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Notes

Dimerization of Aromatic Aldehydes Catalyzed by K[CpFe(CO)$_2$]

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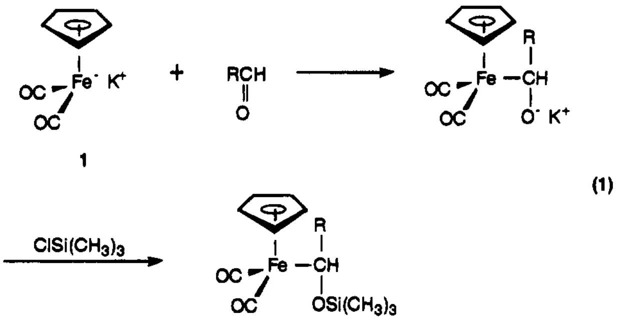
Summary: K[CpFe(CO)$_2$] was found to be an efficient catalyst for the dimerization of aromatic aldehydes to carboxylic esters. In the reactions of para-substituted aromatic aldehydes, the reactivity increased with a decrease in the electron density of their carbonyl carbon. On the basis of these results, the reaction mechanism including the nucleophilic attack of [CpFe(CO)$_2$]$^-$ (Fp anion) at the carbonyl carbon is discussed.

Various metal carbonyl complexes are utilized as catalysts or as quantitative reagents in a wide variety of synthetic reactions.[1–3] Previously, we have reported that dianionic carbonyl complexes such as disodium and dipotassium tetracarbonylferrate ($M_2[Fe(CO)_4]$; M = Na, K) or disodium pentacarbonylchromate ($Na_2Cr(CO)_5$) have been shown to be good catalysts for disproportional dimerization of two molecules of aldehyde to carboxylic ester,[4,5] for example dimerization of two molecules of benzaldehyde to benzyl benzoate, which is used as a solvent for artificial musk, as a perfume fixative, in confectionery, and in chewing gum flavors.

On the other hand, the monoanionic carbonyl complexes $MCpFe(CO)_2$ (M = Na, K) also have been shown to be valuable reagents for various organic and inorganic syntheses. For example, Rosemblum *et al.* reported useful reactions which proceeded via an (η^1-allyl)Fp or (η^2-alkene)Fp$^+$ complex as an intermediate,[6] and (η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH$_3$ has been utilized in various asymmetric syntheses.[7]

More recently, Hossain *et al.* have reported the syntheses of (α-siloxybenzyl)iron complexes **2** from 1 equiv of K[CpFe(CO)$_2$] (**1**) and 1.2–4 equiv of aromatic aldehydes at −78 °C for 1–3 h, followed by trapping the resulting alkoxide with 1–2 equiv of trimethylsilyl chloride[8] (eq 1). We have found, however, that the reaction of aromatic aldehydes with **1** gave completely different results at room temperature; i.e., **1** catalyzed the dimerization of aromatic aldehydes and gave the corresponding esters (eq 2). Furthermore, **1** has much greater catalytic activity than the dianionic complexes previously reported. Now, in this paper, we wish to report the complex **1** catalyzed dimerization of aromatic aldehydes and discuss the reaction mechanism.



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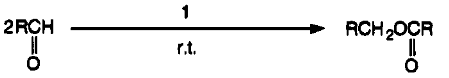
(1)

2a: R = C_6H_5
2b: R = p-$CH_3OC_6H_4$
2c: R = p-ClC_6H_4
2d: R = p-$CH_3C_6H_4$



$$2\underset{\underset{O}{\|}}{RCH} \xrightarrow[\text{r.t.}]{\mathbf{1}} RCH_2O\underset{\underset{O}{\|}}{C}R \qquad (2)$$

3a: R = C_6H_5
3b: R = p-$CH_3OC_6H_4$
3c: R = p-ClC_6H_4

Table 1 illustrates the investigation of the catalytic activity of **1** for the dimerization of benzaldehyde. Benzaldehyde (5–100 equiv) was added to 1 equiv of **1** in THF, and the mixture was stirred at room temperature for a certain reaction time under an argon atmosphere. In our previous studies, the maximum turnover number was 21, obtained by using $Na_2Cr(CO)_5$ at 60 °C after 18 h,[5] whereas it is worth noting that **1** reacted with 100 equiv of benzaldehyde to give **3a** in 95.6% yield (turnover number 48) at room temperature. The catalytic activity of **1** was found to be much greater than that of $M_2Fe(CO)_4$ (M = Na, K) and $Na_2Cr(CO)_5$.

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[1] McQuillin, F. J.; Parker, D. G.; Stephenson, G. R. *Transition Metal Organometallics for Organic Synthesis*; Cambridge University Press: Cambridge, U.K., 1991.

[2] Harrington, P. J. *Transition Metals in Total Synthesis*; Wiley: New York, 1991.

[3] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988.

[4] Yamashita, M.; Ohishi, T. *Appl. Organomet. Chem.* **1993**, *7*, 357 and references cited therein.

[5] Ohishi, T.; Matsumoto, T.; Yamashita, M. *Appl. Organomet. Chem.* **1994**, *8*, 107.

[6] Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191.

[7] Liebeskind, L. S.; Welker, M. E.; Fengel, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (b) Davies, S. G.; Easton, R. J. C.; Sutton, K. H.; Walker, J. C.; Jones, R. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 489. (c) Davies, S. G.; Gravatt, G. L. *J. Chem. Soc., Chem. Commun.* **1988**, 780.

[8] (a) Vargas, R. M.; Theys, R. D.; Hossain, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 777. (b) Vargas, R. M.; Hossain, M. M. *Tetrahedron Lett.* **1993**, *34*, 2727.

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Table 1. Reaction of Benzaldehyde with 1 at Room Temperature

run no.	benzaldehyde/1 molar ratio	time, h	yield,[a,b] %
1	5	1.5	90.0
2	10	2	94.5
3	20	3	91.3
4	100	3	95.6

[a] Yields were determined by GC. [b] Based on the amount of benzaldehyde.

Table 2. Reaction of Benzaldehyde with 1[a] at Various Reaction Temperatures

	reaction conditions		
run no.	*T*, °C	time, h	yield,[b,c] %
1	−78	4	
2	−20	4	trace
3	0	9	82.9
4	10	3	82.6
5	room temp	2	94.5
6	60	0.5	99.2

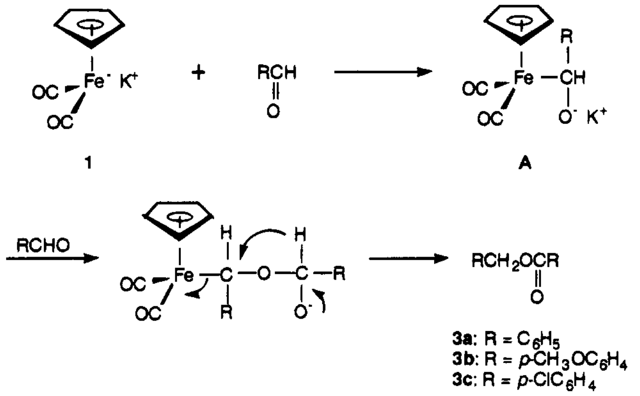
[a] The benzaldehyde/1 molar ratio was 10 in all cases. [b] Yields were determined by GC. [c] Based on the amount of benzaldehyde.

Table 3. Reaction of Aromatic Aldehydes with 1 at Room Temperature

run no.	aldehyde (amt, mmol)	amt of 1, mmol	time, h	yield,[a,b] %
1	C_6H_5CHO (30)	3	2	94.5
2	ClC_6H_4CHO (30)	3	1	98.9
3	$H_3COC_6H_4CHO$ (30)	3	3	14.8

[a] Yields were determined by GC. [b] Based on the amount of benzaldehyde.

Scheme 1



1

A

3a: R = C_6H_5
3b: R = p-$CH_3OC_6H_4$
3c: R = p-ClC_6H_4

Table 2 presents the results of the reaction of **1** and benzaldehyde at various temperatures. At −78 and −20 °C, no **3a** was obtained and only benzaldehyde was recovered. At 0 °C or above, the dimerization proceeded and **3a** was obtained in good yield. This shows that 0 °C is a boundary condition for the dimerization. The reaction was completed in a shorter time at higher temperature.

Under similar conditions, several *para*-substituted aromatic aldehydes gave the corresponding esters. The results of these reactions are listed in Table 3. *p*-Chlorobenzaldehyde, having an electron-withdrawing substituent on the benzene ring, gave the ester **3b** in 98.9% yield, but *p*-anisaldehyde, having an electron-releasing group, produced the ester **3c** only in 14.8% yield. The aldehyde reactivities are influenced by the electron density on their carbonyl carbon.

On the basis of these results, the reaction mechanism is discussed (Scheme 1). First, $[CpFe(CO)_2]^-$ (Fp anion) attacks the carbonyl carbon of the aldehyde nucleophilically to give the adduct **A**. This step is the same as that in Hossain's report,[8] and **A** is enough stable to trap by trimethylsilyl chloride at −78 °C. However, above 0 °C, the addition of the second aldehyde to **A** took place, followed by the loss of the Fp anion, to give the esters. The Fp anion attacks the carbonyl carbon of the other aldehyde again as a catalyst. This mechanism is supported by investigations of the effect of substituents upon the reactivity of *para*-substituted benzaldehydes. It is roughly similar to that of the well-known variations of the base-induced dismutation of aldehydes.[9]

Experimental Section

General Comments. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Hitachi R-600 FT-NMR spectrometer operating at 60 MHz. Peak positions are reported in parts per million relative to tetramethylsilane internal standard. Spectra which were recorded with off-resonance decoupling have peaks reported as singlets (s), doublets (d), triplet(t), quartets (q), or multiplets (m). Infrared (IR) spectra were recorded on a Hitachi 260−10 spectrometer as Nujol mulls (for solids) or liquid films (for liquids). Mass spectra were recorded on a Hitachi M-80B or Shimadzu GCMS-QP2000A instrument. Gas chromatography was performed on a Shimadzu Model GC-14A equipped with a capillary column (CBP 1-W12-100, 0.53 mm i.d. × 12 m) using helium as carrier gas. All melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected.

Column chromatography was done with E. Merck silica gel 60 (230−400 mesh). Analytical thin-layer chromatography (TLC) was done on a 0.25 mm thickness of E. Merch silica gel 60 F-254.

Tetrahydrofuran (THF) was dried and distilled under an argon atmosphere from potassium benzophenone just before use. The complex **1** is prepared by reduction of $[CpFe(CO)_2]_2$ using potassium benzophenone ketyl[10] or $K(s\text{-}C_4H_9)_3BH$.[11] The aldehydes were all commercial products; they were dehydrated over $CaSO_4$ and distilled before use. Other reagents were all commercial products and were used without further purification.

Preparation of Esters. In a typical procedure, 20 mmol of the aldehyde was added to a solution of 2 mmol of **1** in 4 mL of tetrahydrofuran, and the mixture was stirred at room temperature for a certain reaction time under an argon atmosphere. Then the mixture was poured into 20 mL of water and extracted with diethyl ether. After they were dried over $MgSO_4$, the organic extracts were concentrated. The residual crude products were purified by column chromatography. The esters thus obtained were identified by means of their spectral data (IR, NMR, and MS) and by comparison of the retention time of the GLC with those of authentic samples; the yields were determined using internal standards.

Benzyl Benzoate (3a): IR (liquid film) ν 3050, 1730, 1460, 1280, 1120, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.34 (s, 2H), 7.08−8.18 (m, 10H); GC/MS *m/z* (relative intensity) 212 (M^+, 23), 105 (100), 91 (56), 77 (40), 51 (25).

***p*-Methoxybenzyl *p*-Methoxybenzoate (3b):** IR (liquid film) ν 3000, 2860, 1720, 1620, 1520, 1270, 1180, 1120, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (s, 3H), 3.81 (s, 3H), 5.24 (s, 2H), 6.74−8.10 (m, 8H); GC/MS *m/z*(relative intensity) 272 (M^+, 15), 135 (43), 121 (100), 77 (26).

***p*-Chlorobenzyl *p*-Chlorobenzoate (3c):** mp 63−64 °C; IR (Nujol) ν 1740, 1610, 1290, 1220, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.30 (s, 2H), 7.23−8.12 (8H, m, 8H); GC/MS *m/z* (relative intensity) 280 (M^+, 9), 139 (48), 125 (30), 86 (100), 58 (27).

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[9] Geissman, T. A. *Organic Reactions*; Wiley: New York, 1957.
[10] Plotokin, J. S.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 284.
[11] Ohishi, T.; Shiotani, Y.; Yamashita, M. *J. Org. Chem.* **1994**, *59*, 250.