Synthesis, 2D HETCOR NMR Spectra and Unequivocal Assignment of

(*E*)- and (*Z*)-1-ferrocenyl-2-phenylethene, and (*E*)-1,2-diferrocenylethene

(*E*)- and (*Z*)-CpFe[(η^5-C$_5$H$_4$)CH=CHC$_6$H$_5$], and

(*E*)-CpFe[(η^5-C$_5$H$_4$)CH=CH(η^5-C$_5$H$_4$)]FeCp

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Abstract

Reaction of ferrocenecarbaldehyde with benzyltriphenylphosphorane afforded (*E*) and (*Z*)-1-ferrocenyl-2-phenylethene, (**2**-(*E*) and (**2**-(*Z*)) via the conventional Wittig reaction. Based on the 2D HETCOR, the C(3,4) resonates at a lower field than C(2,5) on the Cp(Fe) ring of (*E*)-isomer, whereas the C(2,5) resonates at a lower field than C(3,4) on that of (*Z*)-isomer. The hypothesis to elucidate these data assignments was proposed.

Keywords: Ferrocene, vinyl, anisotropism, resonance, HETCOR NMR

1. Introduction

Previously, We observed that C(3,4) resonates at a lower field than C(2,5) in all Cp(M) (M = W, Fe) metallocene and phenyl derivatives bearing either an electron-donating (-NH$_2$, -OCH$_3$) substituent or an electron-withdrawing substituent (-CHO, -COR) via resonance. The hypothesis to elucidate these data assignments was also proposed [1]. In 1999 [2], we revealed that the vinyl group donates electron density to the adjacent metallocenyl (CpCr(CO)$_2$(NO), ferrocene) Cp ring or phenyl ring via resonance in (*E*)-isomers. In hopes of confirming those hypotheses and the validity of them to the (*Z*)-isomers, in which the sterically hindered conformer may disrupt the resonance, compound CpFe[(η^5-C$_5$H$_4$)CH=CHC$_6$H$_5$] **2**-(*Z*) was synthesized and its ^{13}C NMR data have been examined and compared with the (*E*)-isomer, **2**-(*E*)

The preparations and ^{1}H NMR data of compounds **1**–**3**-(*E*), **1**–**2**-(*Z*), and **4** have been previously reported [3, 4, 5]. However, their ^{13}C NMR data has either not been reported (**2**-(*Z*)) or not unequivocally assigned (**1**-(*E*), **1**-(*Z*), **3**-(*E*)). Herein, we report their unequivocal chemical shifts of the C(2,5) and C(3,4) of the Cp(Fe) ring, and the C(*o*, *m*, *p*) of the phenyl ring, based on the 2D HETCOR correlation spectra.
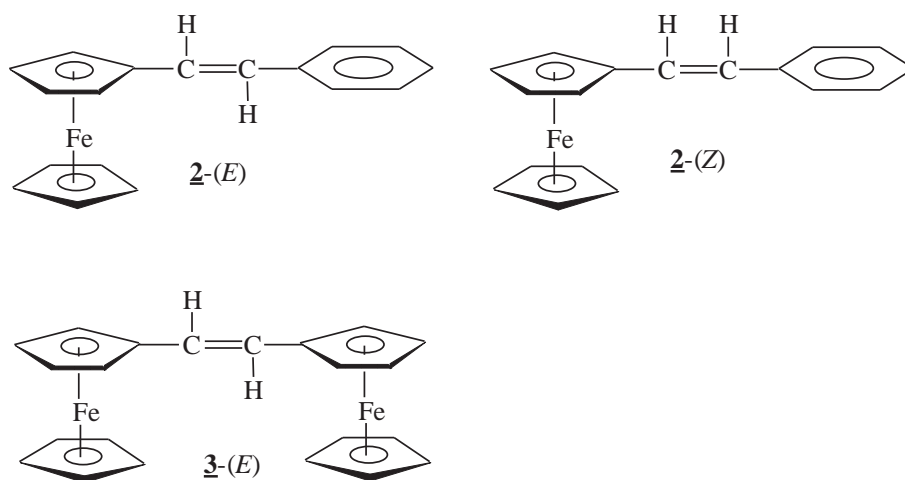
2. Results

2.1. Synthesis

Through the Wittig reaction [6] between ferrocenecarbaldehyde and benzyltriphenylphosphorane, formed from the deprotonation of the corresponding phosphonium iodide with n-butyllithium, (*E*) and (*Z*)-1-ferrocenyl-2-phenylethene, (**2**-(*E*), (**2**-(*Z*)), were obtained in a yield of 53% and 28%, respectively.

$$[C_6H_5CH_2PPh_3]^+ I^- \xrightarrow{\text{n-BuLi}} C_6H_5CH{=}PPh_3 \xrightarrow{\text{FcCHO}} \textbf{2}\text{-}(E) + \textbf{2}\text{-}(Z)$$

2.2 Characterization: ^{1}H NMR

The ^{1}H NMR for compounds **1**—**3**-(*E*), **1**-(*Z*), **2**-(*Z*), and **4** are listed in Table 1 [2—4]. The ^{1}H NMR spectra of compounds **2**-(*E*) and **2**-(*Z*) are consistent with their assigned structures and are similar to other metallocenyl systems [7]. The ^{1}H NMR spectrum (Table 1, Fig. 1) of **2**-(*E*) exhibited two doublets of relative intensity 1H owing to the vinyl protons at $\delta = 6.88$ and 6.70 ppm. The coupling constants of the two protons on the double bond manifested the configuration. The characteristic coupling constant of the *Z*-isomer is about 12 Hz, and that of the *E*-isomer is about 16 Hz. The value of 15.6 Hz revealed the configuration as an *E*. One A_2B_2 pattern, related to the observed triplets, resonating at $\delta = 4.47$ and 4.29 ppm corresponding to the protons H(2,5) and H(3,4) of Cp^1(Fe) were also observed. The downfield triplet can be assigned to the H(2,5) protons of the Cp. This assignment is made on the basis of the fact that the vinyl group would exert a diamagnetic anisotropic effect. As expected, H(2,5) would be

deshielded to a greater extent than the protons on the more remote 3- and 4-positions. Given the same basis, one doublet of relative intensity of 1H and two triplets of relative intensity of 2H, resonating at δ = 7.43, 7.33, and 7.22 ppm were assigned to the ortho, the meta, and the para protons of phenyl ring, respectively. Analogously, chemical shifts of the H(2–5) of Cp(Fe) and H(o, m, p) of phenyl ring on compound **2**-(Z) (Fig. 2) were assigned.

[Table 1, Fig. 1, 2]

2.2 Characterization: ^{13}C NMR

^{13}C NMR chemical shifts of **1**–**3-**(E), **1**-(Z)**, 2-**(Z), and **4** are presented in Table 2 [2—4]. The assignments of ^{13}C NMR spectra were based on standard ^{13}C NMR [8], 2D HETCOR, DEPT correlation techniques, and also by comparison with other ferrocene derivatives [9]. In the case of 2-(E), two relatively less intense signals were observed at δ = 137.94 and 83.34 ppm corresponding to the C(1) of phenyl and Cp(Fe) ring, respectively. The line assignments for the vinyl carbons, the C(2–5) of Cp(Fe), and the C(o, m, p) of phenyl were more difficult to make. Based on the 2D HETCOR results (Fig. 1), in which the magnetic fields of ^{1}H and ^{13}C NMR spectra increase toward the right and upper side, respectively, given the positive slope of FcCH= and PhCH= versus FcCH= and PhCH=, chemical shifts at δ = 126.93 and 126.06 ppm were assigned to FcCH= and PhCH=, respectively. The downfield chemical shifts of C(3,4) correlate with the upfield chemical shifts of H(3,4) (δ = 4.29 ppm) and the upfield chemical shifts of C(2,5) correlate with the downfield chemical shifts of H(2,5) (δ = 4.47 ppm). Accordingly, chemical shifts at δ = 69.00 and 66.85 ppm were assigned to C(3,4) and C(2,5) of Cp(Fe), respectively.

[Table 2]

The assignments, the downfield and upfield chemical shifts assigned to C(3,4) and C(2,5), revealed that the 3,4–positions are more deshielded by the vinyl substituent [2]. Analogous assignments apply to compound **2**-(*Z*) (Fig. 2). Accordingly, chemical shifts at δ = 69.4 and 68.5 ppm were assigned to C(2,5) and C(3,4) of Cp(Fe), respectively, and chemical shifts at δ = 128.71 and 126.64 ppm were assigned to C(*o*) and C(*p*) of phenyl ring, respectively. The assignments for **2**-(*Z*), the downfield and upfield chemical shifts assigned to C(2,5) and C(3, 4), revealed that the 2,5–positions are more deshielded by the vinyl substituent [1]. The assignments for **2**-(*Z*) are opposite to the assignments for **2**-(*E*). The 2D ^{1}H{^{13}C}HETCOR NMR spectrum of **3**-(*E*) is also shown (Fig. 3) for comparison.

[Fig. 3]

3. Discussion

3.1 Vinyl group as an electron-donating group via resonance in E-isomer

Because ^{13}C NMR spectroscopy is less sensitive to the effects of magnetically anisotropic groups and ring current than ^{1}H NMR [10], 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. As is well known, the vinyl group can exert an either electron-donating or electron-withdrawing effect by resonance to its attached group. When an electron-donating group is attached to it, the vinyl group withdraws the electron from the group, and vice versa. Upon examination of the ^{13}C spectra (Table 2)

of **1–3**(*E*) and **4**, a negative value of Δt ($\Delta t = \delta$ [average] $- \delta$ [C(Cp(Fe))] for Cp(Fe) ring or $\Delta t = \delta$ [average] $- \delta$ [C(benzene)] for phenyl ring of corresponding parent compound) was observed. The vinyl group exerts the same kind of electronic effect as the amino group, rather than the carbonyl group, to its adjacent Cp(Fe) ring or phenyl ring.

3.2. 2D HETCOR spectra: a negative slope for E-isomer; a positive slope for Z-isomer

Table 3 illustrated the contracted 2D HETCOR spectra. One interesting feature was observed. The 2D HETCOR correlations of the (*E*)-isomers are opposite to those of (*Z*)-isomers for both Cp(Fe) and phenyl rings. Given that, the H(2,5) of Cp(M) resonates at a lower field than the C(3,4) in all cases due to the anisotropic effect of a vinyl group—deshielding the H(2,5) to a greater extent than does the H(3,4), the outcome of ^{13}C NMR spectra will determine the slope, a positive or a negative. A positive value of $\Delta r_{(C)}$ ($\Delta r_{(C)} = \delta C(2,5) - \delta C(3.4)$ ppm)—in the cases of (*Z*)-isomers—(Table 2) gives a positive slope, whereas a negative value of $\Delta r(C)$—in the cases of (*E*)-isomers—gives a negative slope.

[Table 3]

3.3. Explanation for 3.2
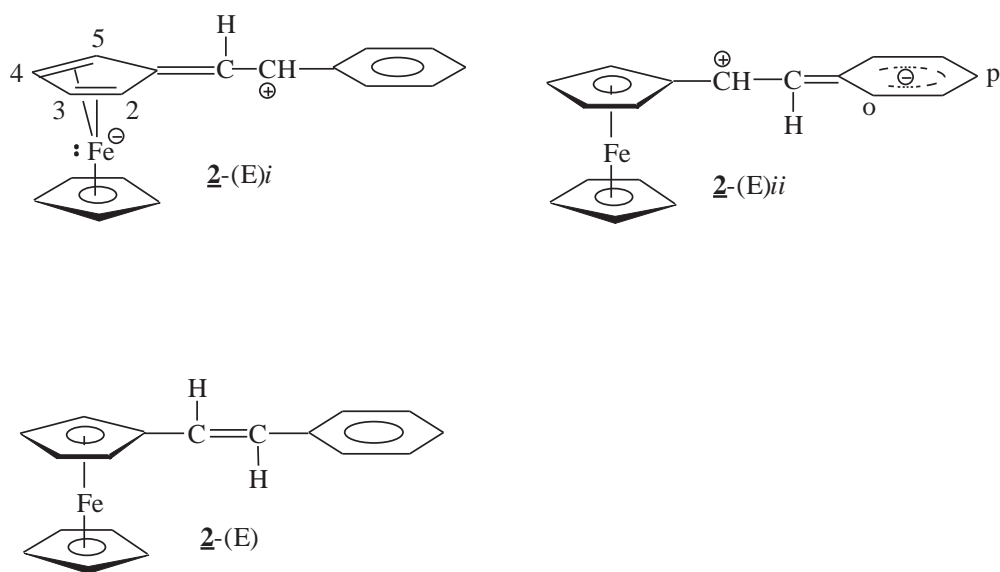
3.3.1. Vinyl substituents on Cp(Fe)

The above assignments reveal that positions 2 and 5 on the substituted Cp ring in (*Z*)-isomers are more deshielded than 3- and 4- positions to the vinyl substituent, contrary to analogous ferrocene derivatives bearing an electron-donating substituent via

resonance [1]. While the 3- and 4-positions of the substituted Cp(Fe) ring in (E)-isomers are more deshielded than 2- and 5- positions to the vinyl substituent, as analogous ferrocene derivatives bearing an electron-donating substituent via resonance [1]. The electronic influence of any substituent is determined by the interplay of two effects that may operate simultaneously: induction and resonance. Induction occurs through the σ framework. It tapers off with distance and is mostly governed by the relative electronegativity of atoms. Resonance takes place through π-bonds. An electron-withdrawing substituent via induction will deshield the nearby C(2,5) of Cp(M) to a greater extent than the more remote C(3,4), and each of these compounds would be anticipated to give a positive value of $\Delta \mathbf{r}_{(C)}$ ($\Delta \mathbf{r}_{(C)} = \delta C(2,5) - \delta C(3,4)$ ppm for the Cp(M); $\Delta \mathbf{r}_{(C)} = \delta C(o) - \delta C(p)$ ppm for the phenyl ring). From Table 2 the Cp(Fe) of compounds **2**-(E), **3**-(E), and **4** gave a negative value of $\Delta \mathbf{r}_{(C)}$ (**2**-(E),–2.15; **3**-(E),–2.30; **4**,–1.90 ppm); As well, the phenyl group of **1**-(E) and **2**-(E) gave a negative value of $\Delta r(C)$ (**1**-(E),–1.50; **2**-(E),–1.00 ppm). It reveals that electron donating via resonance predominantly acts on the (E)-isomers, and this resonance effect deshields the C(3,4) to a greater extent than it does the C(2,5). In the case of (Z)-isomers the inductive effect operates. The Cp(Fe) and phenyl ring of **1**-(Z) or **2**-(Z) gave a positive value of $\Delta \mathbf{r}_{(C)}$ (**1**-(Z), 1.80; **2**-(Z) 0.90, 2.09 ppm) (Table 2).

3.3.2 in E-isomers: vinyl groups acting as a π -Electron donating group via resonance

The greater the contribution of canonical **2**-(E)*i* to structure **2**-(E), the more the deshielding on the C(3,4) exceeding that on the C(2,5). Similarly, the greater the contribution of canonical **2**-(E)*ii* to structure **2**-(E), the more the deshielding on the C(p) exceeding that on the C(o). In (E)-isomers—the p orbitals aligned perpendicularly to the molecular plane form a contiguous interacting array—resonance takes place through π-bonds, and the ethenyl and aryl are coplanar. In (Z)-isomers, the sterically hindered

conformation renders the coplanarity not maintained. The extent of the contribution of

the canonical form **2**-(*E*)*i* or **2**-(*E*)*ii* to the corresponding structure **2**-(*E*) diminished.

Which may lead **2**-(*E*)*i* or **2**-(*E*)*ii* to have an insignificant weight of contribution to **2**-(*E*).

The electron withdrawing by induction, deshielding the nearby carbon (C(2,5)) atoms to

a greater extent than the more distant 3- and 4-positions, may explain the observed data

and the positive slope for (*Z*)-isomers.

3.3.3 Unravel the daunting odds: a negative value of Δr(C) for

electron–donating–via–resonance substituents on Cp(Fe) and phenyl ring

Examining the structures of canonical form **2**-(*E*)*i* and fulvene may help unravel the

mystery. Table 4 lists the ^{13}C NMR data of some selected derivatives of

5-methylenecyclopenta-1,3-diene. It is of interest to note that the C(3,4) was deshielded

to a greater extent than the C(2,5) in all cases. All gave a negative value of $\Delta r_{(C)}$.

4. Experimental details

All the syntheses were carried out under nitrogen by the use of Schlenk techniques. Traces of oxygen in the nitrogen were removed with BASF catalyst and deoxygenated nitrogen was dried over molecular sieves (3 Å) and P_2O_5. Hexane, pentane, benzene, and dichloromethane were dried over calcium hydride and freshly distilled under nitrogen. Diethyl ether was dried over sodium and redistilled under nitrogen from sodium-benzophenone ketyl. All the other solvents were used as commercially obtained. Column chromatography was carried out under nitrogen with Merck Kiesel-gel 60. The silica gel was heated with a heat gun during mixing in a rotary evaporator attached to a vacuum pump for 1 h to remove water and oxygen. The silica gel was then stored under nitrogen until use. ^{1}H- , ^{13}C-NMR, and 2D ^{1}H{^{13}C} HETCOR (HETeronuclear CORrelation) experiments were acquired on a Varian Unity-300 spectrometer. Chemical shifts were referenced to tetramethylsilane.

*4.1 Preparation of (E)-1-ferrocenyl-2-phenylethene (**2**-(E)) and*

*(Z)-1-ferrocenyl-2-phenylethene (**2**-(Z))*

Benzyltriphenylphosphonium iodide (0.48 g, 1.0 mmol) was dissolved in 30 ml of tetrahydrofuran and n-butyl lithium (1.6 M, 0.94 ml, 1.5 mmol) was slowly dropped into while stirring. After the color of solution turned red, the reaction mixture was stirred for 3 h at room temperature ferrocenecarbaldehyde (23) (0.21 g, 1.0 mmol) was added into. The content was continued to stir for 12 h at room temperature. The solution was filtered and concentrated to a brown residue under vacuum. The residue was dissolved in 30 ml of dichloromethane. Ten grams of silica gel were added to the

solution, and the solvent was then removed under vacuum. The residue was added to a dry-packed column (2 x 10 cm) of silica gel. Elution of the column with hexane gave two yellow bands. After removal of solvent under vacuum, the first (yellow) band gave (*Z*)-1-ferrocenyl-2-phenylethene (**2**-(*Z*)), m.p. 44°C, (0.08 g, 28%) and the second (yellow) band gave (*E*)-1-ferrocenyl-2-phenylethene (**2**-(*E*)), m.p. 120°C, (0.15 g, 53%), respectively.

(*E*)-1-ferrocenyl-2-phenylethene (**2**-(*E*)). Proton NMR(CDCl$_3$): δ (relative intensity, multiplicity, assignment): 4.14 (5H, Cp^2(Fe)); 4.29 (2H, s, Cp^1(Fe) H(3,4)); 4.47 (2H, s, Cp^1(Fe) H(2,5)); 6.70 (1H, d, J = 15.6 Hz, Ph-C$\underline{H}$=); 6.88 (1H, d, J = 15.6 Hz, Cp^1(Fe)-C$\underline{H}$=); 7.22 (1H, t, J = 8.1 Hz, *p*-Ph); 7.33 (2H, t, J = 8.1 Hz, *m*-Ph); 7.43 (2H, d, J =8.1 Hz, *o*-Ph). Carbon-13 NMR (CDCl$_3$): δ (assignment): 66.85(Cp^1(Fe), C(2,5)); 69.00 (Cp^1(Fe), C(3,4)); 69.19 (Cp^2(Fe)); 83.34 (Cp^1(Fe), C(1)); 125.79 (*o*-Ph); 126.06 (Ph-C$\underline{H}$=); 126.79 (*p*-Ph); 126.93 (Cp^1(Fe)-C$\underline{H}$=); 128.66 (*m*-Ph); ; 137.94 (ipso-Ph).

(*Z*)-1-ferrocenyl-2-phenylethene (**2**-(*Z*)). Proton NMR(CDCl$_3$): δ (relative intensity, multiplicity, assignment): 4.10 (5H, Cp^2(Fe)); 4.14 (2H, s, Cp^1(Fe) H(3,4)); 4.15 (2H, s, Cp^1(Fe) H(2,5)); 6.31 (1H, d, J = 11.7 Hz, Ph-C$\underline{H}$=); 6.44 (1H, d, J = 15.6 Hz, Cp^1(Fe)-C$\underline{H}$=); 7.22 (1H, t, J = 6.3 Hz, *p*-Ph); 7.29 (2H, t, J = 6.3 Hz, *m*-Ph); 7.33 (2H, d, J = 6.3 Hz, *o*-Ph). Carbon-13 NMR (CDCl$_3$): δ (assignment): 68.50(Cp^1(Fe), C(2,5)); 69.23 (Cp^2(Fe)); 69.40 (Cp^1(Fe), C(3,4)); 81.39 (Cp^1(Fe), C(1)); 126.64 (*p*-Ph); 127.28 (Cp^1(Fe)-C$\underline{H}$=); 128.04 (*m*-Ph); 128.15 (Ph-C$\underline{H}$=); 128.71 (*o*-Ph); 138.30 (ipso-Ph).

Acknowledgements

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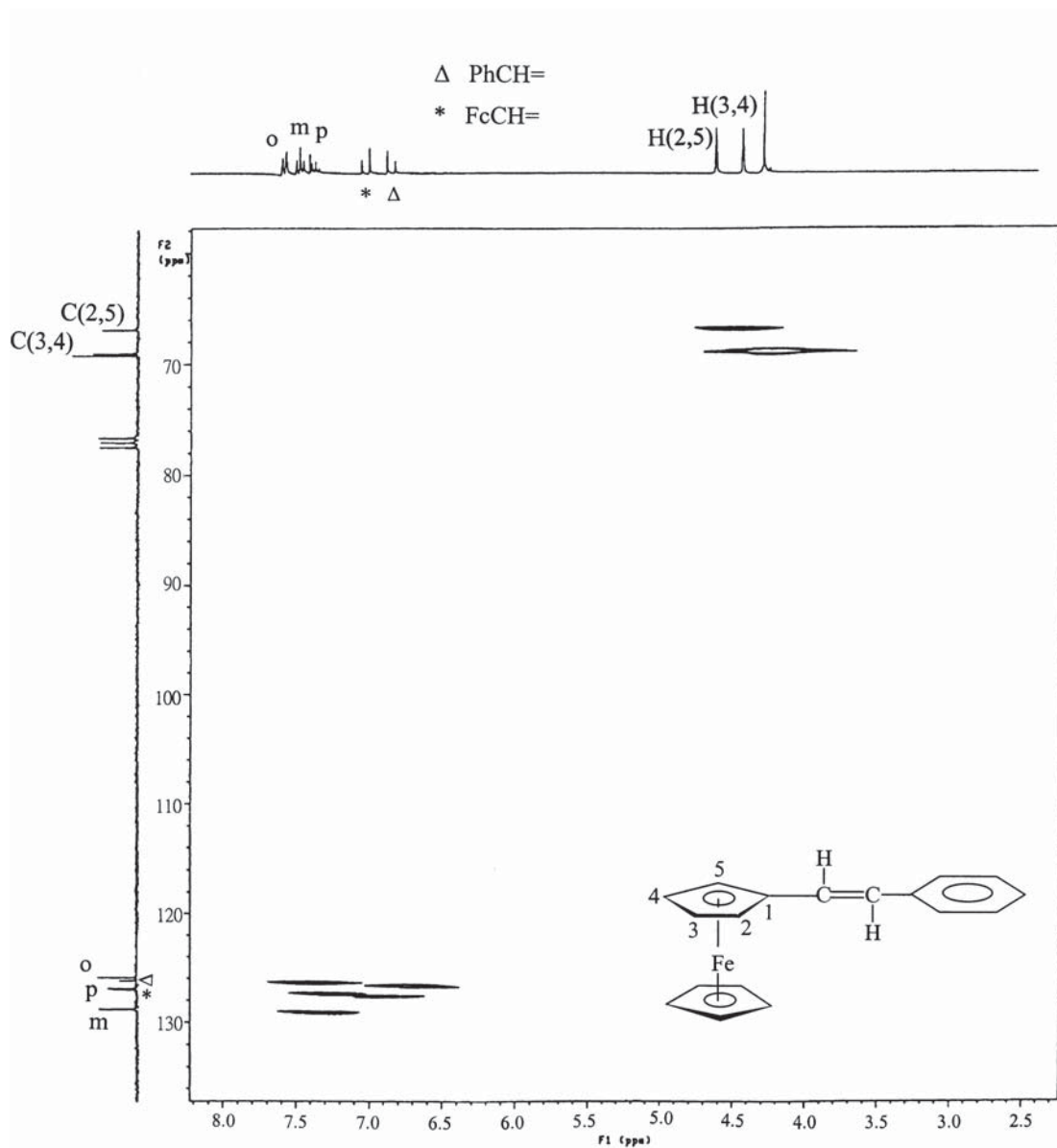
Fig. 1. Two-dimensional ^{1}H-^{13}C HETCOR NMR spectrum of **2**-(*E*) in CDCl$_3$.
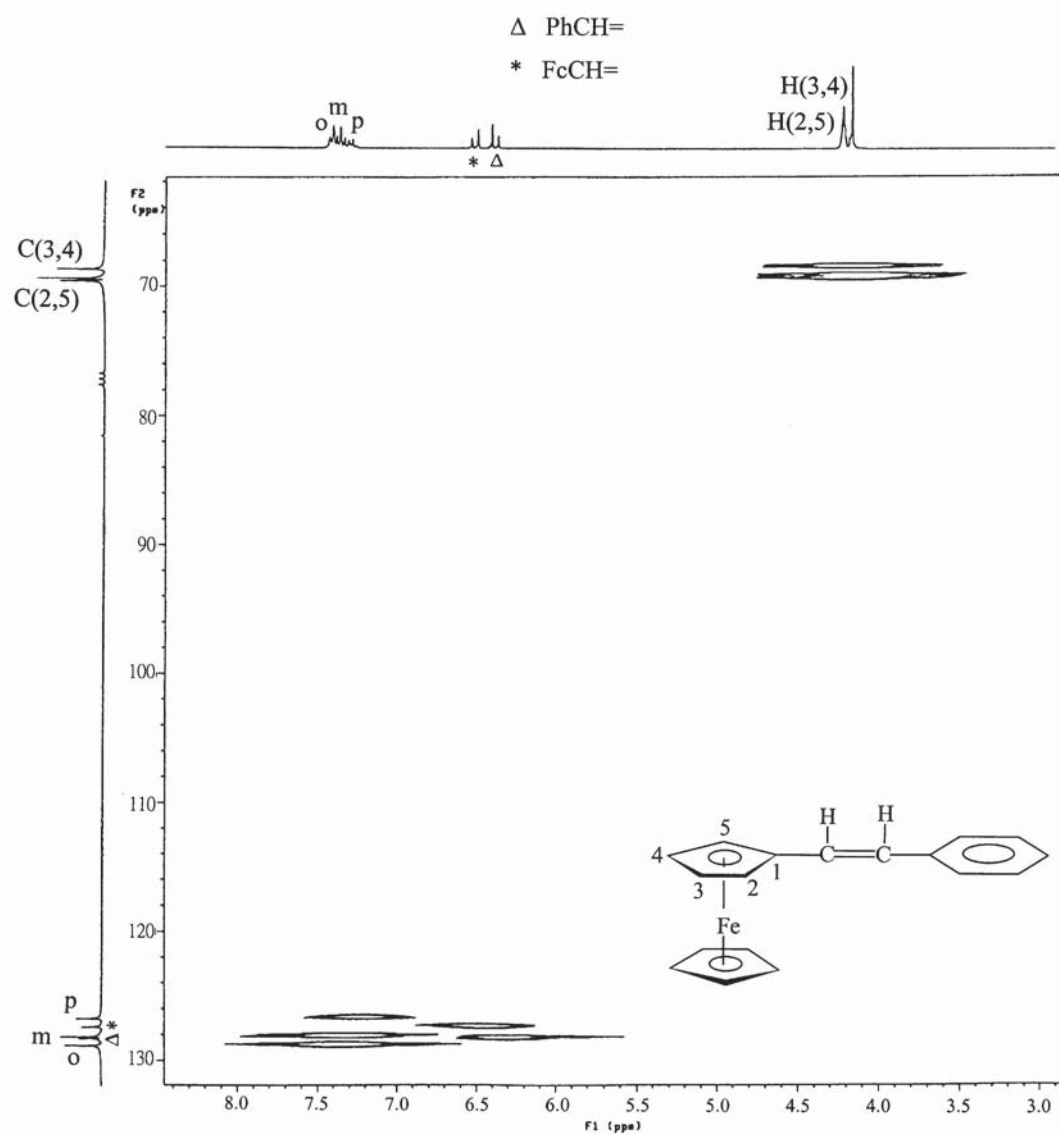
Fig. 2. Two-dimensional ^{1}H-^{13}C HETCOR NMR spectrum of **2**-(*Z*) in CDCl$_3$
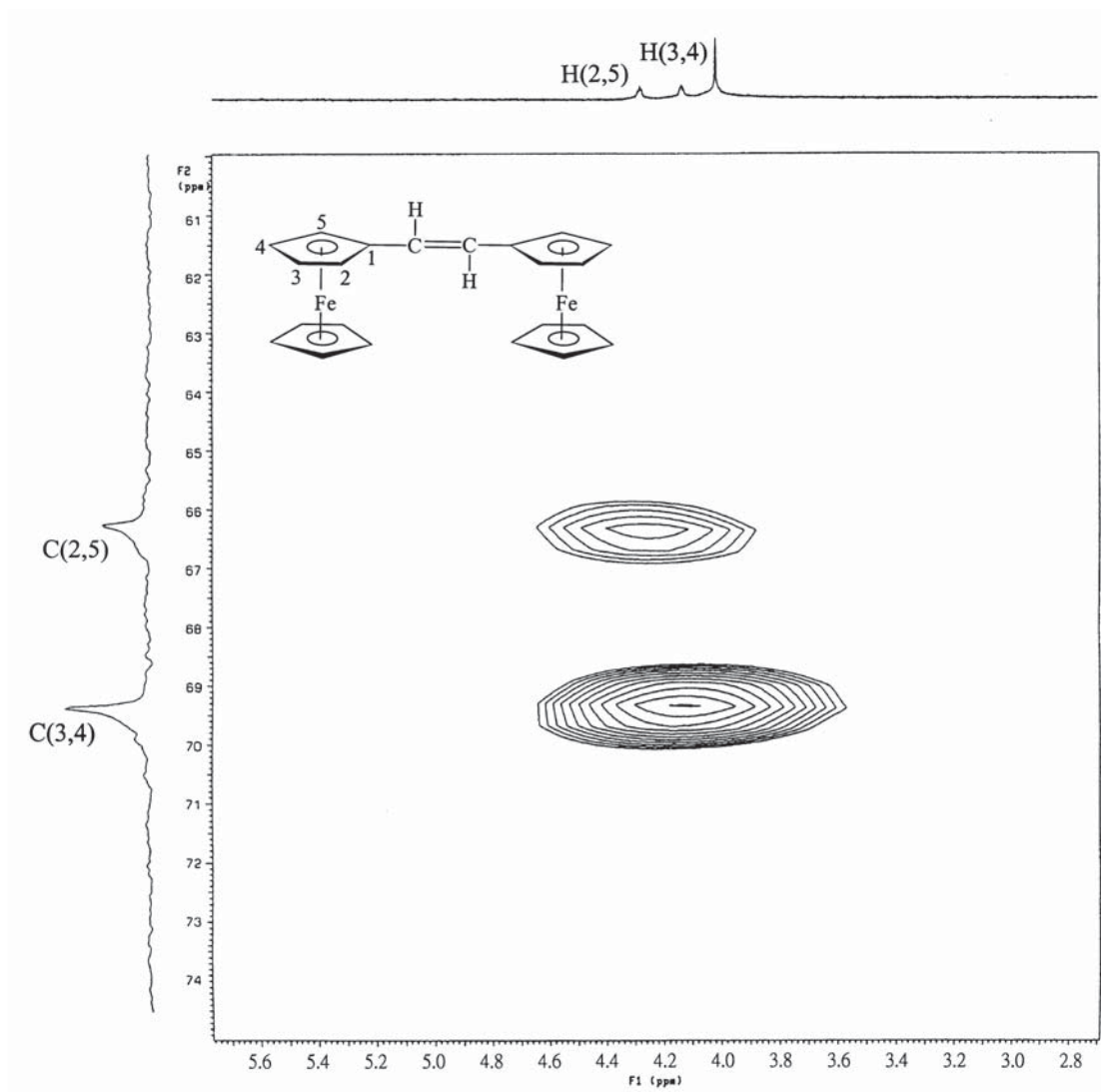
Fig. 3. Two-dimensional ^{1}H-^{13}C HETCOR NMR spectrum of **3-**(*E*) in CDCl$_3$

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

Compound	Cp(Fe) δ (ppm)			C₆H₆ δ (ppm)			Cp(Fe)CH=	PhCH=	others
	H(2,5)	H(3,4)	$\Delta r_{(H)}$[b]	H(2,6)(o)	H(4)(p)	$\Delta r_{(H)}$[b]			
Cp₂Fe	4.04	4.04							
C₆H₆				7.24	7.24				
E-PhCH=CHPh[c,d,f] **1**-(E)				**_7.52_**	7.26	0.26		7.11	7.36(Ph, *m*)
E-CpFe(η⁵-C₅H₄CH=CHC₆H₅)[e] **2**-(E)	**_4.47_**	4.29	0.18	**_7.43_**	7.22	0.21	6.88	6.70	7.33(Ph, *m*)
E-CpFe[(η⁵-C₅H₄)CH=CH(η5-C5H4)FeCp[c,f] **3**-(E)									
	_4.38_	4.24	0.14				6.41		4.12(Cp²(Fe))
CpFe(η⁵-C₅H₄CH=CH₂)[e] **4**	**_4.36_**	4.21	0.15				6.45		5.03, 5.34 (=CH₂)
Z-PhCH=CHPh[d,f] **1**-(Z)				**_7.26_**	7.15	0.11		6.59	7.21(Ph, *m*)
Z-CpFe(η⁵-C₅H₄CH=CHC₆H₅)[f] **2**-(Z)	4.15	4.14	0.01	**_7.33_**	7.22	0.11	6.44	6.31	4.10(Cp²(Fe)), 7.29(Ph, *m*)

[a] in CDCl₃.
[b] $\Delta r_{(H)} = \delta[H(2,5)] - \delta[H(3,4)]$.(+: H(2.5)downfield, H(3,4) upfield; – : H(2,5) upfield, H(3,4) downfield). The lower-field chemical shift of each pair is bold-faced and underlined.
[c] from Ref. [02]. [d] from Ref. [03]. [e] from Ref. [004]. [f] This work.

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

Compound	Cp(Fe) δ (ppm)						C6H6 δ (ppm)						(Cp(Fe)C<u>H</u>=)	(PhC<u>H</u>=)
	C(1)	C(2,5)	C(3,4)	average[b]	**Δt**[c]	**Δr**$_{(C)}$[d]	C(1)	C(2,5)(o)	C(4)(p)	average[b]	**Δt**[c]	**Δr**$_{(C)}$[d]		
FeH	67.88	67.88	67.88											
C6H6							128.5	128.5	128.5					
E-PhCH=CHPh[e,f,h] **1**-(E)							137.2	126.4	**<u>127.6</u>**	127.0	−1.5	−1.2	128.9	128.6(Ph, *m*)
E-CpFe(η^5-C5H4CH=CHC6H5)[g] **2**-(E)	83.34	66.85	**<u>69.00</u>**	67.93	0.05	−2.15	137.94	125.79	**<u>126.29</u>**	126.29	−2.21	−1.00	126.93	126.06 / 69.19(Cp^2(Fe)) / 128.66(Ph, *m*)
E-CpFe[(η^5-C5H4)CH=CH(η^5-C5H4)FeCp][e,h] **3**-(E)	84.33	66.22	**<u>68.73</u>**	67.48	−0.40	−2.51							123.71	69.34(Cp^2(Fe))
CpFe(η^5-C5H4CH=CH2)[e,g] **4**	83.6	66.7	**<u>68.6</u>**	67.65	−0.23	−1.90							134.7	69.3(Cp^2(Fe)) / 111.1(=C<u>H</u>2)
Z-PhCH=CHPh[f,h] **1**-(Z)							137.8	**<u>128.8</u>**	127.0	127.9	−0.60	1.80	130.2	128.1(Ph, *m*)
Z-CpFe(η^5-C5H4CH=CHC6H5)[h] **2**-(Z)	81.39	**<u>69.4</u>**	68.5	68.95	1.07	0.9	138.3	**<u>128.71</u>**	126.64	127.68	−0.82	2.07	127.28	128.15 / 69.23(Cp^2(Fe)) / 128.04(Ph, *m*)

[a] in CDCl$_3$.

[b] average = $1/2\{\delta[C(2,5)] + \delta[C(3,4)]\}$.

[c] **Δt** = δ[average] − δ[C(Cp or phenyl) of corresponding parent compound] (+: [average] downfield, [parent compound] upfield; − : [average] upfield, [parent comound] downfield).

[d] **Δr** = δ[C(2,5)]−δ[C(3,4)]. (+: C(2.5)downfield, C(3,4) upfield; − : C(2,5) upfield, C(3,4) downfield). The lower-field chemical shift of each pair is bold-faced and underlined.

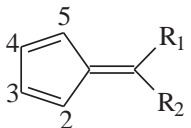[e] From Ref. [02]. [f] From Ref. [03]. [g] From Ref. [04]. [h] This work.

Table 3
The contracted 2D HetCOR spectra.

Compound		^{1}H, Cp(M)[a,c]	2D HetCOR[b]	^{13}C, Cp(M)[a,d,e]
E-PhCH=CHPh **1**-(E)	PhH			
E-CpFe(η^5-C$_5$H$_4$CH=CHC$_6$H$_5$) **2**-(E)	Cp(Fe)			
E-CpFe[(η^5-C$_5$H$_4$)CH=CH(η5-C5H4)FeCp **3**-(E)	Cp(Fe)			
CpFe(η^5-C$_5$H$_4$CH=CH$_2$) **4**	Cp(Fe)			
Z-PhCH=CHPh **1**-(Z)	PhH			
Z-CpFe(η^5-C$_5$H$_4$CH=CHC$_6$H$_5$) **2**-(Z)	Cp(Fe)			

PhH

Table 4

$^{13}C\{^1H\}$ NMR data of selected 5-methylenecyclopenta-1,3-diene (fulvene)[a].

Compound	R$_1$ =	R$_2$ =	C(2,5)	C(3,4)	$\Delta r_{(C)}$[b]		Compound	R$_1$ =	R$_2$ =	C(2,5)	C(3,4)	$\Delta r_{(C)}$[b]
1 fulvene	H	H	124.90	**134.30**	−9.4	4	6-chlorolfulvene	H	Cl	124.79	**131.50**	−6.71
2 6-methyllfulvene	H	CH$_3$	123.13	**131.50**	−8.62	5	6-methoxyfulvene	H	OCH$_3$	120.70	**134.81**	−14.11
			122.63			6	6-hydroxyfulvene	H	OH	120.85	**132.31**	−11.46
3 6-phenylfulvene	H	C$_6$H$_5$	122.32	**131.22**	−8.65	7	6-methyl-6-phenylfulvene	CH$_3$	C$_6$H$_5$	123.74	**129.20**	−5.46
			122.82									

[a] ACD/NMR Predictors.

[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). The lower-field chemical shift of each pair is bold-faced and underlined.

化合物

(*E*)- and (*Z*)-CpFe[(η⁵-C₅H₄)CH=CHC₆H₅]及 (*E*)-CpFe[(η⁵-C₅H₄)CH=CH(η⁵-C₅H₄)]FeCp 的合成, 二維異核 NMR 光譜及化學位移

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摘 要

化合物 (*E*)- and (*Z*)-CpFe[(η⁵-C₅H₄)CH=CHC₆H₅] (**2**-(*E*) and (**2**-*(Z)*) 可經由 FcCHO 與 C₆H₅CH=PPh₃ (Wittig) 反應獲得. 經由二維異核相對應 NMR 光譜儀, 化合物之 ¹³C 化學位移得以確認.並由光譜得知: (*E*)-幾何同分異構物的 C(3,4) 化學位移在較低磁場, C(2,5)的化學位移在較高磁場.但相反地 (*Z*)-幾何同分異構物的 C(2,5) 化學位移在較低磁場, C(3,4)的化學位移在較高磁場. 對此文中提出可能的解釋.

關鍵字: 弗洛笙, 乙烯基, 各向異性, 共振, 異相二維核磁共振