2D HETCOR NMR Spectra of

(η^5-1-carboethoxy-2-methylcyclopentadienyl)dicarbonylnitrosylchromium,

(η^5-1-carboethoxy-3-methylcyclopentadienyl)dicarbonylnitrosylchromium, and

dicarbonyl(η^5-1-carboxy-2-methylcyclopentadienyl)nitrosylchromium

[η^5-2-(CH$_3$)C$_5$H$_3$COOR]Cr(CO)$_2$(NO) (R = H, C$_2$H$_5$) and

[η^5-3-(CH$_3$)C$_5$H$_3$COOC$_2$H$_5$]Cr(CO)$_2$(NO)
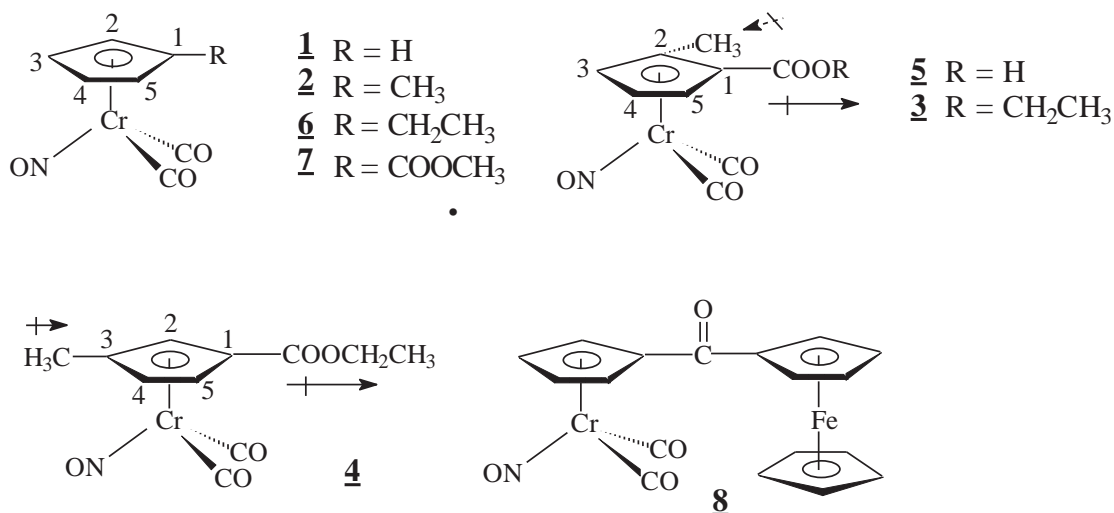
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Abstract

Reaction of sodium methylcyclopentadienide with diethylcarbonate led to a mixture of sodium 1-carboethoxy-2-methylcyclopentadienide and sodium 1-carboethoxy-3-methylcyclopentadienide. After the mixture was refluxed with Cr(CO)$_6$ in DMF, the metal carbonyl anion obtained was converted to the corresponding hydrido complexes [η^5-2-(CH$_3$)C$_5$H$_3$COOC$_2$H$_5$]Cr(CO)$_3$(H) and [η^5-3-(CH$_3$)C$_5$H$_3$COOC$_2$H$_5$]Cr(CO)$_3$(H), by adding acetic acid. A subsequent nitrosylation with N-methyl-N-nitroso-p-toluenesulfonamide gave the corresponding ester complexes **3** and **4**. Chromium acid **5** was obtained after saponification of **3**.The chemical shifts of C(2,5) and C(3,4) on the Cp ring of **3**–**5** have been assigned using two-dimensional HETCOR NMR spectroscopy.

Keywords: Chromium, cynichrodene, ferrocene, 2D HETCOR-NMR

1. Introduction

Functionally substituted η^5-cyclopentadienyl metal compounds have been the subject of continuing interest in our laboratory [1]. We previously reported that in the dicarbonyl(η^5-cyclopentadienyl)nitrosylchromium, CpCr(CO)$_2$(NO), (hereafter called cynichrodene) derivatives, the 2,5-positions of the substituted cyclopentadienyl ring are more sensitive to both electron-donating substituents and electron-withdrawing substituents. The highfield and lowfield chemical shifts are assigned to C(2,5) and C(3,4) for cynichrodene derivatives bearing electron-donating groups, as a methyl group, in the ^{13}C NMR spectra, as are the ferrocene analogs. However an opposite correlation of the assignments of C(2,5) and C(3,4) on the Cp ring between cynichrodene and ferrocene derivatives bearing electron-withdrawing substituents [2] were observed. The carbonyl substituent withdraws the Cp(M) electron via both induction and resonance. In the case of ferrocene derivatives, the carbonyl substituent withdraws the Cp(Fe) electrons via resonance predominantly, deshielding the C(3,4) to a greater extent than the C(2,5). In the case of CpCr(CO)$_2$(NO) derivatives, the carbonyl substituent withdraws the Cp(Cr) electrons via the induction predominantly, deshielding the C(2,5) to a greater extent than the C(3,4).The difference has prompted us to study disubstituted complexes **3, 4,** and **5**, complexes bearing a carbonyl and a methyl group on the Cp ring. An additive behavior would be anticipated and the results would help confirm the hypothesis we proposed earlier.

The preparations and ^{1}H NMR data of **2–5** have been previously reported [3]. However, their ^{13}C NMR data has not been reported and examined. Herein, we report the chemical shifts of the unequivocal assignments made for the C(2,5) and C(3,4) of the Cp(Cr) ring of **2–5,** based on the 2D HETCOR correlation spectra.

2. Results

2.1 Synthesis

Sodium methylcyclopentadienide react with diethylcarbonate to give a mixture of sodium 1-carboethoxy-2-mtehylcyclopentadienide and sodium 1-carboethoxy-3-methylcyclopentadienide. Without isolation, the salt was directly treated with $Cr(CO)_6$ under reflux in N,N-dimethylformamide to give the tricarbonyl salt $[\eta^5\text{-}2\text{-}(CH_3)C_5H_3COOC_2H_5]CrCO)_3^-Na^+$ and $[\eta^5\text{-}3\text{-}(CH_3)C_5H_3COOC_2H_5]CrCO)_3^-Na^+$. Subsequent acidification with acetic acid, followed by nitrosylation with N-methyl-N-nitroso-p-toluenesulfonamide produced the respective dicarbonyl nitrosyl esters **3** and **4**. Saponification of the chromium ester **3** produced the carboxylic acid **5**.
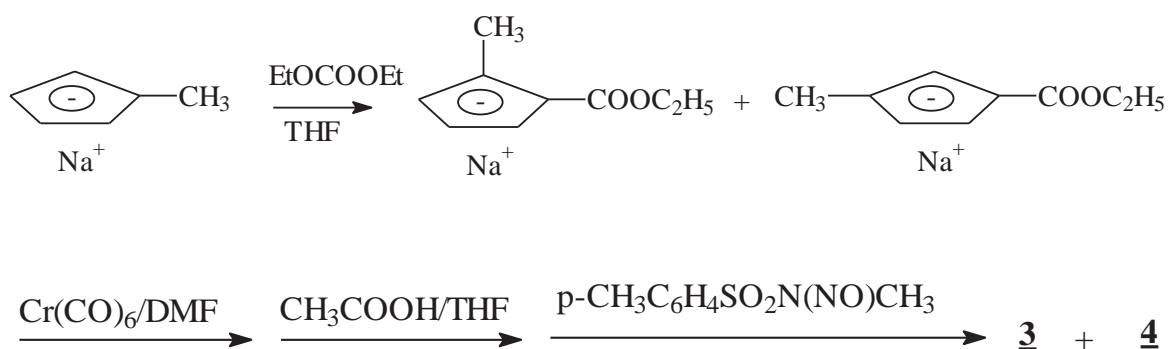
2.2 Characterization: ^{1}H NMR

The ^{1}H NMR spectrum of **4** exhibited a singlet owing to the Cp(CH$_3$) protons at δ 1.90 ppm and two multiplets owing to ethoxy group at 1.21(3H) and 4.14 ppm (2H). Two doublets and one singlet, relative intensity of 1H, were also observed. In which the one at the lowest field can be assigned to H(5) of the Cp ring. This assignment was made on the basis that the carbonyl group would exert a strong diamagnetic anisotropic effect and exhibit an electron-withdrawing property. As expected, H (2,5) would be deshielded to a greater extent than the protons on the more remote 4-position. The electron donating property of methyl group would shield H(2) to a bit higher field. Accordingly, the following assignments were made: H(2), H(4), and H(5) of Cp(Cr) resonate at δ 4.88, δ5.54, and δ 5.63 ppm, respectively, for complex **4**. Similarly, H(2−5) of Cp(Cr) for complexes **3** and **5** were assigned (Table 1) [3, 4].

[Table 1]

2.3 Characterization: ^{13}C NMR

The assignments of ^{13}C NMR spectra for **3**–**5** were based on standard ^{13}C NMR [2, 5], 2D HETCOR (Fig. 1−3), and DEPT correlation techniques. They were also compared with other metallo-aromatic systems [6]. In the case of **4**, five relatively less intense signals were observed at δ 234.96, δ 234.75, δ 164.49, δ 91.27, and δ 110.31 ppm corresponding to the two terminal carbonyl carbons, the carbonyl carbon, and the C(1) and the C(3) of Cp(Cr), respectively. Chemical shifts at δ 13.42, δ 14.08, and δ 60.76 ppm were assigned to Cp methyl carbon, the ethoxy methyl carbon, and the ethoxy methylene carbon, respectively. The line assignments for the C(2, 4, 5) of Cp(Cr) were more difficult to make. Based on the 2D HETCOR results (Fig. 2), in which the magnetic

fields of ^{1}H and ^{13}C NMR spectra increase toward the right and upper side, respectively. The chemical shift of C(5), C(2), and C(4) correlate with the chemical shift of H(5) (δ 5.63 ppm), H(2) (δ 5.54 ppm), and H(4) (δ 4.88 ppm), respectively. Accordingly, chemical shifts at δ 93.59, 92.72, and 91.70 ppm were assigned to C(5), C(2), and C(4), respectively, of Cp(Cr) (Table 2) [2, 7]. Analogous assignments apply to complex **3** (Fig. 1) and **5** (Fig. 3)**.** These assignments reveal that positions 2 and 5 on the substituted Cp ring in **3–5** are more sensitive to electron-withdrawing substituents, as previously found for cynichrodene derivatives [2].

[Fig. 1, 2, 3]
(Table 2)

3. Discussion

3.1 Electron-withdrawing effect of carbonyl and Electron-donating effect of methyl on Cp(Cr) via induction

As ^{13}C NMR spectroscopy is less sensitive to the effects of magnetically anisotropic groups and ring currents than ^{1}H NMR [8], the following discussion on the electron density distribution within a molecule is based upon the chemical shifts of ^{13}C spectra rather than the ^{1}H NMR spectra. Table 3 [1, 6, 9] illustrates the contracted 2D HETCOR spectra of **3–8**. It is interesting to note that all the Cp(Cr) moiety exhibits a positive slope. For **6**, the chemical shifts of H(2,5) and C(2,5) occurred at a higher field than those of H(3,4) and C(3,4), whereas for others the chemical shifts of H(2,5) and C(2,5) occurred at a lower field than those of H(3,4) and C(3,4). This reveals that in the cynichrodenes, the 2,5-positions of the substituted cyclopentadienyl ring are more sensitive to both

electron-donating substituents and electron-withdrawing substituents, as we previously reported for cynichrodene analogs . The contracted 2D 1H{^{13}C}HETCOR NMR spectrum of **8** [9] is also illustrated for comparison. Complex **8**—containing both Cp(Cr) and Cp(Fe)—exhibits a positive slope in the Cp(Cr) moiety, whereas a negative slope in the Cp(Fe) moiety.

(Table 3)

3.2 Chemical shifts from cynichrodene for disubstituted Cp ring carbons may be additive

One may wonder whether for a complex like **4**, in which the C(2) and C(5) are deshileded to a lower field owing to the nearby carbonyl group, however C(2) is also shielded to a higher field due to the nearby methyl group. Given the shielding effect (−0.71 ppm) (Table 2, complex **2**) is less profound than the deshielding effect (2.38 ppm) (Table 2, complex **7**). It would be interesting to see if chemical shift from cynichrodene for disubstituted Cp ring carbons could be approximated by applying the principle of substituent additivity. One would anticipate the chemical shift for C(2) of **4** to be the subtracted value of an ortho methyl group (−0.71 ppm) effect from the chemical shift of C(5). The calculated value is 92.88 ppm (93.59−0.71) and the observed value is 92.71 ppm (Table 3).

4. Conclusion

In summary, the 2D HETCOR-NMR spectra of disubstituted derivatives of CpCr(CO)$_2$(NO), **2**−**5**, further confirmed the hypothesis we proposed earlier. Chemical shifts for disubstituted Cp ring carbons of cynichrodene derivatives can be approximated

by applying the principle of substituent additivity.

5. Experimental

Complexes **2**–**5** [3] were prepared by following the published procedures. The characterizations are given here.

(η^5-C$_5$H$_4$CH$_3$)Cr(CO)$_2$(NO) (**2**). ^{1}H NMR(CDCl$_3$): δ (relative intensity, multiplicity, assignment): 1.89 (3H, s, –CH$_3$); 4.85 (4H, s, Cp(Cr) H(2–5)). ^{13}C NMR (CDCl$_3$): δ (assignment): 13.41 (CH$_3$); 89.12 (Cp(Cr), C(2,5)); 89.83 (Cp(Cr), C(3,4)); 109.52 (Cp(Cr), C(1)); 237.58 (Cr-C≡O).

[η^5-2-(CH$_3$)C$_5$H$_3$COOCH$_2$CH$_3$]Cr(CO)$_2$(NO) (**3**). ^{1}H NMR(CDCl$_3$): δ (relative intensity, multiplicity, assignment): 1.29 (3H, t, J = 6.9 Hz, –OCH$_2$C$\underline{\text{H}}_3$); 2.22 (3H, s, CH$_3$(Cp(Cr))); 4.23 (2H, m, –OCH$_2$–); 4.94 (2H, s, Cp(Cr) H(3,4)); 5.58 (1H, dd, J = 1.8, 3.0 Hz, Cp(Cr) H(5)). ^{13}C NMR (CDCl$_3$): δ (assignment): 13.54 (Cp-$\underline{\text{C}}$H$_3$); 14.19 (–OCH$_2$$\underline{\text{C}}H_3$); 60.70 (OCH$_2$–); 89.83 (Cp(Cr), C(3)); 90.81(Cp(Cr), C(1)); 91.72 (Cp(Cr), C(4)); 93.05(Cp(Cr), C(5)); 113.88 (Cp(Cr), C(2)); 165.25 (–C(O)–); 234.91, 235.26 (Cr-C≡O).

[η^5-3-(CH$_3$)C$_5$H$_3$COOCH$_2$CH$_3$]Cr(CO)$_2$(NO) (**4**): ^{1}H NMR(CDCl$_3$): Proton NMR(CDCl$_3$): δ (relative intensity, multiplicity, assignment): 1.21 (3H, t, J = 7.2 Hz, –OCH$_2$C$\underline{\text{H}}_3$); 1.90 (3H, s, CH$_3$(Cp(Cr))); 4.14 (2H, m, J = 7.2 Hz, OCH$_2$–); 4.88 (1H, s, Cp(Cr) H(4)); 5.54 (1H, s, Cp(Cr) H(2)); 5.63 (1H, s, Cp(Cr) H(5)). ^{13}C NMR (CDCl$_3$): δ (assignment): 13.42 (Cp-$\underline{\text{C}}$H$_3$); 14.08 (OCH$_2$$\underline{\text{C}}H_3$); 60.76 (OCH$_2$–); 91.27(Cp(Cr), C(1)); 91.70 (Cp(Cr), C(4)); 92.72(Cp(Cr), C(2)); 93.59 (Cp(Cr), C(5)); 110.31 (Cp(Cr), C(3));

164.49 (C(O)–); 234.75, 234.96 (Cr-C≡O).

[η^5-2-(CH$_3$)C$_5$H$_3$COOH]Cr(CO)$_2$(NO) (**5**): ^{1}H NMR(CDCl$_3$): δ (relative intensity, multiplicity, assignment): 2.24 (3H, s, CH$_3$); 4.99 (2H, s, Cp(Cr) H(3,4)); 5.67 (1H, s, Cp(Cr) H(5)); ^{13}C NMR (CDCl$_3$): δ (assignment): 13.57 (CH$_3$); 88.86 (Cp(Cr), C(1)); 90.26 (Cp(Cr), C(3)); 92.31(Cp(Cr), C(4)); 94.14 (Cp(Cr), C(5)); 114.64 (Cp(Cr), C(2)); 171.18 (–C(O)–); 234.19, 234.58 (Cr-C≡O).

Acknowledgements

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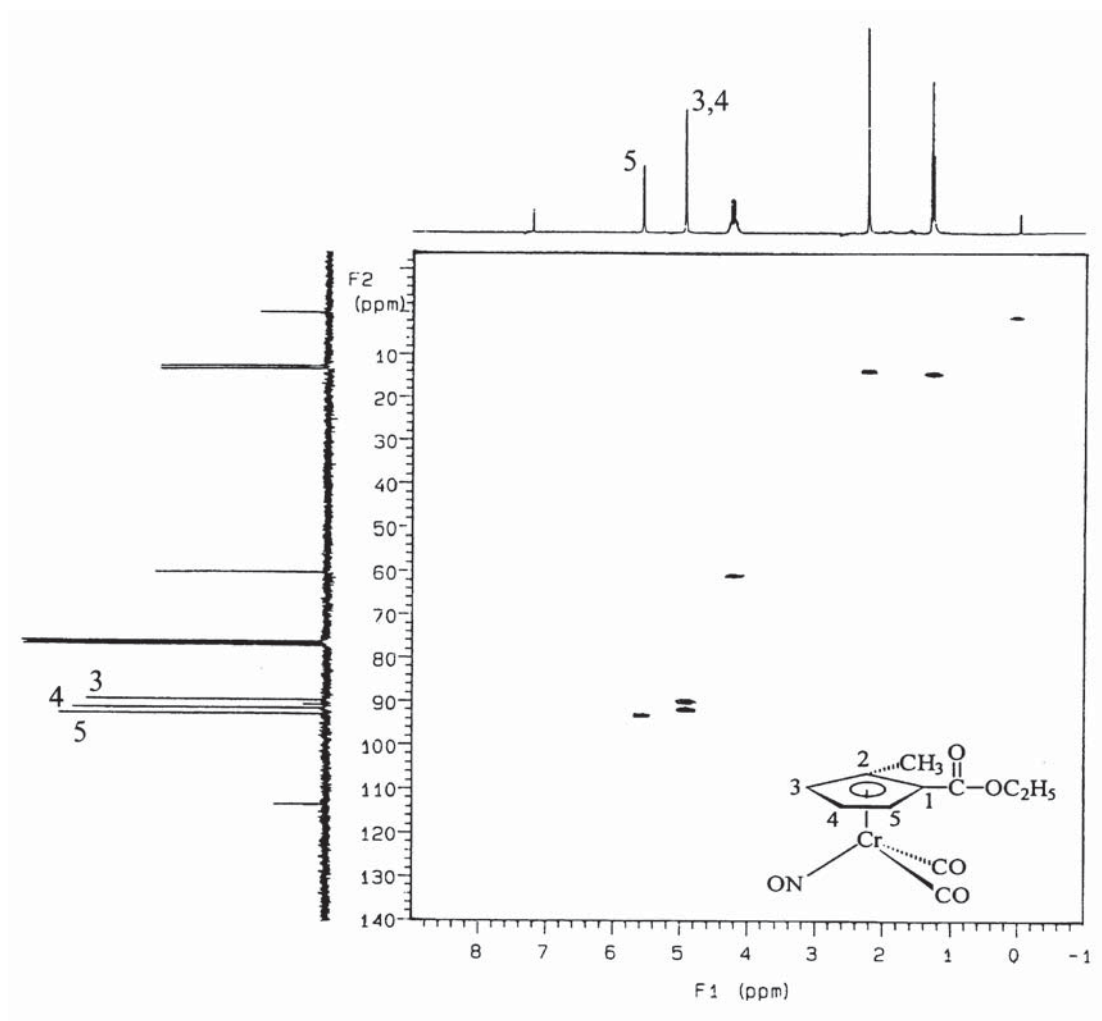[5] J.B. Stotter, Carbon-13-NMR Spectroscopy, Academic Press, New York, 1972, pp.

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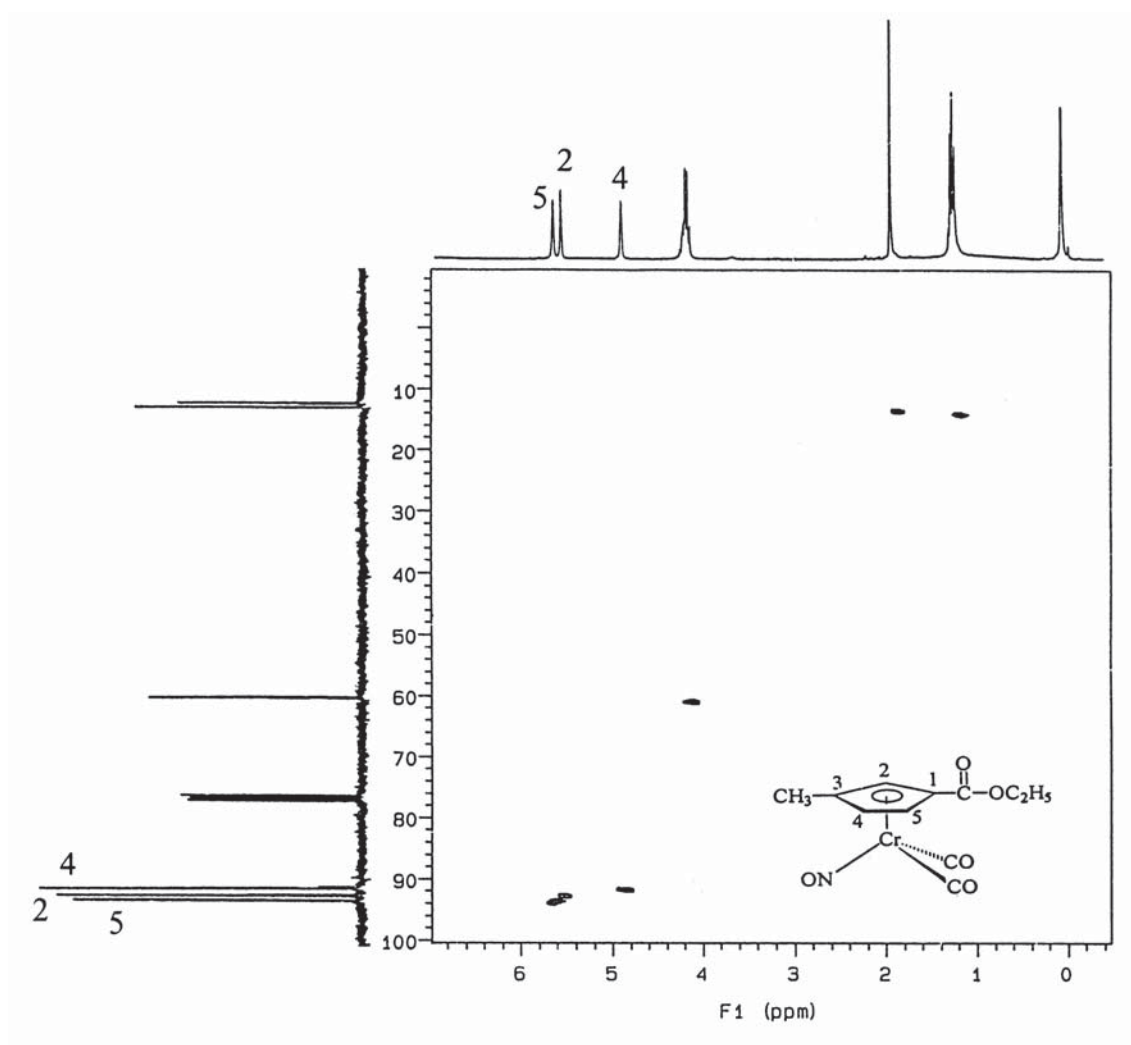
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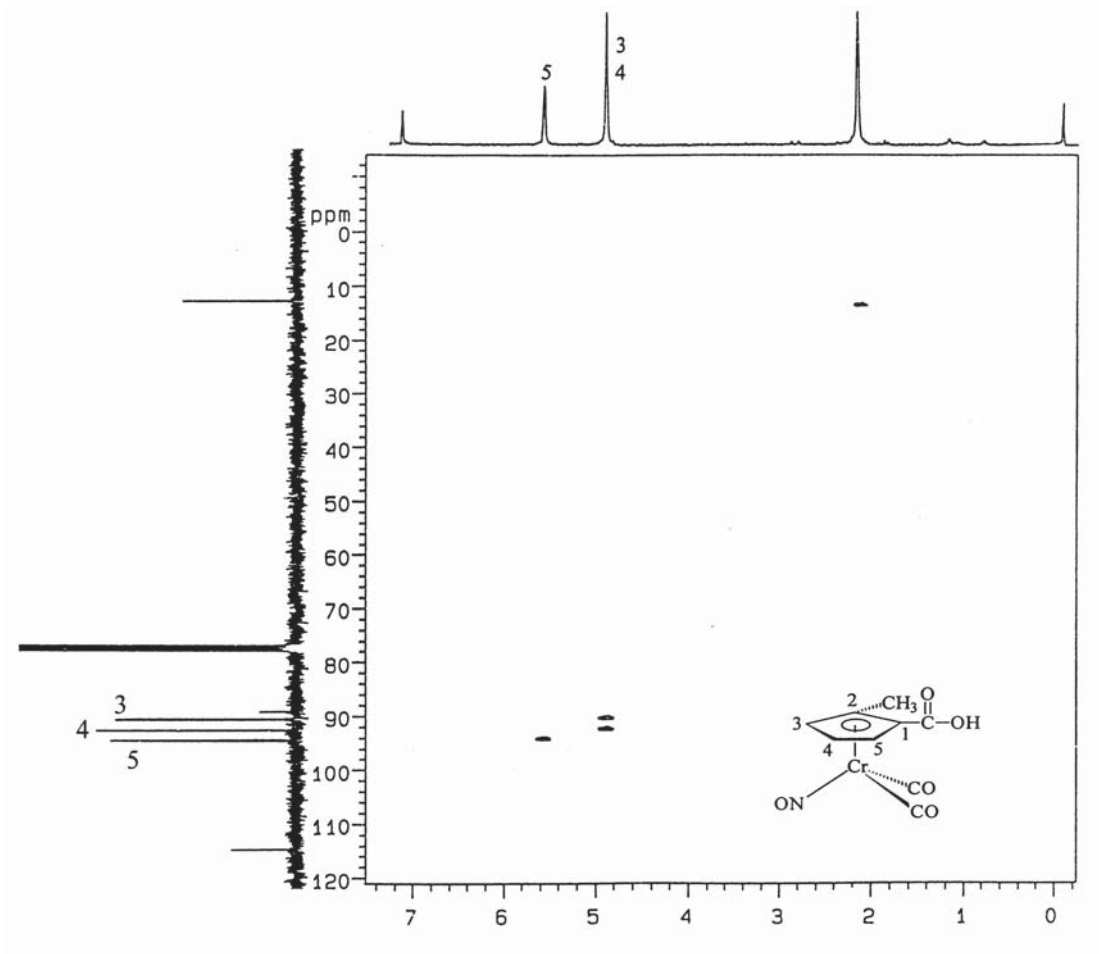[8] A.A. Koridze, P.V. Petrovskii, A.I. Mokhov, A.I. Lutsenko, J. Organomet. Chem. 136 (1977) 57–63.

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Fig. 1. Two-dimensional ^1H-^{13}C HETCOR NMR spectrum of **3** in $CDCl_3$

Fig. 2. Two-dimensional ^1H-^{13}C HETCOR NMR spectrum of **4** in CDCl$_3$.

Fig. 3. Two-dimensional ^1H-^{13}C HETCOR NMR spectrum of **5** in CDCl$_3$

Table 1
^{1}H NMR data[a]

Compound	Cp(Cr) δ (ppm)					Cp(CH$_3$)	Others
	H(2)	H(3)	H(4)	H(5)	Δ[b] (ppm)		
1 (CO)$_2$(NO)Cr(η^5-C$_5$H$_5$)[c]	5.07				0		
2 (CO)$_2$(NO)Cr(η^5-C$_5$H$_4$CH$_3$)	4.85				0	1.89	
3 CO)$_2$(NO)Cr[η^5-2-(CH$_3$)C$_5$H$_3$COOCH$_2$CH$_3$]		5.58	4.94	**<u>5.58</u>**	0.64	2.22	1.29 (CH$_2$C<u>H</u>$_3$), 4.23 (OCH$_2$)
4 CO)$_2$(NO)Cr[η^5-3-(CH$_3$)C$_5$H$_3$COOCH$_2$CH$_3$]	5.54		4.88	**<u>5.63</u>**	0.75	1.90	1.21 (CH$_2$C<u>H</u>$_3$), 4.14 (OCH$_2$)
5 CO)$_2$(NO)Cr[η^5-2-(CH$_3$)C$_5$H$_3$COOH]		4.99	4.99	**<u>5.67</u>**	0.68	2.24	
6 (CO)$_2$(NO)Cr(η^5-C$_5$H$_4$CH$_2$CH$_3$)[d]	4.92	**<u>4.98</u>**	**<u>4.98</u>**	4.92	−0.06		1.23 (CH$_2$C<u>H</u>$_3$), 2.31 (CH$_2$)

[a] in CDCl$_3$.

[b] Δ = δ[H(5)]–δ[H(4)](+: H(5)downfield, H(4) upfield; − : H(5) upfield, H(4) downfield). The lower-field chemical shift of each pair of H(4) and H(5) is underlined.

[c] From Ref. [4].

[d] From Ref. [2]

22

Table 2
^{13}C{1H} NMR data[a]

Compound	Cp(Cr)[c]						Cr(CO)	C=O	others
	C(1)	C(2)	C(3)	C(4)	C(5)	$\Delta r_{(C)}$[b]			
1 CO)$_2$(NO)Cr(η^5-C$_5$H$_5$)[d]	90.31						237.1		
2 (CO)$_2$(NO)Cr(η^5-C$_5$H$_4$CH$_3$)	109.52 (CH$_3$)	89.12	89.83	**89.83**	89.12	−0.71	237.58		13.41(CpCH$_3$)
3 CO)$_2$(NO)Cr(η^5-2-(CH$_3$)C$_5$H$_3$COOCH$_2$CH$_3$)	90.81(C(O))	113.88(CH$_3$)	89.82	91.72	**93.05**		234.91 235.26	165.25	13.54(Cp(CH$_3$)), 14.19(CH$_2$C<u>H</u>$_3$), 60.70(OCH$_2$)
4 CO)$_2$(NO)Cr(η^5-3-(CH$_3$)C$_5$H$_3$COOCH$_2$CH$_3$)	91.27(C(O))	92.72	110.31(CH$_3$)	91.70	**93.59**		234.75 234.96	164.49	13.42(Cp(CH$_3$)), 14.08(CH$_2$<u>C</u>H$_3$), 60.76(OCH$_2$)
5 CO)$_2$(NO)Cr(η^5-2-(CH$_3$)C$_5$H$_3$COOH)	88.86	114.64(CH$_3$)	90.26	92.31	**94.14**		234.19 234.58	171.18	13.57(Cp(CH$_3$))
6 (CO)$_2$(NO)Cr(η^5-C$_5$H$_4$CH$_2$CH$_3$)[e]	116.16	88.62	**89.11**	**89.11**	88.62	-0.49	237.75		14.30(CH$_2$<u>C</u>H$_3$), 21.11(CH$_2$)
7 (CO)$_2$(NO)Cr(η^5-C$_5$H$_4$COOCH$_3$)[d]	92.94	**94.12**	91.74	91.74	**94.12**	2.38	234.67	165.07	52.16(OCH$_3$)

[a] in CDCl$_3$.
[b] $\Delta r_{(C)} = \delta[C(2,5)]-\delta[C(3,4)]$. (+: C(2.5)downfield, C(3,4) upfield; − : C(2,5) upfield, C(3,4) downfield).
[c] The lower-field chemical shift of each pair is in bold and underlined.
[d] From Ref. [7].
[e] From Ref. [2]

Table 3
The contracted 2D HETCOR spectra of **3–8**

Complex	Cp(M)	^{1}H, Cp(Cr)[a,d]	2D HETCOR[b,c]	^{13}C, Cp(M)[a]
(η^5-C$_5$H$_4$CH$_2$CH$_3$)Cr(CO)$_2$(NO)[g] **6**	Cp(Cr)	* o	(diagonal)	* o
(η^5-C$_5$H$_4$COOCH$_3$)Cr(CO)$_2$(NO)[h] **7**	Cp(Cr)	o *	(diagonal)	o *
CO)$_2$(NO)Cr(η^5-2-(CH$_3$)C$_5$H$_3$COOR) (**3** R = CH$_2$CH$_3$, R = H, **5**)	Cp(Cr)	5 3 , 4	(diagonal) e	5 4 3
CO)$_2$(NO)Cr(η^5-3-(CH$_3$)C$_5$H$_3$COOCH$_2$CH$_3$) **4**	Cp(Cr)	5 2 4	(diagonal) f	5 2 4
(CO)$_2$(NO)Cr[(η^5-C$_5$H$_4$)CO(η^5-C$_5$H$_4$)]FeCp[i] **8**	Cp(Cr)	o *	(diagonal)	o *
	Cp(Fe)	o *	(anti-diagonal)	* o

[a] o, (2,5); *, (3,4); the magnetic field increases towards the right.

[b] The magnetic fields of ^{1}H and ^{13}C-NMR spectra increase towards the right and upper side respectively.

[c] o (2,5) versus * (3,4), unless otherwise stated.

[d] Those affected by the anisotropic effect of an organic carbonyl or iminyl group are underlined.

[e] (5) versus (4) or (5) versus (3).

[f] (5) versus (4), (2) versus (4), or (5) versus (2). [g] From Ref.[2]. [h] From Ref. [7]. [i] From Ref. [9].

24

錯合物
CO)$_2$(NO)Cr[η^5-2-(CH$_3$)C$_5$H$_3$COOR] (R = H, C$_2$H$_5$) 及
CO)$_2$(NO)Cr[η^5-3-(CH$_3$)C$_5$H$_3$COOC$_2$H$_5$]
二維異核 NMR 光譜

王玉蘋*, 廖仁海

摘　要

鈉塩 Na$^+$(η^5-C$_5$H$_4$CH$_3$)$^-$與 diethylcarbonate 反應得雙取代 Cp 鈉塩 sodium 1-carboethoxy-2-methylcyclopentadienide 及 sodium 1-carboethoxy-3-methylcyclopentadienide. 加入 Cr(CO)$_6$, 回流後 所得之 metal carbonyl anion 以乙酸酸化,可得 hydrido 錯合物 [η^5-2-(CH$_3$)C$_5$H$_3$COOC$_2$H$_5$]Cr(CO)$_3$(H) 及 [η^5-3-(CH$_3$)C$_5$H$_3$COOC$_2$H$_5$]Cr(CO)$_3$(H). 接下來以 N-methyl-N-nitroso-p-toluenesulfonamide 進行 nitrosylation 可得酯錯合物 [η^5-2-(CH$_3$)C$_5$H$_3$COOCH$_3$]CrCO)$_2$(NO) 3 及 [η^5-3-(CH$_3$)C$_5$H$_3$COOCH$_3$]CrCO)$_2$(NO) 4. 錯合物 3 經 saponication(皂化反應)得錯合物酸 [η^5-2-(CH$_3$)C$_5$H$_3$COOH]CrCO)$_2$(NO) 5. 藉由 HETCOR NMR spectroscopy 錯合物 3–5 Cp 環上的 碳化學位移得以明確地標示出.

關鍵字: 鉻, 二羰(η^5-環戊二烯)亞硝基鉻, 二茂鐵, 2D HETCOR NMR