

Transition Metal Alkoxides. Preparation and Properties of Bis(aryloxo)-iron(II) and Bis(alkoxo)iron(II) Complexes Having 2,2'-Bipyridine Ligands

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A series of bis(aryloxo)iron(II), **2a**—**2g**, and bis(alkoxo)iron(II), **2h**—**2k**, complexes with 2,2'-bipyridine ligands ($\text{Fe}(\text{OC}_6\text{H}_4\text{X})_2(\text{bpy})_n$ and $\text{Fe}(\text{OR})_2(\text{bpy})_n$) have been prepared by the reactions of diethylbis(2,2'-bipyridine)-iron(II) (**1**) with corresponding *p*-substituted phenols and alcohols, respectively. ($\text{X}=\text{NO}_2$, CN , Cl , C_6H_5 , H , and CH_3 ; $\text{R}=\text{CH}_3$, C_2H_5 , *iso*- C_3H_7 , and $\text{CH}_2\text{C}_6\text{H}_5$). These compounds were characterized by IR and NMR spectroscopies and elemental analyses as well as by chemical reactions. Kinetic investigation of the reactions of **1** with phenols by a visible spectroscopic method supports a mechanism involving partial dissociation of the 2,2'-bipyridine ligand, followed by coordination of phenol and activation of the $\text{Fe}-\text{C}_2\text{H}_5$ bonds giving the bis(phenoxo)iron(II) compound. Thermolysis of bis(alkoxo)iron(II) complexes gives not only disproportionation products of the alkoxo ligands (alcohols and aldehydes) but also organic products which are obtained as the result of C—O bond cleavage of the alkoxo groups. Interactions of **2** with acyl and alkyl halides lead to the formation of corresponding esters and ethers. Reactions of these iron(II) complexes with various organic acetates give corresponding acetates *via* an alkoxo exchange reaction. Bis(aryloxo)iron(II) complexes, **2**, are hydrolyzed with H_2O to yield phenols. Catalytic trans-esterification between ester and alcohol and Tishchenko type dimerization of benzaldehyde are effectively promoted under mild conditions by the bis(phenoxo)iron(II) and bis(benzyloxo)iron(II) complexes, respectively.

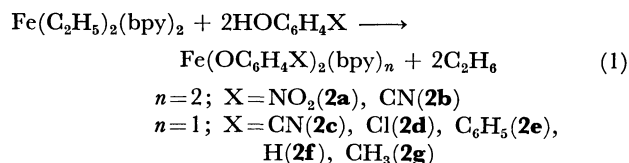
In contrast to non-transition metal alkoxides,¹⁾ which are known to promote the catalytic reactions of carbonyl compounds such as Tishchenko reaction and Meerwein-Ponndorf reaction, and to early transition metal alkoxides, which have been studied mainly from structural interest, the chemistry of Group VIII transition metal alkoxides has been much less explored. Formation of Group VIII transition metal alkoxides as intermediates has been implicitly postulated in reduction of transition metal halides on reactions with alcohols to low valent transition metal complexes,²⁾ or in oxidation of alcohols³⁾ as well as in trans-esterification reactions.^{1a)} The lack of well-characterized group VIII transition metal alkoxides has hindered our understanding of the mechanisms of these reactions. Although a growing number of Group VIII metal alkoxides have been synthesized and their properties studied,⁴⁾ more information is obviously needed concerning the chemistry of the Group VIII transition metal alkoxides to shed light on the mechanisms of transition metal promoted transformation of organic compounds.

We have found that diethylbis(2,2'-bipyridine)-iron(II), $\text{Fe}(\text{C}_2\text{H}_5)_2(\text{bpy})_2$ (**1**) serves well as a starting material for preparing a variety of iron(II) aryloxides and alkoxides and studied their properties including catalytic activities. This paper also deals with the kinetic study of the reaction of **1** with alcohols and substituted phenols to form the alkoxides and aryloxides.

Results and Discussion

Preparation and Spectroscopic Properties of Bis(aryloxo)- and Bis(alkoxo)iron(II) Complexes. A variety of *p*-substituted phenols react with diethylbis(2,2'-bipyridine)iron(II), $\text{Fe}(\text{C}_2\text{H}_5)_2(\text{bpy})_2$ (**1**)⁵⁾ to give bis(phenoxo)iron(II) complexes having bpy ligands, $\text{Fe}(\text{OC}_6\text{H}_4\text{X})_2(\text{bpy})_n$ (**2**) ($n=1$ and 2) with evolution of

two equivalents of ethane at ambient conditions. The bis(phenoxo)iron complexes are highly air sensitive, but thermally very stable.



These complexes were characterized by elemental analyses, IR, and NMR spectroscopies, as well as by chemical reactions. The phenoxide complex **2f** was also prepared *via* an independent route by the reaction of FeCl_2 with NaOC_6H_5 in the presence of bpy, but the contamination of the product with salts prevented isolation of the pure material. Table I summarizes the elemental analyses and the yields of the complexes. The number of coordinating bpy ligand in the bis(phenoxo)iron(II) complexes varies depending on the *p*-substituent in the phenoxo ligand. Electron-withdrawing substituents such as nitro and cyano groups favor the coordination of electron-donating two bpy ligands and less electron-withdrawing substituents give mono-bpy coordinated complexes. Bis(*p*-cyanophenoxo)iron(II) complex lies on the border between the two groups favoring mono- and bis-bpy complexes and both complexes **2b** and **2c** can be isolated under suitable conditions (see Experimental). Complexes **2a** and **2b** having two bpy ligands have considerable solubilities but the other complexes having one bpy ligand are much less soluble in organic solvents. Many metal alkoxides and phenoxides are known to be aggregated,^{1a)} and the coordinatively unsaturated complexes having only one bpy ligand per iron may well have polymeric structures accounting for the poor solubilities. In fact addition of excess bpy to a heterogeneous system of **2c** having one bpy ligand in acetone or toluene with heating caused dissolution of **2c** to give a homogeneous solution from which dark

TABLE 1. ANALYTICAL DATA OF $\text{Fe}(\text{OC}_6\text{H}_4\text{X}-p)(\text{bpy})_n$ COMPLEXES

Complex	Yield/%	Found(Calcd) (%)				
		C	H	N	Cl	
$\text{Fe}(\text{OC}_6\text{H}_4\text{NO}_2-p)_2(\text{bpy})_2$	2a	63	59.0 (59.6)	3.8 (3.8)	13.3 (13.0)	
$\text{Fe}(\text{OC}_6\text{H}_4\text{CN}-p)_2(\text{bpy})_2$	2b	65	67.8 (67.6)	4.0 (4.0)	14.0 (14.0)	
$\text{Fe}(\text{OC}_6\text{H}_4\text{CN}-p)_2(\text{bpy})$	2c	96	64.5 (64.3)	3.9 (3.6)	12.1 (12.5)	
$\text{Fe}(\text{OC}_6\text{H}_4\text{Cl}-p)_2(\text{bpy})$	2d	66	56.2 (56.6)	3.5 (3.5)	5.9 (6.0)	15.0 (15.1)
$\text{Fe}(\text{OC}_6\text{H}_4\text{C}_6\text{H}_5-p)_2(\text{bpy})$	2e	84	72.5 (74.2)	4.6 (4.8)	4.9 (5.1)	
$\text{Fe}(\text{OC}_6\text{H}_5)_2(\text{bpy})$	2f	51	65.7 (66.3)	4.7 (4.6)	6.9 (7.0)	
$\text{Fe}(\text{OC}_6\text{H}_4\text{CH}_3-p)_2(\text{bpy})$	2g	86	66.6 (67.6)	4.9 (5.2)	6.4 (6.6)	

TABLE 2. ^1H NMR AND IR SPECTRA OF $\text{Fe}(\text{OC}_6\text{H}_4\text{X}-p)_2(\text{bpy})_n$ COMPLEXES

Complex	^1H NMR (δ/ppm)			IR $\nu(\text{C}-\text{O})/\text{cm}^{-1}$
	Phenoxo	bpy	Other	
2a	6.2 (d, 9 Hz), 7.8 (d, 9 Hz)	7.4 (m), 8.1 (m), 8.6 (m)		1290
2b	6.6 (d, 8 Hz), 7.4 (d, 8 Hz)	7.5 (m), 8.2 (m), 8.7 (m)		1340
2c	6.4 (m), 7.4 (m)	7.4 (m), 8.1 (m), 8.6 (m)		1310
2d	5.8—7.2 (br)	7.3 (m), 8.1 (m), 8.6 (m)		1280
2f	6.7 (m), 7.2 (m)	7.5 (m), 8.2 (m), 8.7 (m)		1260
2g	6.5 (m), 6.9 (m)	7.4 (m), 8.2 (m), 8.8 (m)	2.2 (s)	1250

d, doublet; m, multiplet; br, broad; s, singlet.

red crystals of **2b** having two bpy ligands were obtained on cooling the solution to -78°C . The bpy ligand may be acting to break the bridging phenoxo bonds.

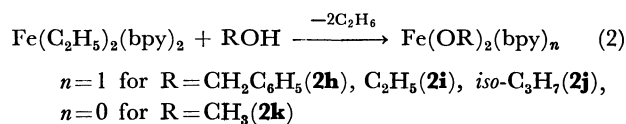
IR spectra of these (*p*-substituted phenoxo)iron(II) complexes showed a strong characteristic $\nu(\text{C}-\text{O})$ band at $1260\text{--}1340\text{ cm}^{-1}$ which is shifted to higher frequency by $10\text{--}15\text{ cm}^{-1}$ compared with $\nu(\text{C}-\text{O})$ of free phenols (Table 2). Cyano and nitro groups in the present complexes do not seem to have an interaction with iron, since no frequency change of $\nu(\text{CN})$ and $\nu(\text{NO}_2)$ from the starting phenols was observed.

^1H NMR spectra of these bis(*p*-substituted diphenoxo)iron(II) complexes (Table 2) showed two doublets assignable to ortho and meta hydrogens in the *p*-substituted phenoxo ligands and three groups of multiplets for the bpy ligand. Bis(phenoxo) complex **2f** showed two kinds of broad signals in a 2 to 3 ratio, one being attributable to ortho hydrogens and the other to meta and para hydrogens. These spectroscopic results suggest that the phenoxo ligand is normally bonded with iron through oxygen unlike the π -bonding between ruthenium and phenoxo ligand in $\text{RuH}(\text{OC}_6\text{H}_5)(\text{PPh}_3)_2$ as observed by Wilkinson *et al.*⁶⁾

In the presence of free bpy ligand, ^1H NMR of **2f** in CD_3OD showed only averaged peaks of bpy ligands coordinated and uncoordinated at room temperature, indicating fast intermolecular exchange process between them in the solution. On the contrary, ^1H NMR of a mixture of **2a** and free bpy showed separated signals for free and coordinated bpy ligands, respectively. Ligand exchange rate of **2a** with free bpy is considered to be slow enough in NMR time scale to separate the peaks. The configuration of the six coordinated complex with two bpy ligands, **2a** and **2b**, is considered to be *cis*, because of the steric requirement. ^1H NMR of bpy ligand in the *cis* con-

figuration has been reported to show two kinds of pyridyl rings giving complicated multiplets.⁷⁾ However, the observed ^1H NMR of the coordinated bpy in **2a** showed a relatively simple pattern. Fast intramolecular exchange of bpy ligands may account for this observation, while a *trans* structure for **2a** is not completely excluded.

The reactions of **1** with aliphatic alcohols (ROH) afforded bis(alkoxo)iron(II) complexes analogously to the reactions with phenols.



The alkoxoiron complexes are extremely sensitive to air to preclude the microanalysis and have been characterized mainly by chemical reactions (*vide infra*). IR spectra of **2h**—**2j** showed a characteristic strong $\nu(\text{C}-\text{O})$ band at *ca.* 1000 cm^{-1} in addition to the bands attributable to the bpy ligand. On the other hand, the IR spectrum of **2k** showed only bands assignable to the methoxo ligands. The aliphatic alkoxoiron complexes, **2h**, **2i**, and **2j**, are all quite insoluble in organic solvents suggesting polymeric structures as are common among other metal alkoxides. Formation of polymeric iron(II) methoxide has been reported by Klein.⁸⁾

Chemical Reactivities of Iron(II) Aryloxides and Alkoxides. The phenoxoiron complex **2f** smoothly reacted with alkyl and acyl halides to give corresponding ethers and esters, respectively (Table 3). The resulted solid product formed in the reaction of **2f** with CH_3COCl was identified as $\text{FeCl}_2(\text{bpy})$ by comparing its IR spectrum with that of the sample prepared by the acidolysis of **1** with HCl.

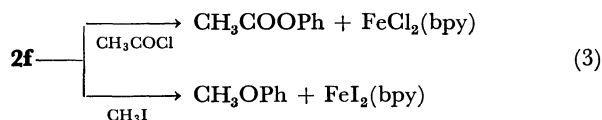
TABLE 3. REACTIONS OF ARYLOXO AND ALKOXOIRON(II) COMPLEXES WITH ALKYL AND ACYL HALIDES AT ROOM TEMPERATURE

Complex	Reagent (mol/Fe)	Solvent	Time/h	Product (mol/Fe)
2a	CH ₃ COCl(excess)	none	24	CH ₃ CO ₂ C ₆ H ₄ NO ₂ (1.64)
2b	CH ₃ COCl(excess)	none	24	CH ₃ CO ₂ C ₆ H ₄ CN (1.54)
2f	CH ₃ COCl (20)	THF	24	CH ₃ CO ₂ C ₆ H ₅ (1.49)
	C ₆ H ₅ CH ₂ Br (4)	toluene	5	C ₆ H ₅ CH ₂ OC ₆ H ₅ (0.57)
	CH ₃ I(excess)	none	3	C ₆ H ₅ OCH ₃ (0.16)
2h	CH ₃ COCl (6)	toluene	2	CH ₃ CO ₂ CH ₂ C ₆ H ₅ (1.52)
2i	CH ₃ COCl (2)	THF	10	CH ₃ CO ₂ C ₂ H ₅ (1.80)
2j	CH ₃ COCl (2)	THF	10	CH ₃ CO ₂ C ₃ H ₇ ⁱ (1.84)
2k	CH ₃ COCl (2)	THF	10	CH ₃ CO ₂ CH ₃ (1.68)

TABLE 4. REACTIONS OF ARYLOXO AND ALKOXOIRON(II) COMPLEXES WITH ESTERS^{a)}

Complex	Ester(mol/Fe)	Product(mol/Fe)
2f	CH ₃ CO ₂ C ₆ H ₄ NO ₂ - <i>p</i> (4)	CH ₃ CO ₂ C ₆ H ₅ (1.71)
	CH ₃ CO ₂ C ₆ H ₄ CN- <i>p</i> (4)	CH ₃ CO ₂ C ₆ H ₅ (1.24)
	CH ₃ CO ₂ C ₆ H ₄ - <i>p</i> -CH ₃ (4)	CH ₃ CO ₂ C ₆ H ₅ (0.76)
	CH ₃ CO ₂ CH ₂ C ₆ H ₅ (4)	CH ₃ CO ₂ C ₆ H ₅ (0)
	CH ₃ CO ₂ C ₂ H ₅ (4)	CH ₃ CO ₂ C ₆ H ₅ (0)
2h	CH ₃ CO ₂ C ₆ H ₅ (4)	CH ₃ CO ₂ CH ₂ C ₆ H ₅ (1.82)
2j	CH ₃ CO ₂ C ₆ H ₅ (4)	CH ₃ CO ₂ C ₃ H ₇ ⁱ (1.64)
2k	CH ₃ CO ₂ C ₆ H ₅ (4)	CH ₃ CO ₂ CH ₃ (1.52)

a) Reactions were carried out at 50 °C in THF for 5 h.



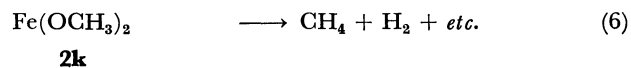
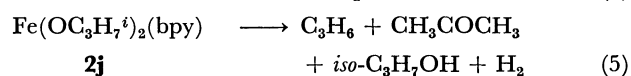
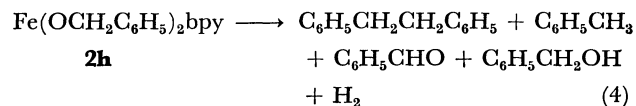
Other bis(*p*-substituted phenoxy)- and bis(alkoxo)iron(II) analogs also gave corresponding organic acetates on reaction with acetyl chloride (Table 3).

Table 4 summarizes the results of the reactions of aryloxoiron(II) and alkoxoiron(II) complexes with various organic esters. *p*-Substituted phenyl acetates reacted with the phenoxoiron(II) complex, **2f**, to give phenyl acetate. Benzyl and ethyl acetates had no tendency to exchange with the phenoxy ligand under the same conditions. On the other hand, phenyl acetate underwent the exchange reaction with the benzyloxy, isopropoxy, and methoxoiron(II) complexes giving benzyl, isopropyl, and methyl acetates, respectively in good yields. The more electrophilic alkoxo ligand seems to have stronger affinity with iron(II). Hydrolysis of **2a**–**2g** with water gave corresponding *p*-substituted phenols.

A greenish grey bis(phenoxo)iron(II) complex, **2f**, is highly air sensitive and it turns red brown immediately on exposure to air at room temperature both in solution and in the solid state. Oxygen uptake by **2f** in solution was roughly half a mol per iron. The resultant red brown complex **2f'**, is almost insoluble in usual solvents and is paramagnetic with a μ_{eff} value of 4.3 B.M., suggesting a high spin Fe(III) species. IR spectrum of **2f'** is very close to that of **2f** indicating the existence of the intact phenoxy and bpy ligands in **2f'**. No absorption band attributable to $\nu(\text{O}=\text{O})$ was detected, whereas most of the dioxygen complexes

show the strong characteristic band at 800–900 cm^{-1} .⁹⁾ Therefore, the present complex **2f'** may be considered as a polymeric oxygen bridged complex having the bpy ligand. An oxygen bridged iron(II) complex has been reported by Teyssie *et al.*¹⁰⁾

Although thermal decomposition of metal alkoxides usually affords exclusively disproportionation products of the alkoxo ligands,¹⁾ alcohols and aldehydes, thermolysis of **2h**–**2k** in the solid state gave unusual products besides the disproportionation products as shown in Table 5.

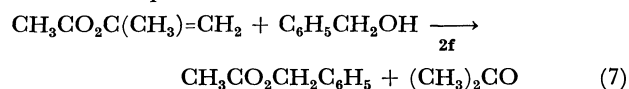


2k

Formation of bibenzyl and toluene from **2h** indicates the involvement of the C–O bond cleavage on thermolysis, whereas benzaldehyde and benzyl alcohol were obtained by the usual disproportionation reaction of the alkoxo ligands. Thermolysis of **2j** gave propylene in addition to the disproportionation products, also suggesting a similar decomposition pathway. Compound **2k** mainly gave methane on thermolysis. The present unusual C–O bond fission may have arisen from the great affinity of iron metal with oxygen. Formation of an alkyl radical by the C–O bond cleavage probably accounts for the pyrolysis products. Analogous C–O bond breakage in a transition metal alkoxo compound is known.¹¹⁾ On the other hand, thermolysis of **2i** and **2f** afforded ethanol and phenol as a major product respectively, although the hydrogen source is not clear.

Catalytic Reactions Promoted by Alkoxoiron(II) Complexes.

The phenoxo complex **2f** was found to catalyze the trans-esterification. Isopropenyl acetate and benzyl alcohol were converted into benzyl acetate and acetone in a 73% yield in the presence of **2f** at room temperature.



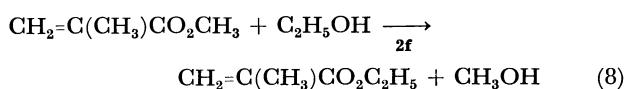
In the trans-esterification reaction isopropene-2-ol may

TABLE 5. THERMAL DECOMPOSITION OF ALKOXOIRON(II) COMPLEXES IN SOLID STATE^{a)}

Complex	Dp/°C	Product (mol/Fe)
Fe(OCH ₂ C ₆ H ₅) ₂ (bpy) 2h	210—220	H ₂ (0.05), C ₆ H ₅ CH ₃ (0.30), C ₆ H ₅ CHO(0.52), C ₆ H ₅ CH ₂ OH(0.23), C ₆ H ₅ CH ₂ CH ₂ C ₆ H ₅ (0.20)
Fe(OC ₂ H ₅) ₂ (bpy) 2i	170	H ₂ (0.03), C ₂ H ₅ OH(0.87)
Fe(OC ₃ H ₇) ₂ (bpy) 2j	185	H ₂ (trace), C ₃ H ₈ (0.28), <i>i</i> -C ₃ H ₇ OH(0.24), (CH ₃) ₂ CO(0.04)
Fe(OCH ₃) ₂ 2k	200—220	H ₂ (0.10), CH ₄ (0.50), C ₂ H ₆ (trace)

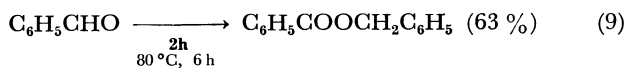
a) The compounds were heated up to 220 °C.

be first formed and transformed to its tautomer, acetone. Methyl methacrylate and ethanol also gave ethyl methacrylate and methanol in a 38% yield in the presence of **2f**.



The phenoxoiron(II) catalyst used was unchanged after the reaction as revealed by IR analysis, suggesting the phenoxo ligand in **2f** is not involved in the catalytic trans-esterification. A similar type of trans-esterification using Cu phenoxide¹²⁾ has been reported and a mechanism involving metal assisted nucleophilic replacement was postulated.

Non-transition metal alkoxides, especially aluminum isopropoxide, are known to catalyze Tishchenko reaction.¹⁾ Among the iron alkoxides prepared in the present study dibenzylxido(2,2'-bipyridine)iron complex **2h** was found to be most effective for the Tishchenko reaction, converting benzaldehyde into benzyl benzoate.



Recently a few transition metal complexes of Ru(II),¹³⁾ Fe(II),¹⁴⁾ and Mn(II)¹⁵⁾ have been reported to serve as catalysts for the dimerization of aldehyde, and formation of alkoxy-transition metal intermediates has been postulated.

Kinetic Study of the Formation of 2f. The rate of the formation of complex **2f** by the reaction of **1** with excess of phenol in THF was studied by following the change in the visible spectrum of the reaction mixture *in vacuo*. The decrease in the absorbance of a band at 590 nm which is known to be a CT band of **1**,¹⁶⁾ was used to estimate the rate of disappearance of **1**. Plot of $\log(A_t - A_\infty)$ against time gave a linear relationship indicating a first-order dependence of the rate on the concentration of **1**.

$$\frac{d}{dt}[\text{2f}] = -\frac{d}{dt}[\text{Fe}(\text{C}_2\text{H}_5)_2(\text{bpy})_2] = k[\text{Fe}(\text{C}_2\text{H}_5)_2(\text{bpy})_2] \quad (10)$$

Figure 1 shows the dependence of the pseudo-first-order rate constant k on the phenol concentration. It is seen that the rate increase with the increase in the phenol concentration is leveled off at higher concentration of phenol and addition of the bpy ligand shows a marked effect to retard the rate of decomposition

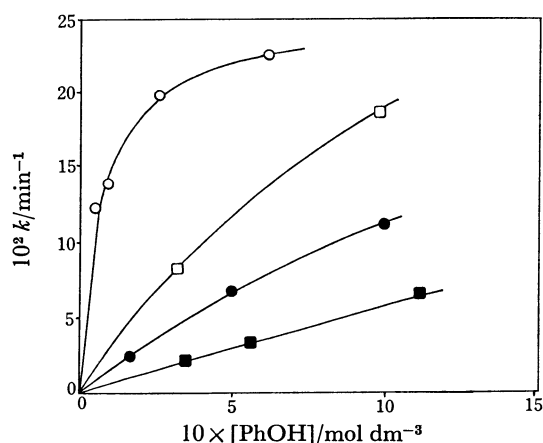


Fig. 1. Effect of [PhOH] on the first order rate constant k in various bpy concentrations for the reaction of **1** with phenol in THF at 23.2 °C. [bpy]=0 mol/dm³, ○; 0.90 × 10⁻³ mol/dm³, □; 2.71 × 10⁻³ mol/dm³, ●; 9.02 × 10⁻³ mol/dm³, ■.

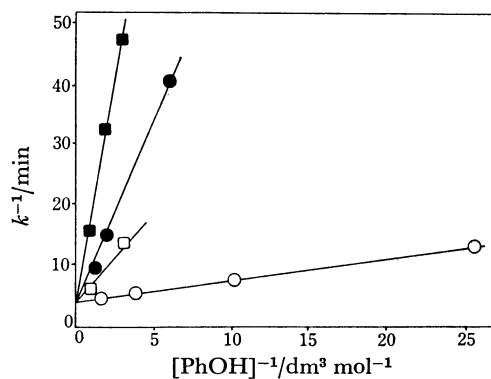


Fig. 2. Plot of the reciprocal of k vs. the reciprocal of [PhOH] in Fig. 1.

of **1**. The both reciprocal plots of k and phenol concentration at various bpy concentration shown in Fig. 2 gives straight lines. The effect of variation of the added bpy concentration on the slopes in Fig. 2 is shown in Fig. 3. These experimental results can be summarized by the following equation;

$$\frac{1}{k} = A + \frac{B + C[\text{bpy}]}{[\text{C}_6\text{H}_5\text{OH}]} \quad (11)$$

where A , B , and C represent constants. A similar kinetic behavior has been previously observed by Yamamoto *et al.*¹⁶⁾ in the reaction of **1** with olefins. The present kinetic behavior can be explained by

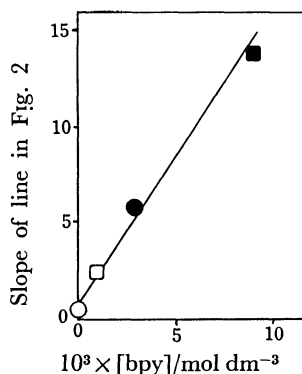
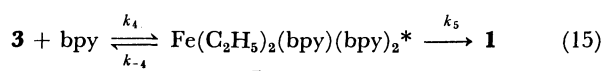
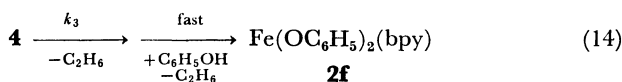
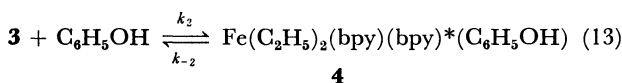
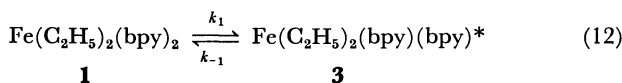


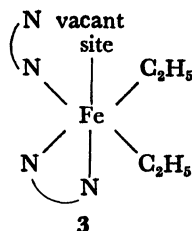
Fig. 3. Plot of the slope of line in Fig. 2 against [bpy].

assuming the following reaction mechanism.



(bpy)*: partially dissociated bpy ligand

A partial dissociation of bpy from **1** takes place to give coordinatively unsaturated species **3** which presumably has a structure as shown below:



where $\widehat{\text{N}}\widehat{\text{N}}$ represents the bpy ligand. Phenol then coordinates at the vacant site in **3** affording **4**. Activation of the Fe–Et bond by coordination of phenol leads to splitting of the ethyl group to give ethane as the rate-determining irreversible process. Further rapid reaction of phenol may follow to give **2f**. A competitive coordination of phenol and bpy toward **3** should be considered; Eq. 15 accounting for the inhibition effect of bpy on the reaction.

Since the starting material **1** and the final product **2f** are the only species observable during the reaction (actually 1:1 reaction mixture of **1** and phenol gave a 1:1 mixture of **1** and **2f**, indicating the absence of isolable reaction intermediates), the concentration of **3**, **4**, and **5** are considered to be negligible. Therefore by applying the steady state approximation for these species the following rate equation is derived.

$$\text{Rate} = -\frac{d}{dt}[\text{1}] = k[\text{1}]$$

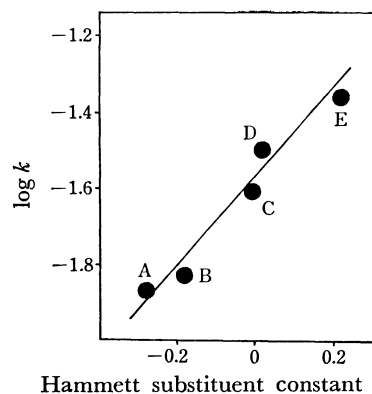


Fig. 4. Relation between $\log k$ in THF at 23.2 °C and Hammett substituent constant. $[\text{XC}_6\text{H}_4\text{OH}] = 1.66 \times 10^{-1} \text{ mol/dm}^3$; A, X=CH₃O; B, X=CH₃; C, X=H; D, X=C₆H₅; E, X=Cl. $[\text{bpy}] = 2.71 \times 10^{-3} \text{ mol/dm}^3$. Under these conditions, k increases with increasing the phenol concentration and does not level off.

$$k = \frac{k_1 k_2 k_3 [\text{C}_6\text{H}_5\text{OH}]}{k_{-1}(k_{-2} + k_3) + k_2 k_3 [\text{C}_6\text{H}_5\text{OH}] + \frac{k_4 k_5 (k_{-2} + k_3) [\text{bpy}]}{k_{-4} + k_5}} \quad (16)$$

When k_{-2} is much greater than k_3 , the observed pseudo-first-order rate constant k is given by

$$\frac{1}{k} = \frac{1}{k_1} + \frac{k_{-1} k_{-2} + \bar{k} [\text{bpy}]}{k_1 k_2 k_3 [\text{C}_6\text{H}_5\text{OH}]} \quad (17)$$

$$\bar{k} = \frac{k_4 k_5 k_{-2}}{k_{-4} + k_5}$$

The experimental results expressed by Eq. 11 is in agreement with Eq. 17 supporting the validity of assumptions as expressed by Eqs. 12–15. Thus from constants A, B, and C in Eq. 11 rate constants and their ratios $1/k_1$, $k_{-1} k_{-2} / k_1 k_2 k_3$, and $\bar{k} / k_1 k_2 k_3$ may be obtained. The $1/k_1$ value of 4.0 min obtained from the intercept in Fig. 2 roughly agrees with the value observed in the reaction of **1** with olefins.¹⁶⁾ The agreement may be taken as additional support for that the similar reaction mechanism involving the partial dissociation of bpy ligand from **1** is operative in the reactions of **1** with phenols and with olefins.

The rates of the reactions of **1** with various *p*-substituted phenols were examined under the same conditions. The relation between $\log k$ and Hammett substituent constant σ ¹⁸⁾ of X is demonstrated in Fig. 4 ($\rho = +1.17$). More electron-withdrawing substituent facilitates the reaction, indicating electrophilic attack of phenols to **1**.

The pseudo-first-order rate constant k was estimated in various solvents such as acetone, THF, and toluene, having dielectric constants of 20.7, 7.6, and 2.4.¹⁸⁾ Figure 5 shows the results under various phenol concentrations. The fact that all the $1/k$ values lie on the same line as plotted *vs.* phenol concentration indicates the absence of solvent effect on the rate. This result suggests that non-polar active intermediate is involved in the rate determining step.¹⁹⁾

Two types of interactions of iron(II) complex with phenol for **4** such as (A) and (B) are plausible.

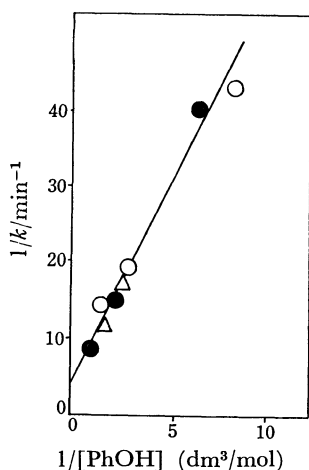
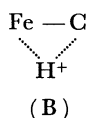
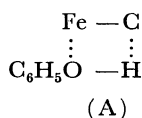


Fig. 5. Plot of the reciprocal of k vs. the reciprocal of $[\text{PhOH}]$ at 23.2°C in various solvents. Acetone, \circ ; THF, \bullet ; toluene, \triangle .



In the usual electrophilic cleavage of metal alkyls by acids, the three centered intermediate (B) has been suggested.²⁰ However, the intermediate (B) is not reasonable in the present reaction of **1** with phenols. The nucleophilic participation by OC_6H_5^- to give four centered intermediate (A) is preferred by the following reasons, although the substituent effect of the phenols on the reaction rate suggests electrophilic attack of phenols at the ethyl ligand bonded to iron(II). Firstly, the absence of solvent effect agrees with the non-polar four centered intermediate rather than the ionic one (B). Secondly, the kinetic behavior of the present reaction is quite similar to that found in the reaction of **1** with olefin, in which facile Fe–C bond activation by the coordination of electron-deficient olefin to iron(II) has been reported.¹⁷ On the other hand, however, the possibility of oxidative addition of phenol to Fe(II) giving Fe(IV) species in **4** followed by the reductive elimination of alkane can not be excluded.²¹

Experimental

All the procedures were carried out under nitrogen or *in vacuo*. The nitrogen gas used was deoxygenated by passing through a trap cooled to -196°C in order to avoid the contamination by a trace of oxygen. Solvents were purified by usual manners under nitrogen and were stored under nitrogen or argon. $\text{Fe}(\text{C}_2\text{H}_5)_2(\text{bpy})_2$ was prepared by the method previously reported.⁵ Phenols and esters were commercial products and used without further purification. Alkyl and acyl halides were used after simple distillation of commercial products. IR and visible spectra were recorded on a Hitachi 295 infrared spectrometer and a Hitachi Type 200 spectrometer, respectively. ^1H NMR spectra were measured on a JEOL PS-100 spectrometer by Mr. Y. Nakamura. Micro analyses of C, H, N, and Cl were performed by using Yanagimoto CHN Corder Type MT-2 by Mr. T. Saito in our laboratory. Magnetic susceptibility was measured with Shimadzu Magnetic Balance Type MB-100. Gases were

analysed by gas chromatography after collecting the gases evolved by a Toepler pump by which the gas volumes were measured. Amounts of the organic products were determined quantitatively by gas chromatography using suitable internal standards.

Preparation of the Bis(aryloxo)- and Bis(alkoxo)iron(II) Complexes and Their Reactions with H_2O and O_2 . Phenol (497 mg, 5.3 mmol) was added to a THF (20 ml) solution of $\text{Fe}(\text{C}_2\text{H}_5)_2(\text{bpy})_2$ (860 mg, 2.0 mmol) at -78°C . After the evacuation of the reaction vessel, the mixture was allowed to react at room temperature for 1 d. The color of the solution changed from deep purple to greenish grey and ethane (4.2 mmol) was detected in the gas phase. The solution was concentrated to *ca.* 10 ml and diethyl ether (30 ml) was added to give a greenish grey powder, which was washed with hexane and diethyl ether a few times and was dried *in vacuo*. (Yield 415 mg, 51%). The compounds **2a**, **2c**, **2d**, **2e**, **2g**, **2h**, **2i**, **2j**, and **2k** were prepared similarly. Elemental analyses, yields, and IR and ^1H NMR spectra of **2a–2g** are summarized in Tables 1 and 2, respectively. Micro analyses of **2h–2k** failed because of their extreme sensitivity toward oxygen. Results of thermolysis of **2h–2k** are listed in Table 5. Hydrolysis of **2f** (170 mg, 0.43 mmol) by distilled water (0.5 ml) in THF (6 ml) gave phenol (0.56 mmol) at 50°C after 10 h. Hydrolysis of the other aryloxides, **2a**, **2b**, **2c**, **2d**, **2e**, and **2g** under similar conditions gave corresponding *p*-substituted phenols, the amount of respective phenols liberated being trace, 1.14, 0.85, 1.09, 1.18, 1.30, and 1.10 mol/complex. Dry air was introduced into the toluene suspension of complex **2e** (310 mg, 0.78 mmol) to give a brown heterogeneous solution. Oxygen absorbed (0.39 mmol) was measured by a gas burette. Resulted brown complex was filtered and dried *in vacuo* (100%). Found: C, 64.9; H, 4.6; N, 6.5%. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_3\text{Fe}$: C, 63.8; H, 4.4; N, 6.8%. $\mu_{\text{eff}} = 4.3$ B.M. IR. $\nu(\text{C}-\text{O}) = 1260\text{ cm}^{-1}$.

Preparation of $\text{Fe}(\text{OC}_6\text{H}_4\text{CN-}p)_2(\text{bpy})_2$ (2b**).** The mixture of **2c** (440 mg) and bpy (320 mg) in dry toluene (10 ml) was heated to 100°C to give a dark red homogeneous solution. After the filtration of this hot solution, it was kept in dry-ice temperature to deposit slowly dark red crystals. The resulted red crystals were filtered off, washed with diethyl ether containing free bpy and dried *in vacuo*.

Reactions of Bis(aryloxo)iron(II) Complexes with Organic Halides. Complex **2e** (41 mg, 0.10 mmol) in THF was treated with CH_3COCl (100 μl , 1.4 mmol) to cause immediate color change from greenish grey to dark red. After 1 d phenyl acetate (0.15 mmol) was detected in the solution. The red compound was obtained by removing all the volatile matter and was identified as $\text{FeCl}_2(\text{bpy})$ by comparing its IR spectrum with that of an authentic sample which was prepared by **1** and HCl. (Yield 10 mg, 25%) Found: C, 42.5; H, 2.0; N, 10.0; Cl, 25.1%. Calcd: C, 43.2; H, 3.0; N, 10.1; Cl, 24.1%. Other reactions of various bis(aryloxo)iron(II) complexes with PhCH_2Br , CH_3I , and CH_3COCl were performed similarly and the results are summarized in Table 3.

Reaction of the Bis(aryloxo)iron(II) Complexes with *p*-Nitrophenyl Acetate. Complex **2f** (210 mg, 0.50 mmol) in THF (10 ml) was treated with *p*-nitrophenyl acetate (350 mg, 1.9 mmol) to give a dark red heterogeneous solution. After 5 h at room temperature phenyl acetate (0.83 mmol) was found in the solution by gas chromatography. The reactions of iron phenoxides and alkoxides with other organic acetates were carried out analogously and the results are shown in Table 4.

Catalytic Trans-esterification. Isopropenyl acetate (1 ml)

was mixed with benzyl alcohol (1 ml) in the presence of **2f** (90 mg, 0.23 mmol) to give immediately a red purple solution. After 2 d at room temperature acetone (6.6 mmol) and benzyl acetate (6.6 mmol) were detected in solution. (73% based on isopropenyl acetate). IR spectrum of the catalyst recovered was identical with that of **2f**. Transesterification of methyl methacrylate (3 ml) and ethanol (3 ml) in the presence of **2f** (110 mg, 0.28 mmol) also gave ethyl methacrylate (11.2 mmol) and methanol (11.2 mmol) in 1 d at room temperature (38% based on methyl methacrylate).

Tishchenko Type Reaction of Benzaldehyde Promoted by 2h. Benzaldehyde (5 ml, 50 mmol) was heated to 80 °C for 6 h in the presence of **2h** (120 mg) to afford a homogeneous blue solution. Benzyl benzoate (16 mmol, 63%) was found in the liquid phase by gas chromatography.

Kinetics. The rate of the formation of **2f** from **1** and phenol in THF was estimated by following the disappearance of the visible spectrum of **1** at 590 nm under vacuum. The pseudo-first order rate constants obtained by measuring the change at various wave lengths gave the same values. The solvent for spectroscopic measurements was dried over benzophenone ketyl and was introduced by a trap-to-trap distillation into the reaction mixture containing **1** and phenol.

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