6.35 (1H, s, Cp<sup>1</sup>(Fe) H(4)); 6.44 (1H, s, Cp(Cr) H(5)); 6.58 (1H, s, Cp<sup>1</sup>(Fe) H(3)); 8.12 (1H, s, CH). Carbon-13 NMR

(CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$  (assignment): 79.51 (Cp<sup>1</sup>(Fe), C(2)); 82.00 (Cp<sup>1</sup>(Fe), C(5)); 83.06 (Cp<sup>2</sup>(Fe)); 92.04 (Cp(Cr), C(2)); 93.60 (Cp<sup>1</sup>(Fe), C(4)); 94.19 (Cp(Cr), C(4)); 94.32 (Cp<sup>1</sup>(Fe), C(3)); 97.07 (Cp(Cr), C(3)); 99.09 (Cp<sup>1</sup>(Fe), C(1)); 99.85 (Cp(Cr), C(1)); 100.33 (Cp(Cr), C(5)); 120.0 (CH); 234.78 (Cr–C $\equiv$ O). IR Spectrum. (CDCl<sub>3</sub>): cm<sup>-1</sup> (intensity): 3350bm, 2010vs, 1945vs, 1690vs, 1520vs, 815w, 620w.

## Results and discussion

Reduction of ketone **3** with sodium borohydride in aqueous ethanol produced the corresponding secondary alcohol **5** in 90% yield. Treatment of **3** with 1/1 lithium aluminum hydride/aluminum chloride led to the hydrogenolysis product cynchrodenylferrocenylmethane **6** in 41% yield.



All compounds **4–6** exhibit two carbonyl stretching bands, the symmetric mode occurring at 2010–2040 cm<sup>-1</sup> and the asymmetric mode at 1945–1969 cm<sup>-1</sup>. A nitrosyl stretching band is also observed at 1690–1717 cm<sup>-1</sup>. The normal absorption of the hydroxy group of **5** appeared at 3550 cm<sup>-1</sup>.

The <sup>1</sup>H NMR spectrum of **6** exhibits a singlet cyclopentadienyl resonance at  $\delta$  4.10 corresponding to the protons of Cp<sup>2</sup>(Fe), a pair of triplets at  $\delta$  4.09 and 4.11 for the protons of Cp<sup>1</sup>(Fe), another pair of apparent triplets at  $\delta$  4.87 and 4.94 corresponding to the protons of Cp(Cr), and a 2H singlet at  $\delta$  3.29 for methylene protons. As expected, the chemical shifts of protons on both Cp<sup>1</sup>(Fe) and Cp(Cr) occur at a higher field than those of the corresponding protons of **1** ( $\delta$  4.18) and **2**

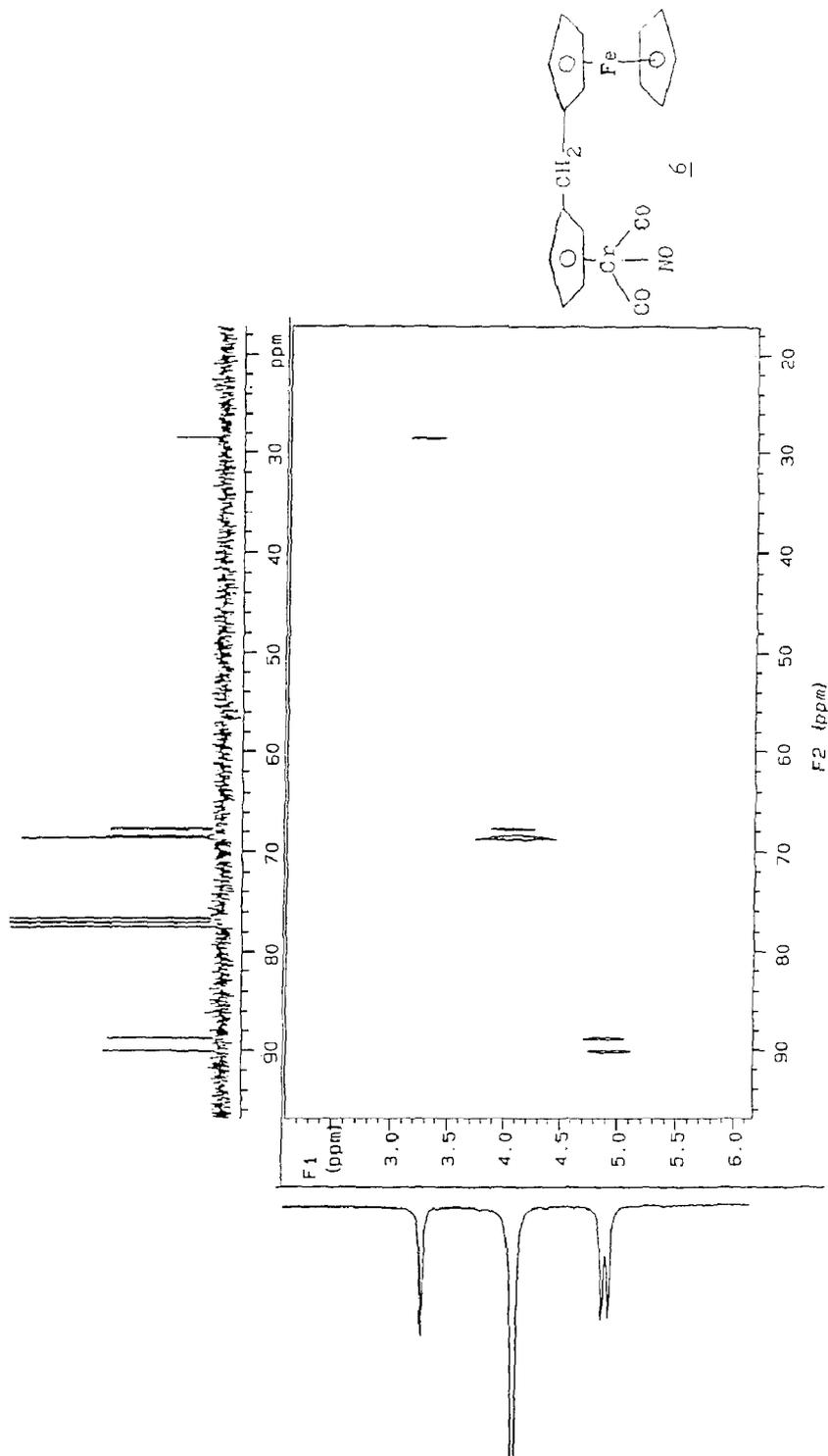


Fig. 1. Two-dimensional  $^1\text{H}$ - $^{13}\text{C}$  HetCOR NMR spectrum of **6** in  $\text{CDCl}_3$ .

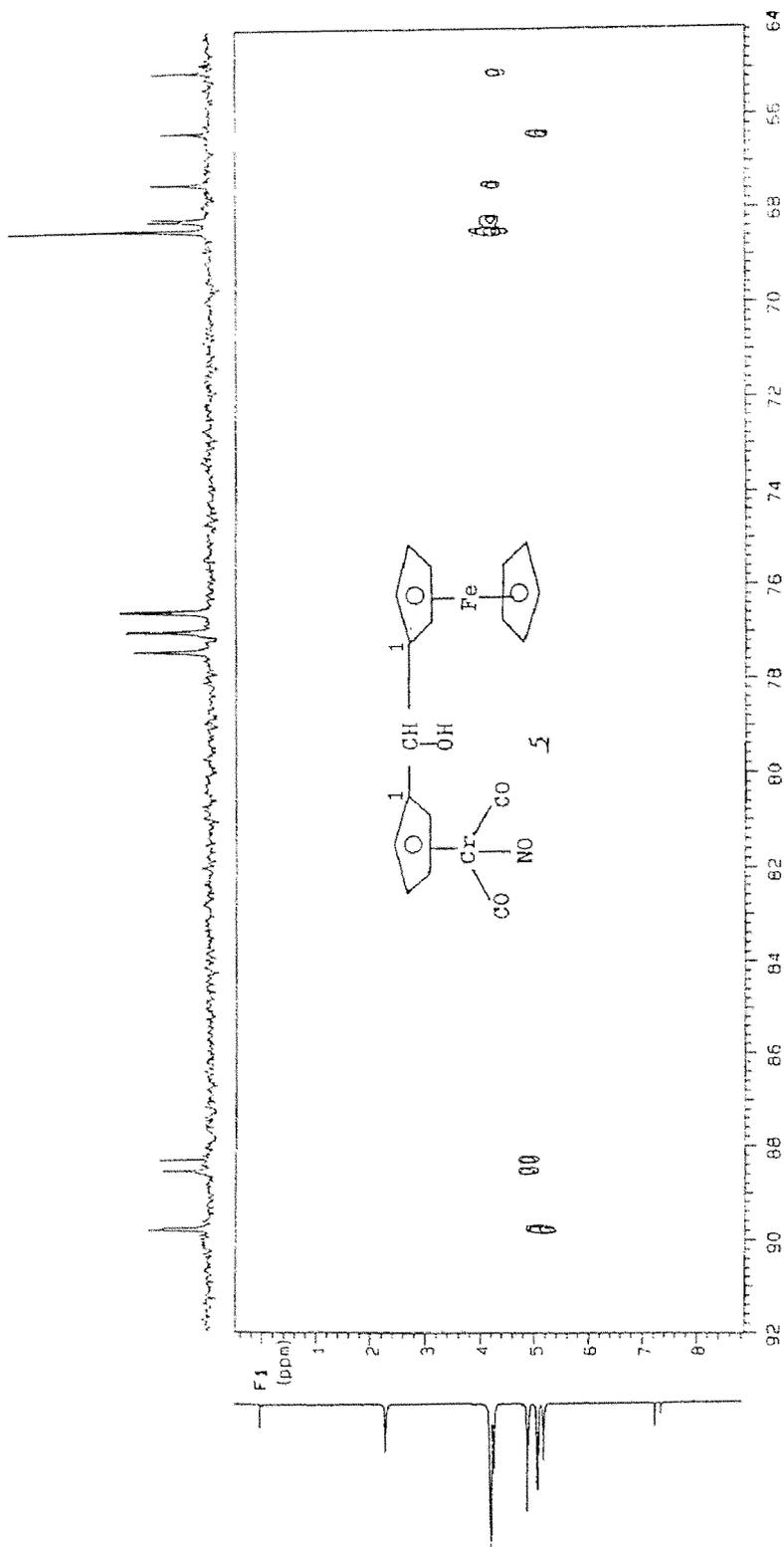


Fig. 2. Two-dimensional  $^1\text{H}$ - $^{13}\text{C}$  HETCOR NMR spectrum of **5** in  $\text{CDCl}_3$ .

( $\delta$  5.07). This suggests that both  $\text{CH}_2(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)$  and  $\text{CH}_2(\text{C}_5\text{H}_4)\text{Cr}(\text{CO})_2\text{-}(\text{NO})$  possess electron-releasing properties.

The hydroxyl substituted carbon in the alcohol **5** is chiral and is thus expected to exhibit two  $\text{A}_2\text{BB}'$  patterns for the protons of  $\text{Cp}^1(\text{Fe})$  and  $\text{Cp}(\text{Cr})$ . For each pattern, it would consist of two closely spaced quartets of relative intensity 1H downfield and a triplet of relative intensity 2H upfield. The two downfield quartets can be assigned to the H(2,5) protons since the protons nearer to the alcohol would be expected to show the greater diastereotopic effect, whereas a proton at either the 3- and 4-position would show little or no diastereotopic effect. Accordingly, a triplet of relative intensity 2H at  $\delta$  4.89 was assigned to the H(3,4) protons of  $\text{Cp}(\text{Cr})$  and two closely spaced multiplets of relative intensity 1H at  $\delta$  5.07 and 5.08 were assigned to H(2,5) protons.

The assignments of the  $^{13}\text{C}$  NMR spectra of compounds **5** and **6** are based on standard  $^{13}\text{C}$  NMR correlations [13]; 2D-HetCOR; DEPT technique and compared with other metallo-aromatic systems [14]. In the case of **6**, three relatively less intense singlets were observed at  $\delta$  237.62, 113.41 and 86.17 corresponding to terminal carbonyl carbon, C(1) of  $\text{Cp}(\text{Cr})$  and C(1) of  $\text{Cp}^1(\text{Fe})$  respectively. Carbons of  $\text{Cp}^2(\text{Fe})$  resonate at  $\delta$  68.68. Chemical shifts at  $\delta$  28.59 was assigned to  $\text{CH}_2$  carbon. The line assignments for C(2–5) of  $\text{Cp}(\text{Cr})$  and  $\text{Cp}^1(\text{Fe})$  were more difficult to make. Based on 2D HetCOR (Fig. 1) chemical shifts at  $\delta$  88.66 and 90.09 were assigned to C(3,4) and C(2,5) of  $\text{Cp}(\text{Cr})$  ring respectively, and at  $\delta$  67.73 and 68.47 were assigned to C(2,5) and C(3,4) of  $\text{Cp}^1(\text{Fe})$  respectively. Analogously, in the case of **5** (Fig. 2), chemical shifts at  $\delta$  88.28 and 88.53 were assigned to C(3,4) of  $\text{Cp}(\text{Cr})$  ring, at  $\delta$  89.78 was assigned to C(2,5) of  $\text{Cp}(\text{Cr})$  ring, at  $\delta$  65.09 and 67.51 were assigned to C(2,5) of  $\text{Cp}^1(\text{Fe})$  ring, at  $\delta$  68.25 and 68.29 were assigned to C(3,4) of  $\text{Cp}^1(\text{Fe})$  ring and at  $\delta$  66.41 was assigned to  $\text{CH}(\text{OH})$ .

There are two surprising findings in the study of  $^{13}\text{C}$  spectra of **5** and **6**. The first is that the highfield and lowfield chemical shifts are assigned to C(2,5) and C(3,4), respectively, for both electron-releasing and electron-withdrawing substituents on a Cp ring of ferrocene derivatives which is analogous to that reported in the literature [15]. 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 second finding is that, in the case of **5**, the greater diastereotopic shift was observed for C(2,5) ( $\Delta$  2.42 ppm) than that for C(3,4) ( $\Delta$  0.04 ppm) of the  $\text{Cp}^1(\text{Fe})$  ring which is analogous to that reported in the literature [15]. However, the greater diastereotopic shift was observed for C(3,4) ( $\Delta$  0.25 ppm) than that of for C(2,5) ( $\Delta$   $\sim$  0 ppm) of the  $\text{Cp}(\text{Cr})$  ring.

Protonation of **5** with 48% aqueous fluoroboric acid in acetic anhydride/ether gave  $\alpha$ -cynichrodenyl- $\alpha$ -ferrocenylmethylum tetrafluoroborate **4** in 88% yield. Attempts to grow single crystals of **4** suitable for X-ray diffraction studies, have so far been unsuccessful.

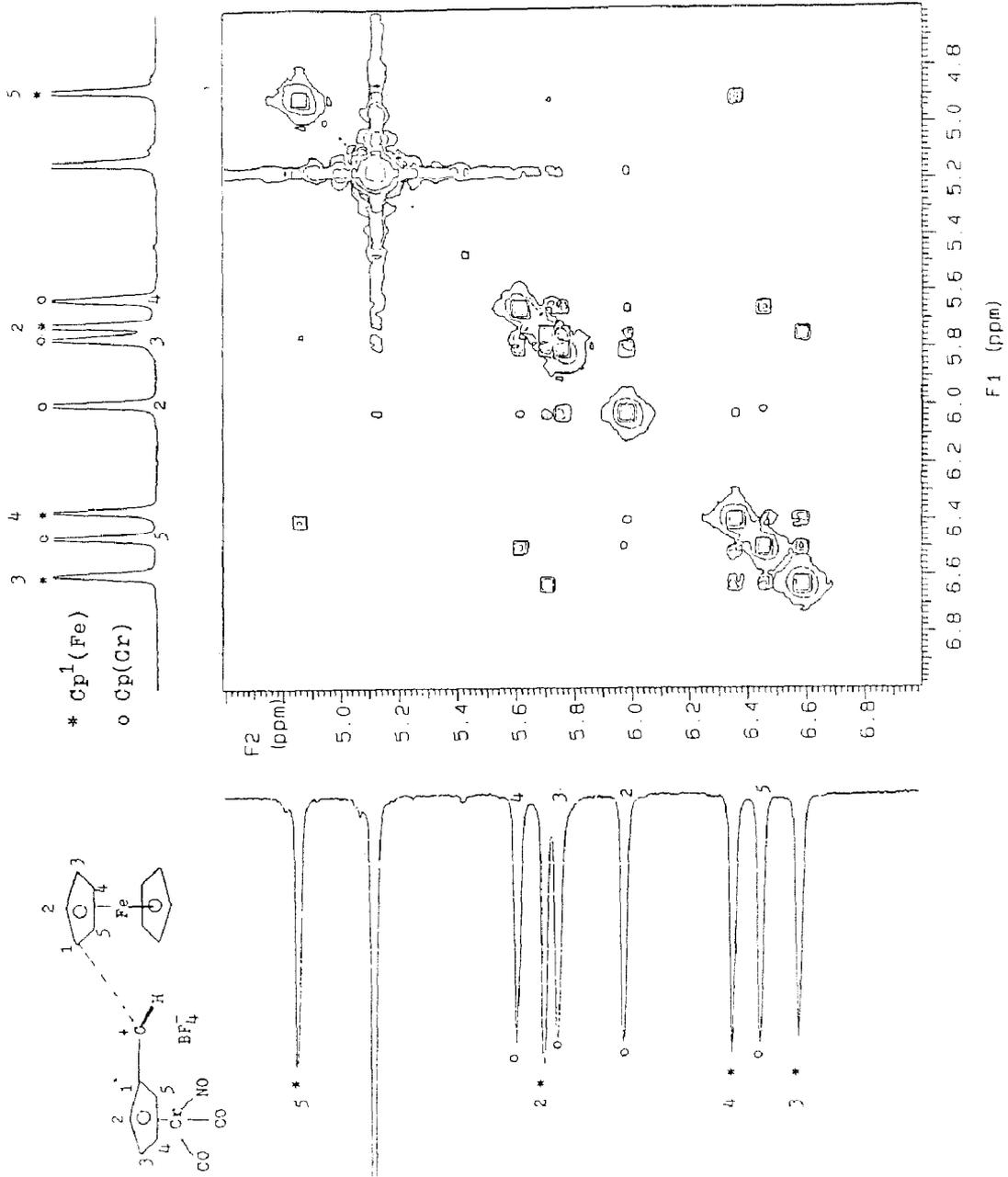


Fig. 3. Two-dimensional  $^1\text{H}$ -COSY NMR spectrum of **4** in  $\text{CD}_3\text{COCD}_3$ .

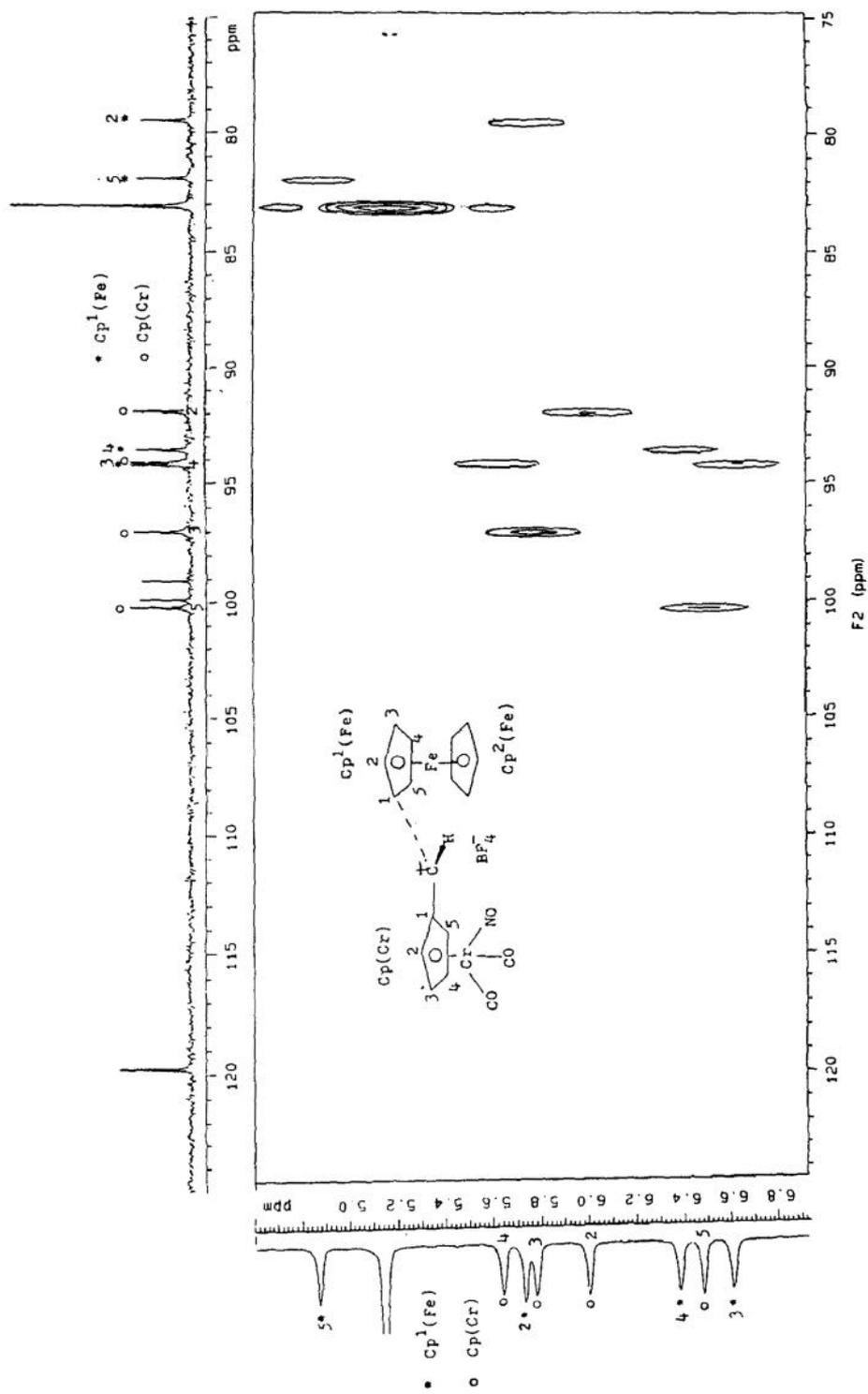
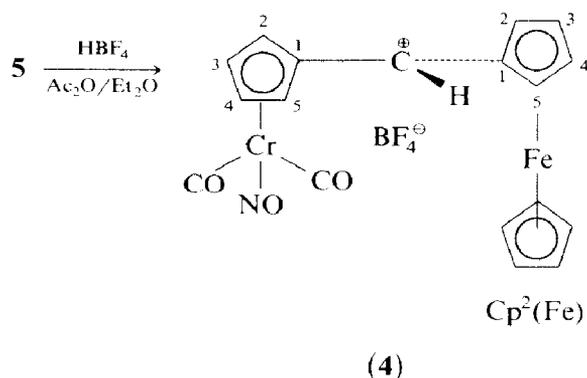


Fig. 4. Two-dimensional  $^1\text{H}$ - $^{13}\text{C}$  HetCOR NMR spectrum of **4** in  $\text{CD}_3\text{COCD}_3$ .



The  $^1\text{H}$  NMR spectrum of carbonium ion **4** exhibits a singlet cyclopentadienyl resonance at  $\delta$  5.11 corresponding to the protons of  $\text{Cp}^2(\text{Fe})$  and a 1H singlet at  $\delta$  8.12 for the methine proton. The diastereotopism of the H(2,5) and H(3,4) pairs of both of the  $\text{Cp}(\text{Cr})$  and  $\text{Cp}^1(\text{Fe})$  rings was observed originating in hindered rotation about the exocyclic C(1)–C( $\alpha$ ) bonds. Four protons of each  $\text{Cp}(\text{Cr})$  and  $\text{Cp}^1(\text{Fe})$  are magnetically non-equivalent. The line assignments for H(2–5) of  $\text{Cp}(\text{Cr})$  and  $\text{Cp}^1(\text{Fe})$  were difficult to make. Based on 2D  $^1\text{H}$ – $^1\text{H}$  correlated spectrum (Fig. 3) and analogy to the related metallo-aromatic system [16,17] four separately spaced multiplets at  $\delta$  4.86, 5.70, 6.35 and 6.58 were assigned to H(5), H(2), H(4) and H(3) of  $\text{Cp}^1(\text{Fe})$  ring respectively. The resonances at  $\delta$  5.61, 5.75, 5.98 and 6.44 were assigned to H(4), H(3), H(2) and H(5) of  $\text{Cp}(\text{Cr})$  respectively.

The  $^{13}\text{C}$  NMR spectrum of **4** exhibits three relatively less intense singlets at  $\delta$  99.09, 99.85 and 234.78 corresponding to C(1) of  $\text{Cp}^1(\text{Fe})$ , C(1) of  $\text{Cp}(\text{Cr})$  and (Cr–C $\equiv$ O). Carbons of  $\text{Cp}^2(\text{Fe})$  resonate at  $\delta$  83.06. The line assignments for C(2–5) of  $\text{Cp}(\text{Cr})$  and  $\text{Cp}^1(\text{Fe})$  were based on 2D HetCOR (Fig. 4). Chemical shifts at  $\delta$  79.51, 82.00, 93.60 and 94.32 were assigned to C(2), C(5), C(4) and C(3) of  $\text{Cp}^1(\text{Fe})$  respectively analogous to literature reports [15]. The resonances of the C(3,4) carbons occur at significantly lower field than that of C(2,5) carbons, a situation which parallels that found for the  $^1\text{H}$  resonances in the  $^1\text{H}$  spectra. Resonances at  $\delta$  92.04, 94.19, 97.07 and 100.33 were assigned to C(2), C(4), C(3) and C(5) of  $\text{Cp}(\text{Cr})$  respectively.

The  $^{13}\text{C}$  chemical shift assignments of **4** and **5** and the difference ( $\Delta\delta$ ) between the  $\delta$  values of the individual carbon atoms of **4** and **5** are listed in Table 1. The

Table 1

 $^{13}\text{C}$  Chemical shifts for **4**, **5** and  $\Delta\delta$ <sup>a</sup>

Cp(Cr)	Cp(Cr)			Cp <sup>1</sup> (Fe)		Cp <sup>2</sup> (Fe)	Cr–C $\equiv$ O	CH	
	C(1)	C(2,5)	C(3,4)	C(1)	C(2,5)				C(3,4)
<b>5</b>	115.58	89.78	88.28	92.83	65.09	68.25	68.49	236.98	66.41
<b>4</b>	99.85	100.33	94.19	99.09	79.51	93.60	83.06	234.78	120.00
		92.04	97.07		82.00	94.32			
$\Delta\delta$	-15.73	10.55	5.78	6.26	13.21	25.33	14.57	-2.2	53.59
		2.26	9.66		15.70	26.05			

<sup>a</sup>  $\Delta\delta = \delta$  (cation, **4**) –  $\delta$  (alcohol, **5**).

significant downfield shift of  $^{13}\text{C}$  resonances of both of ferrocenyl and cynichrodenyl carbon atoms of **4** compared to the resonances of the alcohol **5** reveals that the positive charge is effectively delocalized throughout both of the ferrocenyl and cynichrodenyl moieties [16]. The larger  $\Delta\delta$  values found for ferrocenyl carbon atoms than that for cynichrodenyl carbon atoms suggested that a higher concentration of the positive charge is delocalized to the ferrocenyl moiety than to the cynichrodenyl moiety.

The  $\Delta\delta$  values associated with the sets of C(1), C(2,5) and C(3,4) of  $\text{Cp}^1(\text{Fe})$ , C(1-5) of  $\text{Cp}^2(\text{Fe})$  and C( $\alpha$ ) are favorably compared with literature reported values for some ferrocenylalkylium ions [16].

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