Organometallics 1988, 7, 1155–1161

Reaction of Iron–η^1-Dienyl Complexes with Dienophiles. X-ray Structures of the [4 + 2] Cycloaddition Adducts

Gene-Hsiang Lee and Shie-Ming Peng*

Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

Shie-Fu Lush, David Mu, and Rai-Shung Liu*

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

Received October 2, 1987

$CpFe(CO)_2$(η^1-pentadienyl) (**1**) and the corresponding η^1-2,4-hexadien-1-yl (**3**) undergo [4 + 2] cycloaddition with tetracyanoethylene and maleic anhydride to give the adducts $CpFe(CO)_2CH_2CHC(CN)_2C(CN)_2CH_2CH{=}CH_2$ (**2**) and $CpFe(CO)_2CH_2CHCHCOOCOCHCHRCH{=}CH$ (R = H (**4**), CH_3 (**5**)) in moderate yields. Reflux of PPh_3 with **4** and **5** gave the acyl compounds in two diastereoisomers with good yields. Complex **1** undergoes insertion with alkynes dimethyl acetylenedicarboxylate and hexafluoro-2-butyne. The insertion products have been fully characterized by means of appropriate physical methods. The molecular structures of **2**, **4**, and **5** have been characterized by an X-ray diffraction study. Crystallographic data for **2**: space group $Pca2_1$; a = 13.174 (2) Å, b = 10.601 (2) Å, c = 12.315 (3) Å; Z = 4; R_F = 4.3, R_{wF} = 3.0. For **4**: space group $P2_12_12_1$; a = 8.167 (1) Å, b = 10.006 (2) Å, c = 17.700 (4) Å; Z = 4; R_F = 2.7, R_{wF} = 3.0. For **5**: $P2_1/c$, a = 9.197 (2) Å, b = 12.498 (3) Å, c = 13.622 (2) Å, β = 90.79 (2)°; Z = 4; R_F = 3.2, R_{wF} = 2.6.

Introduction

In recent years, there has been a resurgence of interest in the chemistry of acyclic transition-metal–pentadienyl complexes.[1-3] Numerous studies have focused on synthesis, structure, and physical and chemical properties of the η^3- and η^5-pentadienyl complexes. In contrast, the chemistry of the η^1-pentadienyl compound has received much less attention. We have recently reported the synthesis of an iron–pentadienyl complex $CpFe(CO)_2$(η^1-pentadienyl) (**1**).[4] We are particularly interested in its chemistry because the related compound Me_3Si(η^1-pentadienyl) has shown versatile reactivity in organic reactions.[5] The latter compound has been shown to undergo [4 + 2] cycloaddition and electrophilic additions with various electrophiles.[5] Nevertheless, if complex **1** is considered to be a high homologue of $CpFe(CO)_2$(η^1-allyl), it would undergo [3 + 2] cycloaddition with reactive electrophiles such as tetracyanoethylene (TCNE) and organic isocyanates.[6] In order to clarify the reaction pathway, we have investigated its reaction with reactive alkenes and alkynes such as tetracyanoethylene, maleic anhydride, dimethyl acetylenedicarboxylate, and hexafluoro-2-butyne.

Table I. Atomic Coordinates and Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of the Molecule 2

atom	x	y	z	B(iso)[a]
Fe	0.06184 (5)	0.47847 (6)	0.4483	3.46 (3)
C(1)	0.1901 (4)	0.5285 (5)	0.3601 (4)	5.1 (4)
C(2)	0.1910 (4)	0.3986 (5)	0.3748 (6)	5.8 (4)
C(3)	0.1924 (4)	0.3780 (5)	0.4876 (5)	6.3 (5)
C(4)	0.1956 (5)	0.4938 (7)	0.5378 (5)	6.8 (5)
C(5)	0.1925 (4)	0.5879 (5)	0.4619 (7)	5.5 (3)
C(6)	−0.0268 (4)	0.3595 (4)	0.3559 (4)	3.0 (2)
C(7)	−0.0241 (3)	0.2182 (4)	0.3826 (4)	2.6 (2)
C(8)	−0.0951 (3)	0.1811 (4)	0.4723 (4)	3.0 (3)
C(9)	−0.1531 (3)	0.0808 (4)	0.4748 (4)	3.1 (3)
C(10)	−0.1567 (3)	−0.0180 (4)	0.3875 (4)	3.3 (2)
C(11)	−0.0662 (4)	−0.0035 (4)	0.3077 (4)	3.3 (2)
C(12)	−0.0514 (4)	0.1398 (4)	0.2782 (4)	3.1 (3)
C(13)	−0.0890 (4)	−0.0754 (5)	0.2061 (5)	4.7 (3)
C(14)	0.0284 (4)	−0.0505 (4)	0.3573 (5)	4.4 (4)
C(15)	−0.1478 (4)	0.1863 (5)	0.2308 (4)	3.7 (3)
C(16)	0.0305 (4)	0.1545 (5)	0.1977 (5)	4.7 (4)
C(17)	−0.0141 (4)	0.5993 (5)	0.4014 (5)	4.9 (4)
C(18)	−0.0144 (4)	0.4550 (5)	0.5632 (5)	5.7 (4)
N(1)	−0.1108 (4)	−0.1262 (5)	0.1304 (4)	7.5 (4)
N(2)	0.1009 (3)	−0.0850 (4)	0.3963 (5)	6.9 (5)
N(3)	−0.2223 (4)	0.2199 (4)	0.1968 (4)	5.5 (4)
N(4)	0.0978 (4)	0.1655 (5)	0.1422 (5)	8.0 (4)
O(1)	−0.0633 (4)	0.4445 (5)	0.6388 (3)	10.0 (4)
O(2)	−0.0664 (3)	0.6772 (4)	0.3662 (4)	7.9 (4)

[a] B(iso) is the mean of the principal axes of the thermal ellipsoid.

Results and Discussion

Stirring of **1** with an equimolar amount of TCNE at 0 °C for 2 h gave a deep blue solution. After evaporation of the solvent to dryness, the residues were extracted with chloroform and recrystallized from $CHCl_3$/hexane to produce yellow blocks of **2** in moderate yields (35%). However, the reaction of TCNE and $CpFe(CO)_2$(η^1-2,4-hexadien-1-yl) (**3**)[4b] fails to give an analogous [4 + 2] cycloadduct except a blue solid of undetermined composition. The IR and ^{1}H and ^{13}C NMR spectra and an X-ray

---

(1) For recent review papers on acyclic pentadienyl–transition-metal complexes, see: (a) Ernst, R. D. *Acc. Chem. Res.* **1985**, *15*, 56. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15.

(2) (a) Ma, H.; Weber, P.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 854. (b) Ernst, R. D.; Ma, H.; Sergeson, G.; Zahn, T.; Ziegler, M. L. *Ibid.* **1987**, *6*, 848. (c) Williams, G. M.; Fisher, R. D.; Heyn, R. H. *Ibid.* **1986**, *5*, 818. (d) Kowalcski, R. M.; Basolo, F.; Trogler, W. C.; Ernst, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6046. (e) Wilson, D. R.; Dilullo, A. A.; Ernst, R. D. *Ibid.* **1980**, *102*, 5928.

(3) (a) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576. (b) Bleeke, J. R.; Hays, M. K. *Ibid.* **1987**, *6*, 1367. (c) Bleeke, J. R.; Donaldson, A. J. *Ibid.* **1986**, *5*, 2401. (d) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417.

(4) (a) Lush, S.-F.; Liu, R.-S. *Organometallics* **1986**, *5*, 1908. (b) Lee, G.-H.; Peng, S.-M.; Lee, T.-W.; Liu, R.-S. *Ibid.* **1986**, *5*, 2378. (c) Lee, G.-H.; Peng, S.-M.; Lush, S.-F.; Liao, M.-Y.; Liu, R.-S. *Ibid.*, in press. (d) Lee, T.-W.; Liu, R.-S. *J. Organomet. Chem.* **1987**, *320*, 211.

(5) (a) Seyferth, D.; Pornet, J.; Weinstein, R. M. *Organometallics* **1982**, *1*, 1651. (b) Yasuda, H.; Nishi, T.; Miyanaga, S.; Nakamura, A. *Ibid.* **1985**, *4*, 359. (c) Horsomi, A.; Saito, M.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 3783.

(6) For examples, see: (a) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (b) Williams, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 3116. (c) Cutler, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosau, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149. (d) Hu, Y.-R.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1987**, *6*, 1561. (e) Bucheister, A.; Klemarczyk, P.; Rosenblum, M. *Ibid.* **1982**, *1*, 1679.

0276-7333/88/2307-1155$01.50/0

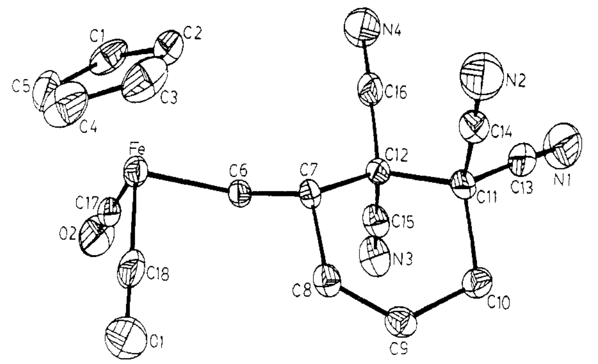
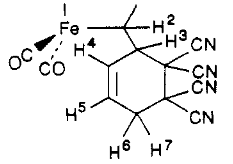


Figure 1. ORTEP drawing of the molecule 2.

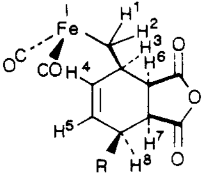
Table II. Bond Distances (Å) and Bond Angles (deg) of the Molecule 2

Bond Distances					
Fe–C(1)	2.077 (5)	Fe–C(2)	2.106 (5)	Fe–C(3)	2.080 (5)
Fe–C(4)	2.085 (5)	Fe–C(5)	2.082 (5)	Fe–C(6)	2.062 (4)
Fe–C(17)	1.724 (5)	Fe–C(18)	1.753 (5)	C(1)–C(2)	1.389 (8)
C(1)–C(5)	1.403 (9)	C(2)–C(3)	1.406 (9)	C(3)–C(4)	1.375 (9)
C(4)–C(5)	1.368 (9)	C(6)–C(7)	1.534 (6)	C(7)–C(8)	1.499 (6)
C(7)–C(12)	1.573 (6)	C(8)–C(9)	1.309 (6)	C(9)–C(10)	1.501 (6)
C(10)–C(11)	1.553 (6)	C(11)–C(12)	1.574 (6)	C(11)–C(13)	1.495 (7)
C(11)–C(14)	1.475 (7)	C(12)–C(15)	1.482 (7)	C(12)–C(16)	1.474 (7)
C(13)–N(1)	1.114 (7)	C(14)–N(2)	1.129 (6)	C(15)–N(3)	1.124 (7)
C(16)–N(4)	1.125 (7)	C(17)–O(2)	1.160 (6)	C(18)–O(1)	1.138 (7)

Bond Angles			
C(1)–Fe–C(2)	38.8 (2)	C(1)–Fe–C(3)	65.2 (2)
C(1)–Fe–C(4)	64.5 (2)	C(1)–Fe–C(5)	39.4 (2)
C(1)–Fe–C(6)	109.2 (1)	C(1)–Fe–C(17)	96.1 (2)
C(1)–Fe–C(18)	157.6 (2)	C(2)–Fe–C(3)	39.3 (2)
C(2)–Fe–C(4)	64.9 (2)	C(2)–Fe–C(5)	65.9 (2)
C(2)–Fe–C(6)	88.5 (2)	C(2)–Fe–C(17)	128.6 (2)
C(2)–Fe–C(18)	138.8 (2)	C(3)–Fe–C(4)	38.6 (2)
C(3)–Fe–C(5)	65.4 (2)	C(3)–Fe–C(6)	106.4 (2)
C(3)–Fe–C(17)	159.7 (2)	C(3)–Fe–C(18)	102.3 (2)
C(4)–Fe–C(5)	38.3 (2)	C(4)–Fe–C(6)	144.9 (2)
C(4)–Fe–C(17)	127.5 (2)	C(4)–Fe–C(18)	93.9 (2)
C(5)–Fe–C(6)	148.6 (2)	C(5)–Fe–C(17)	95.3 (2)
C(5)–Fe–C(18)	119.2 (2)	C(6)–Fe–C(17)	86.6 (2)
C(6)–Fe–C(18)	92.0 (2)	C(17)–Fe–C(18)	92.5 (2)
Fe–C(1)–C(2)	71.7 (3)	Fe–C(1)–C(5)	70.5 (3)
C(2)–C(1)–C(5)	109.2 (5)	Fe–C(2)–C(1)	69.5 (3)
Fe–C(2)–C(3)	69.4 (3)	C(1)–C(2)–C(3)	106.4 (5)
Fe–C(3)–C(2)	71.4 (3)	Fe–C(3)–C(4)	70.9 (3)
C(2)–C(3)–C(4)	107.9 (4)	Fe–C(4)–C(3)	70.5 (3)
Fe–C(4)–C(5)	70.7 (3)	C(3)–C(4)–C(5)	110.0 (5)
Fe–C(5)–C(1)	70.1 (3)	Fe–C(5)–C(4)	71.0 (3)
C(1)–C(5)–C(4)	106.5 (4)	Fe–C(6)–C(7)	117.8 (3)
C(6)–C(7)–C(8)	113.6 (3)	C(6)–C(7)–C(12)	109.6 (3)
C(8)–C(7)–C(12)	108.7 (3)	C(7)–C(8)–C(9)	126.5 (4)
C(8)–C(9)–C(10)	124.6 (4)	C(9)–C(10)–C(11)	111.1 (3)
C(10)–C(11)–C(12)	109.6 (3)	C(10)–C(11)–C(13)	109.0 (3)
C(10)–C(11)–C(14)	110.7 (4)	C(12)–C(11)–C(13)	108.9 (4)
C(12)–C(11)–C(14)	108.5 (3)	C(13)–C(11)–C(14)	110.1 (4)
C(7)–C(12)–C(11)	110.5 (3)	C(7)–C(12)–C(15)	110.0 (3)
C(7)–C(12)–C(16)	109.0 (3)	C(11)–C(12)–C(15)	107.8 (3)
C(11)–C(12)–C(16)	110.4 (3)	C(15)–C(12)–C(16)	109.1 (4)
C(11)–C(13)–N(1)	176.4 (6)	C(11)–C(14)–N(2)	179.0 (5)
C(12)–C(15)–N(3)	178.2 (5)	C(12)–C(16)–N(4)	175.0 (6)
Fe–C(17)–O(2)	177.0 (5)	Fe–C(18)–O(1)	177.3 (5)



2



4, R=H^9
5, R=CH$_3$

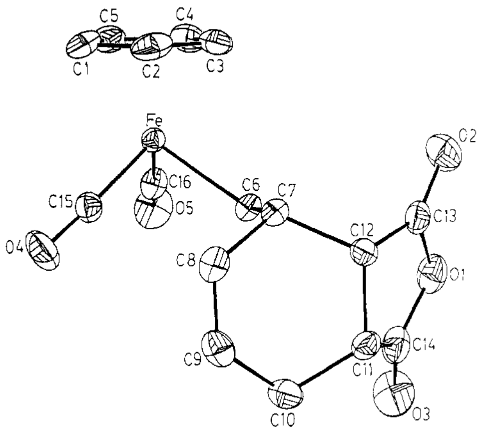


Figure 2. ORTEP drawing of the molecule 4.

structural analysis of 2 have established the structure depicted. The ^1H NMR spectrum shows the resonances of H^1 and H^2 as an AB quartet at δ 1.15 and 2.16, respectively, further split by H^3 and the resonances of the two olefinic protons H^4 and H^5 at δ 6.00 and 5.70, respectively. The IR spectrum shows the ν(CO) bands at 2001 and 1952 cm^{-1} as well as the ν(CN) bands at 2200 and 2180 cm^{-1}, in addition to the weak ν(C=C) band at 1630 cm^{-1}. The elemental analyses were consistent with the given formula. An X-ray diffraction study of 2 has been undertaken. An ORTEP drawing of the molecular structure is shown in Figure 1, and the atomic coordinates and the bond distances and angles are given in Table I and II, respectively. The crystal structure confirms that $C_2(CN)_4$ undergoes 1,4 addition to the diene moiety. The coordination geometry about the iron atom is approximately a distorted tetrahedron with two carbonyls, one α-carbon, and a Cp group occupying the four coordination sites. The L–Fe–L angles are 125.1 (2)°, 126.4 (2)°, 123.1 (2)°, 92.5 (3)°, 86.6 (2)°, and 92.0 (2)° for Cp–Fe–C(17), Cp–Fe–C(18), Cp–Fe–C(6), C(17)–Fe–C(18), C(17)–Fe–C(6), and C(18)–Fe–C(6), respectively. (Cp is the centroid of the cyclopentadienyl group). The $CpFe(CO)_2$ subunit bonds to the C(6) atom away from the four cyano groups to minimize the steric hindrance, and the cyclohexene moiety tilts toward the Fe–C(18)–O(1) side. In such a conformation, the Fe(II) center is approximately in a site of C_1 symmetry. In solution, the two carbonyl groups are also nonequivalent as revealed by their ^{13}C NMR spectrum. The lengths of the C(11)–C(12) bond (1.574 (6) Å, the C(7)–C(8) bond (1.499 (6) Å), and the C(9)–C(10) bond (1.501 (6) Å) are indicative of single bonds in comparison with the normal C(sp^3)–c(sp^3) (nonsubstituted) distance of 1.54 Å.[7] The C(8)–C(9) bond, 1.309 (6) Å, and the four independent cyano bonds, 1.114 (7)–1.129 (7) Å, are consistent with double- and triple-bond distances, respectively.[7] The remaining bond distances conform to the proposed structure.

The reaction of maleic anhydride with both 1 and 3 gives the [4 + 2] cycloadducts $CpFe(CO)_2CH_2$-CHCHCOOCOCHCHRCH=CH (R = H (4), CH_3 (5)) in moderate yields. Each product exists as only one stereoisomer as revealed by its spectroscopic data. The ^1H and ^{13}C NMR data of both products resemble those of 2. Further characterization of the solid structures was accomplished by an X-ray diffraction study. ORTEP drawings of the molecules are shown in Figures 2 and 3, respectively; their selected bond distances, angles and atomic coordinates are given in Tables III–VI. For 4, the coordination geometry about the iron atom is approximately a distorted tetrahedron. The L–Fe–L angles are 122.3 (2)°, 125.9 (2)°,

---

[7] (a) Huheey, J. E. *Inorganic Chemistry, Principles of Structures and Reactivity*; 3rd ed.; Harper and Row: New York, 1983. (b) Britton, D. *Perspect. Struct. Chem.* **1967**, *1*, 109.

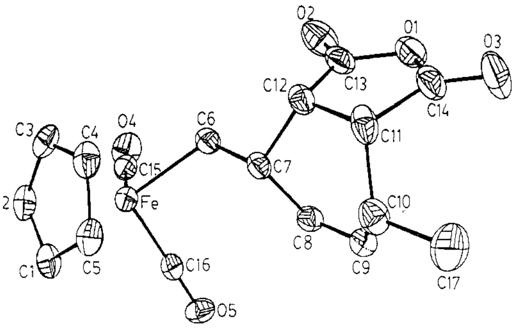


Figure 3. ORTEP drawing of the molecule 5.

Table III. Atomic Coordinates and Thermal Parameters (Å²) for the Non-Hydrogen Atoms of the Molecule 4

atom	*x*	*y*	*z*	*B*(iso)
Fe	0.74626 (7)	0.22044 (5)	0.22360 (3)	2.49 (2)
C(1)	0.7884 (6)	0.0139 (4)	0.2239 (3)	5.0 (2)
C(2)	0.8252 (7)	0.0667 (5)	0.1516 (3)	4.9 (2)
C(3)	0.9500 (6)	0.1589 (5)	0.1601 (3)	4.9 (2)
C(4)	0.9922 (6)	0.1653 (6)	0.2373 (3)	4.9 (2)
C(5)	0.8911 (6)	0.0738 (5)	0.2760 (3)	4.8 (2)
C(6)	0.7316 (5)	0.3861 (3)	0.1542 (2)	2.6 (1)
C(7)	0.6857 (5)	0.3563 (4)	0.0712 (2)	2.6 (1)
C(8)	0.5092 (5)	0.3158 (4)	0.0644 (2)	3.2 (2)
C(9)	0.3916 (5)	0.4039 (5)	0.0610 (2)	3.7 (2)
C(10)	0.4223 (6)	0.5526 (5)	0.0625 (3)	4.2 (2)
C(11)	0.5872 (5)	0.5906 (4)	0.0283 (2)	3.3 (2)
C(12)	0.7117 (4)	0.4784 (4)	0.0181 (2)	2.8 (2)
C(13)	0.8716 (6)	0.5450 (5)	0.0331 (3)	4.0 (2)
C(14)	0.6778 (7)	0.6933 (5)	0.0720 (3)	4.5 (2)
C(15)	0.5344 (5)	0.2002 (5)	0.2219 (3)	3.4 (2)
C(16)	0.7432 (7)	0.3292 (4)	0.3010 (2)	3.7 (2)
O(1)	0.8453 (5)	0.6694 (4)	0.0662 (2)	4.8 (2)
O(2)	1.0072 (4)	0.5075 (4)	0.0237 (2)	6.1 (2)
O(3)	0.6290 (6)	0.7851 (4)	0.1066 (2)	7.3 (2)
O(4)	0.3962 (4)	0.1822 (4)	0.2240 (2)	5.9 (2)
O(5)	0.7445 (7)	0.3979 (4)	0.3520 (2)	6.7 (2)

124.7 (2)°, 91.5 (2)°, 88.0 (2)°, and 94.1 (2)° for Cp–Fe–C(6), Cp–Fe–C(15), Cp–Fe–C(16), C(6)–Fe–C(15), C(6)–Fe–C(16), and C(15)–Fe–C(16), respectively (Cp is the centroid of the cyclopentadienyl group). The bulky group $CpFe(CO)_2$ subunit links to the C(6) atom away from the anhydride moiety and lies on the same side as the C(8)–C(9) double bond. The Fe(II) ion center is in a site of C_1 symmetry. In the bicyclic $C_9H_9O_3$ group, three bonds, C(8)–C(9), C(13)–O(2), and C(14)–O(3), are double bonds (1.305 (6), 1.182 (6), 1.174 (7) Å, respectively), while the rest are single bonds. The atoms C(7), C(8), C(9), and C(10) are coplanar (plane A) with a maximum deviation of 0.003 (6) Å. The atoms C(7), C(10), C(11), and C(12) also form a plane (plane B) with a maximum deviation of 0.126 (6) Å. The dihedral angles between various planes are listed in Table VII. The six-member ring of the cyclohexene moiety is approximately in a boat geometry with the atoms C(8), C(9), C(11), and C(12) forming a basal plane with a maximum deviation of 0.083 (6) Å. The C(7) and C(10) atoms lie 0.599 (6) and 0.246 (7) Å above this plane, respectively. Notably, the C(6) atom occupies the axial position of the cyclohexene moiety and lies in the position endo to the five-member ring of the anhydride moiety. The plane of the latter lies away from the C(8)–C(9) double bond. This stereochemical arrangement reveals that the cyclization is controlled by the endo addition.[8] The preference for this addition arises from a combination of dipolar and van der Waals attraction as well as orbital interaction of the diene system with the

Table IV. Bond Distances (Å) and Bond Angles (deg) of the Molecule 4

Bond Distances			
Fe–C(1)	2.095 (4)	C(7)–C(8)	1.502 (6)
Fe–C(2)	2.099 (4)	C(7)–C(12)	1.556 (5)
Fe–C(3)	2.100 (5)	C(8)–C(9)	1.305 (6)
Fe–C(4)	2.097 (5)	C(9)–C(10)	1.509 (7)
Fe–C(5)	2.100 (5)	C(10)–C(11)	1.525 (6)
Fe–C(6)	2.067 (3)	C(11)–C(12)	1.525 (6)
Fe–C(15)	1.742 (4)	C(11)–C(14)	1.484 (7)
Fe–C(16)	1.750 (4)	C(12)–C(13)	1.490 (6)
C(1)–C(2)	1.417 (8)	C(13)–O(1)	1.392 (7)
C(1)–C(5)	1.383 (8)	C(13)–O(2)	1.182 (6)
C(2)–C(3)	1.382 (8)	C(14)–O(1)	1.393 (7)
C(3)–C(4)	1.410 (8)	C(14)–O(3)	1.174 (7)
C(4)–C(5)	1.4–9 (8)	C(15)–O(4)	1.144 (5)
C(6)–C(7)	1.545 (5)	C(16)–O(5)	1.136 (5)
Bond Angles			
C(1)–Fe–C(2)	39.4 (2)	C(1)–C(2)–C(3)	107.9 (5)
C(1)–Fe–C(3)	65.3 (2)	Fe–C(3)–C(2)	70.7 (3)
C(1)–Fe–C(4)	65.3 (2)	Fe–C(3)–C(4)	70.2 (3)
C(1)–Fe–C(5)	38.5 (2)	C(2)–C(3)–C(4)	108.4 (5)
C(1)–Fe–C(6)	143.3 (2)	Fe–C(4)–C(3)	70.5 (3)
C(1)–Fe–C(15)	92.8 (2)	Fe–C(4)–C(5)	70.5 (3)
C(1)–Fe–C(16)	127.9 (2)	C(3)–C(4)–C(5)	107.3 (5)
C(2)–Fe–C(3)	38.4 (2)	Fe–C(5)–C(1)	70.5 (3)
C(2)–Fe–C(4)	65.4 (2)	Fe–C(5)–C(4)	70.2 (3)
C(2)–Fe–C(5)	65.4 (2)	C(1)–C(5)–C(4)	108.2 (5)
C(2)–Fe–C(6)	104.1 (2)	Fe–C(6)–C(7)	115.1 (2)
C(2)–Fe–C(15)	102.1 (2)	C(6)–C(7)–C(8)	111.1 (3)
C(2)–Fe–C(16)	159.3 (2)	C(6)–C(7)–C(12)	112.9 (3)
C(3)–Fe–C(4)	39.3 (2)	C(8)–C(7)–C(12)	107.1 (3)
C(3)–Fe–C(5)	65.5 (2)	C(7)–C(8)–C(9)	121.9 (4)
C(3)–Fe–C(6)	87.9 (2)	C(8)–C(9)–C(10)	122.9 (4)
C(3)–Fe–C(15)	138.0 (2)	C(9)–C(10)–C(11)	112.7 (4)
C(3)–Fe–C(16)	127.8 (3)	C(10)–C(11)–C(12)	116.9 (4)
C(4)–Fe–C(5)	39.3 (2)	C(10)–C(11)–C(14)	113.9 (4)
C(4)–Fe–C(6)	109.6 (2)	C(12)–C(11)–C(14)	103.8 (4)
C(4)–Fe–C(15)	157.3 (2)	C(7)–C(12)–C(11)	114.6 (3)
C(4)–Fe–C(16)	95.0 (3)	C(7)–C(12)–C(13)	111.3 (3)
C(5)–Fe–C(6)	148.8 (2)	C(11)–C(12)–C(13)	103.5 (4)
C(5)–Fe–C(15)	119.1 (2)	C(12)–C(13)–O(1)	109.9 (4)
C(5)–Fe–C(16)	95.5 (2)	C(12)–C(13)–O(2)	130.9 (5)
C(6)–Fe–C(15)	91.5 (2)	O(1)–C(13)–O(2)	119.2 (5)
C(6)–Fe–C(16)	88.0 (2)	C(11)–C(14)–O(1)	109.4 (5)
C(15)–Fe–C(16)	94.1 (3)	C(11)–C(14)–O(3)	130.1 (5)
Fe–C(1)–C(2)	70.4 (3)	O(1)–C(14)–O(3)	120.4 (5)
Fe–C(1)–C(5)	71.0 (3)	Fe–C(15)–O(4)	176.3 (4)
C(2)–C(1)–C(5)	108.2 (4)	Fe–C(16)–O(5)	178.2 (5)
Fe–C(2)–C(1)	70.1 (3)	C(13)–O(1)–C(14)	109.6 (4)
Fe–C(2)–C(3)	70.8 (3)		

Table V. Atomic Coordinates and Thermal Parameters (Å) for the Non-Hydrogen Atoms of the Molecule 5

atom	*x*	*y*	*z*	*B*(iso)
Fe	0.21087 (4)	0.09121 (3)	0.11452 (2)	3.09 (1)
C(1)	0.0281 (3)	−0.0010 (2)	0.1554 (2)	4.3 (1)
C(2)	−0.0199 (3)	0.0926 (3)	0.1104 (2)	4.6 (1)
C(3)	0.0326 (3)	0.1802 (3)	0.1664 (2)	4.9 (1)
C(4)	0.1122 (3)	0.1388 (2)	0.2470 (2)	4.8 (1)
C(5)	0.1112 (3)	0.0269 (2)	0.2400 (2)	4.3 (1)
C(6)	0.3957 (3)	0.1718 (2)	0.1629 (2)	3.7 (1)
C(7)	0.4794 (3)	0.1198 (2)	0.2484 (2)	3.3 (1)
C(8)	0.5943 (3)	0.0395 (2)	0.2195 (2)	3.8 (1)
C(9)	0.6791 (3)	−0.0027 (2)	0.2887 (2)	4.2 (1)
C(10)	0.6543 (3)	0.0268 (2)	0.3936 (2)	4.7 (1)
C(11)	0.6443 (3)	0.1520 (2)	0.4018 (2)	4.5 (1)
C(12)	0.5568 (3)	0.2028 (2)	0.3167 (2)	3.9 (1)
C(13)	0.6693 (3)	0.2681 (2)	0.2614 (2)	4.7 (1)
C(14)	0.7926 (3)	0.2053 (2)	0.3961 (2)	5.4 (1)
C(15)	0.2322 (3)	0.1552 (2)	0.0025 (2)	3.9 (1)
C(16)	0.3186 (3)	−0.0170 (2)	0.0787 (2)	3.2 (1)
C(17)	0.7636 (4)	−0.0226 (3)	0.4655 (2)	7.8 (2)
O(1)	0.8019 (2)	0.2658 (2)	0.3117 (1)	5.2 (1)
O(2)	0.6597 (3)	0.3173 (2)	0.1877 (2)	6.9 (1)
O(3)	0.8929 (2)	0.2012 (2)	0.4518 (2)	7.9 (1)
O(4)	0.2494 (2)	0.1953 (2)	−0.0721 (1)	6.0 (1)
O(5)	0.3851 (2)	−0.0887 (1)	0.0513 (1)	4.4 (1)

---

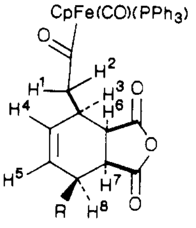
[8] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry: Part B: Reactions and Synthesis*, 2nd ed.; Plenum: New York, 1977.

Table VI. Bond Distances (Å) and Bond Angles (deg) of the Molecule 5

Bond Distances			
Fe–C(1)	2.106 (3)	C(7)–C(12)	1.556 (3)
Fe–C(2)	2.101 (3)	C(8)–C(9)	1.321 (4)
Fe–C(3)	2.099 (3)	C(9)–C(10)	1.496 (4)
Fe–C(4)	2.113 (3)	C(10)–C(11)	1.571 (4)
Fe–C(5)	2.106 (3)	C(10)–C(17)	1.517 (4)
Fe–C(6)	2.062 (3)	C(11)–C(12)	1.536 (4)
Fe–C(15)	1.736 (3)	C(11)–C(14)	1.509 (4)
Fe–C(16)	1.744 (3)	C(12)–C(13)	1.518 (4)
C(1)–C(2)	1.388 (4)	C(13)–O(1)	1.380 (3)
C(1)–C(5)	1.413 (4)	C(13)–O(2)	1.179 (4)
C(2)–C(3)	1.415 (4)	C(14)–O(1)	1.380 (4)
C(3)–C(4)	1.406 (4)	C(14)–O(3)	1.180 (3)
C(4)–C(5)	1.402 (4)	C(15)–O(4)	1.146 (3)
C(6)–C(7)	1.528 (3)	C(16)–O(5)	1.147 (3)
C(7)–C(8)	1.506 (4)		
Bond Angles			
C(1)–Fe–C(2)	38.53 (12)	Fe–C(3)–C(2)	70.42 (15)
C(1)–Fe–C(3)	65.34 (12)	Fe–C(3)–C(4)	71.05 (15)
C(1)–Fe–C(4)	65.22 (11)	C(2)–C(3)–C(4)	107.7 (3)
C(1)–Fe–C(5)	39.20 (10)	Fe–C(4)–C(3)	69.95 (15)
C(1)–Fe–C(6)	145.84 (10)	Fe–C(4)–C(5)	70.31 (14)
C(1)–Fe–C(15)	125.67 (11)	C(3)–C(4)–C(5)	108.1 (2)
C(1)–Fe–C(16)	95.69 (12)	Fe–C(5)–C(1)	70.40 (14)
C(2)–Fe–C(3)	39.37 (12)	Fe–C(5)–C(4)	70.87 (15)
C(2)–Fe–C(4)	65.41 (10)	C(1)–C(5)–C(4)	107.8 (2)
C(2)–Fe–C(5)	65.33 (10)	Fe–C(6)–C(7)	115.58 (17)
C(2)–Fe–C(6)	144.72 (11)	C(6)–C(7)–C(8)	115.2 (2)
C(2)–Fe–C(15)	95.55 (11)	C(6)–C(7)–C(12)	112.9 (2)
C(2)–Fe–C(16)	124.38 (12)	C(8)–C(7)–C(12)	106.9 (2)
C(3)–Fe–C(4)	39.00 (11)	C(7)–C(8)–C(9)	118.8 (2)
C(3)–Fe–C(5)	65.45 (11)	C(8)–C(9)–C(10)	119.3 (3)
C(3)–Fe–C(6)	105.39 (11)	C(9)–C(10)–C(11)	108.8 (2)
C(3)–Fe–C(15)	98.55 (12)	C(9)–C(10)–C(17)	114.2 (3)
C(3)–Fe–C(16)	161.04 (12)	C(11)–C(10)–C(17)	113.4 (2)
C(4)–Fe–C(5)	38.82 (12)	C(10)–C(11)–C(12)	112.9 (2)
C(4)–Fe–C(6)	86.82 (10)	C(10)–C(11)–C(14)	112.5 (2)
C(4)–Fe–C(15)	132.49 (12)	C(12)–C(11)–C(14)	103.6 (2)
C(4)–Fe–C(16)	134.79 (11)	C(7)–C(12)–C(11)	113.7 (2)
C(5)–Fe–C(6)	106.65 (10)	C(7)–C(12)–C(13)	111.4 (2)
C(5)–Fe–C(15)	160.73 (11)	C(11)–C(12)–C(13)	104.5 (2)
C(5)–Fe–C(16)	100.44 (11)	C(12)–C(13)–O(1)	109.7 (2)
C(6)–Fe–C(15)	87.42 (11)	C(12)–C(13)–O(2)	131.3 (3)
C(6)–Fe–C(16)	90.48 (11)	O(1)–C(13)–O(2)	119.1 (3)
C(15)–Fe–C(16)	92.36 (11)	C(11)–C(14)–O(1)	110.5 (2)
Fe–C(1)–C(2)	70.56 (16)	C(11)–C(14)–O(3)	129.3 (3)
Fe–C(1)–C(5)	70.40 (15)	O(1)–C(14)–O(3)	120.2 (3)
C(2)–C(1)–C(5)	108.3 (3)	Fe–C(15)–O(4)	178.0 (2)
Fe–C(2)–C(1)	70.90 (15)	Fe–C(16)–O(5)	176.7 (2)
Fe–C(2)–C(3)	70.21 (15)	C(13)–O(1)–C(14)	111.2 (2)
C(1)–C(2)–C(3)	108.1 (2)		

anhydride moiety in the transition state of the cyclization.[9] The X-ray structure of 5 is also in accord with the endo rule. The structure resembles closely that of 4, but some structural deviations are noteworthy. The $CpFe(CO)_2$ unit tilts away from the anhydride moiety. The six-member ring of the cyclohexene moiety has almost a "boat" geometry with the four atoms C(8), C(9), C(11), and C(12) forming a basal plane having a maximum deviation of 0.030 (4) Å. In contrast with 4, the C(6) and C(17) atoms occupy the two equatorial positions to avoid the increasing steric hindrance at the two axial positions. The anhydride plane lies toward the C(8)–C(9) double bond and cis to the C(6) and C(17) atoms.

Reflux of a benzene solution of 4 and 5 with excess PPh_3 produced the acyl compounds 6 and 7 in high yields. Orange crystals with analytic purity were obtained by cooling a saturated tetrahydrofuran solution at −25 °C.



6, $R=H^9$
7, $R=CH_3$

The structure depicted was supported by its spectroscopic data. A single absorption band at 1910 cm^{-1} was observed in the 1800–2200 cm^{-1} region, indicative of a single terminal CO group.[10] The proton resonances of H^1 and H^2 were shifted downfield to δ 3.10–4.10, and the ^{13}C resonances of CH^1H^2 were shifted to δ 65–66. This information suggests that CO has inserted into the σ-Fe–CH^1H^2 bond.[10] The presence of an acyl group was further indicated by an IR absorption peak at 1590 cm^{-1} and the ^{13}C NMR resonances of a doublet at 272–273 ppm (J_{Pc} = 21 Hz).[10,11] The ^1H and ^{13}C NMR data reveal that these two acyl complexes exist as two diastereoisomers, arising from the two chiral centers at Fe and the CH_3 carbon, respectively. The chiral center at the CH^3 carbon has no significant effect on the product diastereoselectivity, and the intensities of the proton resonances of the two diastereoisomers are almost equal. For 6, the major isomer has resonances of H^1 and H^2 as an ABX pattern at δ 3.12 and 3.95, respectively, and the minor species have resonances at δ 3.45 and 3.71, respectively; the intensity ratio is 52:48. However, for 7, the ABX patterns at δ 3.57 and 3.88 become the major species whereas the ABX patterns at δ 3.25 and 4.04 are the minor species; the intensity ratio is 55:45. For both 7 and 8, for the methylene protons of the isomer having the greater separation in their chemical shifts, the higher field hydrogen showed a smaller coupling constant with the methine proton than did the lower field methylene hydrogen. In contrast, the isomer characterized by a smaller separation in the chemical shifts of the methylene protons had a reversed magnitude of vicinal coupling constants to the higher and lower field methylene hydrogens. A similar phenomenon has been previously reported for the related complex $CpFe(CO)(PPh_3)(COCH_2CHR(NHR))$ (R = alkyl).[12a] Attempts to separate the isomers by fractional crystallization and column chromatography were unsuccessful. For this reason we cannot further determine the *RR* (*SS*), *RS* (*SR*) configuration. These acyl compounds are not particularly stable in solution. When the solution was allowed to stand at 23 °C for days, monitored by IR and ^1H NMR spectra, a slow decarbonylation occurred to yield the starting compounds 4 and 5. Such a process with loss of the phosphine group contrasts with photolytic decarbonylation of the related compound $CpFe(CO)(PPh_3)(-COCH_3)$.[12b]

Like the reactive alkenes tetracyanoethylene and maleic anhydride, the alkynes dimethyl acetylenedicarboxylate and hexafluoro-2-butyne are well-known to undergo [4 + 2] cycloaddition with numerous dienophiles.[8,13,14] Interestingly, complex 1 undergoes a novel reaction pathway

---

[9] (a) Kobuke, Y.; Sugimoto, T.; Furukawa, J.; Funco, T. *J. Am. Chem. Soc.* **1972**, *94*, 3633. (b) Williamson, K. L.; Hsu, Y.-F. *Ibid.* **1970**, *92*, 7385.

[10] (a) Green, M.; Westlake, D. J. *J. Chem. Soc. A* **1971**, 367. (b) Butler, I. S.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1967**, *6*, 2074.

[11] Todd, L. J.; Wilkenson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151.

[12] (a) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (b) Davision, A.; Martinez, N. *J. Organomet. Chem.* **1974**, *74*, C 17.

[13] Wright, M. E. *Organometallics* **1983**, *2*, 559.

[14] Wright, M. E.; Hoover, J. F.; Nelson, G. O.; Scott, C. P.; Glass, R. S. *J. Org. Chem.* **1984**, *49*, 3059.

Table VII. Dihedral Angles between Planes A and B

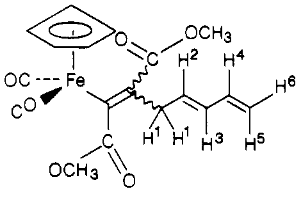
planes		dihedral angles, deg		
A	B	2	4	5
1	2	6.0 (2)	39.5 (3)	51.7 (2)
1	3	0.9 (6)	0.4 (5)	1.6 (3)
1	4	14.1 (4)	30.3 (4)	47.7 (2)
1	5		22.7 (2)	69.3 (1)
2	3	6.4 (3)	39.8 (4)	50.5 (2)
2	4	19.8 (4)	30.7 (3)	45.3 (2)
2	5		58.1 (2)	120.9 (1)
3	4	14.2 (4)	30.3 (4)	48.0 (2)
3	5		22.2 (5)	70.4 (2)
4	5		35.7 (2)	98.9 (1)

plane 1: C7, C8, C9, C10
plane 2: C7, C10, C11, C12
plane 3: C7, C8, C9
plane 4: C9, C10, C11
plane 5: C11, C12, C13, C14, O1

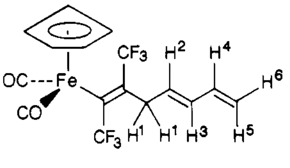
Equation of Plane: $Ax + By + Cz = D$

plane	A	B	C	D
1 of 2	9.69 (3)	−5.36 (2)	5.56 (4)	0.73 (2)
2 of 2	10.54 (2)	−4.53 (2)	5.19 (5)	0.59 (2)
3 of 2	9.69 (3)	−5.47 (7)	5.41 (9)	0.64 (5)
4 of 2	7.24 (7)	−6.47 (6)	7.02 (3)	1.704 (15)
1 of 4	−0.64 (2)	−0.08 (3)	17.64 (4)	0.79 (2)
2 of 4	3.26 (2)	4.33 (2)	14.31 (3)	4.75 (2)
3 of 4	−0.64 (2)	−0.16 (8)	17.643 (5)	0.76 (3)
4 of 4	3.51 (4)	−0.89 (5)	15.91 (5)	1.98 (2)
5 of 4	−0.84 (2)	−3.92 (2)	16.18 (2)	2.26 (2)
1 of 5	6.02 (1)	9.31 (1)	−1.38 (2)	3.655 (7)
2 of 5	7.336 (7)	0.55 (2)	−8.20 (1)	1.56 (1)
3 of 5	6.02 (1)	9.25 (2)	−1.74 (6)	3.56 (2)
4 of 5	8.983 (4)	0.59 (4)	1.96 (5)	6.66 (1)
5 of 5	−2.57 (1)	9.89 (1)	7.45 (2)	2.90 (1)

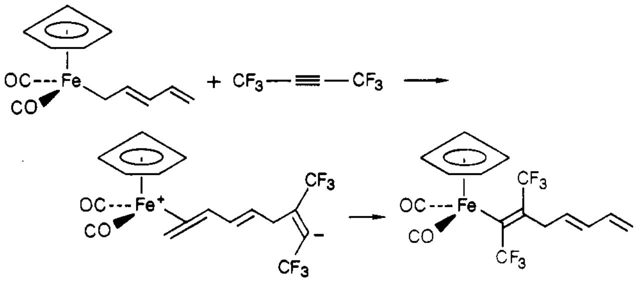
with these alkynes. Dimethyl acetylenedicarboxylate reacts rapidly with 1 at 23 °C in CH_2Cl_2 to give a deep red oil of 8 (58% yield) analyzed as a 1:1 adduct after purification through alumina chromatography. The structure depicted was assigned based on its IR and ^1H and ^{13}C NMR spectra. The $\nu(CO)$ stretching frequencies are appreciably higher ($\sim$30 cm^{-1}) than those of the parent η^1-pentadienyl complex, suggesting insertion of an electron-withdrawing group into the σ-Fe–C bond.[5b] The chemical shift of the methylene protons was 1.20 ppm further downfield than that of the precursor η^1-pentadienyl complex, additionally supporting the assigned structure. The presence of the iron–alkenyl group was further indicated by the ^{13}C NMR resonances at δ 139 and 153 assignable to the C_α and C_β carbons, respectively.[5b,15,16] The remaining ^1H and ^{13}C NMR resonances conform to the structure. The absolute configuration of the Z and E form of 8 is unclear at present stage because only one isomer has been detected spectroscopically. The reaction of 3 with dimethyl acetylenedicarboxylate did not proceed at 23 °C, and only the starting material was recovered after a 6-h reaction time. Elevated reaction temperatures were precluded by the thermal instability of 3. The reaction of 1 with hexafluoro-2-butyne proceeds rapidly at room temperature. A similar insertion product 9 was obtained in moderate yield (32%) after workup. The $\nu(CO)$ band are about 40–50 cm^{-1} higher than for the parent η^1-dienyl complex. The ^1H and ^{13}C NMR patterns resemble those of 7 with the chemical shifts of the methylene protons at δ 2.91. The iron–alkenyl bond was indicated by the ^{13}C NMR resonances of the C_α and C_β carbons at 139 and 141 ppm, respectively.[15,16] The E configuration is established by the ^{19}F NMR which shows two singlets of the two CF_3 groups at δ 62.4 and 56.6.[6a] The expected Z configuration should have the characteristic coupling pattern $^5J_{CF_3-CF_3} \sim$ 12–14 Hz.[6a,17] In contrast, the reaction of 3 with hexafluoro-2-butyne did not give a similar insertion product, and the resulting red oil appeared to be very unstable to allow characterization. Related to our work is the reaction of $CpFe(CO)_2(\eta^1\text{-allyl})$ with hexafluoro-2-butyne, which gave an insertion adduct with the two CF_3 groups mutually cis.[6b] In the latter case, hexafluoro-2-butyne was believed to bond to the metal center first, followed by cis addition of the iron–σ-allyl bond. In our mechanism, we propose that the insertion reaction is initiated by the electrophilic attack of hexafluoro-2-butyne on the ϵ-carbon of the dienyl ligand to give the ionic intermediate I. This intermediate is assumed to have the two CF_3 groups mutually trans to minimize the steric hindrance. A subsequent rearrangement through attack by the negative CCF_3 terminus on the iron center gives the alkenyl complex. This mechanism is analogous to the 1,3-allyl rearrangement in the SO_2 insertion reaction mechanism of the complex $CpFe(CO)_2(\eta^1\text{-allyl})$.[18] In fact, in our previous paper we showed that the electrophilic addition of 1 and 3 may occur at the γ- and ϵ-carbons of the dienyl ligand.[4c] The regiochemistry of addition was shown to vary greatly depending on the substituents on the ϵ-carbon. The above results show that the reactive alkenes and alkynes such as TCNE, maleic anhydride, dimethyl acetylenedicarboxylate, and hexafluoro-2-butyne undergo two independent routes with the iron–η^1-pentadienyl complexes. Among them, the alkyne insertion into the Fe–σ-pentadienyl bond is of great significance and novelty because the competitive [4 + 2] cycloaddition is known to be a facile and common process.[8,13,14] For example, the closely related complex $CpFe(CO)_2(\eta^1\text{-}C_5H_5)$ has been shown to undergo [4 + 2] cycloaddition with hexafluoro-2-butyne and dimethyl acetylenedicarboxylate.[13,14] Although the data presented in this paper show that [4 + 2] cycloaddition is the preferred reaction pathway in the reaction of the η^1-dienyl ligand with the alkenes, the possibility of [3 + 2] cycloadditions is not excluded. The latter in principle can be made possible if the ϵ-carbon of the pentadienyl ligand is disubstituted with bulky groups. In this manner, the required σ-*cis*-diene geometry for the Diels–Alder reaction



8



9



I

---

(15) Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *Organometallics* **1984**, *3*, 134.

(16) Reger, D. L.; Belmore, K. A. *Organometallics* **1985**, *4*, 305.

(17) Cutler, A.; Ehntholt, D.; Gierinin, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Taucrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

(18) Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1971**, *93*, 5299.

would encounter difficulties owing to the increasing steric hindrance.[8] Progress in this direction is under current study.

Experimental Section

All operations were carried out under argon in a Schlenk apparatus or in a glovebox. The solvents benzene, diethyl ether, tetrahydrofuran, and pentane were dried with sodium/benzophenone and distilled before use. Dichloromethane and chloroform were dried over P_2O_5 and distilled. Dimethyl acetylenedicarboxylate, hexafluoro-2-butyne, maleic anhydride, TCNE, and $[CpFe(CO)_2]_2$ were obtained from commercial sources and used without further purification. The synthesis of 1 and 3 has been described in our previous paper.[4a,c] All ^1H (400 MHz), ^{13}C (100 MHz), and ^{19}F (93.6 MHz) NMR experiments were operated on either a Bruker AM-400 or a JEOL FX-100 spectrometer. ^1H and ^{13}C spectra were referenced to tetramethylsilane. ^{19}F spectra were referenced to $CFCl_3$. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. Elemental analyses were performed at National Taiwan University.

(A) Synthesis of $CpFe(CO)_2CH_2CHC(CN)_2CH_2CH{=}CH$ (2). Tetracyanoethylene (0.42 g, 3.28 mmol) was added to **1** (0.73 g, 3.00 mmol) with rapid stirring at 23 °C. The solution first turned green and finally blue after a period of 45 min. The solution was evaporated to dryness, and the residues were extracted with 10 mL of chloroform twice. Further crystallization from $CHCl_3$/hexane gave yellow blocks of **2** (0.390 g, 1.05 mmol). Anal. Calcd for $C_{18}H_{12}N_4FeO_2$: C, 58.06; H, 3.23. Found: C, 57.42; H, 3.62. IR (Nujol): $\nu(CN)$ 2200 (s) and 2180 (s) cm^{-1}, $\nu(CO)$ 2001 (s) and 1952 (s) cm^{-1}, $\nu(C{=}C)$ 1630 (w) cm^{-1}. ^1H NMR (C_6D_6, 400 MHz): δ 1.10 (dd, 1 H, H^1), 2.00 (dd, 1 H, H^2), 2.83 (m, 1 H, H^3), 3.07 (complex m, 2 H, $H^6 + H^7$), 4.87 (s, 5 H, C_5H_5), 5.70 (dd, 1 H, H^4), 6.00 (m, 1 H, H^5), J_{12} = 10.8 Hz, J_{13} = 1.5 Hz, J_{23} = 11.6 Hz, J_{34} = 2.0 Hz, J_{45} = 10.0 Hz. $^{13}C\{H\}$ NMR (C_6D_6, 100 MHz): δ 1.1 (CH^1H^2), 16.2 (CH^6H^7), 32.3, 44.8 ($C(CN)_2C(CN)_2$), 47.8 (CH^3), 85.8 (C_5H_5), 112.2, 111.4, 110.8, 108.9 (4 CN), 120.4, 128.3 ($CH^4 + CH^5$), 215.4, 216.4 (2 CO).

(B) Synthesis of $CpFe(CO)_2CH_2CHCHCOOCOCH$-$CH_2CH{=}CH$ (4). Maleic anhydride (0.36 g, 3.68 mmol) was added to **1** (0.58 g, 2.38 mmol) with rapid stirring at 23 °C for 2 h. The solution was evaporated to dryness, and the residues were extracted with dichloromethane. Further recrystallization from CH_2Cl_2/ether afforded orange blocks of crystals (0.56 g, 1.64 mmol). Anal. Calcd for $C_{16}H_{14}FeO_5$: C, 56.14; H, 4.09. Found: C, 56.52; H, 4.14. IR (Nujol): $\nu(CO)$ 1998 (s), 1950 (s), 1770 (s) cm^{-1}, $\nu(C{=}C)$ 1640 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 1.43 (dd, 1 H, H^1), 1.68 and 2.37 (complex m, 2 H, $H^8 + H^9$), 1.80 (dd, 1 H, H^2), 2.17 (m, 1 H, H^3), 2.46 (dd, 1 H, H^7), 2.67 (dd, 1 H, H^6), 4.01 (s, 5 H, C_5H_5), 5.53 (br s, 1 H, H^5), 5.87 (br s, 1 H, H^4), J_{12} = 10.0 Hz, J_{13} = 4.0 Hz, J_{23} = 10.0 Hz, J_{36} = 6.2 Hz, J_{67} = 9.0 Hz. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 0.41 (CH^1H^2), 21.9 (CH^8H^9), 39.6, 41.5, 47.1 ($CH^3 + CH^6 + CH^7$), 84.8 (C_5H_5), 125.0, 135.1 ($CH^4 + CH^5$), 173.9, 171.4 (COOCO), 216.5, 217.3 (2 CO).

(C) Synthesis of $CpFe(CO)_2CH_2CHCHCOOCOCHCH$-$(CH_3)CH{=}CH$ (5). This complex was prepared similarly from the reaction of **3** with maleic anhydride, and the yield was 51%. Anal. Calcd for $C_{17}H_{16}FeO_5$: C, 57.30; H, 4.50. Found: C, 56.98; H, 4.52. IR (Nujol): $\nu(CO)$ 2000 (s), 1950 (s), 1778 (s) cm^{-1}, $\nu(C{=}C)$ 1645 (w) cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 1.20 (d, 3 H, CH_3), 1.85 (dd, 1 H, H^1), 1.91 (dd, 1 H, H^2), 1.99 (m, 1 H, H^3), 2.23 ndd, 1 H, H^7), 2.60 (dd, 1 H, H^6), 4.01 (s, 5 H, C_5H_5), 5.44 (m, 1 H, H^5), 5.77 (m, 1 H, H^4), J_{12} = 10.0 Hz, J_{13} = 4.0 Hz, J_{23} = 10.0 Hz, J_{36} = 6.3 Hz, J_{67} = 9.4 Hz, J_{78} = 7.7 Hz, J_{8-CH} = 7.2 Hz, J_{45} = 10 Hz. $^{13}C\{H\}$ NMR (100 MHz, C_6D_6): δ 2.4 (CH^1H^2), 16.4 (CH_3), 30.5, 43.1 ($CH^3 + CH^8$), 49.1, 49.9 ($CH^6 + CH^7$), 85.7 (C_5H_5), 133.5, 136.5 ($CH^4 + CH^5$), 171.6 (COOCO), 216.5, 217.8 (2 CO).

(D) Synthesis of $CpFe(CO)(PPh_3)(-COCH_2$-$CHCHCOOCOCHCH_2CH{=}CH)$ (6). Triphenylphosphine (0.52 g, 0.20 mmol) was added to **2** (0.34 g, 0.10 mol) in 20 mL of benzene. The solution was then refluxed under argon for 4 h. After evaporation of the solvent, the residues were extracted with ether/THF (5:1). The extract was reduced to a saturated solution and cooled at −25 °C to give an orange crystalline solid (0.46 g, 7.6 × 10^{-2} mmol). Anal. Calcd for $C_{34}H_{29}FePO_5$: C, 67.55; H, 4.80. Found: C, 67.01; H, 4.40. IR (Nujol): $\nu(CO)$ 1912 (s), 1768 (s), 1585 (m) cm^{-1}, $\nu(C{=}C)$ 1648 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): major species, δ 1.28 (m, 1 H, H^9), 2.12 (m, 1 H, H^8), 2.21 (m, 1 H, H^3), 2.38 (dd, 1 H, H^7), 3.12 (dd, 1 H, H^1), 3.24 (dd, 1 H, H^6), 3.95 (dd, 1 H, H^2), 4.41 (s, 5 H, C_5H_5), 5.08 (m, 1 H, H^5), 5.35 (m, 1 H, H^4), 7.05, 7.70 (m, 15 H, $P(C_6H_5)_3$), J_{12} = 18.1 Hz, J_{13} = 3.9 Hz, J_{23} = 10.4 Hz, J_{67} = 8.2 Hz; minor species, δ 1.46 (m, 1 H, H^9), 2.21 (m, 1 H, H^8), 2.26 (m, 1 H, H^3), 2.28 (m, 1 H, H^7), 2.41 (m, 1 H, H^6), 3.45 (dd, 1 H, H^1), 3.71 (dd, 1 H, H^2), 4.17 (s, 5 H, C_5H_5), 5.38 (m, 1 H, H^5), 5.48 (m, 1 H, H^4), J_{12} = 17.9 Hz, J_{13} = 7.2 Hz, J_{23} = 6.4 Hz. $^{13}C\{H\}$ NMR (100 MHz, C_6D_6): major species, δ 24.0 (CH^8H^9), 32.0 (CH^3), 40.8, 43.4 ($CH^6 + CH^7$), 65.9 (d, J_{PC} = 5 Hz, CH^1H^2), 85.6 (C_5H_5), 126.0, 129.3, 129.2, 132.5 (PPh_3), 127.3, 134.2 ($CH^4 + CH^5$), 174.5, 172.9 (-COOCO), 221.1 (d, J_{CP} = 31 Hz, CO), 273.0 (d, J_{PC} = 20 Hz, $-COCH_2$).

Table VIII. Crystal and Diffraction Data

compd	**2**	**4**	**5**
space group	$Pca2_1$	$P2_12_12_1$	$P2_1/c$
a (Å)	13.174 (2)	8.167 (1)	9.197 (2)
b (Å)	10.601 (2)	10.006 (2)	12.498 (3)
c (Å)	12.315 (3)	17.700 (4)	13.622 (2)
β (deg)			90.79 (2)
Z	4	4	4
cryst dimens (mm)	0.45 × 0.50 × 1.0	0.45 × 0.50 × 0.60	0.30 × 0.40 × 0.70
cryst color	yellow	brick red	yellow
radiatn source (λ = 0.7093 Å)	Mo Kα	Mo Kα	Mo Kα
scan parameter	0.65 + 0.35 tan θ	0.65 + 0.35 tan θ	0.65 + 0.35 tan θ
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
2θ range (Å)	3–55	3–55	3–55
h,k,l range	$0 \le h \le 17$ $0 \le k \le 13$ $0 \le l \le 16$	$0 \le h \le 10$ $0 \le k \le 13$ $0 \le l \le 23$	$0 \le h \le 11$ $0 \le k \le 16$ $-13 \le l \le 13$
no. of reflects meased	2059	1906	3538
no. of reflects with $I > 3\,\sigma(I)$	1556	1716	2381
no. of variables	225	200	208
abs coeff (cm^{-1})	8.91	10.60	9.87
abs correctn	Ψ rotation	Ψ rotation	Ψ rotation
final R_F	4.3	2.7	3.2
final R_{wF}[a]	3.0	3.0	2.6
final D map max, e/Å^3	0.46	0.35	0.34
goodness of fit S[b]	2.87	2.76	2.61

[a] $w = 1/(\sigma^2(F_o))$. [b] $S = [\sum(w(F_o - F_c)^2)/(N_o - N_c)]^{1/2}$, where N_o is the number of observations and N_c is the number of variables.

(E) Synthesis of $CpFe(CO)(PPh_3)(COCH_2$-$CHCHCOOCOCHCH(CH_3)CH{=}CH)$ (7). This complex was prepared similarly from refluxing a benzene solution of **3** with PPh_3 under argon for 4 h. The yield is 56%. Anal. Calcd for $C_{35}H_{31}FePO_5$: C 67.96; H, 5.10. Found: C, 67.42; H, 4.84. IR (Nujol): $\nu(CO)$ 1918 (s), 1769 (s), 1592 (s) cm^{-1}, $\nu(C{=}C)$ 1652 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): major species, δ 1.10 (d, 3 H, CH_3), 1.68 (m, 1 H, H^8), 2.13 (dd, 1 H, H^7), 2.30 (m, 1 H, H^3), 2.37 (dd, 1 H, H^6), 3.57 (dd, 1 H, H^1), 3.88 (dd, 1 H, H^2), 4.10 (s, 5 H, C_5H_5), 5.33 (m, 1 H, H^4), 5.55 (m, 1 H, H^5), 7.06, 7.17 (m, 15 H, PPh_3), J_{12} = 18.0 Hz, J_{13} = 7.1 Hz, J_{23} = 6.8 Hz, J_{36} = 3.5 Hz, J_{67} = 8.9 Hz, J_{8-CH_3} = 7.2 Hz; minor species, δ 1.12 (d, 3 H, CH_3), 1.47 (m, 1 H, H^8), 2.12 (m, 1 H, H^3), 2.22 (dd, 1 H, H^7), 3.25 (dd, 1 H, H^2), 3.25 (dd, 1 H, H^6), 4.04 (dd, 1 H, H^1), 4.40 (s, C_5H_5), 5.10 (m, 1 H, H^4), 5.25 (m, 1 H, H^5), 7.00, 7.70 (m, 15 H, PPh_3), J_{12} = 16.5 Hz, J_{13} = 8.0 Hz, J_{23} = 3.2 Hz, J_{36} = 3.6 Hz, J_{67} = 9.0 Hz, J_{8-CH_3} = 7.0 Hz. $^{13}C\{H\}$ NMR (100 MHz, C_6D_6, selected peaks): δ 65.90, 66.37 (d, d, J_{PC} = 5 Hz, CH^1H^2), 171.4, 171.7, 172.6, 172.9 (–COOCO), 220.8, 221.4 (d, d, J_{PC} = 31 Hz, CO), 272.1, 273.0 (d, d, J_{PC} = 20 Hz, $FeCOCH_2$).

(F) Synthesis of $CpFe(CO)_2(COOMe{=}COOMeCH_2CH{=}CHCH{=}CH_2)$ (8). Dimethyl acetylenedicarboxylate (0.54 g, 3.8

mmol) was added to **1** (0.70 g, 2.96 mmol) in 20 mL of CH_2Cl_2 with rapid stirring for 2 h. The solvent was then removed in vacuo, and the residues were chromatographed through a neutral alumina column using benzene as the eluting solvent. A red band was rapidly developed and collected. Removal of the solvent under reduced pressure gave a red oil, **8** (0.68 g, 1.71 mmol). Anal. Calcd for $C_{18}H_{18}FeO_6$: C, 56.05; H, 4.66. Found: C, 56.24; H, 4.73. IR (Nujol): ν(CO) 2030 (s), 1980 (s), 1770 (s) cm^{-1}, ν(C═C) 1605 cm^{-1} (s). ^1H NMR (400 MHz, C_6D_6): δ 3.40 (d, 2 H, H^1), 3.45 (s, 3 H, CH_3), 3.46 (s, 3 H, CH_3), 4.39 (s, 5 H, C_5H_5), 4.87 (dd, 1 H, H^6), 5.05 (dd, 1 H, H^5), 5.87 (m, 1 H, H^2), 6.19 (dd, 1 H, H^3), 6.28 (m, 1 H, H^4), J_{12} = 6.2 Hz, J_{23} = 13.3 Hz, J_{34} = 11.0 Hz, J_{45} = 15.6 Hz, J_{46} = 9.4 Hz, J_{56} = 1.2 Hz. $^{13}C\{H\}$ NMR (100 MHz, C_6D_6): δ 28.1 (CH_3), 30.2 (CH_3), 38.9 (CH^1), 86.8 (C_5H_5), 115.4 (CH^5H^6), 132.3, 133.0, 137.6 (CH^2 + CH^3 + CH^4), 139.3 (Fe*C*═), 153.4 (FeC═*C*), 170.0, 177.1 (–COOMe), 214.0 (CO).

(G) Synthesis of CpFe(CO)$_2$(–CF$_3$C═CCF$_3$CH$_2$CH═CHCH═CH$_2$) (9). Hexafluoro-2-butyne (0.44 g, 0.30 mmol) was condensed with **1** (0.56 g, 0.23 mmol) in 20 mL of CH_2Cl_2 at −195 °C. The solution was then warmed to 23 °C and left standing for 6 h. The solvent was then removed in vacuo, and the residues were chromatographed through a neutral alumina column using benzene as the eluting solvent. Removal of the solvent under reduced pressure gave a red oil, **9** (0.29 g, 7.2×10^{-2} mmol). Anal. Calcd for $C_{16}H_{12}FeF_6O_2$: C, 47.27; H, 2.96. Found: C, 47.54; H, 3.04. IR (Nujol): ν(CO) 2040 (s), 2000 (s), ν(C═C) 1600 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 2.91 (m, 2 H, H^1), 4.2 (s, 5 H, C_5H_5), 4.90 (d, 1 H, H^6), 5.01 (d, 1 H, H^5), 5.58 (dt, 1 H, H^2), 6.06 (dd, 1 H, H^3), 6.14 (dt, 1 H, H^4), J_{12} = 7.2 Hz, J_{1-F} = 5.4 Hz, J_{23} = 15.0 Hz, J_{34} = 10.8 Hz, J_{46} = 10.8 Hz, J_{45} = 16.4 Hz. ^{13}C NMR (100 MHz, C_6D_6): δ 36.8 (CH^1), 86.2 (C_5H_5), 115.9 (CH^5H^6), 132.2, 133.1, 135.5 (CH^2 + CH^3 + CH^4), 139.0 (Fe*C*═C, q, J_{C-F} = 29 Hz), 141.2 (Fe–C═*C*, q, J_{C-F} = 29 Hz), 129.5, 133 (2CF_3, q, J_{CF} = 270 Hz), 213.6 (CO). ^{19}F NMR (93.6 MHz, C_6D_6): δ 56.6 (s), 62.4 (s).

(H) X-ray Diffraction Study of 2, 4, and 5. Intensity data were collected at room temperature on a CAD4 diffractometer, using graphite-monochromated Mo Kα radiation. All data reduction and structure refinement were performed by using the NRCC-SDP-VAX package on a VAX-785 computer. Crystal date, data collection, and structure analysis are summarized in Table VIII. The structure of three compounds were solved by the Patterson method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were added at idealized positions and included in the structure factor calculations.

Acknowledgment. We wish to thank the Chinese National Science Council for financial support of this work.

Registry No. **1**, 103225-91-8; **2**, 113404-08-3; **3**, 109638-07-5; **4**, 113404-09-4; **5**, 113404-10-7; **6** (isomer 1), 113404-11-8; **6** (isomer 2), 113472-63-2; **7** (isomer 1), 113404-12-9; **7** (isomer 2), 113472-64-3; **8**, 113404-13-0; **9**, 113404-14-1; TCNE, 670-54-2; maleic anhydride, 108-31-6; dimethyl acetylenedicarboxylate, 762-42-5; hexafluoro-2-butyne, 692-50-2.

Supplementary Material Available: Table IX, calculated atomic coordinates and estimated thermal parameters for the hydrogen atoms of molecule **2**, **4**, and **5** (1 page); listings of structure factors for **2**, **4**, and **5** (51 pages). Ordering information is given on any current masthead page.

Synthesis of Fluorosilanes from Chlorosilanes: The Use of Hexafluorosilicates

Robert Damrauer* and Roger A. Simon

Department of Chemistry, University of Colorado, Denver, Colorado 80202

Bernard Kanner

5 Robin Lane, West Nyack, New York 10994

Received October 5, 1987

The conversion of chlorosilanes to fluorosilanes has been studied by using sodium and ammonium hexafluorosilicate. Of particular interest has been their efficacy in the conversion of highly hindered chlorosilanes like dimesityldichlorosilane and di-*tert*-butyldichlorosilane. Ammonium hexafluorosilicate is found to be the superior reagent for these conversions, since its reactions are more easily worked up and give higher yields. In addition, ammonium hexafluorosilicate does not affect the Si–H, Si–Si, or Si–O–Si linkages as do many reagents which bring about chlorosilane to fluorosilane conversions.

The chemistry of organofluorosilanes has recently been revitalized by reports of their use in the preparation of pentacoordinate siliconates and highly hindered organosilanes.[1-3] Pentacoordinate siliconates are made in high yields by reacting organofluorosilanes such as diphenyldifluorosilane with fluoride ion solubilized in toluene by 18-crown-6 (eq 1).[2] Although hindered silanes have recently been prepared by reaction of either SiF_4 or a substituted trifluorosilane with hindered Grignard or organolithium reagents (eq 2–4),[3] the utility of fluorosilanes in such couplings was first recognized by Eaborn in 1952.[4] Indeed, many recent studies by Eaborn and co-workers have heightened interest in highly hindered silicon compounds as have studies where bulky substituents on silicon stabilize otherwise reactive silicon intermediates.[5,6]

$$(C_6H_5)_2SiF_2 \xrightarrow[\text{18-crown-6}\atop\text{toluene}]{\text{KF}} (C_6H_5)_2\bar{S}iF_3 + K^+(\text{18-crown-6}) \tag{1}$$

---

[1] Kanner, B. *Silicon Compounds, Register and Review, 1987*, Petrarch Systems Catalog, 40.

[2] (a) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490. (b) A variation of this method has also been used recently by Corriu and co-workers to solubilize potassium methoxide, personal communication.

[3] (a) Nakadaira, Y.; Ohara, K.; Sakurai, H. *J. Organomet. Chem.* **1986**, *309*, 247. (b) Wiberg, N.; Neruda, B. *Chem. Ber.* **1966**, *99*, 740. (c) Weidenbruch, M.; Kramer, K. *J. Organomet. Chem.* **1985**, *291*, 159.

[4] Eaborn, C. *J. Chem. Soc.* **1952**, 2840.

0276-7333/88/2307-1161$01.50/0 © 1988 American Chemical Society