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Formation of $[\eta^5,\eta^1\text{-}C_5H_4C(OCOR){=}C(OCOR)CO]Fe(CO)_2$ Complexes via Triple CO Insertion into Cyclopentadienyl Anions by $Fe(CO)_5$

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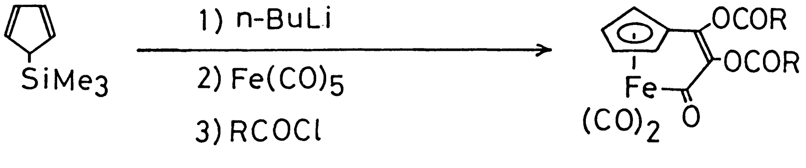
The reaction of cyclopentadienyl anions with $Fe(CO)_5$ in the presence of acyl chlorides gave $[\eta^5,\eta^1\text{-}C_5H_4C(OCOR){=}C(OCOR)CO]Fe(CO)_2$ complexes, accompaning a triple CO insertion into the anions and a double acylation.

Anionic acyliron complexes, derived from the reaction of organolithium or 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. We now report that the reaction of stable carbanions generated from compounds containing a cyclopentadiene ring with $Fe(CO)_5$ in the presence of acyl chlorides affords $[\eta^5,\eta^1\text{-}C_5H_4C(OCOR){=}C(OCOR)CO]Fe(CO)_2$ complexes (Scheme 1). To our knowledge, this reaction constitues the first example of triple CO insertion into organic anions by use of transition-metal carbonyls.



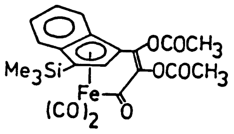
1a 2a-d

2a: R=Methyl 2b: R=Ethyl, 2c: R=Cyclohexyl, 2d: R=Phenyl
Scheme 1.

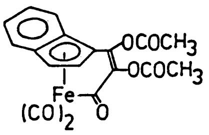
To a solution of 5-trimethylsilyl-1,3-cyclopentadiene (1a, 3.0 mmol) in tetrahydrofuran (15 cm^3) were added successively n-BuLi (3.3 mmol) and $Fe(CO)_5$ (3.0 mmol) at 0 °C, and the mixture was stirred at room temperature for 3 h. Acetyl chloride (6.0 mmol) was then added at 0 °C, and the resulting mixture was stirred at room temperature over night. The solvent was evaporated and the residue was chromatographed on silica gel. Elution with ethyl acetate-benzene (1:9) gave $[\eta^5,\eta^1\text{-}C_5H_4C(OCOR){=}C(OCOR)CO]Fe(CO)_2$ (2a) as yellow crystals in 54% yield. When acetyl chloride was replaced by the other acyl halides, the corresponding 2,3-diacyloxypropenoyliron complexes (2b-d) were obtained. The results are summarized in Table 1.

Table 1. The reaction of cyclopentadienyl anions with $Fe(CO)_5$ in the presence of acyl chlorides

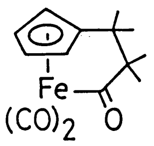
Compd	Acyl chloride	Product	Mp/°C	Yield/%
1a	CH_3COCl	2a	149-150	54
1a	CH_3CH_2COCl	2b	114-115	49
1a	cy-$C_6H_{11}COCl$	2c	105-106	53
1a	C_6H_5COCl	2d	198-199	51
1b	CH_3COCl	2a	149-150	10
1c	CH_3COCl	2e	oil	21
1d	CH_3COCl	2f	oil	18



2e



2f



3

Similar treatments of cyclopentadiene (1b), 1-trimethylsilylindene (1c), and indene (1d) with $Fe(CO)_5$ in the presence of acetyl chloride gave the iron complexes 2a, 2e, and 2f, respectively. The results are also given in Table 1. The desilylation occured in the reaction of 1a, but no desilylation was observed in the reaction of 1c.

The structures of the products were confirmed by their spectral data (Table 2) and elemental analyses.[3] Recently, Eilbracht and coworkers have reported the preparation of 3-(cyclopentadienyl)propionyliron complexes (3) from the reaction of spiro[2.4]hepta-4,6-diene derivatives with $Fe_2(CO)_9$.[4] The comparison of NMR spectra of the iron complexes 2a-d with those of 3 revealed that the spectral characteristics of both of the iron complexes resemble each other, supporting the structure assignment for 2a-d.

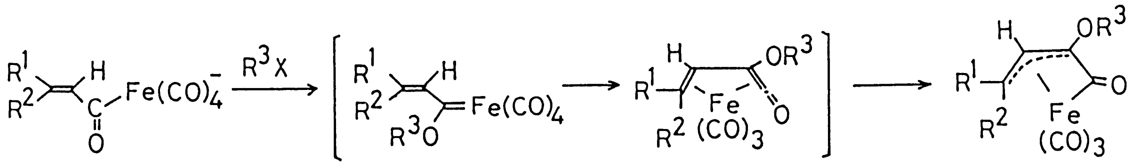
A remarkable feature of this reaction is that the triple CO insertion into cyclopentadienyl anions occurs successively, accompaning double acylations.

The detailed mechanism of the reaction is obscure at present. However, Mitsudo and coworkers have previously reported the reaction of $[(\eta^1\text{-acryloyl})Fe(CO)_4]^-$ 4 with acyl halides to give $(\eta^3,\eta^1\text{-allylacyl})Fe(CO)_3$ 5.[5] They have demonstrated that this reaction proceeds via CO insertion into (η^1-vinylcarbene)iron complexes 6 to form (η^4-vinylketene)iron complexes 7 (Scheme 2). This mechanism suggests that the present reaction also proceeds via the carbene iron complexes (12 and 13) and the ketene iron complexes 14 as represented in Scheme 3.

Table 2. Spectral data of the iron complexes 2a-f

	IR(KBr)			mass	^{1}H NMR(CDCl$_3$)		^{13}C NMR(CDCl$_3$)			
				m/z	ppm			ppm		
2	CO$^{a)}$	CO$^{b)}$	OCO$^{c)}$	(M+)	Cp	CO$^{a)}$	CO$^{b)}$	OCO$^{c)}$	C=C	Cp
2a	2020	1620	1780	346	5.60-5.55(2H,m)	211.6	233.8	166.8	148.2	104.6
	1990		1765		4.93-4.80(2H,m)			166.6	143.7	90.4
										87.6
2b	2018	1608	1775	374	5.68-5.61(2H,m)	211.7	233.8	170.5	148.2	104.8
	1990		1760		4.99-4.88(2H,m)			170.3	143.8	90.3
										87.5
2c	2020	1622	1770	482	5.69-5.57(2H,m)	211.7	233.7	172.0	148.5	105.0
	1990		1765		4.98-4.87(2H,m)			171.7	143.7	90.3
										87.4
2d	2020	1620	1740	470	5.77-5.62(2H,m)	211.3	232.7	162.5	148.4	104.4
	1970		1730		5.05-4.90(2H,m)			162.4	143.7	90.3
										87.5
2e	2040	1620	1780	468	5.44(1H,s)	214.7	238.0	167.2	148.5	97.6
	1980		1765			214.4		167.0	144.0	96.9
										87.5
2f	2040	1620	1780	396	5.42(1H,d,J=2 Hz)	213.8	237.5	166.4	147.8	104.6
	1980		1765		7.70-7.05(1H)$^{d)}$	211.0		166.3	143.7	95.0
										90.3

a) Two terminal carbonyls in [Fe(CO)$_2$] moiety. b) η^1-Propenoyl carbonyl in [C=CCOFe] moiety. c) Acyloxy carbonyls in [C(OAc)=C(OAc)] moiety.
d) Signals of aromatic protons are overlapped with the signals of cyclopentadienyl protons.



4 6 7 5

Scheme 2.

One of the driving forces of this reaction may be the formation of the iron complexes stabilized by the η^5-cyclopentadienyl ligand after triple CO insertion. The silyl group serves as a carbanion stabilizing group and also as a good leaving group.$^{6)}$

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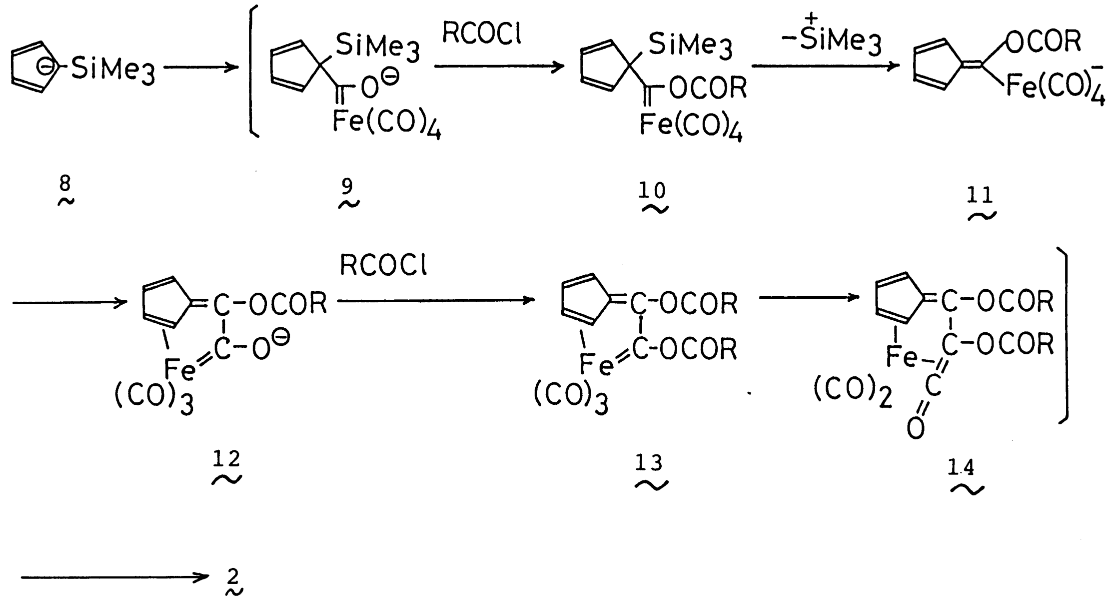

Scheme 3.

References

1) For examples, see: E. O. Fischer, Adv. Organomet. Chem., 14, 1 (1976); D. J. Cardin, Chem. Rev., 72, 545 (1972).

2) Y. Sawa, M. Ryang, and S. Tsutsumi, J. Org. Chem., 35, 4183 (1970); M. F. Semmelhack and J. Park, J. Am. Chem. Soc., 109, 935 (1987) and references cited therein.

3) All the new compounds gave satisfactory elemental analyses for C and H, except oily compounds 2e and 2f. However, both 2e and 2f gave the reasonable spectral properties(mass, IR and NMR) as shown in Table 2.

4) P. Eilbracht, W. Fassmann, and W. Diehl, Chem. Ber., 118, 2314 (1985).

5) T. Mitsudo, Y. Watanabe, H. Nakanishi, I. Morishima, and Y. Takegami, J. Chem. Soc., Dalton, 1978, 1298; T. Mitsudo, A. Ishihara, M. Kadokura, and Y. Watanabe, Organometallics, 5, 238 (1986).

6) The reaction of 1a with n-BuLi in THF at 0 °C, followed by treatment with benzyl bromide at 10 °C, gave 1-benzyl-1-trimethylsilyl-2,4-cyclopentadiene in 68% yield along with a small amount of a mixture of other benzylated trimethylsilylcyclopentadienes. However, the reaction of the anion of 1c generated from 1c and n-BuLi with methyl iodide gave 3-methyl-1-trimethylsilylindene in 77% yield as a sole isolable product. These results suggest that in the case of 1a, the carbanion 8 is a major primary intermediate for the CO insertion reaction and the desilylation occurs probably via the pathway represented in Scheme 3; whereas in the case of 1c, a major primary intermediate for the CO insertion reaction may be 1-trimethylsilyl-3-indenide which leads to 2e without desilylation.

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