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Studies on Reactions of Metallic Iron with Mixtures of Aryl Carboxylic Acids (ArCOOH) and Organic Halides Relevant to Corrosion of Steel. Preparation of $[FeX(OCOAr)]_n$ (X = Cl, Br, I) and Its Characterization

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Crystalline, multinuclear $[FeX(OCOAr)]_n$ *(X = Cl, Br, I; Ar =* C_6H_5, $C_6H_5CH{=}CH$, $C_6H_5CH_2$*) is produced by reactions of metallic iron with mixtures of carboxylic acids (ArCOOH) and alkyl halides (RX). The reactions proceed smoothly above 180 °C, and the formation of* $[FeX(OCOAr)]_n$ *is accompanied by formation of ester (ArCOOR), and* H_2*; the stoichiometry of the reaction is expressed by an equation,* $Fe + 2\,ArCOOH + RX \rightarrow (1/n)[FeX(OCOAr)]_n + ArCOOR + H_2$. $[FeX(OCOAr)]_n$ *has been characterized by elemental analysis, its chemical reactivities with basic ligands, IR spectroscopy, powder X-ray diffraction pattern, thermogravimetric analysis, and magnetic susceptibility. A reaction mechanism involving a successive reaction of ArCOOH and RX with iron is proposed to elucidate the formation of* $[FeX(OCOAr)]_n$*. A reaction of metallic iron with a mixture of* C_6H_5COOH *and* CCl_4 *gives* C_6H_5COCl *in a good yield.*

Introduction

The reaction of metallic iron with carboxylic acids in an aqueous solution is well known. However, the reaction of metallic iron with gaseous mixtures of carboxylic acids (acetic acid, benzoic acid, *etc.*) and organic halides (methyl iodide, ethyl bromide, *etc.*) has been much less explored. Recently such mixtures of carboxylic acids and organic halides are often used in the chemical industry [1, 2], and elucidation of the corrosion process of the reaction of iron with the mixture is considered to be of importance.

Previously we reported [3] that crystals of polymeric $[FeX(OCOAr)]_n$ grew on the surface of an iron plate when the iron plate was treated with a mixture of aromatic carboxylic acid (ArCOOH) and organic halide (RX). We now report details of the reaction between iron and the mixture of ArCOOH and RX, as well as characterization and chemical properties of the product, $[FeX(OCOAr)]_n$.

Results and Discussion

Reactions of Iron with Mixtures of ArCOOH and RX

When an iron plate is exposed to vapor containing benzoic acid, PhCOOH (Ph = C_6H_5), and ethyl bromide, EtBr, at temperatures higher than 180 °C, a rapid reaction proceeds to produce crystals of $[FeBr(OCOPh)]_n$, *1*, on the surface of the iron plate. Gas chromatographic analyses of the liquid and gaseous products reveal formation of equimolar amounts of PhCOOEt and H_2 per mol of FeBr(OCOPh) unit in *1*, as well as small amounts of C_2H_4 and C_2H_6 originated from EtBr. Formation of *1*, PhCOOEt, and H_2 indicates the following stoichiometry of the reaction,

$$Fe + 2PhCOOH + EtBr \longrightarrow (1/n)\underbrace{[FeBr(OCOPh)]_n}_{1} + PhCOOEt + H_2 \qquad (1)$$

When a 1:1 mixture [4] of PhCOOH and EtBr is employed at 180 °C, the whole surface of the iron plate is covered with about 0.3 mg/mm^2 of *1* after about 10 h, after which time the reaction is retarded. At 200 °C, the rate of the reaction is considerably faster, and the whole of the surface is covered with *1* after 4 h. At 150 °C, the reaction proceeds to some extent, but the rate of the reaction is

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TABLE I. Yield, Analytical Data, and IR Data of $[FeX(OCOAr)]_n$, *1–6*.

Compound	Color	Yield[a] (mg)	D.p.[b] (°C)	μ_{eff} (B.M.)	Analytical Data[c]			IR data (cm^{-1})	
					C	H	X	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$
1	brownish yellow	*ca.* 350[d]	425	4.82	32.5 (32.7)	1.9 (2.0)	31.4 (31.1)	1540	1390
2	pale brown	390	435	4.98	40.0 (39.6)	2.5 (2.4)	16.9 (16.7)	1540	1410
3	deep green	600	390	4.99	27.4 (27.7)	1.4 (1.6)	42.9 (42.7)	1530	1370
4	light yellow	36	388	5.15	37.7 (38.2)	2.4 (2.5)	27.5 (28.2)	1540	1400
5	reddish brown	220	430	4.90	34.7 (35.5)	2.6 (2.6)	30.5 (29.5)	1540	1380
6	pink	170	250	5.26	35.1 (35.5)	2.7 (2.6)	30.4 (29.5)	1620	1390

[a] Yield at 200 °C. Reaction time = 10 h. ArCOOH = 27 mmol. RX = 27 mmol. Iron plate (1 × 10 × 50 mm) was used for the preparation of *1–3*, whereas stainless steel plate (SUS 304, 0.1 × 10 × 50 mm) was used to prepare *4–6* (see text). [b] Decomposition point where fast decrease of mass was observed, determined by TGA. [c] Calculated values in parentheses. [d] Average of 5 experiments.

much slower. When the iron plate is exposed to vapors of PhCOOH and EtBr separately at 200 °C, certain uncharacterized reactions proceed with evolution of H_2 and a mixture of H_2, C_2H_4, and C_2H_6, respectively. However, loss of weight of the iron plate in the reaction with PhCOOH or EtBr is much smaller than that observed in the reaction of the iron plate with the mixture of PhCOOH and EtBr, indicating that reaction (1) is a uniquely rapid process caused by synergism of PhCOOH and EtBr.

The rate of reaction (1) depends on the ratio between PhCOOH and EtBr, reaching a maximum when the PhCOOH/EtBr ratio [4] is about 1. When the PhCOOH/EtBr ratio largely deviates from 1, the rate of the reaction becomes considerably lower. However, the products (*1*, PhCOOEt, H_2) and ratios between the products do not vary over a wide range of the PhCOOH/EtBr ratio (PhCOOH/EtBr = 0.3–3.0), supporting that reaction (1) proceeds uniquely in the presence of both PhCOOH and EtBr.

Use of other organic bromides including butyl bromide, 2-methylisopropyl bromide, pentyl bromide in combination with PhCOOH gives *1* in comparable yields to that obtained in the PhCOOH–EtBr system, and in those cases the formation of *1* is also accompanied by formation of the corresponding ester (*e.g.*, butyl benzoate) and H_2. A PhCOOH–cyclohexyl bromide system also gives *1*, but its yield is considerably lower (about ¼) than those attained with the other PhCOOH–alkyl bromide systems described above, demonstrating a lower reactivity of cyclohexyl bromide against iron. In contrast to the alkyl bromides having sp^3 C–Br bonds, use of phenyl bromide having an aromatic sp^2 C–Br bond in combination with PhCOOH does not afford *1*. For example, the reaction of the iron plate with a PhCOOH–PhBr mixture at 200 °C leads to formation of a small amount of uncharacterized compound on the iron plate, but loss of weight of the iron plate (measured after removing the uncharacterized compound) is very small. The low reactivity of PhBr against iron agrees with the known lower reactivity of aromatic sp^2 C–Br bond than aliphatic sp^3 C–Br bond [5].

Use of an alkyl chloride, $(CH_3)_3Cl$, and an alkyl iodide, EtI, gives $[FeCl(OCOPh)]_n$, *2*, and $[FeI(OCOPh)]_n$, *3*, respectively, with formation of the corresponding ester and H_2:

$$\mathrm{Fe} + 2\mathrm{PhCOOH} + (\mathrm{CH_3})_3\mathrm{CCl} \longrightarrow \underset{2}{[\mathrm{FeCl(OCOPh)}]_n} + \mathrm{PhCOOC(CH_3)_3} + \mathrm{H_2} \qquad (2)$$

$$\mathrm{Fe} + 2\mathrm{PhCOOH} + \mathrm{EtI} \longrightarrow \underset{3}{[\mathrm{FeI(OCOPh)}]_n} + \mathrm{PhCOOEt} + \mathrm{H_2} \qquad (3)$$

Use of other aromatic acids (PhCH=CHCOOH, p-$CH_3C_6H_4COOH$, and $PhCH_2COOH$), instead of

PhCOOH, in combination with EtBr gives analogues of *1–3*:

$$\mathrm{Fe + 2ArCOOH + EtBr \longrightarrow}$$
$$\mathrm{[FeBr(OCOAr)]_n + ArCOOEt + H_2} \qquad (4)$$

4–6

$\mathrm{Ar = -OCOCH{=}CHPh}$ (*4*)
$\mathrm{-OCOC_6H_4CH_3}$ (*5*),
$\mathrm{-OCOCH_2Ph}$ (*6*)

Table I shows yields, analytical data, some physical properties and IR data of *1–6*.

When aliphatic carboxylic acids such as acetic and propionic acid are used with EtBr, the reaction with the iron plate proceeds smoothly with evolution of ethyl carboxylate and H_2. However, the reddish brown compounds formed were not crystalline and no further characterization was made except that a carboxylato ligand was contained in the product as revealed by IR spectra. Use of a $\mathrm{PhCOOH{-}CCl_4}$ mixture leads to an unprecedented reaction producing PhCOCl, $COCl_2$, HCl, and some organic halides such as C_2Cl_4 and $CHCl_3$:

$$\mathrm{Fe + PhCOOH + CCl_4 \longrightarrow PhCOCl + COCl_2 + HCl +}$$
$$1 \quad : \quad 1 \qquad (82\%/\mathrm{PhCOOH})$$
$$+ \text{Fe compound} + \mathrm{C_2Cl_4}\ \textit{etc.}$$
$$(\text{small amount}) \qquad (5)$$

The iron compound contains Cl, as revealed by a flame test.

Reaction Mechanism

Since vapors of ArCOOH and of RX have only low reactivity against iron when used separately, the reactions described in this paper apparently proceed through synergic attack of ArCOOH and RX to iron. The reaction pathway probably involves a successive reaction of the carboxylic acid and alkyl halide with iron. As for the reaction mechanism, the following two mechanisms are conceivable:

$$\mathrm{Fe + ArCOOH \longrightarrow FeH(OCOAr)} \qquad (6)$$
$$\Big\downarrow\ +\mathrm{RX} \qquad (7)$$
$$\mathrm{FeH(X) + ArCOOR}$$
$$\Big\downarrow\ +\mathrm{ArCOOH} \qquad (8)$$
$$\mathrm{FeX(OXOAr) + H_2}$$
$$\downarrow$$
$$\mathrm{[FeX(OCOAr)]_n}$$

Mechanism 1

$$\mathrm{Fe + RX \longrightarrow FeR(X)} \qquad (9)$$
$$\Big\downarrow\ +\mathrm{ArCOOH} \qquad (10)$$
$$\mathrm{FeH(X) + ArCOOR}$$
$$\Big\downarrow\ +\mathrm{ArCOOH} \qquad (11)$$
$$\mathrm{FeX(OCOAr) + H_2}$$
$$\downarrow$$
$$\mathrm{[FeX(OCOAr)]_n}$$

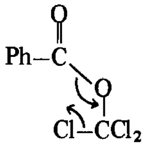
Mechanism 2

As for Mechanism 1, oxidative addition of carboxylic acid to transition metal compounds to produce hydrido(carboxylato)–transition metal complexes (*cf.* eqn. 6) [6], liberation of ester by reaction of metal carboxylate with organic halide (*cf.* eqn. 7) [7], and evolution of H_2 by reactions of metal hydrides with carboxylic acids (*cf.* eqn. 8) [6] all have precedents. As for mechanism 2, oxidative addition of RX to transition metal or transition metal compounds to yield organo(halo)transition metal compounds (*cf.* eqn. 9) is well known [8]. At the moment we do not have evidence to prove or disprove the mechanisms. However, evolution of a small amount of ethane and ethylene originated from C_2H_5Br suggests that a certain alkyliron intermediate like FeR(X) may have been formed according to eqn. 9, at least partially. It has been reported that an isolated alkyliron complex liberates ethane and ethylene on thermolysis [9].

It is known that metals including iron react with CCl_4 to produce metal chlorides and a $\cdot CCl_3$ radical which further reacts with hydrogen donors such as NH_4OH and alcohols to abstract hydrogen from them to yield $CHCl_3$ [10]. If we assume a similar radical formation reaction between Fe and CCl_4 in the presence of PhCOOH, the formation of PhCOCl is explained by the following mechanism involving $PhCOOCCl_3$ as the intermediate:

$$\mathrm{Fe + nCCl_4 \longrightarrow FeCl_{n-m} + m{\cdot}Cl + n{\cdot}CCl_3} \qquad (12)$$

$$\mathrm{PhCOOH + {\cdot}CCl_3 \longrightarrow PhCOOCCl_3 + {\cdot}H} \qquad (13)$$



$$\longrightarrow \mathrm{PhCOCl + COCl_2} \qquad (14)$$

$$\mathrm{{\cdot}H + {\cdot}Cl \longrightarrow HCl} \qquad (15)$$

$$\mathrm{{\cdot}H + {\cdot}CCl_3 \longrightarrow CHCl_3} \qquad (16)$$

$$\mathrm{2{\cdot}CCl_3 \longrightarrow C_2Cl_4 + C_2Cl_6 + Cl_2},\ \textit{etc.} \qquad (17)$$

TABLE II. Powder X-ray Diffraction Data.[a]

$[FeBr(OCOC_6H_5)]_n$ *1*			$[FeCl(OCOC_6H_5)]_n$ *2*			$[FeI(OCOC_6H_5)]_n$ *3*		
2θ (°)	d (Å)	$100I/I_0$	2θ (°)	d (Å)	$100I/I_0$	2θ (°)	d (Å)	$100I/I_0$
13.1	6.76	100	12.2	7.25	90.4	12.9	6.89	100
19.3	4.60	8.2	18.4	4.83	100	21.8	4.08	5.1
25.6	3.48	13.9	24.5	3.63	4.3	25.9	3.45	48.0
31.9	2.81	22.6	29.7	3.09	3.7	32.5	2.76	35.6
49.6	1.84	2.9	35.6	2.52	3.1	39.2	2.30	10.5
						53.1	1.73	10.4
$[FeBr(OCOCH{=}CHC_6H_5)]_n$ *4*			$[FeBr(OCOC_6H_4\text{-}p\text{-}CH_3)]_n$ *5*			$[FeBr(OCOCH_2C_6H_5)]_n$ *6*		
9.4	9.31	54.5	9.7	9.20	52.0	11.4	7.73	100
14.2	6.24	100	14.6	6.07	100	17.1	5.17	73.4
21.8	4.08	6.4	20.6	4.31	6.1	22.9	3.88	16.6
28.8	3.10	6.4	29.6	3.02	7.7	28.8	3.10	10.4
29.4	3.05	7.4	34.7	2.59	3.5	34.7	2.59	8.3
35.4	2.54	4.7	39.8	2.27	2.5	53.2	1.72	9.6

[a] K_α (Cu) (λ = 1.5418 Å) was irradiated.

Characterization and Chemical Reactivity of $[FeX(OCOAr)]_n$

As described above, compounds *1–6* grow as crystals on the surface of the iron plate and washing the compounds with organic solvents give analytically pure samples, as shown in Table I. Use of iron powder and excess of ArCOOH and RX leads to complete disappearance of the iron powder by the reaction, and removal of soluble materials in organic solvents also gives analytically pure compounds. X-ray diffraction patterns of *1–6* show sharp diffraction bands supporting the theory that they are crystalline compounds; the data are summarized in Table II. Complexes *1–6* show paramagnetism with μ_{eff} values of 5.04 ± 0.22 B.M. (see Table I) corresponding to 4 unpaired electrons, the high spin character of *1–6* suggesting tetrahedral configuration around Fe; actually tetrahedral complexes such as $[FeCl_4]^{2-}$ and $[FeBr_4]^{2-}$ reportedly have μ_{eff} values of about 5.0 B.M. [11].

Compounds *1–6* are insoluble in non-coordinating solvents such as hydrocarbons (benzene, toluene, *etc.*), halogenated hydrocarbons (CH_2Cl_2, $CHCl_3$, *etc.*), ethers, alcohols, and acidic and alkaline water. However, they are soluble in coordinating solvents such as pyridine and triethylamine, suggesting that they have multinuclear structures which are degraded by coordination of the coordinating solvent to Fe. Their high thermal stabilities, as revealed by thermogravimetric analysis (Fig. 1), may also be taken as an indication of the polynuclear structure. IR spectra of *1–5* show $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ around 1540 cm^{-1} and 1400 cm^{-1}, respectively. The positions of $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ are characteristic of metal compounds having bridging carboxylato ligands between metals [12], supporting the proposed multinuclear structure. Based on the properties and IR spectroscopic data of the compounds, we propose the following multinuclear structure having bridging halo and carboxylato ligands for *1–5*:

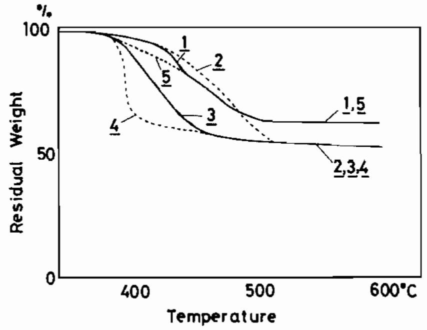
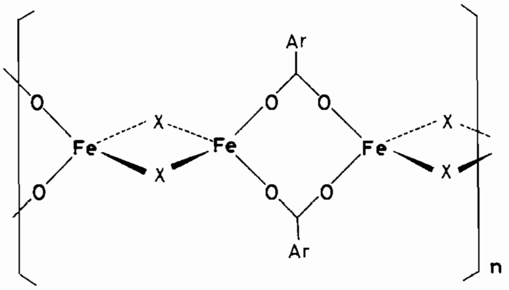


Fig. 1. Thermogravimetric analysis of $[FeX(OCOAr)]_n$.



As for *6*, it has lower thermal stability than *1–5* and its IR spectrum shows a somewhat different pattern concerning ν(COO). Therefore, *6* may have a different structure from that shown above, though *6* is still insoluble in the non-coordinating solvents.

Evaporation of the pyridine and triethylamine solutions of *1–6* gives compounds whose IR spectra clearly show formation of pyridine- and triethylamine-coordinated complex. However, isolation of the complexes failed. On the contrary, treatment of *1–3* with solvents containing 2,2′-bipyridine (bpy) gives isolatable complexes formulated as $[Fe(bpy)_3]X_2$ [13] and insoluble $Fe(OCOPh)_2$ which is isolated as an adduct with isonicotinic hydrazide (INH) [14]:

$$2[FeX(OCOPh)]_n + 3n\text{bpy} \longrightarrow$$

$$n[Fe(bpy)_3]X_2 + nFe(OCOPh)_2 \qquad (18)$$

$$\Big\downarrow{+\text{INH}}$$

$$Fe(OCOPh)_2(INH) \qquad (19)$$

Treatment of *1–3* with PPh_3 gave adducts of PPh_3 as proved by IR spectroscopy, but isolation of the PPh_3 adducts was not feasible. Compounds *1–6* have moderate stability in air, but after 24 h their color changes (usually to red), presumably due to partial oxidation of Fe(II) to Fe(III). The non-conducting compounds *1–6* are converted to substances showing certain electric conductivity (σ = *ca.* 10^{-5} S cm^{-1}) after exposure to air.

Experimental

Materials and Manipulation

Iron plate (JIS-SUYP, Fe > 98%), pure iron powder (guaranteed grade), and stainless steel (SUS 304) were purchased from Nisshin Kohki Co. Ltd., Yoneyama Chemical Industries Co. Ltd., and Japan Lamp Industrial Co. Ltd., respectively. Carboxylic acids, organic halides, bpy, PPh_3, and isonicotinic hydrazide were used as purchased from Tokyo Kasei Co. Ltd. Organic solvents were dried over CaH_2 or Na wires, distilled under N_2, and stored under N_2. N_2 was bubbled into distilled water and the water was stored under N_2. Pressure bottles used for the reaction were purchased from Japan Taiatsu Glass Co. Ltd. The reactions and manipulation of compounds *1–6* were carried out under N_2 using Schlenk type tubes.

Elemental and Instrumental Analysis

Microanalysis of C, H, N, and halogen was performed by Mr. T. Saito of our laboratory by using a Yanagimoto CHN Autocorder Type MT2 and a Yazawa halogen analyzer.

IR and NMR spectra were recorded on a Hitachi spectrometer 295 and a Japan Electron Optics Laboratory Model PS-100 spectrometer, respectively. The magnetic susceptibility was measured with the aid of a Shimadzu MB-100 magnetic balance at room temperature.

X-ray diffraction patterns were obtained with a Phillips PW-1051 X-ray diffractometer. The electric conductivity was measured by a Takeda Riken TR-8651 electrometer after molding the compound into a disk. Thermogravimetric analysis was performed by using a Shimadzu DT-30 thermoanalyzer. Gas chromatographic (GC) analysis was performed by using a Shimadzu GC-3BT or a Shimadzu GC-6A gas chromatograph (carrier gas = He; column = active charcoal for gaseous products and SDC-550 from Gasukuro Kogyo Inc. for liquid products).

Reaction of Iron with the Mixture of ArCOOH and RX

A pressure bottle (equipped with a needle valve) containing an iron plate (1 × 10 × 50 mm), PhCOOH (3.3 g, 27 mmol), and EtBr (2.9 g, 27 mmol) was evacuated. After introducing N_2, the pressure bottle was heated at 200 °C for 10 h in a thermostatted oil bath. After cooling to room temperature, the needle valve was open, and the amount of gas evolved was measured volumetrically. GC analysis of the gas showed evolution of H_2 (*ca.* 1.4 mmol) and small amounts of C_2H_6 and C_2H_4. GC analysis of the liquid product showed formation of PhCOOEt (1.3 mmol). The iron plate was taken out from the pressure bottle, and crystals of *1* were scraped off carefully with a spatula. The crystals were washed repeatedly with acetone under N_2 in a Schlenk tube and dried under vacuum: yield = 360 mg. Compounds *2* and *3* were prepared analogously. Use of stainless steel plates in the reactions with PhCOOH–RX (X = Br, Cl, I) mixtures also gave *1–3* with somewhat lower yields (about 60% of the yields attained by using the iron plate). The compounds *1–3* thus obtained were also analytically pure, and their IR spectra and powder X-ray diffraction patterns were identical to those of *1–3* prepared by using the iron plate. Stainless steel contains Ni and Cr, but it was confirmed that Ni and Cr did not react with the mixture of ArCOOH and RX, and the product obtained by using the stainless steel did not contain Ni and Cr. Compounds *4–6* were prepared analogously.

A mixture of Fe (powder, 580 mg, 10 mmol), PhCOOH (2.5 g, 21 mmol), and CCl_4 (2.0 cm^3, 21 mmol) was heated at 200 °C for 10 h in a pressure bottle (under N_2) equipped with a needle valve. When the needle valve was opened, a gas which produced smoke in air came out. The gas contained $COCl_2$, HCl and H_2, as proved by GC. Liquid products were extracted with ether and analyzed by GC which showed formation of 17 mmol (82%) of PhCOCl, $CHCl_3$, C_2Cl_6, C_2Cl_4, and $CCl_2{=}CCl{-}CCl{=}CCl_2$. A black solid (presumably containing iron compounds) was obtained.

Reactions of 1–3 *with Bpy*

A mixture of *1* (200 mg, 0.77 mmol as the monomer unit) and bpy (360 mg, 2.3 mmol) was stirred in 50 cm^3 of toluene at room temperature under N_2. After 1 day, a red solution and a brownish green precipitate were obtained. After removing toluene by evaporation under vacuum, CH_2Cl_2 (30 cm^3) was added to obtain a red solution containing $[Fe(bpy)_3]Br_2$. After filtration, the filtrate was cooled to −20 °C to yield red crystals of $[Fe(bpy)_3]Br_2$ (100 mg). The compound was characterized by comparing its IR and NMR spectra with those of an authentic sample prepared according to the literature [13]. To the brownish green precipitate remaining after extracting $[Fe(bpy)_3]Br_2$ was added isonicotinic hydrazide (INH, 210 mg, 1.5 mmol) and 10 cm^3 of H_2O. After stirring the mixture for 10 h at room temperature under N_2, the INH adduct of $Fe(OCOPh)_2$ formed was washed with H_2O repeatedly and dried under vacuum. $Fe(OCOPh)_2(INH)$ thus formed was identified by comparing its IR spectrum with that of an authentic sample prepared according to the literature [14]. The reactions of *2* and *3* with bpy were carried out analogously.

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