Journal of Organometallic Chemistry, 395 (1990) 187–193
Elsevier Sequoia S.A., Lausanne
JOM 21113

Synthesis and reactivity of (tricarbonyl)-(η^5-2-methylpentadienyl)iron(+1) cation

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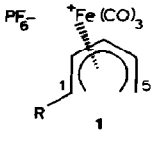
(Received March 6th, 1990)

Abstract

The (tricarbonyl)(η^5-2-methylpentadienyl)iron(+1) cation was prepared by the protonation of (tricarbonyl)(4-methyl-2,4-pentadienol)iron. Reaction of the cation with H_2O, allyl-TMS, $NaBH_3CN$, PPh_3, malonate and 3-furyl cuprate gave (η^4-1,3-diene)$Fe(CO)_3$ complexes. The regioselectivity for the nucleophilic attack appears to be sterically controlled.

There has been considerable recent interest in the application of acyclic butadiene iron tricarbonyl complexes in organic synthesis [1]. In comparison, although the corresponding open (η^5-pentadienyl)iron(+1) cations (**1**) have been known for nearly 27 years [2], there are few examples of the reaction of these cations with carbon nucleophiles [3–5]. Recently we reported upon the reactivity of (1-substituted-pentadienyl)iron cations **1** with malonate nucleophiles and with alkynyl nucleophiles [4]. To our knowledge, there are no reported examples of the synthesis or reactivity of (2-substituted-pentadienyl)iron cations [6 **]. We herein report on the sysnthesis of (tricarbonyl)(2-methylpentadienyl)iron(+1) hexafluorophosphate (**2**) and its reaction with a variety of carbon and heteroatom nucleophiles.



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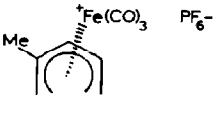

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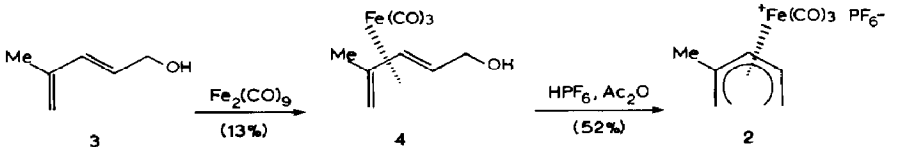
** Reference number with asterisk indicates a note in the list of references.

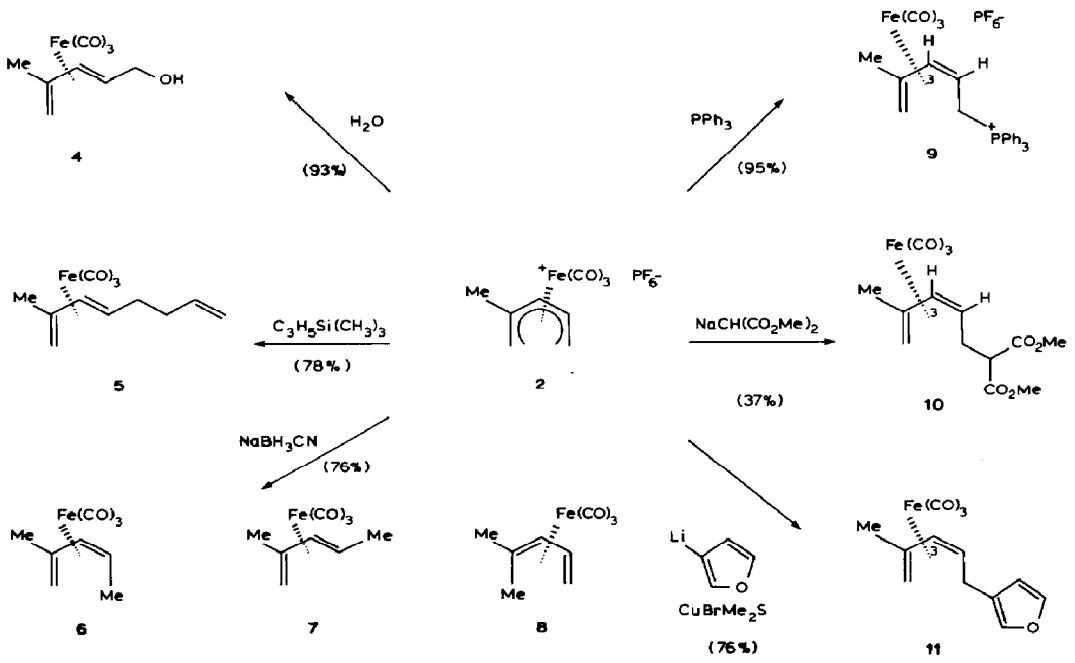
0022-328X/90/$03.50

Results and discussion

Trans-4-methyl-2,4-pentadienol (**3**) was prepared by the literature procedure [7]. Complexation of **3** with $Fe_2(CO)_9$ gave the dienol complex (**4**) as a yellow oil. The *trans* stereochemistry of the complex was assigned on the basis of its ^1H NMR spectral data. Notably the signal corresponding to H3 appears at δ 5.20 as a doublet (J 9 Hz), and the signal for H1endo appears far upfield at δ 0.45 (d, J 2 Hz). Treatment of **4** with $HPF_6/Ac_2O/Et_2O$ gave the cation **2** as an off-white solid. The pentadienyl ligand was assigned the "U" geometry on the basis of its ^1H NMR coupling data [8]. It should be noted that the ^{13}C NMR chemical shifts of C1 and C5 are relatively similar (δ 60.2, 62.0). This might be interpreted to indicate that the electronic character of the two termini are nearly identical.



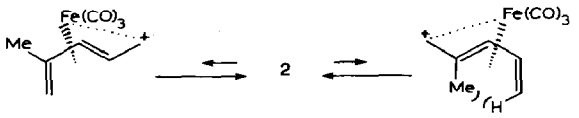
The results of the reaction of **2** with water, allyltrimethylsilane, $NaBH_3CN$, triphenylphosphine, sodio dimethylmalonate, and 3-furyl lithium/CuBr appear in Scheme 1. In nearly all cases a single product was isolated, while the reaction of **2** with $NaBH_3CN$ gave a mixture of known methylpentadiene complexes [9]. The sole or predominant product in each case arises from nucleophilic attack at C5. The structural assignments for these products are based on their ^1H NMR spectral data (experimental section). In particular, the appearance of a single internal diene hydrogen (H3) signal as a doublet indicates that nucleophilic attack occurs at C5.



Scheme 1

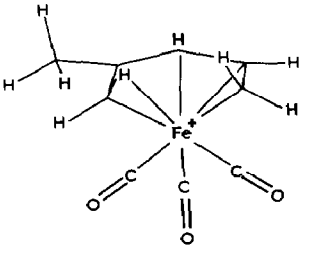
The diene geometry (*trans* vs. *cis*) may be tentatively assigned on the basis of the magnitude of H3–H4 coupling; 8–9 Hz for *trans* and 6–8 Hz for *cis*. The *trans* vs. *cis* geometry may be more positively identified from the chemical shift of the H1*endo* signal. The H1*endo* signal of the *trans*-diene complexes **4**, **5**, and **7** appear significantly upfield ($\sim \delta$ 0.4) compared to the corresponding *cis*-diene complexes **6**, **9**, **10**, and **11** ($\sim \delta$ 1.60).

The hydrolysis of **2** presumably occurs via attack of water on the less stable "S" form of the pentadienyl ligand [10]. There are two possibilities for the *transoid* structure (**A** and **B**), however, it would appear, on the basis of steric hindrance, that structure **A** would be the predominant isomer. In a similar fashion, attack of the weak allylsilane nucleophile occurs via attack of the more reactive "S" form of the cation (**A**) [5,11].

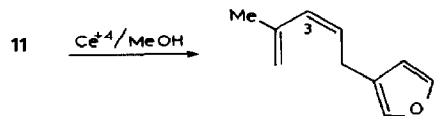


A B

For more reactive nucleophiles, attack occurs on the "U" form of the pentadienyl ligand. The predominant site of hydride attack is at C5, the less sterically-hindered site. The importance of steric factors in the addition of $NaBH_3CN$ to (pentadienyl)iron(+1) cations has previously been reported [12]. It should be noted that the regioselectivity of hydride addition to the cyclic analog, (2-methylcyclohexadienyl)$Fe(CO)_3^+$, is dependent upon temperature as well as the hydride donor [13]. Exclusive nucleophilic attack of triphenylphosphine at C5 is not surprising; nucleophilic attack of PPh_3 at the less hindered pentadienyl terminus has previously been observed for cations **1** [14]. The regiospecificity observed for attack by malonate anion on **2** may be compared to the relative lack of regioselectivity observed for malonate attack on cation **1** (R = alkyl) [4a]. We have previously attributed this lack of regioselectivity to offsetting weak steric and electronic influences. Since the electronic character at C1 and C5 of **2** is not greatly different, the regiospecificity for attack at C5 appears to the result of steric hindrance. It should be noted that the cyclic analog (2-CH_3-C_6H_6)$Fe(CO)_3^+$ gives predominantly the product of malonate attack at C5 [13]. Nucleophilic attack of 3-furyl cuprate occurs at the less hindered terminus. This result is consistent with the regioselectivity observed for the attack of alkyl [15] and alkynyl cuprates [4b] with dienyl iron cations. It would thus appear that the rate of nucleophilic attack on the "U" form of the 2-substituted-pentadienyl ligand at C5 is faster than the rate of nucleophilic attack at C1 due to the steric hindrance of the C2 methyl substituent. A molecular mechanics generated structure [16] for **2** which illustrates this hindrance appears below.



The oxidative decomposition of **11** was accomplished using Ce^{+4}/MeOH to afford 3-(*Z*-4-methyl-2,4-pentadienyl)furan (**12**). This pleasant swelling compound is the Δ^3-isomer of the terpene lepalin, isolated from the essential oil of *Ledum palustre* [17*]. It should be noted that the oxidative decomplexation of **11** occurs without any isomerization about the diene, as evidenced by the appearance of H3 in the NMR spectrum of **12** as a doublet (δ 5.89, J 11 Hz).



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In summary, these results indicate that attack by a variety of nucleophiles on the 2-methylpentadienyl ligand is predominantly controlled by steric effects. This may be compared to the regioselectivity observed for nucleophilic attack on 1-substituted pentadienyl iron cations [3–5,11]. We are presently examining the reaction of a series of 1,2- and 1,4-disubstituted pentadienyl cations in order to determine the cooperativity or countervailing nature of substituents in these positions on the regioselectivity of nucleophilic attack.

Experimental

General data. Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected. Spectrograde solvents were used without further purification with the exception of diethylether and tetrahydrofuran which were distilled from the sodium and potassium benzophenone ketyls.

(Tricarbonyl)(η^4-4-methyl-2,4-pentadienol)iron (4). To a solution of 4-methyl-2,4-pentadienol (11.19 g, 0.114 mol) in degassed THF/ether (200 ml, 1 : 1) was added diiron nonacarbonyl (31.2 g, 0.086 mol). The reaction mixture was stirred under N_2 for 48 h, and then concentrated to give a dark red oil. The oil was filtered through a bed of SiO_2 (60–200 mesh) with hexanes and benzene elution. The resultant solution was concentrated and distilled (Kugelrohr) under high vacuum. The first fraction contained the starting dienol (40–70 °C/0.07 mmHg) followed by the product **4** as a golden yellow oil: 2.75 g, 11.5 mmol, 13%. bp 90 °C/0.4 mmHg; 60 MHz ^{1}H NMR (CCl_4) δ 5.29 (d, J 9 Hz, H3), 3.45 (m, H5, H5′, OH), 2.11 (s, CH_3), 1.75 (br s, H1*exo*), 0.85 (m, H4), 0.45 (br d, J 2 Hz, H1*endo*); ^{13}C[^{1}H] NMR ($CDCl_3$), δ 211.1 (M–C=O), 100.4 (C2), 86.7 (C3), 64.8 (C5), 59.2 (C4), 43.6 (C1), 22.8 (CH_3); HRMS, m/z 237.9933 [calcd for $C_9H_{10}O_4Fe$, 237.9928].

(Tricarbonyl)(2-methylpentadienyl)iron(+ 1) hexafluorophosphate (5). To a cold solution of HPF_6 (4 ml, 60% in H_2O) in acetic anhydride (5 ml) was added a solution of **4** (2.75 g, 11.5 mmol) in acetic anhydride (5 ml). The solution immediately became dark black. The solution was slowly added dropwise to a large excess of ether (600 ml). The ether was decanted and the resultant precipitate was dissolved in nitromethane (3 ml). The nitromethane solution was slowly added dropwise to an excess of ether (700 ml). The resultant precipitate was collected by vacuum filtration and was dissolved in nitromethane and reprecipitated again in excess ether (700 ml). The resultant off-white precipitate was collected by vacuum filtration and dried in vacuo to give **2**: 2.19 g, 5.98 mmol, 52%. mp > 220 °C (dec.);

60 MHz ^{1}H NMR (CD_3NO_2) δ 6.97 (d, J 7 Hz, H3), 6.14 (ddd, J 7, 10, 12 Hz, H4), 3.68 (dd, J 3, 10 Hz, H5*exo*), 3.56 (m, H1*exo*), 2.40 (s, CH_3), 2.29 (dd, J 3, 12 Hz, H5*endo*), 1.83 (d, J 4 Hz, H1*endo*); ^{13}C{^{1}H} NMR (CD_3NO_2) δ 122.2 (C2), 99.1 (C4), 94.6 (C3), 62.0, 60.2 (C5, C1), 20.8 (CH_3); Anal. Found: C, 29.70; H, 2.40. $C_9H_9O_3FePF_6$ calcd: C, 29.53, H, 2.48%.

Reaction of 2 with water. A sample of **2** (0.248 g, 0.677 mmol) was added to water (75 ml) and the suspension was vigorously stirred for 1 h. The reaction mixture was extracted with ether (2 × 50 ml) and the combined ethereal extracts were washed with brine (25 ml). The organic layer was dried ($MgSO_4$), and the solvent evaporated, and dried in vacuo to afford a yellow oil: 0.150 g, 0.630 mmol, 93%. This was identified by ^{1}H and ^{13}C{^{1}H} NMR as consisting of **4**.

Reaction of 2 with allyl trimethylsilane. To a solution of **2** (0.247 g, 0.675 mmol) in THF (20 ml) and CD_3NO_2 (2 ml) was added allyl trimethylsilane (0.12 ml, 0.75 mmol). The dark yellow-green solution immediately paled to a light yellow green. The reaction was stirred for 24 h, and then poured into dilute aqueous $NaHCO_3$ and extracted with ether (2 × 50 ml). The combined ethereal extracts were dried ($MgSO_4$) and concentrated. The residue was chromatographed on SiO_2 (60–200 mesh). Elution with hexanes gave a golden yellow fraction which was concentrated and dried in vacuo to give **5** as a golden yellow oil: 0.139 g, 0.526 mmol, 78%. **5**: 300 MHz ^{1}H NMR ($CDCl_3$) δ 5.80 (ddt, J 10.2, 17.1, 6.7 Hz, H7), 5.12 (d, J 8.3 Hz, H3), 5.04 (dd, J 3.4, 17.1 Hz, H8), 4.98 (dd, J 3.4, 10.2 Hz), 2.15 (s, CH_3 and H6), 1.74 (d, J 2.3 Hz, H1*exo*), 1.70 (m, H5), 0.82 (dt, J 8.2, 7.0 Hz, H4), 0.31 (d, J 2.3 Hz, H1*endo*); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 212.0 (M–C=O), 137.6 (C7), 115.2 (C8), 99.2 (C2), 88.2 (C3), 61.2 (C4), 43.0 (C1), 36.1, 33.8 (C5 and C6), 22.8 (CH_3).

Reaction of 2 with $NaBH_3CN$. To a suspension of **2** (0.260 g, 0.710 mmol) in THF (20 ml) at 0 °C was added solid $NaBH_3CN$ (0.055 h, 0.832 mmol). The solid rapidly dissolved and the reaction mixture was stirred for 3 h. The clear yellow solution was diluted with water (50 ml) and extracted with petroleum ether (3 × 30 ml). The combined extracts were dried ($MgSO_4$), and the solvent evaporated, and dried in vacuo to afford a yellow oil: 0.120 g, 0.540 mmol, 76%. This was identified by ^{1}H and ^{13}C{^{1}H} NMR as a mixture of **6**, **7**, and **8** (10 : 1 : 2). **6**: 300 MHz ^{1}H NMR δ 5.25 (d, J 7.6 Hz, H3), 2.57 (pentad, J 7.4 Hz, H4), 2.18 (s, CH_3), 1.88 (d, J 2.8 Hz, H1*exo*), 1.54 (d, J = 2.8, H1*endo*), 1.04 (d, J 7.3 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 211.3 (M–C=O), 107.4 (C2), 88.0 (C3), 49.7 (C4), 43.3 (C1), 24.4 (CH_3), 13.4 (C5). **7**: 300 MHz ^{1}H NMR δ 5.11 (d, J 8.3 Hz, H3), 2.15 (s, CH_3), 1.72 (d, J 2.3 Hz, H1*exo*), 1.41 (d, J 6.3 Hz, CH_3), 0.88 (dq, J 8.3, 6.3 Hz, H4), 0.32 (d, J 2.3 Hz, H1*endo*). **8**: 300 MHz ^{1}H NMR δ 5.25 (m, H2), 5.18 (d, J 5.2 Hz, H3), 1.76 (dd, J 3.0, 7.8 Hz, H1*exo*), 1.56 (s, CH_3*exo*), 1.54 (m, H1*endo*), 1.15 (s, CH_3*endo*). For ^{13}C NMR spectral data of **7** and **8** see ref. 9.

Reaction of 2 with triphenylphosphine. To a solution/suspension of **2** (0.22 g, 0.60 mmol) in CH_2Cl_2 (20 ml) was added triphenylphosphine (0.16 g, 0.61 mmol). The suspension rapidly dissolved and the golden yellow solution was stirred for 16 h. The reaction mixture was concentrated under reduced pressure and the resultant oil was dissolved in CH_2Cl_2 and treated with extraction grade ether until cloudy. After standing for 1 h, **9** was collected as a golden yellow precipitate: 0.36 g, 0.57 mmol, 95%. mp 146–150 °C; 60 MHz ^{1}H NMR ($CDCl_3/CD_3CN$) δ 7.9–7.4 (m, 15H, C_6H_5), 5.06, (br d, J 6 Hz, H3), 3.37 (br d, J 12 Hz, H5), 2.77 (br d, J 12 Hz, H5′), 2.40 (m, H4), 2.07 (m, H1*exo*), 1.93 (s, CH_3), 1.60 (d, J 3 Hz, H1*endo*);

$^{13}C\{^1H\}$ NMR (CD_3CN) δ 208.8 (M–C=O), 135.2 (J(PC) 2 Hz), 133.3 (J(PC) 10 Hz), 130.5 (J(PC) 13 Hz), 117.1 (J(PC) 84 Hz), 110.1 (C2), 84.7 (J(PC) 2 Hz, C3), 44.9 (C1), 38.3 (J(PC) 11 Hz, C4), 24.2 (J(PC) 43 Hz, C5), 22.8; $^{31}P\{^1H\}$ NMR (CD_3CN) δ 22.5 (wrt H_3PO_4); Anal. Found: C, 50.46; H, 3.83. $C_{27}H_{24}O_3P_2F_6Fe \cdot \frac{1}{2}H_2O$ calcd: C, 50.89; H, 3.95%.

Reaction of 2 with sodium dimethylmalonate. To a solution of sodium dimethylmalonate (0.655 mmol, freshly prepared from excess. NaH and dimethylmalonate) in THF (25 ml) cooled to 0 °C was added solid **2** (0.228 g, 0.623 mmol). The reaction mixture was stirred for 1 h and then poured into saturated aqueous NaCl (50 ml) and extracted with ether (2 × 50 ml). The combined ethereal extracts were dried ($MgSO_4$) and concentrated. The residue was chromatographed over SiO_2 (60–200 mesh). Elution with hexanes gave $Fe_3(CO)_{12}$ as a green fraction. Elution with benzene gave **9** as a golden oil: 0.078 g, 0.222 mmol, 37%. **10**: 300 MHz ^1H NMR ($CDCl_3$) δ 5.17 (d, J 7.8 Hz, H3), 3.70 (s, OCH_3), 3.28 (dd, J 6.4, 8.3 Hz, CHE_2), 2.29 (ddd, J 4.8, 7.8, 12.7 Hz), 2.14 (s, CH_3), 2.13 (ddd, J 4.8, 6.4, 14.1 Hz, H5), 1.93 (d, J 3.2 Hz, H1*exo*), 1.62 (ddd, J 8.3, 12.7, 14.1 Hz), 1.53 (d, J 3.2 Hz, H1*endo*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 210.5 (M–C=O), 168.9 (COOR), 108.7 (C2), 86.3 (C3), 54.5, 52.5, 51.0 (C4, CHE_2, OCH_3), 43.6 (C1), 28.4 (C5), 24.3 (CH_3); HRMS, m/z 269.0350 [calcd for $C_{12}H_{16}O_5Fe$ (M − 2 CO), 296.0347].

Reaction of 2 with 3-furyl cuprate. To a solution of 3-bromofuran (0.72 g, 4.92 mmol) in ether (5 ml), cooled to −78 °C, was added via syringe a solution of n-butyl lithium (5.0 mmol). The mixture was stirred at −78 °C for 45 min after which $CuBrMe_2S$ (0.34 g, 1.64 mmol) was added. The reaction mixture was diluted with ether (15 ml) and stirred for 1 h. Solid **2** (0.60, 1.64 mmol) was added in one portion and the mixture was stirred at −78 °C for 2 h. The reaction mixture was warmed to room temperature and stirred for 1 h. The mixture was treated with conc. aqueous NH_4OH (2 ml) and then with saturated aqueous NH_4Cl (30 ml). The layers were separated and the aqueous layer was extracted with ether (2 × 30 ml). The combined organic layers were washed with saturated aqueous NH_4Cl. The ethereal layer was dried ($MgSO_4$) and concentrated. The residue was chromatographed on SiO_2 (60–200 mesh). Elution with hexanes gave a golden yellow fraction which was concentrated and dried in vacuo to give **11** as a golden yellow oil: 0.361 g, 1.25 mmol, 76%. **11**: 300 MHz ^1H NMR ($CDCl_3$) δ 7.34, 7.19, 6.23 (three s, furyl H), 5.26 (d, J 7.3 Hz, H3), 2.60 (m, H4, H5′), 2.21 (s, CH_3), 2.15 (dd, J 10.9, 16.5 Hz, H5), 1.97 (d, J 2.8 Hz, H1*exo*), 1.60 (d, J 2.8 Hz, H1*endo*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 210.9 (M–C=O), 142.8, 138.7, 126.0, 110.6 (furyl C), 108.4 (C2), 86.3 (C3), 55.2 (C4), 43.5 (C1), 24.3, 23.6 (C5, CH_3); HRMS, m/z 260.0135 [calcd for $C_{12}H_{12}O_3Fe$ (M − CO) 260.0136].

Cleavage of 11. To a solution of **11** (0.336, 1.16 mmol) in methanol (50 ml) was added ceric ammonium nitrate (0.64 g, 1.16 mmol) with concomitant gas evolution. The reaction mixture was stirred for 1 h after which a second sample of ceric ammonium nitrate was added (0.64 g). Addition of a third equivalent of Ce^{+4} caused no further gas evolution. The reaction mixture was stirred for 2 h, and then poured into water (100 ml). The aqueous solution was extracted with ether (2 × 50 ml), and the combined ether extracts were washed with water (50 ml). The ether layer was dried ($MgSO_4$) and concentrated to give a pale oil. Distillation (Kugelrohr) under high vacuum gave **12** as a clear oil: 0.076 g, 0.513 mmol, 44%. **12**: bp 20 °C/0.2 mmHg (Kugelrohr); ^1H NMR (CCl_4) δ 7.23, 7.10, 6.17 (three narrow m,

furyl H), 5.89 (d, *J* 11 Hz, H3), 5.43 (dt, *J* 11, 7 Hz, H4), 4.92, 4.82 (2 m, C=CH_2), 3.31 (d, *J* 7 Hz, H5), 1.82 (s, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 142.9, 141.4, 139.0, 131.9, 128.6, 115.4, 110.9, 24.4, 23.3; GC/MS: *m/z*(int.) 148 (M^+, 21), 133 (76), 105 (100), 119 (76).

Acknowledgments

Financial support for this research was provided by the National Institutes of Health (GM42641-01). We are grateful to the National Science Foundation (CHE-8905465) for partial funding of the purchase of the 300 MHz NMR spectrometer used in this research. High resolution mass spectral determinations were performed at the Midwest Center for Mass Spectrometry, an NSF Regional Instrumentation Center.

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