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2D HETCOR NMR spectra and unequivocal assignments of (*E*)- and (*Z*)-1-ferrocenyl-2-phenylethene, and (1*E*,3*E*)- and (1*Z*,3*E*)-1-ferrocenyl-4-phenyl-1,3-butadiene, (*E*)-1,2-diferreocenylethene, and (1*E*,3*E*)-1,4-diferrocenyl-1,3-butadiene in ^{13}C NMR spectra

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ABSTRACT

Reaction of ferrocenecarbaldehyde with benzyltriphenylphosphorane and (*E*)-Cinnamyltriphenylphosphorane, respectively, afforded (*E*)- and (*Z*)-1-ferrocenyl-2-phenylethene ([(*E*)-**5**] and ([(*Z*)-**5**]), and (1*E*,3*E*)- and (1*Z*,3*E*)-1-ferrocenyl-4-phenyl-1,3-butadiene ([(1*E*,3*E*)-**6**] and [(1*Z*,3*E*)-**6**]), respectively, via the conventional Wittig reaction. An analogous reaction between (ferrocenylmethyl)triphenylphosphorane and (*E*)-1-ferrocenyl-2-formylethene **9** gave (1*E*,3*E*)-1,4-diferrocenyl-1,3-butadiene **8**.

From the 2D HETCOR, we observed that the C(3,4) of Cp ring (or C(para) of phenyl ring) resonates at a lower field than the C(2,5) of Cp ring (or C(ortho) of phenyl ring) in *E* isomers, whereas the C(2,5) (or C(ortho)) resonates at a lower field than the C(3,4) (or C(para)) in *Z* isomers. In the ^{1}H NMR spectra, the H(2,5) (or H(ortho)) and the vinyl protons in *E* isomers resonate at a lower field than those of corresponding protons in *Z* isomers. The hypotheses to elucidate these data assignments are proposed.

1. Introduction

Since the advent of ^{1}H and ^{13}C NMR spectrometry in 1960s and 1970s, respectively, those two sophisticated techniques have been widely used in identifying organic compounds. In 2009, Alonso [1], etc. reported the chemical shifts of ^{1}H and ^{13}C spectra for (*E*)- and (*Z*)-Stilbene ([(*E*)-**2**] and [(*Z*)-**2**]). However, the chemical shifts of ^{13}C NMR spectra were not unequivocally assigned. Two puzzles aroused. Firstly, the diamagnetic anisotropy of vinyl group exerting on the phenyl rings of the *E* isomer is significant greater than that exerting on those of the *Z* isomer, observed in ^{1}H NMR spectra ($\Delta = 0.26$ ppm for ortho protons). Secondly, C(ortho) or C(para), would be anticipated to be more sensitive to the vinyl substituent via resonance than the other (C(para) of C(ortho)) in both E and Z isomer. The downfiled and upfield chemical shifts would be assigned to C(ortho) and C(para), respectively, for both (*E*)-Stilbene and (*Z*)-Stilbene, or vice versa.

In 2015, 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 [2]. Earlier, in 1999 [3], we revealed that the vinyl group donates electron density to the adjacent metallocenyl (CpCr$(CO)_2$(NO), ferrocene) Cp and phenyl rings via resonance in *E* isomers. In hopes of resolving the above two puzzles, confirming those hypotheses, and the validity of them to *Z* isomers, in which the sterically hindered conformer may disrupt the resonance, compounds (*Z*)-CpFe(η^5-C_5H_4CH=CHC_6H_5) [(*Z*)-**5**] and (1*Z*,3*E*)-FcCH=CHCH=CHPh [(1*Z*(Fe),3*E*)-**6**], compounds containing both Cp(Fe) and phenyl ring, and with a *Z* configuration, were synthesized. For the purpose of comparison, compound (1*E*,3*E*)-FcCH=CHCH=CHFc [(1*E*,3*E*)-**8**] was also prepared.

Herein, we report the syntheses of new compounds, [(*Z*)-**5**], [(1*Z*(Fe),3*E*)-**6**], and [(1*E*,3*E*)-**8**], and the results of spectral studies on compounds **1**–**9**. ^{1}H and ^{13}C NMR spectral comparisons among **1**–**9** and probable rationalizations are presented.

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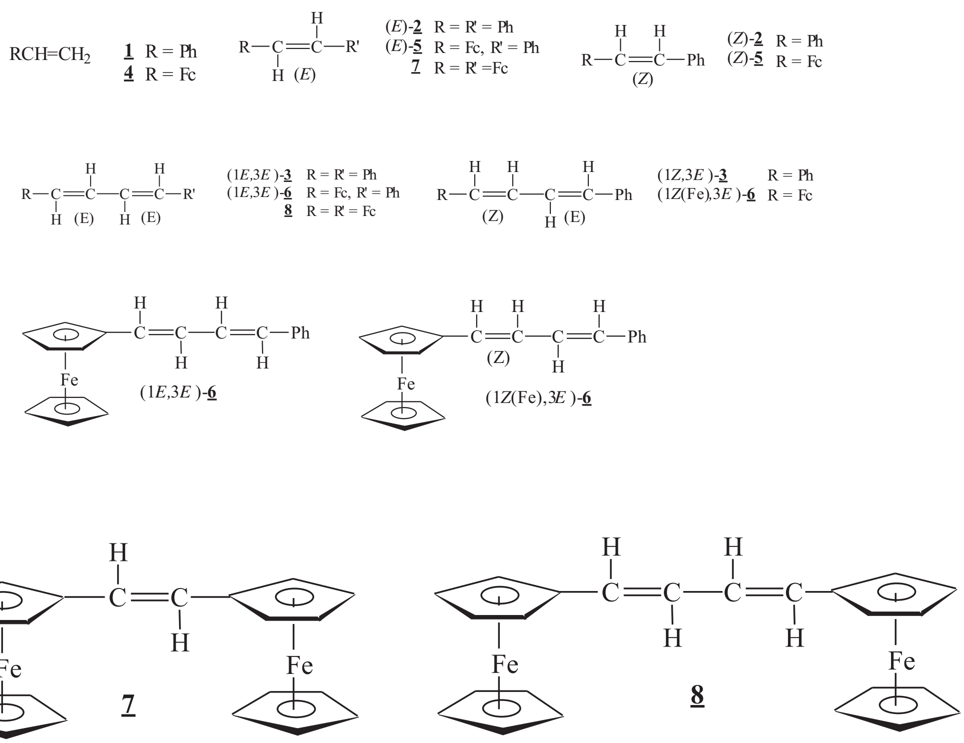

2. Results

2.1. Synthesis

Through the Wittig reaction [4] between ferrocenecarbaldehyde and benzyltriphenylphosphorane, formed from the deprotonation of the corresponding phosphonium iodide with n-butyllithium, (*E*)- and (*Z*)-1-ferrocenyl-2-phenylethene ([(*E*)-**5**], [(*Z*)-**5**]), were obtained in a yield of 53% and 28%, respectively.

$$[C_6H_5CH_2PPh_3]^+I^- \xrightarrow{\text{n-BuLi}} C_6H_5CH{=}PPh_3 \xrightarrow{\text{FcCHO}} [(E)-\underline{5}] + [(Z)-\underline{5}]$$

$$[(E)-C_6H_5CH{=}CHCH_2PPh_3]^+I^- \xrightarrow{\text{n-BuLi}} (E)-C_6H_5CH{=}CHC{=}PPh_3 \xrightarrow{\text{FcCHO}} [(1E,3E)-\underline{6}] + [(1Z(Fe),3E)-\underline{6}]$$

$$[FcCH_2PPh_3]^+I^- \xrightarrow{\text{n-BuLi}} FcCH{=}PPh_3 \xrightarrow{(E)-FcCH{=}CHCHO\ \underline{9}} \underline{8}$$

An analogous reaction between (*E*)-Cinnamyltriphenylphosphorane and ferrocenecarbaldehyde gave compounds [(1*E*,3*E*)-**6**] and [(1*Z*(Fe),3*E*)-**6**], in a yield of 52 and 16, respectively. Compound **8** was prepared in a yield of 40% from the reaction of (ferrocenylmethyl)triphenylphosphorane and (*E*)-1-ferrocenyl-2-formylethene **9**.

2.2. Characterization: ^1H NMR

The ^1H NMR chemical shifts of **1**–**9** are listed in Table 1 [1,3,5–8]. The ^1H NMR spectra of compounds **4**, [(*E*)-**5**], [(*Z*)-**5**], [(1*E*,3*E*)-**6**], [(1*Z*(Fe),3*E*)-**6**], **7**, **8**, and **9** are consistent with their assigned structures and are similar to other metallocenyl systems [6].

The ^1H NMR spectrum (Fig. 1) of [(*E*)-**5**] exhibited an AB quartet of relative intensity of 2H owing to the vinyl protons at δ = 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 *E*. One A_2B_2 pattern, related to the observed triplets, resonating at δ = 4.47 and 4.29 ppm corresponding to the protons H(2,5) and H(3,4) of Cp^1(Fe), was 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 2H, two triplets of relative intensity of 2H and 1H, respectively, resonating at δ = 7.43, 7.33, and 7.22 ppm were assigned to the ortho, meta, and para proton of the phenyl ring, respectively. Analogously, the chemical shifts of the H(2–5) of Cp(Fe) and the H(2–6) of phenyl ring for compounds [(1*E*,3*E*)-**3**], [(1*Z*,3*E*)-**3**], **4**, [(*Z*)-**5**] (Fig. 2), [(1*E*,3*E*)-**6**], [(1*Z*(Fe),3*E*)-**6**], **7**, **8**, and **9** were assigned.

2.3. Characterization: ^{13}C NMR

^{13}C NMR chemical shifts of **1**–**9** are presented in Table 2 [1,3,5,7]. The assignments of ^{13}C NMR spectra were based on standard ^{13}C NMR [9], 2D HETCOR, and DEPT correlation techniques and also by comparison with other ferrocene derivatives [10]. In the case of [(*E*)-**5**], 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(2–6) of phenyl were more difficult to make. Based on the 2D HETCOR results (Fig. 1), in which the magnetic fields of ^1H and ^{13}C NMR spectra increase toward the right and upper side, respectively, given the positive slope of FcC<u>H</u> = and PhC<u>H</u> = versus Fc<u>C</u>H = and Ph<u>C</u>H=, chemical shifts at δ = 126.93 and 126.06 ppm were assigned to Fc<u>C</u>H = and Ph<u>C</u>H=, 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

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