Multicarbonylation of Cyclopentadienyl and Cycloheptatrienyl Anions by $Fe(CO)_5$

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The reaction of cyclopentadienyl anions with $Fe(CO)_5$ in the presence of acyl chlorides or carboxylic anhydrides gave cyclic acyliron complexes $[\eta^5\text{-}C_5H_4C(OCOR)=C(OCOR)CO]Fe(CO)_2$ via triple carbonylation of the anions and a double acylation. The structure of $[\eta^5\text{-}C_5H_4C(OCOCH_2CH_3)=C(OCOCH_2CH_3)CO]Fe(CO)_2$ thus obtained was confirmed by the X-ray analysis. Diastereomers of indenyl derivative $[\eta^5\text{-}C_9H_6C(OCOCH_2CH_3)=C(OCOCH_2CH_3)CO]Fe(CO)(P(OCH_3)_3)$ were prepared by substitution of CO ligand with trimethyl phosphite and the structure of the diastereomers were characterized by NMR spectroscopy using 2D technique. Treatment of cycloheptatrienyl anion with $Fe(CO)_5$ and acyl chloride resulted in double carbonylation to give $[\eta^5\text{-}C_7H_6C(OCOR)=C(OCOR)]Fe(CO)_2$. The mechanism of the reaction is proposed.

Anionic acyliron complexes, derived from the reaction of organolithium and organomagnesium compounds with $Fe(CO)_5$, are key intermediates for the synthesis of Fischer-type carbene iron complexes[1] and also in organic synthesis.[2] This reaction usually gives monocarbonylation products. In the course of study on the reaction of $Fe(CO)_5$ with carbanions such as cyclopentadienyl and indenyl anions, we have found triple carbonylation of these anions by $Fe(CO)_5$. That is, cyclopentadienyl anions reacted with $Fe(CO)_5$ in the presence of acyl halides to give cyclic acyliron complexes $[\eta^5\text{-}C_5H_4C(OCOR)=C(OCOR)CO]Fe(CO)_2$ (**2**) which were formed via triple carbonylation and double acylation. Similar treatment of indenyl anions also gave tricarbonylated complexes $[\eta^5\text{-}C_9H_6C(OCOR)=C(OCOR)CO]Fe(CO)_2$ (**4**) which are planar chiral complexes. To examine the stereochemistry of **4**, the diastereomers of **4** have been prepared by substitution of one of two CO ligands with trimethyl phosphite.

This triple carbonylation of carbanions by $Fe(CO)_5$ is unique but complicated because the reaction involves incorporation of three CO and two acyl groups. It is therefore important to determine the structure of the complex unambiguously and to study on the structural characteristics of the complexes.

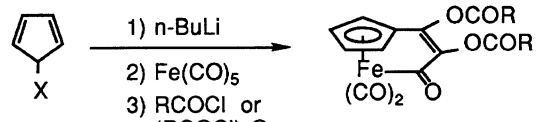
In this paper we have investigated the reaction scope and features of the carbonylation of carbanions and also the stereochemistry of the complexes. The reaction mechanism is also discussed. Part of this work has been the subject of two preliminary communications.[3,4]

Results and Discussion

Formation of Carbonylated Complexes. 5-(Trimethylsilyl)-1,3-cyclopentadiene (**1a**) reacted successively with butyllithium, $Fe(CO)_5$ and acyl chlorides or carboxylic anhydrides to give cyclic acyliron complexes **2** via triple carbonylation of the anions and double acylation accompanying with desilylation as shown in Scheme 1. Complexes **2** were also formed starting from 1,3-cyclopentadiene (**1b**) in lower yield.

Similar treatments of 1-(trimethylsilyl)indene (**3a**) and indene (**3b**) afforded the corresponding complexes **4** (Scheme 2). Both of complexes **2** and **4** are air-stable solids or oily substances and their structures are fully characterized by spectroscopic data and also X-ray analysis (in next section). Results are summarized in Table 1.

The remarkable feature of the complexes is that com-



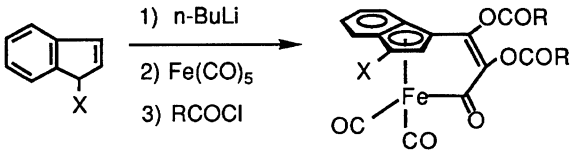
1a,b

1a; X=Me_3Si
1b; X=H

2a-d

2a : R=CH_3
2b : R=CH_3CH_2
2c : R=cyclo-C_6H_{11}
2d : R=C_6H_5

Scheme 1.



3a,b

3a; X=Me_3Si
3b; X=H

4a-e

4a : X=Me_3Si, R=CH_3
4b : X=H, R=CH_3
4c : X=H, R=CH_3CH_2
4d : X=H, R=cyclo-C_6H_{11}
4e : X=H, R=C_6H_5

Scheme 2.

Table 1. The Reaction of Cyclopentadienyl Anions with $Fe(CO)_5$ in the Presence of Acyl Chlorides or Carboxylic Anhydrides

Compd	Acyl chloride or anhydride	Product	Yield%[a]
1a	CH_3COCl	**2a**	54
1b	CH_3COCl	**2a**	10
1a	CH_3CH_2COCl	**2b**	49
1a	*cyclo*-$C_6H_{11}COCl$	**2c**	53
1a	C_6H_5COCl	**2d**	51
1a	$(CH_3CO)_2O$	**2a**	35
1a	$(CH_3CH_2CO)_2O$	**2b**	44
1a	$(C_6H_5CO)_2O$	**2d**	43
1a	$(CF_3CO)_2O$	**2e**	0
3a	CH_3COCl	**4a**	21
3b	CH_3COCl	**4b**	18
3b	CH_3CH_2COCl	**4c**	21
3b	*cyclo*-$C_6H_{11}COCl$	**4d**	30
3b	C_6H_5COCl	**4e**	19

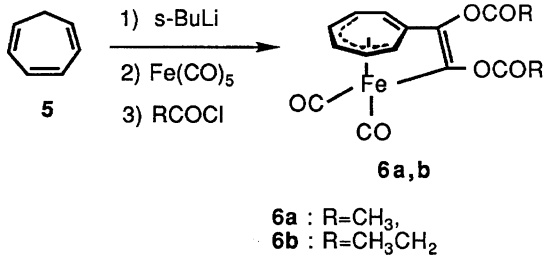
a) Isolated yields based on **1** and **3** used.

plexes **2** have no silyl group in the cyclopentadienyl ring starting from **1a** whereas complexes **4** have silyl group at 3-position of the indenyl ring starting from **3a**.

Reaction of cycloheptatrienyl anion with $Fe(CO)_5$ in the presence of acyl halides gave cyclic vinyliron complexes **6a** and **6b** in 32 and 38% yields, respectively, via double carbonylation (Scheme 3). Complexes **6** are air-sensitive and also unstable in solution under inert atmosphere. The structure of these complexes are assigned on the basis of the spectral data.

Similar reaction of fluorene and 9-(trimethylsilyl)-fluorene gave no corresponding carbonylated complex.

Some significant features of the spectral data are worthy of remark: 1) IR spectra of the complexes **2** and **4** showed clearly the characteristic absorption bands due to propenoyl carbonyl attached to iron atom (1608—1632 cm^{-1}) and two coordinated carbonyl groups (1970—1990, 2020—2040 cm^{-1}), and also exhibited absorption bands due to two ester carbonyl groups (1730—1765, 1740—1780 cm^{-1}). 2) Parent peak (M^+) and three fragment peaks (M^+-CO), (M^+-2CO), and (M^+-3CO) appeared in the mass spectra of **2** and **4**. 3) ^{13}C NMR spectra of the complexes **2** and **4** showed the characteristic signals assigned to propenoyl carbonyl carbons (233—238 ppm) and also enediol carbons (143—144, 147—148 ppm). 4) IR and NMR spectra of



Scheme 3.

6a and **6b** revealed the lack of acyliron group indicating that insertion of the third CO molecule did not occur. ^1H NMR spectra of **6a** and **6b** exhibited two inequivalent cycloheptatrienyl protons in 0.7—1.0 and 5.2—6.2 ppm regions (1 : 1). Signals of cycloheptatrienyl carbons did not appear as sharp signals in their ^{13}C NMR spectra in the range of 25°C to −70°C. This suggests the fluxional nature of the cycloheptatrienyl ligand.

Crystal Structure of $[\eta^5$-$C_5H_4C(OCOCH_2CH_3)$=$C(OCOCH_2CH_3)CO]Fe(CO)_2$ (2b). The molecular structure of **2b** is shown in Fig. 1. Bond distances and angles are listed in Tables 2 and 3. The geometry of the complex resembles well that of similar iron complexes which were synthesized by the reaction of spiro-cyclopentadiene compounds with $Fe_2(CO)_9$,[5—7] and also by the reaction of tricarbonyl(8, 8-dibromobicyclo[5.1.0]octa-2,4-diene)iron with methyllithium.[8] A conspicuous feature of the structure involves the propenoyl side chain as an intramolecular lincage between the dicarbonyliron moiety and the cyclopentadienyl ring. The seven atoms C(1), C(2), C(3), C(4), O(1), O(4), and O(6) constitute a plane (within 0.057°) which is nearly orthogonal (85.9+0.4°) to the cyclopentadienyl plane. All bond lengths of Fe–C(1), C(1)–C(2), C(2)–C(3), and C(3)–C(4) are close agreement with the values reported for the similar iron complexes.[8] Moreover, a large inclination angle (10.8°) of C(3)–C(4) bond to the cyclopentadienyl plane is also observed. This is smaller than 14.8° found for the iron complex.[8] The C(2)–C(3) bond distance is 1.309+0.016 Å, which is slightly shorter than normal carbon–carbon double bond length. This double bond constitutes the enediol group derived from incorporation of two CO

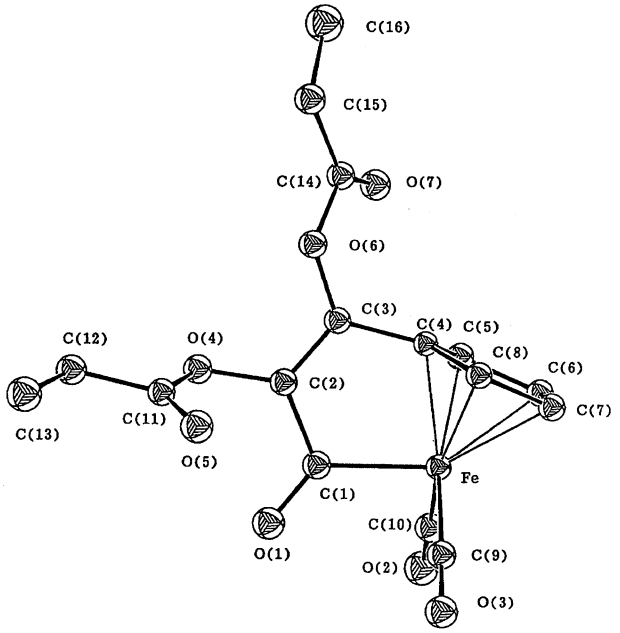


Fig. 1. Molecular structure of $[\eta^5$-$C_5H_4C(OCOCH_2CH_3)$=$C(OCOCH_2CH_3)CO]Fe(CO)_2$ (**2b**).

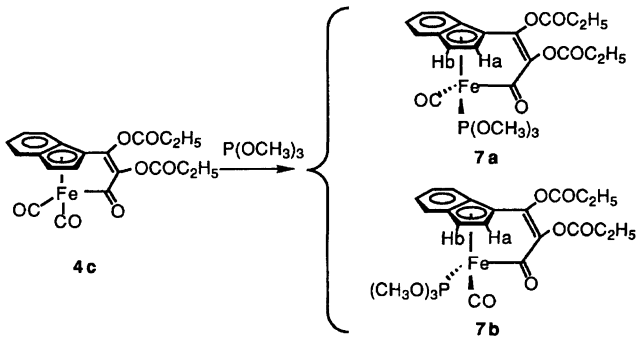
Table 2. Bond Distances of $[\eta^5$-$C_5H_4C(OCOC_2H_5)$=C-$(OCOC_2H_5)CO]Fe(CO)_2$

Fe–C(1)	1.977(12)	C(12)–C(13)	1.489(32)
Fe–C(4)	2.042(7)	C(14)–C(15)	1.481(10)
Fe–C(5)	2.053(14)	C(14)–O(6)	1.374(18)
Fe–C(6)	2.155(15)	C(14)–O(7)	1.197(18)
Fe–C(7)	2.153(10)	C(15)–C(16)	1.490(25)
Fe–C(8)	2.090(7)	C(5)–H(5)	0.96(1)
Fe–C(9)	1.751(14)	C(6)–H(6)	0.96(1)
Fe–C(10)	1.747(9)	C(7)–H(7)	0.96(1)
C(1)–C(2)	1.483(8)	C(8)–H(8)	0.96(1)
C(2)–C(3)	1.309(16)	C(12)–H(121)	0.96(1)
C(4)–C(5)	1.372(20)	C(12)–H(122)	0.96(1)
C(4)–C(8)	1.442(14)	C(13)–H(131)	0.96(1)
C(5)–C(6)	1.427(11)	C(13)–H(132)	0.96(1)
C(6)–C(7)	1.403(18)	C(13)–H(133)	0.96(2)
C(7)–C(8)	1.420(16)	C(15)–H(151)	0.96(1)
C(9)–O(3)	1.147(18)	C(15)–H(152)	0.96(1)
C(10)–O(2)	1.153(12)	C(16)–H(161)	0.96(2)
C(11)–C(12)	1.499(15)	C(16)–H(162)	0.96(1)
C(11)–O(4)	1.356(20)	C(16)–H(163)	0.96(2)
C(11)–O(5)	1.197(14)		

The standard deviation of the least significant figure of each distance is given in parenthesis.

molecules. Each oxygen atom of the enediol group is linked by a propanoyl group. The acyl iron group (C-(1) and O(1)) is made up by the third incorporated CO molecule.

Substitution of CO Ligand with $P(OMe)_3$ in the Complex 4c. Indenyl complexes **4** are planar chiral complexes. To examine the stereochemistry of **4**, diastereomers of **4c** were prepared by substitution of CO ligand. The complex **4c** reacted with a slight excess of trimethyl phosphite in benzene at 80°C for 20 h to give a mixture of diastereomers **7a** and **7b** (1 : 1) in 72% yield (Scheme 4), which were separated by column chromatography on silica gel (CH_2Cl_2 : ethyl acetate=1 : 1). Treatment of **4c** with triphenylphosphine and triphenyl phosphite did not give the corresponding substituted complexes, but resulted in decomposition of **4c**. A striking difference in the ^1H NMR spectra of **7a** and **7b** was observed as shown in Fig. 2. The spectrum of **7b** exhibited two doublet signals assigned to cyclopentadienyl protons (Ha and Hb), while that of **7a** showed a double–



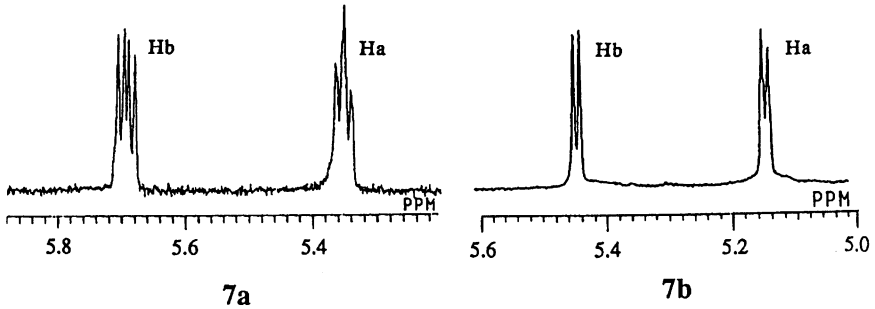
Scheme 4.

Table 3. Bond Angles of $[\eta^5$-$C_5H_4C(OCOC_2H_5)$=C-$(OCOC_2H_5)CO]Fe(CO)_2$

C(1)–Fe–C(9)	88.9(6)
C(1)–Fe–C(10)	89.4(5)
C(9)–Fe–C(10)	92.2(5)
Fe–C(1)–C(2)	112.8(8)
C(1)–C(2)–C(3)	117.5(10)
C(5)–C(4)–C(8)	108.8(8)
C(4)–C(5)–C(6)	108.6(10)
C(5)–C(6)–C(7)	107.6(11)
C(6)–C(7)–C(8)	108.6(8)
C(4)–C(8)–C(7)	106.3(11)
Fe–C(9)–O(3)	178.7(11)
Fe–C(10)–O(2)	179.3(13)
C(12)–C(11)–O(4)	109.3(10)
C(12)–C(11)–O(5)	127.1(15)
O(4)–C(11)–O(5)	123.6(11)
C(11)–C(12)–C(13)	114.9(11)
C(15)–C(14)–O(6)	109.0(12)
C(15)–C(14)–O(7)	128.7(13)
O(6)–C(14)–O(7)	122.2(6)
C(14)–C(15)–C(16)	113.9(14)
C(4)–C(5)–H(5)	125.4(9)
C(6)–C(5)–H(5)	126.1(13)
C(5)–C(6)–H(6)	126.3(12)
C(7)–C(6)–H(6)	126.1(8)
C(6)–C(7)–H(7)	125.6(12)
C(8)–C(7)–H(7)	125.7(13)
C(4)–C(8)–H(8)	127.1(10)
C(7)–C(8)–H(8)	126.6(9)
C(11)–C(12)–H(121)	108.1(10)
C(11)–C(12)–H(122)	107.7(13)
C(13)–C(12)–H(121)	108.7(14)
C(13)–C(12)–H(122)	108.3(11)
H(121)–C(12)–H(122)	109.0(13)
C(12)–C(13)–H(131)	109.2(18)
C(12)–C(13)–H(132)	108.6(17)
C(12)–C(13)–H(133)	108.9(14)
H(131)–C(13)–H(132)	109.9(13)
H(131)–C(13)–H(133)	110.3(19)
H(132)–C(13)–H(133)	109.9(20)
C(14)–C(15)–H(151)	108.4(8)
C(14)–C(15)–H(152)	109.4(10)
C(16)–C(15)–H(151)	108.7(11)
C(16)–C(15)–H(152)	108.9(10)
H(151)–C(15)–H(152)	108.4(16)
C(15)–C(16)–H(161)	108.8(14)
C(15)–C(16)–H(162)	108.7(19)
C(15)–C(16)–H(163)	109.0(12)
H(161)–C(16)–H(162)	109.8(13)
H(161)–C(16)–H(163)	110.5(22)
H(162)–C(16)–H(163)	110.1(15)

The standard deviation of the least significant figure of each angle is given in parenthesis.

doublet and a multiplet signals, indicating the presence of spin–spin coupling of Ha,b protons with phosphorus atom. To investigate the structural feature in detail, 2D NOESY spectra of **7a** and **7b** were recorded. NOE was observed between Ha,b protons and methyl protons of phosphite ligand in the spectrum of **7a** as shown in



7a **7b**

Fig. 2. ^{1}H NMR spectra of **7a** and **7b**.

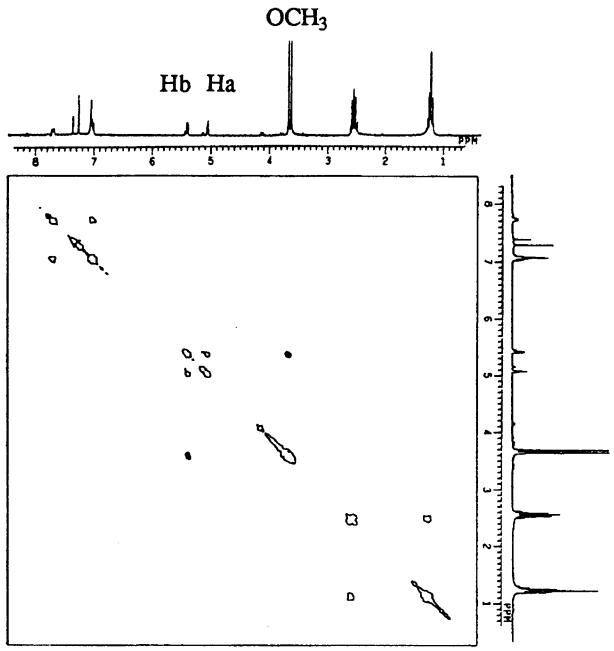


Fig. 3. 2D NOESY spectrum of **7a**.

Fig. 3, but no NOE was detected in the case of **7b**. From these results, the structure of **7a** and **7b** were estimated as illustrated in Scheme 4. These diastereomers did not interchange upon heating up to 110°C in toluene.

Reaction Mechanism of the Carbonylation. The detailed mechanism has not yet been elucidated. However, Mitsudo and co-workers have previously reported the reaction of $[(acryloyl)Fe(CO)_4]^-$ **8** with acyl halides to give $(allylacyl)Fe(CO)_3$ **11**.[9] They have demonstrated that the reaction proceeds via CO insertion into (vinylcarbene)iron complexes **9** to form (vinylketene)iron complexes **10** (Scheme 5). This mechanism suggests that the present reaction also proceeds via the carbene iron complexes (**16** and **17**) and the ketene iron complexes (**18**) as represented in Scheme 6.

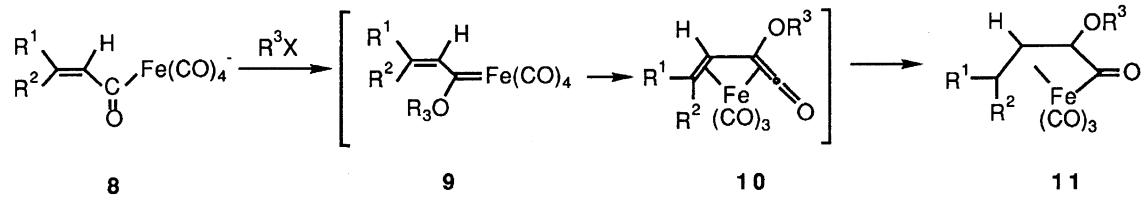
As mentioned above, complexes **2** have no trimethylsilyl group starting from 5-(trimethylsilyl)-1,3-cyclopentadiene in contrast to 1-(trimethylsilyl)indene. Attempt was made to examine the structure of carbanions generated in situ by treatment of silylated compounds with butyllithim. Carbanions thus generated were treated with methyl iodide or benzyl bromide to give alkylated products as shown in Scheme 7. These results suggest that in the case of **1a**, the carbanion **12** is a primary intermediate for the CO insertion reaction and the desilylation occurs probably via the pathway represented in Scheme 6, whereas a primary intermediate for the CO insertion in the case of **3a** may be 3-trimethylsilyl-1-indenide which leads to **4** without desilylation. The silyl group serves as a carbanion-stabilizing group and also as a good leaving group. Attempts to characterize other intermediates in the reaction were unsuccessful. One of the driving forces of the tricarbonylation reaction may be the formation of the iron complexes stabilized by the η^5-cyclopentadienyl ligand after triple CO insertion. On the other hand, the reaction of cycloheptatrienyl anion resulted in dicarbonylation. The complexes **6a** and **6b** may be more stable than the corresponding tricarbonylated acyliron complexes because carbon–carbon double bond interposed between η^5-cyclopentadienyl ligand and the enediol group.

Experimental

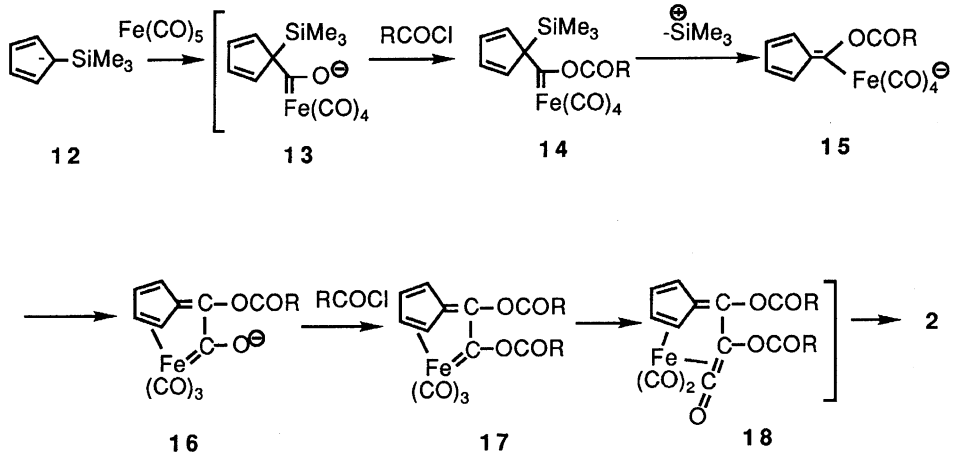
General. The IR spectra were recorded on a JASCO IRA-16 spectrometer. The NMR spectra were measured in a $CDCl_3$ solution using TMS as internal standard with a JOEL JNM-GX 270 spectrometer. Mass spectra were run on Shimadzu LKB 9000. Elemental analyses were carried out on a Yanaco CHN CORDER.

Materials. 5-(Trimethylsilyl)-1,3-cyclopentadiene (**1a**),[10] 1-(trimethylsilyl)indene,[11] and 9-(trimethylsilyl)-fluorene[12] were prepared by modification of the method previously reported.

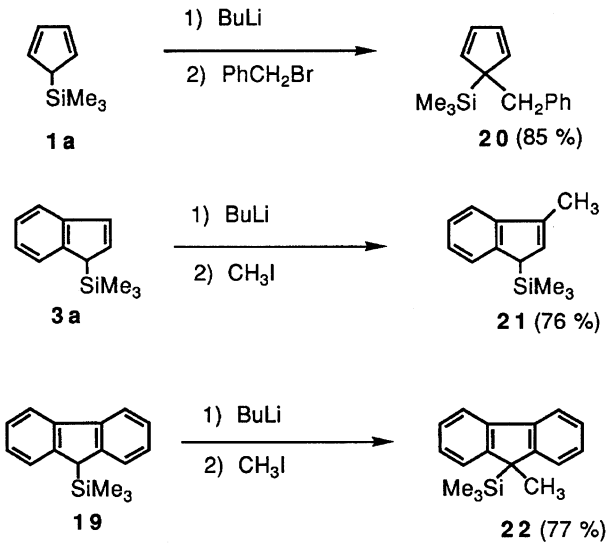
Reaction of Carbanion with $Fe(CO)_5$ in the Presence of Acyl Halides or Carboxylic Anhydrides. General Procedure: To a solution of cyclopentadiene derivatives (or 1,3,5-cycloheptatriene) (3.0 mmol) in freshly distilled tetrahydrofuran (15 ml) were added successively butyllithium (3.3 mmol, 1.6 M (1 M =1 mol dm^{-3}) hexane solution) and $Fe(CO)_5$ (3.0 mmol) at 0°C under argon, and the mixture was stirred at room temperature for 3 h. Acyl chloride (or carboxylic anhydride)(6.0 mmol) was then added at 0°C, and the resulting mixture was stirred at room temperature for 16 h. The solvent was evapolated and the residue was chromatographed on silica gel. Elution with ethyl acetate–benzene (1 : 9) gave the product.



Scheme 5.



Scheme 6.



Scheme 7.

2a: Yellow needles (from hexane–dichloromethane); mp 149—150°C; IR (KBr) 2020, 1990 (CO), 1780, 1765 (OCO), 1630 cm^{-1}(FeCO); ^1H NMR ($CDCl_3$) δ=5.60—5.55 (2H, m, Cp), 4.93—4.80 (2H, m, Cp), 2.22 (3H, s, CH_3), 2.15 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ=233.8 (FeCO), 211.6 (CO), 166.8, 166.6 (OCO), 148.2, 143.7 (C=C), 104.6, 90.4, 87.4 (Cp), 20.7, 20.0 (CH_3); MS *m/z* 346 (M^+), 318, 290, 262. Found: C, 48.65; H, 2.98%. Calcd for $C_{14}H_{10}O_7Fe$: C, 48.59; H, 2.91%.

2b: Yellow needles (from hexane–dichloromethane); mp 114—115°C; IR (KBr) 2018, 1990 (CO), 1775, 1760 (OCO), 1608 cm^{-1}(FeCO); ^1H NMR ($CDCl_3$) δ=5.68—5.61 (2H, m, Cp), 4.99—4.88 (2H, m, Cp), 2.55 (2H, q, *J*=7.2 Hz, CH_2), 2.48 (2H, q, *J*=7.2 Hz, CH_2), 1.21 (3H, t, *J*=7.2 Hz, CH_3), 1.18 (3H, t, *J*=7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ=233.8 (FeCO), 211.7 (CO), 170.5, 170.3 (OCO), 148.2, 143.8 (C=C), 104.6, 90.3, 87.5 (Cp), 27.4, 26.8 (CH_2), 9.0, 8.7 (CH_3); MS *m/z* 374 (M^+), 346, 318, 290. Found: C, 51.19; H, 3.54%. Calcd for $C_{16}H_{14}O_7Fe$: C, 51.36; H, 3.77%.

2c: Yellow needles (from hexane–dichloromethane); mp 105—106°C; IR (KBr) 2020, 1990 (CO), 1770, 1765 (OCO), 1622 cm^{-1}(FeCO); ^1H NMR ($CDCl_3$) δ=5.69—5.57 (2H, m, Cp), 4.98—4.87 (2H, m, Cp), 2.52—2.40 (2H, m, CH), 2.00—1.15 (20H, m, C_6H_{10}); ^{13}C NMR ($CDCl_3$) δ=233.7 (FeCO), 211.7 (CO), 172.0, 171.7 (OCO), 148.5, 143.7 (C=C), 105.0, 90.3, 87.4 (Cp), 42.8, 42.4, 28.9, 28.7, 25.7, 25.6, 25.2, 25.1 (C_6H_{11}); MS *m/z* 482 (M^+), 454, 426, 398. Found: C, 59.85; H, 5.31%. Calcd for $C_{24}H_{26}O_7Fe$: C, 59.76; H, 5.43%.

2d: Yellow needles (from hexane–dichloromethane); mp 198—199°C; IR (KBr) 2020, 1970 (CO), 1740, 1730 (OCO), 1622 cm^{-1}(FeCO); ^1H NMR ($CDCl_3$) δ=8.20—7.20 (10H, m, arom), 5.77—5.62 (2H, m, Cp), 5.05—4.90 (2H, m, Cp); ^{13}C NMR ($CDCl_3$) δ=232.7 (FeCO), 211.3 (CO), 162.7, 162.4 (OCO), 148.4, 143.7 (C=C), 135.0—105.8 (m, arom), 104.4, 90.3, 87.5 (Cp); MS *m/z* 470 (M^+), 442, 414, 386. Found: C, 61.51; H, 2.98%. Calcd for $C_{24}H_{14}O_7Fe$: C, 61.30; H, 3.00%.

4a: Dark red oil; IR (neat) 2040, 1980 (CO), 1780, 1765 (OCO), 1620 cm^{-1}(FeCO); ^1H NMR ($CDCl_3$) δ=7.75—7.11 (4H, m, arom), 5.44 (1H, s, Cp), 2.27 (3H, s, CH_3), 2.24 (3H, s, CH_3), 0.40 (9H, s, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ=238.0 (FeCO), 214.7, 211.4 (CO), 167.2, 167.0 (OCO), 148.5, 144.0 (C=C), 128.9, 127.6, 127.3, 124.8, 110.4, 109.4 (arom), 97.6, 96.9, 86.5 (Cp), 21.0, 20.4 (CH_3), 0.02 ($SiCH_3$); MS *m/z* 468

Table 4. Crystal, Data Collection, and Refinement Parameters for $[\eta^5$-$C_5H_4C(OCOCH_2H_5)$=C-$(OCOCH_2H_5)CO]Fe(CO)_2$

Formula	$C_{16}H_{14}O_7Fe$
FW	374.1
Space group	$C2/c$ (No. 15)
Syst absences	(hkl): $h+k$=2n+1, $(h0l)$: h, l=2n+1, $(0kl)$: $k+l$=2n+1, $(hk0)$: k=2n+1, (00): l=2n+1, $(h00)$: h=2n+1, $(0k0)$: h=2n+1
a/Å	19.533(7)
b/Å	12.951(2)
c/Å	20.241(8)
β/deg	139.7(1)
V/Å^3	3321(4)
Z	8
d_{calcd}/g cm^{-3}	1.50
Crystal dimens/mm	0.2×0.2×0.4
Temp/°C	20
Radiation (wavelength/Å)	Mo $K\alpha$ (0.71073)
Linear abs coeff/cm^{-1}	9.24
Scan speed/deg min^{-1}	4
Scan technique	θ–2θ
2θ range/deg	3—46
Scan width/deg	1.20+0.50 tan θ
hkl limits	−13 to 13, 0 to 14, 0 to 22
F_{000}/e	1536
No. of data collected	3805
No. of data obsd with ($F_o > 4\sigma(F_o)$)	1861
No. of parameters	218
R,[a] R_w[b]	0.059, 0.083
Goodness of fit[c]	2.24
$\Delta(\rho)_{max}$/e Å^{-3}	1.50
Largest Δ/σ in Final cycle	0.25

a) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$

b) $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ $w=1$ *for* $F_o \leqq 50.0$; $w=(1+(F_o-50.0)\times 0.020)^{-1}$ *for* $F_o > 50.0$

c) goodness of fit$=[\Sigma w(|F_o|-|F_c|)^2/(n_o-n_v)]^{1/2}$ where n_o is the number of observations, n_v is the number of parameters.

(M^+), 440, 412, 384. Found: C, 53.77; H, 4.42%. Calcd for $C_{21}H_{20}O_7SiFe$: C, 53.86; H, 4.30%.

4b: Dark red oil; IR (neat) 2040, 1980 (CO), 1780, 1765 (OCO), 1620 cm^{-1}(FeCO); ^{1}H NMR ($CDCl_3$) δ=7.70—7.05 (4H, m, arom), 5.44—5.40 (2H, m, Cp), 2.27 (3H, s, CH_3), 2.23 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ=237.5 (FeCO), 213.8, 211.1 (CO), 166.8, 166.6 (OCO), 147.9, 143.9 (C=C), 128.1, 127.8, 125.6, 124.0, 106.2, 104.6 (arom), 95.1, 90.3, 78.0 (Cp), 20.7, 20.1 (CH_3); MS m/z 396 (M^+), 368, 340, 312. Found: C, 54.33; H, 3.16%. Calcd for $C_{18}H_{12}O_7Fe$: C, 54.57; H, 3.05%.

4c: Dark red oil; IR (neat) 2020, 1980 (CO), 1770, 1764 (OCO), 1610 cm^{-1}(FeCO); ^{1}H NMR ($CDCl_3$) δ=7.66—7.02 (4H, m, arom), 5.42—5.37 (2H, m, Cp), 2.56 (2H, q, J=7.2 Hz, CH_2), 2.53 (2H, q, J=7.2 Hz, CH_2), 1.21 (3H, t, J=7.2 Hz, CH_3), 1.18 (3H, t, J=7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ=237.8 (FeCO), 214.0, 211.3 (CO), 171.4, 170.5 (OCO), 148.2, 143.8 (C=C), 128.3, 128.1, 127.8, 125.6, 124.0, 106.2 (arom), 104.6, 95.3, 90.3 (Cp), 27.4, 26.8 (CH_2), 9.0, 8.7 (CH_3); MS m/z 424 (M^+), 396, 368, 340. Found: C,56.55; H, 3.78%. Calcd for $C_{20}H_{16}O_7Fe$: C, 56.63; H, 3.80%.

4d: Dark red oil; IR (neat) 2020, 1985 (CO), 1775, 1760 (OCO), 1620 cm^{-1}(FeCO); ^{1}H NMR ($CDCl_3$) δ=7.68—7.07 (4H, m, arom), 5.44—5.39 (2H, m, Cp), 2.56—1.23 (22H, m, C_6H_{10}); ^{13}C NMR ($CDCl_3$) δ=237.9 (FeCO), 213.9, 211.2 (CO), 172.0, 171.9 (OCO), 148.3, 143.9 (C=C), 128.3, 128.0, 127.7, 125.7, 124.0, 106.3 (arom), 104.6, 95.3, 90.2 (Cp), 43.2—25.1 (m,C_6H_{11}); MS m/z 532 (M^+), 504, 476, 448. Found: C, 63.27; H, 5.18%. Calcd for $C_{28}H_{28}O_7Fe$: C, 63.17; H, 5.30%.

4e: Dark red oil; IR (neat) 2020, 1980 (CO), 1740, 1732 (OCO), 1620 cm^{-1}(FeCO); ^{1}H NMR ($CDCl_3$) δ=8.25—7.07 (14H, m, arom), 5.55—5.38 (2H, m, Cp); ^{13}C NMR ($CDCl_3$) δ=237.7 (FeCO), 214.5, 211.0 (CO), 162.8, 162.3 (OCO), 148.2, 143.5 (C=C), 135.1—106.0 (m, arom), 105.5, 90.2, 88.8 (Cp); MS m/z 520 (M^+), 492, 464, 436. Found: C, 64.49; H, 3.27%. Calcd for $C_{28}H_{16}O_7Fe$: C, 64.64; H, 3.10%.

6a: Dark red oil; IR (neat) 2080, 1997 (CO), 1789, 1760 (OCO); ^{1}H NMR ($CDCl_3$) δ=6.10—5.20 (3H, m, HC=), 2.38—2.12 (6H, m, CH_3), 1.00—0.80 (3H, m, CH=); ^{13}C NMR ($CDCl_3$) δ=213.4, 212.6 (CO), 171.2, 170.0 (OCO), 148.0, 146.0 (C=C), 20.5, 20.1 (CH_3); MS m/z 344 (M^+), 316, 288. Found: C, 52.45; H, 3.34%. Calcd for $C_{15}H_{12}O_6Fe$: C, 52.35; H, 3.52%.

6b: Dark red oil; IR (neat) 2075, 1990 (CO), 1790, 1766 (OCO); ^{1}H NMR ($CDCl_3$) δ=6.55—6.20 (3H, m, HC=), 2.66—2.33 (4H, m, CH_2), 1.35—1.16 (6H, m, CH_3); ^{13}C NMR ($CDCl_3$) δ=213.2, 212.3 (CO), 170.6, 170.0 (OCO), 148.3, 142.5 (C=C), 27.5, 26.5 (CH_2), 9.1, 8.6 (CH_3); MS *m/z* 372 (M^+), 344, 316. Found: C, 54.74; H, 4.51%. Calcd for $C_{17}H_{16}O_6Fe$: C, 54.86; H, 4.33%.

Substitution of CO Ligand with $P(OCH_3)_3$ in the Complex 4c. A mixture of **4c** (0.5 mmol), trimethyl phosphite (0.6 mmol), and benzene (5 ml) was heated at 80°C under argon for 20 h. After evapolation of the solvent, the residue was chromatographed on silica gel. Elution with dichloromethane–ethyl acetate (1 : 1) gave **7a** and **7b** (1 : 1) as red oil in 72% yield. R_f values were 0.83 for **7a** and 0.70 for **7b**.

7a: Brown oil; IR (neat) 1958 (CO), 1766 (OCO), 1598 cm^{-1}(FeCO); ^{1}H NMR ($CDCl_3$) δ=7.70—7.00 (4H, m, arom), 5.39 (1H, dd, *J*=2.8, 4.4 Hz, Cp), 5.08—5.04 (1H, m, Cp), 3.64 (9H, d, J_{HP}=11.7 Hz, $POCH_3$), 2.53 (2H, q, *J*=7.5 Hz, CH_2), 2.52 (2H, q, *J*=7.5 Hz, CH_2), 1.20 (3H, t, *J*=7.5 Hz, CH_3), 1.19 (3H, t, *J*=7.5 Hz, CH_3); ^{13}C NMR{^{1}H} ($CDCl_3$) δ=248.4 (d, J_{CP}=32.3 Hz, FeCO), 215.4 (d, J_{CP}=47.0 Hz, CO), 171.1, 170.8 (OCO), 147.2, 145.1 (C=C), 128.0, 127.4, 127.0, 125.7, 124.2, 123.7 (arom), 103.5, 94.1, 92.8 (Cp), 27.5, 26.8 (CH_2), 9.1, 8.8 (CH_3); MS *m/z* 520 (M^+), 492, 464. Found: C, 50.88; H, 4.80%. Calcd for $C_{22}H_{25}O_9PFe$: C, 50.79; H, 4.84%.

7b: Brown oil; IR (neat) 1957 (CO), 1776 (OCO), 1598 cm^{-1}(FeCO); ^{1}H NMR ($CDCl_3$) δ=7.72—7.04 (4H, m, arom), 5.43 (1H, d, *J*=2.8 Hz, Cp), 5.13 (1H, d, *J*=2.8 Hz, Cp), 3.39 (9H, d, J_{HP}=11.7 Hz, $POCH_3$), 2.54 (2H, q, *J*=7.7 Hz, CH_2), 2.52 (2H, q, *J*=7.7 Hz, CH_2), 1.20 (3H, t, *J*=7.7 Hz, CH_3), 1.19 (3H, t, *J*=7.7 Hz, CH_3); ^{13}C NMR {^{1}H} ($CDCl_3$) δ=247.8 (d, J_{CP}=32.4 Hz, FeCO), 218.5 (d, J_{CP}=51.1 Hz, CO), 170.9, 170.8 (OCO), 147.1, 145.3 (C=C), 128.0, 127.4, 126.5, 126.0, 125.7, 124.2 (arom), 105.2, 92.8, 90.7 (Cp), 27.4, 26.8 (CH_2), 9.0, 8.8 (CH_3); MS *m/z* 520 (M^+), 492, 464. Found: C, 50.93; H, 4.87%. Calcd for $C_{22}H_{25}O_9PFe$: C, 50.79; H, 4.84%..

Alkylation of Silylated Cyclopentadiene Derivatives. To a solution of cyclopentadiene derivative (3.0 mmol) in freshly distilled tetrahydrofuran (15 ml) was added at 0°C butyllithium (3.0 mmol, 1.6 M hexane solution) followed by addition of alkyl halide (4.0 mmol). The resulting mixture was stirred at room temperature for 4 h. The usual work-up followed by silica-gel column chromatography afforded the alkylated products. 5-Benzyl-5-trimethylsilyl-1, 3-cyclopentadiene **20** decomposed gradually to give 5-benzyl-1,3-cyclopentadiene via desilylation, whereas silylated indene and fluorene derivatives (**21** and **22**) were stable.

20: ^{1}H NMR ($CDCl_3$) δ=7.24—7.00 (4H, m, arom), 6.55—5.83 (4H, m, Cp), 3.77—3.68 (1H, m, Cp), 2.85 (2H, d, *J*=7.2 Hz, CH_2), 0.01 (9H, s, $SiCH_3$).

21: ^{1}H NMR ($CDCl_3$) δ=7.51—7.22 (5H, m, arom), 3.33 (1H, s, Cp), 2.25 (3H, s, CH_3), −0.03 (9H, s, $SiCH_3$).

22: ^{1}H NMR ($CDCl_3$) δ=7.80—7.10 (8H, m, arom), 1.88 (3H, s, CH_3), 0.01 (9H, s, $SiCH_3$).

X-Ray Structural Determination of 2b. Single crystals of **2b** were grown from a saturated dichloromethane-hexane solution. The crystal data for [η^5-C_5H_4C-($OCOCH_2CH_3$)=C($OCOCH_2CH_3$)CO]Fe(CO)$_2$ (**2b**): $C_{16}H_{14}O_7Fe$, F.W.=374.1. Crystal, data collection, and refinement parameters are given in Table 4. The complex **2b** was crystallized in space group *C*2/*c* with cell dimensions *a*=19.533(7), *b*=12.951(2), *c*=20.241(8) Å, *V*=3321 Å^3, *Z*=8, ρ_{calcd}=1.50 g cm^{-3}. From a crystal of dimensions 0.2×0.2×0.4 mm sealed in an X-ray capillary tube, 3805 independent reflections were measured over a 2 θ range of 3—46° using Mo $K\alpha$ radiation (λ=0.71073 Å). The Fe atom was found from a three dimensional Patterson map, and other nonhydrogen atoms were located by subsequent difference Fourier syntheses. All hydrogen atoms were included at calculated positions. Block diagonal least-squares refinement using 1861 reflections with $|F_o|<4\sigma$ (F_o) converged to final agreement factors R=0.059, R_w=0.083 with GOF=2.24.

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