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Redox Reaction of Aromatic Aldehydes with $Fe_3(CO)_{12}$

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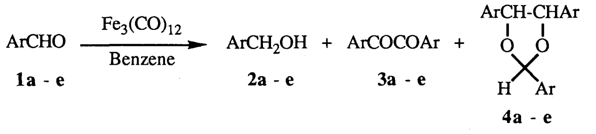
Aromatic aldehydes react with $Fe_3(CO)_{12}$ in refluxing benzene ultimately to give arylmethyl alcohols and 1,2-diaryl-1,2-ethanedione in a 1:1 ratio. In some cases, small amounts of 2,4,5-triaryl-1,3-dioxolanes are formed as minor products. Dinuclear iron complex (1,2-diphenyl-1,2-ethanedioxido)$Fe_2(CO)_7$ has been isolated as an intermediate in the reaction of benzaldehyde with $Fe_3(CO)_{12}$. The mechanism of this redox reaction of aromatic aldehydes are discussed on the basis of the kinetic study of the reaction and also of the reactivity of the isolated dinuclear iron complex.

Iron carbonyl complexes induce a variety of organic transformations.[1] However, no systematic information is yet available, especially about the chemical properties of polynuclear iron complexes. Previously, we reported that a trinuclear iron complex $Fe_3(CO)_{12}$ has a strong reducing ability toward oxygen-containing compounds and induces the reductive deoxygenation of 1,2-oxazines to give pyrroles.[2] We now report the reactivity features of $Fe_3(CO)_{12}$ toward aromatic aldehydes.

Takegami and co-workers have reported that aromatic aldehydes undergo a Tishchenko type reaction to give esters upon treating with $Na_2Fe(CO)_4$.[3] In this reaction, the ferrate complex acts as both of base and hydride-transfer agent. However, neutral iron complexes such as $Fe(CO)_5$ and $Fe_2(CO)_9$ exhibit no or little reactivity toward aromatic aldehydes in less polar solvents under ordinary conditions. We now report that $Fe_3(CO)_{12}$ gives rise to the redox reaction of aromatic aldehydes in benzene to afford arylmethyl alcohols and 1,2-diaryl-1,2-ethanediones as major products. We also discuss the mechanistic features of this reaction on the basis of the reactivity of a dinuclear iron complex isolated from the reaction mixture and also of the kinetic study of the reaction.

Results and Discussion

Reaction of Aromatic Aldehydes with $Fe_3(CO)_{12}$. The reaction of benzaldehyde (**1a**) with one tenth molar equiv of $Fe_3(CO)_{12}$ in refluxing benzene for 20 h, followed by acidification of the reaction mixture with an aqueous HCl, gave benzyl alcohol (**2a**) and 1,2-diphenyl-1,2-ethanedione (**3a**) approximately in a 1:1 ratio, along with a small amount of 2,4,5-triphenyl-1,3-dioxolane (**4a**). These products, except **2a**, were formed only after treating the reaction mixture with an aqueous HCl. Other aromatic aldehydes (**1b**—**e**) reacted similarly with $Fe_3(CO)_{12}$, giving arylmethyl alcohols (**2b**—**e**) and 1,2-diaryl-1,2-ethanediones (**3b**—**e**) as major products. In some cases, 1,3-dioxolanes were obtained as minor products. The results are given in Table 1. For this reaction, $Fe(CO)_5$ was



a : Ar=C_6H_5 **b** : Ar=p-$CH_3C_6H_4$ **c** : Ar=p-$CH_3OC_6H_4$ **d** : Ar=p-ClC_6H_4
e : Ar=2-Furyl

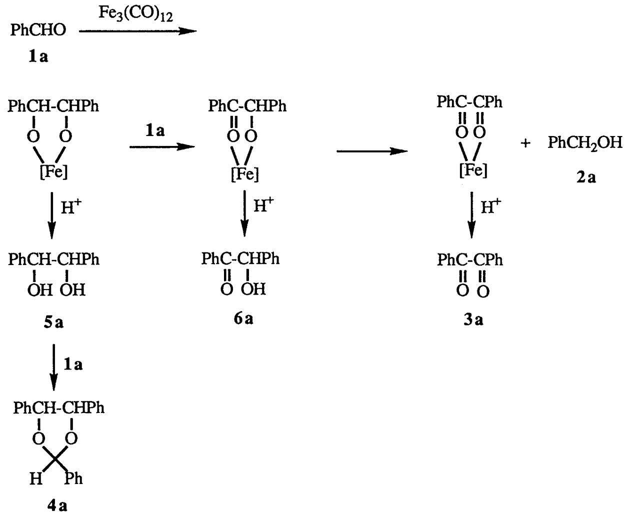
Table 1. Reaction of Aromatic Aldehydes with Iron Carbonyls[a)]

ArCHO	Iron carbonyl	Products[b)] (yield/%[c)])		
		Alcohol	Diketone	1,3-Dioxolane
1a: Ar=C_6H_5	$Fe(CO)_5$	**2a** (Trace)	**3a** (Trace)	**4a** (Trace)
1a:	$Fe_2(CO)_9$	**2a** (3.0)	**3a** (4.5)	**4a** (Trace)
1a:	$Fe_3(CO)_{12}$	**2a** (56)	**3a** (56)	**4a** (4.0)
1b: Ar=*p*-$CH_3C_6H_4$	$Fe_3(CO)_{12}$	**2b** (60)	**3b** (65)	**4b** (3.0)
1c: Ar=*p*-$CH_3OC_6H_4$	$Fe_3(CO)_{12}$	**2c** (38)	**3c** (38)	**4c** (Trace)
1d: Ar=*p*-ClC_6H_4	$Fe_3(CO)_{12}$	**2d** (60)	**3d** (64)	**4d** (Trace)
1e: Ar=Furyl	$Fe_3(CO)_{12}$	**2e** (18)	**3e** (18)	—

a) The reaction was carried out in refluxing benzene for 20 h by using an excess aldehyde (20 mmol) and an iron complex ($Fe(CO)_5$: 6.0 mmol, $Fe_2(CO)_9$: 3.0 mmol, $Fe_3(CO)_{12}$: 2.0 mmol). b) The products **3a**—**e** and **4a**—**d** were isolated after acidification of the reaction mixtures with an aqueous HCl. c) Isolated yields based on iron carbonyls used.

ineffective, and $Fe_2(CO)_9$ was effective but its efficiency was extremely low as compared with that of $Fe_3(CO)_{12}$.

To elucidate the reaction pathways, kinetic study for the reaction of **1a** with $Fe_3(CO)_{12}$ was carried out under the same conditions as those of the preparative reaction. The reaction was followed by analyzing products produced at appropriate time intervals. The result is shown in Fig. 1. This result suggests that the reaction proceeds via the pathways outlined in Scheme 1. An important feature of this reaction is that **3a**, **5a**, and **6a** exist in the reaction mixture as their iron complexes which can be hydrolyzed with HCl. In the actual reaction, the iron complex of 1,2-diphenyl-1,2-ethanediol (**5a**) is produced at the initial stage. This is converted to final products **2a** and **3a** via the iron complex of 2-hydroxy-1,2-diphenylethanone (**6a**). A separate experiment indicated that in the conversion of the iron complexes of **5a** to **3a**, **1a** acts as a hydrogen acceptor; hence **2a** and **3a** are produced in a 1:1 molar ratio (see later). The acid hydrolysis of the iron complexes gives **3a**, **5a**, and **6a**. Compound **4a** can be formed by the acid-catalyzed condensation of **5a** with **1a**.



Scheme 1.

Isolation Intermediary Iron Complex. Compound **1a** was allowed to react with $Fe_3(CO)_{12}$ in benzene at 80 °C for 30 min. Careful work-up of the reaction mixture gave (1,2-diphenyl-1,2-ethanedioxido)$Fe_2(CO)_7$ (**7**) in a 46% yield. The same iron complex was also obtained by treating **5a** with $Fe_3(CO)_{12}$ in benzene. The structural formula of this complex was assigned from its spectral data and elemental analysis. The elemental analysis was consistent with the assigned structural formula. In the mass spectrum, the parent peak (M^+, *m/z* 520) was not observed. However, several fragment peaks that support the assigned structural formula were observed. The peaks appeared at *m/z* 518 (M^+-H_2) and 504 (M^+-16) that are assignable to $[(PhCOCOPh)Fe_2(CO)_7]^+$ and $[(PhCH{=}C(OH)Ph)Fe_2(CO)_7]^+$ or $[(PhCH_2COPh)Fe_2(CO)_7]^+$, re-

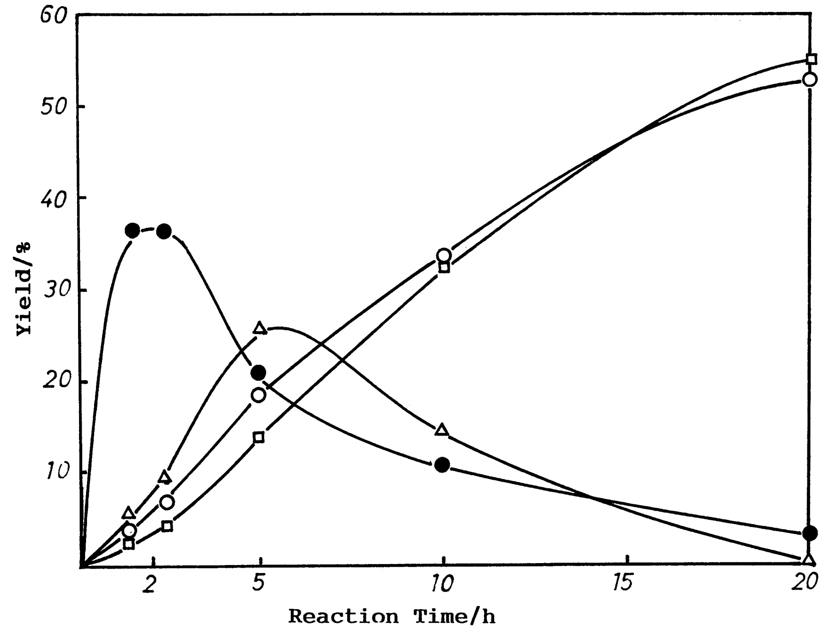
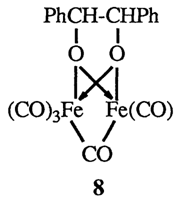


Fig. 1. Kinetic study of the reaction of **1a** with $Fe_3(CO)_{12}$ (**1a**: 20 mmol, $Fe_3(CO)_{12}$: 2.0 mmol, benzene: 15 cm^3. Reaction temperature: 80 °C). ○: Benzyl alcohol (**2a**), □: 1,2-Diphenyl-1,2-ethanedione (**3a**), ●: 1,2-Diphenyl-1,2-ethanediol (**5a**)+2,4,5-triphenyl-1,3-dioxolane (**4a**), △: 2-Hydroxy-1,2-diphenylethanone (**6a**). Compounds **3a**, **4a**, **5a**, and **6a** were isolated after acidification of the reaction mixture with an aqueous HCl.

spectively. Organic fragments were also observed at *m/z* 214, 210, 196, and 107 which can be assigned to $[PhCH(OH)CH(OH)Ph]^+$, $[PhCOCOPh]^+$, $[PhCH_2COPh]^+$, and $[PhCHOH]^+$, respectively. Similar fragmentation pattern was observed in the mass spectrometry of **5a** which is the organic ligand of the complex.[4] The IR spectrum in a KBr disk showed complex absorptions due to the CO ligands attached to Fe at 2035, 1990, 1980, 1965, 1950, 1930, and 1815 cm^{-1}. The lowest absorption suggests the existence of one bridging CO ligand. The ^1H NMR spectrum in $CDCl_3$ exhibited two broad signals at δ=4.88 and 7.28 in the relative intensities of 1:5. These signals can apparently be assigned to the methylidyne and phenyl groups, respectively. The ^{13}C NMR spectrum in $CDCl_3$ at room temperature showed only one broad signal for the CO carbon atom at δ=211.9 where is the region of terminal CO ligands in binuclear iron complexes.[5] This implies that all seven CO groups are scrambled rapidly over two Fe atoms on the NMR time scale at room temperature in a $CDCl_3$ solution. This result indicates that the complex is a sort of a fluxional molecule in the sense that bridging and terminal CO groups are interchanging with each other. This kind of fluxionality in CO ligands has been found also in the other binuclear Fe complexes such as $(Ph_2PCH_2PPh_2)Fe_2(CO)_7$[5] and (1,2-diazine)$Fe_2(CO)_7$.[6] The other feature in the ^{13}C NMR spectrum was that the CH carbon signal in the organic ligand initially appeared at δ=78, but this signal gradually disappeared. This suggests that $[PhCH(O)CH(O)Ph]Fe_2(CO)_7$ is converted to $(PhCOCOPh)Fe_2(CO)_7$ during the NMR measurement. The instability and the limited solubility at lower temperatures of this complex have prevented us from obtaining more detailed information about the structure of the complex. However, from the above results, we propose **8** as a tentative structure of complex **7** by reference to the established structures of dinuclear Fe complexes of the type $XYFe_2(CO)_7$;[5,6] in this structure, the formal 18 electron configuration is attained at each Fe atom.



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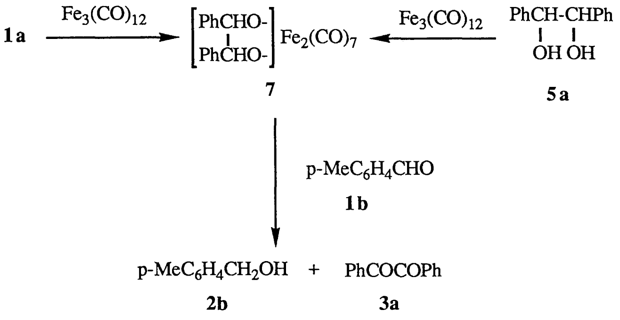
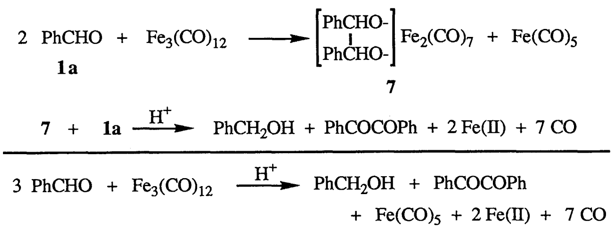
Reaction of Intermediary Iron Complex. Treatment of **7** with excess *p*-methylbenzaldeyde (**1b**) in benzene at 80 °C for 15 h afforded *p*-methylbenzyl alcohol (**2b**) and **3a** in a 1:1 molar ratio in good yields. These products were formed after acidification of the reaction mixture with an aqueous HCl. The results are summarized in Scheme 2.



Scheme 2.



Scheme 3.

Stoichiometry. The reaction of **1a** with one tenth molar equiv of $Fe_3(CO)_{12}$ in benzene was carried out in a sealed vessel. This enabled measurement of the volume of a gas evolved during the reaction. The reaction was started by heating the system at 80 °C. The gas evolution started after 3 h, and ceased after 20 h. A comparison of this result with that of Fig. 1 indicates that CO starts to evolve after **1a** is converted to **7**. The GLC analysis of the evolved gas showed that approximately seven molar equiv of CO are evolved from one molar equiv of $Fe_3(CO)_{12}$ at the end of the reacion.

In a separate experiment, a volatile material produced from the reaction of **1a** with $Fe_3(CO)_{12}$ was collected in a cooled vessel. The collected liquid was identified as $Fe(CO)_5$ from its characteristic IR spectrum. Furthermore, the quantitative analysis of this liquid after converting it to Fe(II) ion by oxidizing with nitric acid indicated that one molar equiv of $Fe(CO)_5$ is produced from one molar equiv of $Fe_3(CO)_{12}$. In this reaction, the production of $Fe(CO)_5$ ceased within 1.5 h. This result indicates that $Fe(CO)_5$ is formed only at the initial stage of the reaction. All of the above results can be explained in terms of the stoichiometric equations shown in Scheme 3.

The initial step is the formation of the diiron complex **7** by the reaction of **1a** with $Fe_3(CO)_{12}$, accompanied with elimination of $Fe(CO)_5$. At the second step, the iron complex reacts further with **1a** to give **2a** and the iron complex of **3a** with evolution of CO, probably accompanying production of Fe(II) ion. During this reaction, hydride migration occurs from **7** to **1a**. This reaction may be assisted by an intramolecular electron transfer from $[Fe_2(CO)_7]$ to the 1,2-diphenyl-1,2-ethanedioxido ligand in **7**.

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded on HITACHI R-24B and JEOL FT-270 spectrometers using TMS as an internal standard. The IR, UV, and MS spectra were taken with Shimadzu IR 27G, Hitachi 228, and JEOL JMS-DX300 spectrometers, respectively. GLC analyses were performed on a Shimadzu GC 4CPF chromatograph using a column packed with SE 30 (10%) (3 mm×1 m). Aromatic aldehydes were all commercial products and purified by distillation prior to use. Benzene was purified by a standard procedure and stored under an argon atmosphere. 1,2-Diphenyl-1,2-ethanediol was prepared from 2-hydroxy-1,2-diphenylethanone.[7] Pentacarbonyliron (0) was a commercial product and used without further purification. Nonacarbonyldiiron (0)[8] and dodecacarbonyltriiron (0)[9] were prepared from $Fe(CO)_5$.

General Procedure for the Reaction of Aromatic Aldehydes with Iron Carbonyls. A mixture of benzaldehyde (20 mmol) and $Fe_3(CO)_{12}$ (2.0 mmol) in benzene (15 cm^3) was heated with stirring at 80 °C for 20 h under N_2 atmosphere, and then acidified with 6 M HCl (10 cm^3, 1 M=1 mol dm^{-3}) at room temperature. The mixture was extracted with ether (30 cm^3). The extract was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue on silica gel successively with benzene, benzene/ether (9/1), and hexane gave 1,2-diphenyl-1,2-ethanedione, benzyl alcohol, and 2,4,5-triphenyl-1,3-dioxolane in 56%, 56%, and 4% yields, respectively. The reactions of other aldehydes with $Fe_3(CO)_{12}$ were carried out in a similar manner. The results are summarized in Table 1. The products were identified by comparison of their IR and NMR spectra with those of authentic specimens. In all cases, when GLC analyses of the reaction mixtures were carried out before acidification with HCl, only benzyl alcohols were detected. Spectral data of the products were as follows.

2a: Bp 205.0—206.0 °C; IR(neat) 3300, 1036, 1022, 736, 696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.81 (s, 1H), 4.68 (s, 2H), 7.24 (m, 5H).

2b: Mp 59.5—60.2 °C; IR(neat) 3400, 1035, 812 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.88 (s, 1H), 2.36 (s, 3H), 4.60 (s, 2H), 7.17 (m, 4H).

2c: Mp 23.2—24.0 °C; IR(neat) 3400, 1030, 815 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.93 (s, 1H), 3.80 (s, 3H), 4.55 (s, 2H), 6.83 (d, J=4.12 Hz, 2H), 7.24 (d, J=4.12 Hz, 2H).

2d: Mp 72.4—73.2 °C; IR(neat) 3400, 1030, 830 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.10 (s, 1H), 4.59 (s, 2H), 7.26 (s, 4H).

2e: Bp 168—170 °C; IR(neat) 3380, 1145, 1020, 740 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.70 (s, 1H), 4.50 (s, 2H), 6.15 (m, 2H), 7.32 (m, 1H).

3a: Mp 94.5—94.9 °C; IR (KBr) 1655, 1592, 1210, 716 cm^{-1}; ^{1}H NMR δ=7.21—7.65 (m, 6H), 7.67—8.02 (m, 4H).

3b: Mp 104—105 °C; IR(KBr) 3060, 2920, 1665, 1600, 1210, 1165 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.38 (s, 6H), 7.16 (d, J=4.10 Hz, 4H), 7.76 (d, J=4.10 Hz, 4H).

3c: Mp 132—133 °C; IR(KBr) 3030, 1660, 1600, 1210 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.83 (s, 6H), 6.89 (d, J=4.12 Hz, 4H), 7.86 (d, J=4.12 Hz, 4H).

3d: Mp 195—196 °C; IR(KBr) 3030, 1665, 1600, 1165 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=7.36 (d, J=4.12 Hz, 4H), 7.89 (d, J=4.12 Hz, 4H).

3e: Mp 163—165 °C; IR(KBr) 2835, 1645, 1450, 751 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=6.59 (dd, J=1.80, 3.53 Hz, 2H), 7.58 (d, J=3.53 Hz, 2H), 7.73 (d, J=1.80 Hz, 2H).

4a: Mp 83—84 °C; IR(KBr) 3030, 2840, 1606, 1100, 1065, 1015, 1000, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=4.68 (s, 2H), 6.18 (s, 1H), 7.08—7.26 (m, 15H).

4b: Mp 87—89 °C; IR(KBr) 3030, 2920, 1610, 1120, 1080, 1035, 1020, 810 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.23 (s, 9H), 4.58 (s, 2H), 6.12 (s, 1H), 6.88—7.34 (m, 12H).

4c: Mp 102—103 °C; IR(KBr) 3030, 2930, 1605, 1230, 1080, 1035, 1020, 805 cm^{-1}; ^{1}H NMR δ=3.73 (s, 9H), 4.67 (s, 2H), 6.18 (s, 1H), 6.55—7.56 (m, 12H).

4d: Mp 97—98 °C; IR(KBr) 3030, 2940, 1610, 1120, 1085, 1035, 835, 810 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=4.60 (s, 2H), 6.15 (s, 1H), 7.06—7.70 (m, 12H).

Kinetic Study of Reaction of 1a with $Fe_3(CO)_{12}$. A solution of **1a** (20 mmol) and $Fe_3(CO)_{12}$ (2.0 mmol) in benzene (15 cm^3) was heated under N_2 at 80 °C for a given period of time. The mixture was acidified with aqueous 6M HCl (10 cm^3). The benzene solution was washed with water, dried, and analyzed by GLC using pyrene as an internal standard. The product analyses were performed in a similar manner by changing reaction time. The results are shown in Fig. 1.

5a: Mp 116.2—119.0 °C; IR(KBr) 3630, 3520, 3380, 3060, 2980, 1190, 1038, 770, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=4.43 (s, 2H), 4.53 (s, 2H), 7.10 (m, 10H).

6a: Mp 132—134 °C; IR(KBr) 3450, 3050, 2980, 1680, 1600, 1283, 1260, 1085, 1068, 978, 680 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=4.50 (br d, 1H), 5.89 (br d, 1H), 7.26—7.40 (m, 8H), 7.73—7.92 (m, 2H).

Isolation of Iron Carbonyl Complex Produced from Reaction of 1a with $Fe_3(CO)_{12}$. A solution of benzaldehyde (20 mmol) and $Fe_3(CO)_{12}$ (2.0 mmol) in benzene (15 cm^3) was heated at 80 °C under N_2 for 30 min. The solvent was evaporated and the residue was washed with ether and then with petroleum ether until excess of benzaldehyde and $Fe_3(CO)_{12}$ were completely removed. The residual solid was dissolved in THF (10 cm^3) and filtered. Concentration of the filtrate gave 480 mg of a dark brown solid. The IR spectral data of the solid were identical in all respects with those of the complex which was prepared from 1,2-diphenyl-1,2-ethanediol (see below).

Preparation of (1,2-Diphenyl-1,2-ethanedioxido)$Fe_2(CO)_7$. All operations were performed under argon. A solution of 1,2-diphenyl-1,2-ethanediol (1.0 mmol) and $Fe_3(CO)_{12}$ (1.0 mmol) in benzene (10 cm^3) was heated at 80 °C for 3 h. The resulting mixture was evaporated to dryness under reduced pressure, and the residue was washed several times with petroleum ether. The residue was taken up in THF (10 cm^3) and filtered. Evaporation of the filtrate gave 260 mg of (1,2-diphenyl-1,2-ethanedioxido)$Fe_2(CO)_7$ as a dark brown solid. IR(KBr) 2035 (s), 1990 (s), 1980 (s), 1965 (sh), 1950 (m), 1930 (sh), 1815 cm^{-1} (m). ^{1}H NMR (CDCl$_3$) δ=4.88 (br s, 2H), 7.28 (br s, 10H). ^{13}C NMR (CDCl$_3$) δ=78.0, 127.3, 128.2, 128.3, 211.9. Found: C, 48.02; H, 2.56; Fe, 21.50%. Calcd for $C_{21}H_{12}O_9Fe_2$: C, 48.50; H, 2.33; Fe, 21.48%. FD-MS (rel intensity) m/z 518 (0.7), 392 (3), 214 (100), 210 (12), 196 (12), 107 (145) under rapidly increasing emitter current intensities, and m/z 504 (2.5), 214 (37), 210 (100), 197 (7), 107 (147 under slowly increasing current intensities.

Reaction of (1,2-Diphenyl-1,2-ethanedioxido)$Fe_2(CO)_7$ with *p*-Methylbenzaldehyde. A solution of benzaldehyde (2 mmol) and $Fe_3(CO)_{12}$ (2.0 mmol) in benzene (15 cm^3) was heated at 80 °C under N_2 for 1.5 h. *p*-Tolualdhyde (**1b**) (15 mmol) was then added to the mixture. The resulting mixture was heated at 80 °C for 15 h, and acidified with 6 M HCl (10 cm^3). The products were isolated as described above. Compounds **3a** and **2b** were obtained in 62% and 58% yields, respectively.

A mixture of 1,2-diphenyl-1,2-ethanediol (1.3 mmol) and $Fe_3(CO)_{12}$ (1.5 mmol) in benzene (10 cm^3) was heated at 80 °C under N_2 for 2 h. Compound **1b** (15 mmol) was added. The resulting mixture was heated at 80 °C for 15 h and acidified with 6 M HCl (10 cm^3). The products were isolated as described above. Compounds **3a** and **2b** were obtained in 56% and 56% yields, respectively.

Quantitative Determination of Evolved CO. A solution of **1a** (10 mmol) and $Fe_3(CO)_{12}$ (1.0 mmol) in benzene (6 cm^3) was placed in a sealed vessel which was connected with a gas burette. The mixture was heated at 80 °C under N_2 atmosphere. At the initial stage, no gas evolution was observed. The gas evolution started after heating for 3 h, but the rate of the gas evolution was moderate. The gas evolution ceased after heating for 20 h. The evolved gas was analyzed by GLC. The analysis showed that the evolved gas contained 6.77 mmol of CO and 0.03 mmol of H_2. The molar ratios of these gases to $Fe_3(CO)_{12}$, which was used initially, were 6.77 for CO and 0.03 for H_2, respectively.

Quantitative Determination of Evolved $Fe(CO)_5$. A solution of **1a** (10 mmol) and $Fe_3(CO)_{12}$ (1.0 mmol) in benzene (5 cm^3) was placed in a flask equipped with a gas trap which was immersed in a Dry Ice-acetone bath. The mixture was heated at 80 °C under N_2 atmosphere for several hours. Benzene and volatile materials were collected in the trapping flask at reduced pressure. The IR spectrum of the trapped material showed that it contained $Fe(CO)_5$. The trapped material was oxidized by adding 4 M HNO_3 (10 cm^3) at room temperature. The resulting aqueous solution was subjected to a Fe(II) ion analysis. The analysis was accomplished by a standard 1,10-phenanthroline method.[10)]

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