*Journal of Organometallic Chemistry*, 364 (1989) 373–379
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09634

# Investigation of complexes of the type $\eta^5$-$C_5H_5Fe(CO)_2(\eta^1$-$C_5H_4X)$ (X = $CH_3$, CONHTs). Crystal and molecular structure of 5-[$\eta^5$-$C_5H_5Fe(CO)_2$]-1-[TsNHCO]cyclopentadiene

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(Received July 19th, 1988; in revised form September 6th, 1988)

## Abstract

The new complex Fp($\eta^1$-$C_5H_4CH_3$) (**2**) was prepared and its fluxionality studied. Complex **2** was found to have a higher energy barrier for the fluxional process than the related systems Fp($\eta^1$-$C_5H_5$), $\eta^5$-$C_5Me_5Fe(CO)_2(\eta^1$-$C_5H_5)$, and Fp($\eta^1$-$C_5H_4$CONHTs) (**3**). Reaction of **2** with dimethyl acetylenedicarboxylate gave a mixture of two cycloadducts where the methyl-group was found in the 5- and the 1-position in a ratio of 3/1, respectively. In both cycloadducts the Fp moiety was found regio- and stereoselectively in the 7-position and *anti* to the carboxylate groups. The molecular structure of crystalline **3** was determined and showed that the CONHTs substituent of the $\eta^1$-ring was in the 1-position.

## Introduction

Recently, there has been considerable interest in the use of allyl-metal complexes in organic syntheses [1*], for example, Fp($\eta^1$-$C_5H_5$) (Fp = $\eta^5$-$C_5H_5Fe(CO)_2$] (**1**) is a synthetic equivalent for methyl 1,3-cyclopentadiene-5-carboxylate [2] and 5-amino-1,3-cyclopentadiene [3] in cycloaddition reactions. The $\eta^1$-$C_5H_5$ ligand of complex **1** reacts with a variety of electron poor alkenes and alkynes to stereo- and regioselectively yield cycloadducts [2–4] whose iron group can be stereospecifically replaced by a carbomethoxy or an amino group.

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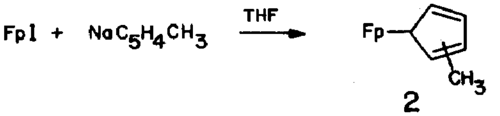
* Reference numbers with asterisks indicate notes in the list of references.

To investigate the synthetic utility of substituted $\eta^1$-cyclopentadienyl ligands in these reactions we have prepared the new complex Fp($\eta^1$-$C_5H_4CH_3$) (**2**) and examined its reactions with dimethyl acetylenedicarboxylate (DMAD). The fluxional behavior of **2** is also presented as well as the related system Fp($\eta^1$-$C_5H_4$CONHTs) (**3**). The crystal and molecular structure of **3** is reported and provides a definitive structure for the complex in the solid state.

Complex **2** is readily prepared from the reaction of FpI with sodium methylcyclopentadienide in tetrahydrofuran (THF) (eq. 1). It is interesting that **2** is obtained in ca. 40% yield or more than twice that typically achieved in the synthesis of Fp($\eta^1$-$C_5H_5$).



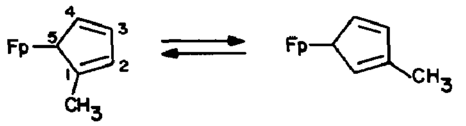
2

(1)

The fluxionality of metal systems containing $\sigma$-bonded cyclopentadienyl ligands has received a great deal of attention over the past two decades [5*]. Among these studies is the effect of alkyl substitution on the $\sigma$-bonded cyclopentadienyl ligand in the fluxional process [6*]. In certain cases, the fluxional process ceases, however, in the related system Rp($\eta^1$-$C_5H_4CH_3$) (Rp = $\eta^5$-$C_5H_5Ru(CO)_2$], the methyl substitution is reported to only slow the migration of the Rp group around the methylated $\eta^1$-ring [5e*]. Like the Ru compound, complex **2** is fluxional and the rearrangement process is retarded [10*]. Selected proton NMR spectra ($CS_2$) for **2** at temperatures of 313, 273, and 213 K are displayed in Fig. 1. When the sample is cooled to ca. 283 K the resonances attributed to the $\eta^1$-$C_5H_4CH_3$ vinyl protons coalesce. Further cooling of the sample to 213 K produces resonances in the $^1$H NMR spectrum which appear to arise from a mixture of two static forms of **2**.

The structures of isomers **2a** and **2b** are assigned on the basis of spectroscopic data. The H(5) resonances appear as a broad singlet ($\delta$ 3.73) and a relatively sharp singlet ($\delta$ 3.04). The H(5) proton is expected to couple with the 1- and 4-vinyl proton(s) [5a,e*], therefore, the broad singlet is assigned to **2b** and the sharper resonance to **2a**. The occurrence of **2b** as the major isomer is consistent with relieving steric interactions between the $\eta^1$-$C_5H_4CH_3$ ligand and the iron group. In contrast, for Rp($\eta^1$-$C_5H_4CH_3$) at 243 K the predominant isomer has the methyl group in the 1-position. Further cooling of the sample changes the relative equilibrium concentrations for **2b** and **2a** (**2b**/**2a**: 2.5 (213 K), 2.9 (173 K)]; however, this change is very small relative to that observed with Rp($\eta^1$-$C_5H_4CH_3$) [5e*]. Another important difference between **2** and the Ru analog is that **2** is not found by NMR spectroscopy to exist in a static form in which the Fp and the methyl group are both bound to the 5-carbon of the $\eta^1$-cyclopentadienyl ligand. This observation and the positional isomer differences mentioned above are likely the result of the smaller coordination geometry of Fe [11,12*] relative to the Ru [13] atom.

The evidence showing the absence of significant amounts of the 5,5-substituted isomer of **2** stimulated our interest in the iron system Fp($\eta^1$-$C_5H_4$CONHTs) (**3**), which gave spectroscopic data consistent with the 5,5-isomer [4b]. Complex **3** displays two multiplets at $\delta$ 6.75 and 5.63 ppm for the $\eta^1$-ring protons in its $^1$H NMR (in acetone-$d_6$) spectrum at 303 K. However, cooling of the sample to 223 K shows complete coalescence of these two resonances and further cooling to 193 K



2a 2b

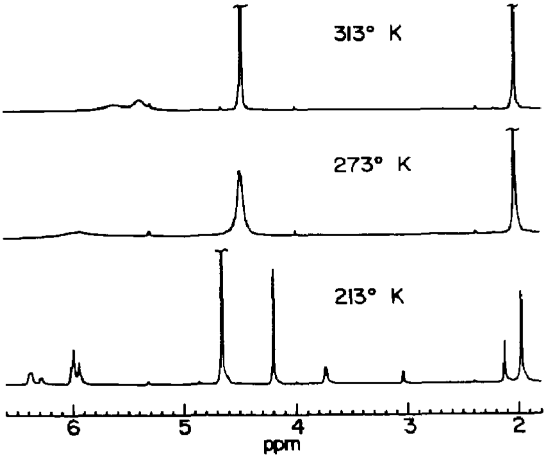


Fig. 1. $^1H$ NMR spectra of **2** in $CS_2$ at selected temperatures.

produces a new, very broad resonance, appearing at $\delta$ 6.46 ppm. Complex **3** is a fluxional molecule and therefore does not exist as the static 5,5-isomer. The low coalescence temperature is indicative of a low energy of activation for the fluxional process in comparison the related systems Fp($\eta^1$-$C_5H_5$) [5a*] and **2**. This observation is consistent with a mechanism which involves a transition state that has some zwitterionic character in the form of $Fp^+(\eta^2\text{-}C_5H_5^-)$. Hence, electron withdrawing substituents, such as CONHTs, on the $\eta^1$-cyclopentadienyl ring should stabilize this type of intermediate and lower the energy barrier of the rearrangement. The increased energy barrier for Fp($\eta^1$-$C_5H_4CH_3$) relative to Fp($\eta^1$-$C_5H_5$) is consonant with the electron-donating nature of the methyl group. Also in accord with this analysis is that the $\eta^5$-pentamethylcyclopentadiene ligand has been shown to slightly lower the energy barrier [12*]. It would appear from the work of Rosenblum et al. [14] and our laboratory [12*] that substitution on the $\eta^5$-ring has little, if any, effect on the energy barrier for the fluxional process. The present study demonstrates that substitution on the $\eta^1$-Cp ring does significantly effect the energy barrier for the fluxional process. The substituent effects observed for the $\eta^1$-Cp ring qualitatively agree with some negative charge developing on the fluxional ring (using standard Hammett $\sigma$'s).

To explore the static structure of **3** a single-crystal X-ray diffraction study was undertaken. An ORTEP perspective drawing of **3** and the labeling scheme employed is presented in Fig. 2. Selected geometric parameters for **3** are listed in Table 1. Complete details and parameters for the structure determination can be found in the supplemental material for this paper. The bond angles and lengths are quite normal in the structure [5a*,11,12*]. A point of interest lies in the substitution pattern on the $\eta^1$-cyclopentadienyl ring. The Fp group is in the 5-position as

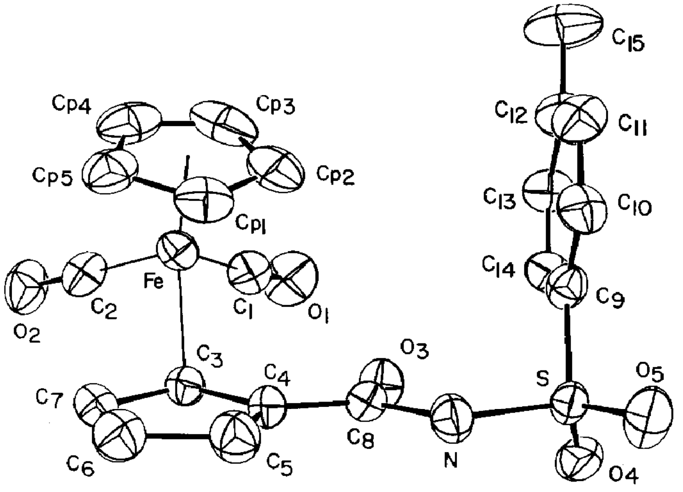
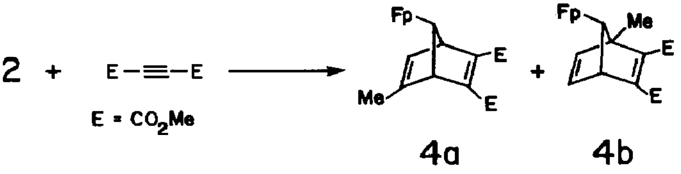


Fig. 2. ORTEP drawing of **3** including the labeling scheme.

anticipated but the CONHTs group is located on the 1-carbon of the $\eta^1$-ring. The C(4)–C(8)–O(3) bond angle is significantly distorted indicating some steric interaction between the carbonyl oxygen and the Fp moiety. It seems that in Fp compounds the 5,5-isomer is higher in energy than its positional isomers; however, this by no means implies that such a species could not be a short lived intermediate in the migration of the Fp group around the $\eta^1$-ring.

Reaction of **2** with DMAD (2 equiv., 0.5 h, 25 ° C) in dichloromethane produces two cycloadducts, **4a** and **4b**, in a ratio of 3/1 respectively (87% total yield) (eq. 2). Medium pressure chromatography of the mixture on alumina-III followed by crystallization permits isolation of pure **4a**, but **4b** could not be efficiently separated from **4a**. Consequently, the spectroscopic data for **4b** was determined from a mixture of **4a** and **4b** highly enriched in **4b**.



(2)

Table 1

Selected geometric parameters for crystalline **3** [a]

| Atoms | Bond length (Å) | Atoms | Bond angle (deg) |
|---|---|---|---|
| Fe–C(3) | 2.159(8) | C(7)–C(3)–C(4) | 102.9(6) |
| C(3)–C(4) | 1.462(10) | Fe–C(3)–C(4) | 113.5(5) |
| C(3)–C(7) | 1.462(10) | Fe–C(3)–C(7) | 106.8(5) |
| C(7)–C(6) | 1.344(12) | C(3)–C(4)–C(5) | 109.1(6) |
| C(6)–C(5) | 1.439(11) | C(3)–C(7)–C(6) | 110.8(7) |
| C(4)–C(5) | 1.325(10) | C(4)–C(8)–N | 116.2(6) |
| C(4)–C(8) | 1.462(9) | O(3)–C(8)–N | 120.3(6) |
| C(8)–O(3) | 1.218(8) | C(4)–C(8)–O(3) | 123.6(8) |

[a] See Fig. 2 for labeling of atoms. Numbers in parentheses are the standard deviation of the last digit(s) reported.

The structure of **4a** is unambiguously assigned by spectroscopic data to be the 5-methyl isomer. Complex **4a** is formed regio- and stereo-selectivity as expected from previous cycloaddition reactions of Fp($\eta^1$-$C_5H_5$) [2,3]. The structure of adduct **4b** is assigned on the basis of spectroscopic data as was **4a**.

Through the independent work of Rosenblum et al. [15] and Wojcicki et al. [16] concerning the cycloaddition reactions of Fp($\eta^1$-allyl) it was established that the reactions involve a step-wise mechanism which proceed through a zwitterionic intermediate. It is conceivable that a similar type of mechanism could be operative for Fp($\eta^1$-$C_5H_5$); however, the latter complex has the possibility of a concerted [$4\pi + 2\pi$] mechanism which should be considered. In fact, evidence for a concerted mechanism for the cycloaddition of **1** with the isomeric 2-butenedinitriles has recently been presented [4c].

In conclusion, additional evidence has been presented which supports zwitterionic character in an intermediate or transition-state complex involved in the fluxional process of Fp($\eta^1$-cyclopentadienyl) systems. In examining the cycloaddition chemistry of **2**, moderate product selectivity is obtained with respect to the methyl substituent on the $\eta^1$-ring; but as expected, the Fp moiety is found regio- and stereo-selectivity in the cycloadducts.

## Experimental

*General.* All manipulations of compounds and solvents were carried out by using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were degassed and purified by distillation under nitrogen from standard drying agents [17]. Spectroscopic measurements utilized the following instrumentation: $^1$H NMR, Varian XL 300; $^{13}$C NMR, Varian XL 300 (at 75.4 MHz). $^1$H NMR chemical shifts are reported in $\delta$ vs. $Me_4Si$ and the $CDCl_3$ resonance is used as the reference in $^{13}$C spectra at 77.00 ppm. The DMAD and methylcyclopentadiene were freshly distilled prior to use. The FpI was purchased from Aldrich Chemical Co. and used as received.

*Fp($\eta^1$-$C_5H_4Me$) (2).* A THF (100 ml) solution containing FpI (5.00 g) was treated with a THF solution of Na($C_5H_4Me$) ($\sim$ 1.0 *M*, 16 ml) and the resulting mixture stirred at ambient temperature for 4 h. The mixture was diluted with pentane (100 ml) and filtered through a pad of alumina. The solvents were removed under reduced pressure and the crude **2** was subjected to column chromatography (alumina-III, hexane/benzene, 7/3, v/v). Final purification was achieved using medium pressure chromatography on a 15 × 500 mm column of alumina-III (Woelm N32-60, hexane/benzene, 1/1, v/v). **2**: $^1$H NMR ($CDCl_3$): $\delta$ 5.74 (br 2, 2H, CH=), 5.46 (br, s, 2 H, CH=), 4.50 (s, 5H, ($C_5H_5$), 2.04 (s, 3H, $CH_3$); $^{13}$C NMR ($CDCl_3$): $\delta$ 216.22 (CO), 85.81 ($C_5H_5$), 15.64 ($CH_3$); IR ($CH_2Cl_2$): $\nu$(CO): 2011, 1960 $cm^{-1}$. Low temperature NMR spectra for complex **2**: is isomer **2a**: $^1$H NMR ($CS_2$, 213 K): $\delta$ 6.37 (br s, 1H, HC=), 6.00 (m, 1H, HC=), 4.65 (s, 5H, $C_5H_5$), 3.73 (s, 1H, Fe–CH), 1.97 (s, 3H, $CH_3$): $^{13}$C NMR ($\delta$, $CS_2$, 213 K) 216.7 (CO), 87.1 ($C_5H_5$), 31.7 (Fe–CH), 17.4 ($CH_3$). The vinyl carbon resonances for both **2a** and **2b** appear at 154.8 ($CH_3C$=), 145.9, 143.6, 140.2 (HC=), 131.5 ($CH_3C$=), 124.5, 121.2, 120.5 (HC=). isomer **2b**: $^1$H NMR ($CS_2$, 213 K): $\delta$ 6.28 (m, 1H, HC=), 5.92 (m, 2H, HC=), 4.20 (s, 5H, $C_5H_5$), 3.04 (s, 1H, FeCH), 2.12 (s, 3H, $CH_3$): $^{13}$C NMR ($CS_2$, 213 K): $\delta$ 215.9 (CO), 85.4 ($C_5H_5$), 27.5 (FeCH), 16.0 ($CH_3$).

*Reaction of 2 with DMAD.* A methylenechloride solution containing **2** (1.00 g, 3.9 mmol) was treated with DMAD (0.52 ml, 4.2 mmol) at ambient temperature for 1 h with stirring. The solvent was removed under reduced pressure and crude product was flashed chromatographed down a column of alumina using benzene and the solvent removed (1.35 g, 87%). The orange oil was crystallized from cold pentanes to afford pure **4a** as orange needles. The mother liquor contained **4b** and small amounts of **4a** which could not be completely removed. Spectroscopic data for complex **4a**: $^1$H NMR ($CDCl_3$): $\delta$ 6.18 (m, 1H, HC=), 4.70 (s, 5H, $C_5H_5$), 3.81 (br s, 1H, H(7)), 3.77 (s, 3H, $CO_2CH_3$), 3.76 (s, 3H, $CO_2CH_3$), 3.67 (m, 1H, H(1)), 3.44 (m, 1H, H(4)), 1.95 (d, 3H, $J$ 1.8 Hz, $CH_3$); $^{13}$C NMR ($CDCl_3$) $\delta$ 216.9 (CO), 166.2 (C=O), 155.9, 154.8, 152.6 (C–C=), 133.9 (HC=), 85.7 ($C_5H_5$), 82.9, 69.0, 64.8 (CH), 51.8 ($CO_2CH_3$), 17.0 ($CH_3$); IR (cm$^{-1}$ in $CH_2Cl_2$); $\nu$(CO) 2006, 1949, 1726, 1706. HRMS: Mass calcd 398.045. Mass found: 398.043. Spectroscopic data for complex **4b**: $^1$H NMR ($CDCl_3$): $\delta$ 6.77 (dd, 1H, $J$ 5.0, 3.3 Hz, H(6)), 6.43 (d, 1H, $J$ 5.0 Hz, H(5)), 4.73 (s, 5H, $C_5H_5$), 4.10 (s, 1H, H(7)), 3.84 (d, 1H, $J$ 3.3 Hz, H(4)), 3.81 (s, 3H, $CO_2CH_3$), 3.71 (s, 3H, $CO_2CH_3$), 1.42 (s, 3H, $CH_3$): $^{13}$C ($CDCl_3$); $\delta$ 217.3 (CO), 168.0, 162.4 (C=O), 151.2 (C=), 146.1, 142.1 (C(5), C(6)), 141.7 (C=), 88.9 (C(4)), 85.7 ($C_5H_5$), 70.4 (C(1)), 62.6 (C(7)), 51.7 ($CO_2CH_3$), 15.8($CH_3$).

### *Single crystal diffraction study on complex 3*

X-ray quality single crystals of **3** were obtained by slow diffusion of $Et_2O$ into an acetone solution containing **3**. Single crystals of **3** were at 20°C monoclinic: space group $P2_1/c$ (No. 14); $a$ 18.085(2), $b$ 15.033(4), $c$ 12.547(3) Å, $\beta$ 90.18 (2)°; $Z = 4$. Complete details of the structure determination can be found in Table E (Crystallographic Report) of the supplementary material. Three-dimensional X-ray diffraction data were collected for the 3493 independent reflections having $3° < 2\theta < 50.8°$ on a computer controlled four-circle Syntex P1 autodiffractometer using graphite-monochromated Mo-$K_\alpha$ radiation and the $\omega$ scanning technique. The structure was solved using the heavy-atom technique. The hydrogen atoms bonded to N and C(3) were located from a difference Fourier synthesis and refined as independent isotropic atoms. The terminal methyl group (C(15) and its hydrogens) was included in the refinement as a rigid rotor with $sp^3$-hybridized geometry and C–H bond lengths of 0.96 Å; hydrogen atoms on all $sp^2$-hybridized carbons were placed in their calculated positions using idealized $sp^2$ geometry and a C–H bond length of 0.96 Å. The isotropic thermal parameters for all hydrogen atoms except those bonded to N and C(3) were fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon to which they were covalently bonded. The resulting structural parameters for **3** have been refined to convergence ($R_1 = 0.059$: and $R_w = 0.076$ for 1946 independent absorption corrected reflections having $I > 3\sigma(I)$) using counter-weighted cascade block-diagonal least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms. A complete listing of final atomic coordinates, thermal parameters, bond lengths, and bond angles can be found in Tables A-D of the supplementary material.

*Supplemental material available.* Tables of the atomic positions, thermal parameters, bond lengths and angles, crystallographic report, and the structure factor amplitude for **3** (21 pages), may be obtained from the authors.

## Acknowledgment

M.E.W. wishes to thank the Office of the Vice President for Research at Utah State University for partial funding of this work. R.S.G. makes acknowledgement to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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