Formation of  $[n^5, n^1-c_{5}H_4C(OCOR)=C(OCOR)CO]Fe(CO)_2$ Complexes via Triple CO Insertion into Cyclopentadienyl Anions by Fe(CO)<sub>5</sub>

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The reaction of cyclopentadienyl anions with Fe(CO)<sub>5</sub> in the presence of acyl chlorides gave  $[n^5, n^1-C_5H_4C(OCOR)=C(OCOR)CO]$ Fe(CO)<sub>2</sub> 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)<sub>5</sub>, are key intermediates for the synthesis of Fischer-type carbene iron complexes<sup>1)</sup> and also in organic synthesis.<sup>2)</sup> 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)<sub>5</sub> in the presence of acyl chlorides affords  $[n^5, n^1-C_5H_4C(OCOR)=C(OCOR)CO]Fe(CO)_2$  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.



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<sup>3</sup>) were added successively n-BuLi (3.3 mmol) and Fe(CO)<sub>5</sub> (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  $[n^5, n^1-C_5H_4C(OCOR)=C(OCOR)CO]Fe(CO)_2$  (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.

| Compd                 | Acyl chloride                          | Product | Mp/°C   | Yield/% |
|-----------------------|--|---------|---------|---------|
| la<br>~               | CH3COC1                                | 2a      | 149-150 | 54      |
| $\stackrel{1a}{\sim}$ | сн <sub>3</sub> сн <sub>2</sub> сос1   | 2b<br>≫ | 114-115 | 49      |
| la                    | cy-C <sub>6</sub> H <sub>11</sub> COC1 | 2c      | 105-106 | 53      |
| la                    | C <sub>6</sub> H <sub>5</sub> COC1     | 2d      | 198-199 | 51      |
| 1b                    | CH3COC1                                | 2a      | 149-150 | 10      |
| 1c                    | CH3COC1                                | 2e      | oil     | 21      |
| 1d                    | CH <sub>3</sub> COC1                   | 2f      | oil     | 18      |

Table 1. The reaction of cyclopentadienyl anions with Fe(CO)<sub>5</sub> in the presence of acyl chlorides



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.<sup>3)</sup> 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  $Fe_2(CO)_9$ .<sup>4)</sup> 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  $[(n^1-acryl$  $oyl)Fe(CO)_4]^- 4$  with acyl halides to give  $(n^3, n^1-allylacyl)Fe(CO)_3 5.^{5}$ They have demonstrated that this reaction proceeds via CO insertion into  $(n^1-vinylcarbene)$  iron complexes 6 to form  $(n^4-vinylketene)$  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.

| IR(KBr) |                  |                  |                   | mass        | <sup>1</sup> H NMR(CDC1 <sub>3</sub> ) | <sup>13</sup> C NMR(CDCl <sub>3</sub> ) |                  |                          |       |       |
|---------|------------------|------------------|-------------------|-------------|--|---|------------------|--------------------------|-------|-------|
| 2~      | co <sup>a)</sup> | co <sup>b)</sup> | oco <sup>c)</sup> | m/z<br>(M+) | ppm<br>Cp                              | co <sup>a)</sup>                        | co <sup>b)</sup> | ppm<br>OCO <sup>C)</sup> | 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  |
| 2đ      | 2020             | 1620             | 1740              | 470         | 5.77-5.62(2H,m)                        | 211.3                                   | 232.7            | 162.5                    | 148.4 | 104.4 |
| $\sim$  | 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  |
| $\sim$  | 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 |
| $\sim$  | 1980             |                  | 1765              |             | 7.70-7.05(1H) <sup>d)</sup>            | 211.0                                   |                  | 166.3                    | 143.7 | 95.0  |
|         |                  |                  |                   |             |  |   |                  |                          |       | 90.3  |
|         |                  |                  |                   |             |  |   |                  |                          |       |       |

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

a) Two terminal carbonyls in [Fe(CO)<sub>2</sub>] moiety. b) n<sup>1</sup>-Propencyl 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.



Scheme 2.

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

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Scheme 3.

## References

- For examples, see: E. O. Fischer, Adv. Organomet. Chem., <u>14</u>, 1 (1976);
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- 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.
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- 5) T. Mitsudo, Y. Watanabe, H. Nakanishi, I. Morishima, and Y. Takegami, J. Chem. Soc., Dalton, <u>1978</u>, 1298; T. Mitsudo, A. Ishihara, M. Kadokura, and Y. Watanabe, Organometallics, 5, 238 (1986).
- 6) The reaction of la with n-BuLi in THF at 0 °C, followed by treatment with benzyl bromide at 10 °C, gave 1-benzyl-1-trimethylsilyl-2,4-cyclopenta-diene 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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