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Selective Generation of Fe_1, Fe_3, and Fe_4 Carbonyl Anions in Aminated Polystyrenes

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ABSTRACT: Di- and monoaminated polystyrenes of **I** and **II** were prepared by reactions of chloromethylated polystyrene with *N,N*-dimethyl-1,3-propanediamine and diethylamine, respectively. Treatment of the diaminated polystyrene (**I**) with $Fe_3(CO)_{12}$ in aqueous medium at 50 °C for 6 h gave a polymer-bound $[Fe_3(CO)_{11}]^{2-}$ complex. However, under refluxing conditions, a polymeric $[Fe_4(CO)_{13}]^{2-}$ complex was formed. When $Fe(CO)_5$ was used as a starting material, selective formation of the above Fe_4 complex resulted after a long reaction time, 16 h. Treatment with $Fe(CO)_5$ at room temperature afforded a polymeric $[HFe(CO)_4]^-$ complex. Reactions of **II** with $Fe_3(CO)_{12}$ and $Fe(CO)_5$ attained selective generation of a $[HFe_3(CO)_{11}]^-$ species in the polymer, respectively. Furthermore, these polymer-bound Fe_3 and Fe_4 complexes could be also obtained by ion exchange reactions of both **I** and **II** with the corresponding ionic Fe compounds. Reaction of **I** with $Ru_3(CO)_{12}$ at room temperature for 24 h gave polymer-bound $[HRu_3(CO)_{11}]^-$ complex. $[Ru_6(CO)_{18}]^{2-}$ species could be selectively fixed in **I** by using the above ion exchange method. The Fe and Ru carbonyl anionic species are stabilized through forming an ion pair in the polymer matrix.

Introduction

Recently, synthetic methodology for metal clusters has been extensively developed not only because unprecedented chemical reactions might occur on multimetal centers as catalysts but also because metal clusters are useful precursors of guest materials in nanocomposites for nonlinear optical applications.[1] Basset and Gates have reported that use of basic surfaces of solid materials causes selective formation of metal cluster complexes.[2] We have also found formation of metal carbonyl anion clusters in polymers by the action of basic organic polymers. Various Rh carbonyl cluster anions of Rh_6, Rh_7, and Rh_{14} species could be generated selectively in the aminated polymer matrix under CO and H_2O, and such polymer-bound Rh cluster complexes catalyzed selective deoxygenation of various N−O bonds and hydrohydroxymethylation of olefins.[3,4] Fe carbonyl compounds have been widely used as reagents and catalysts because of their unique reactivities in organic synthesis.[5] It can be expected that polymer-bound Fe carbonyl complexes might have novel "hybrid" catalytic functions,[6] accompanied by similar reactivities of the corresponding homogeneous Fe complexes. In this paper, we applied our *in situ* method to the synthesis of Fe carbonyl clusters in polymer matrices. Polymer-bound Fe, Fe_3, and Fe_4 carbonyl complexes were selectively obtained by selection between monoamino and diamino moieties of the polymers (**I** and **II**). It is known that polymer-bound metal cluster complexes have been prepared by using the ion exchange reaction of quaternary ammonium moieties bound to a polymer support with metal cluster anions.[7,8] In contrast, the present *in situ* method leads to metal carbonyl anions bound to polymers *directly from the interaction of neutral metal complexes* with the aid of amino moieties in the polymers in an aqueous environment.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere. All solvents were dried, distilled by literature procedures[9] and stored under a nitrogen atmosphere. Distilled H_2O was also stored under a nitrogen atmosphere. *p*-(Chloromethyl)styrene from Seimi Chemicals was purified before use. $Fe(CO)_5$ was used as purchased from Aldrich. $Fe_3(CO)_{12}$,[10] $[HNEt_3][HFe_3(CO)_{11}]$,[10] $[PPN]_2[Fe_3(CO)_{11}]$,[11] $[PPN][HFe(CO)_4]$,[12] $[Fe(py_6)][Fe_4(CO)_{13}]$,[13] $[PPN]_2[Fe_4(CO)_{13}]$,[13] $[pyH][HFe_4(CO)_{13}]$,[14] $[PPN][HFe_4(CO)]_{13}]$,[15] $Ru_3(CO)_{12}$,[16] $[PPN][HRu_3(CO)_{11}]$,[17] and $[PPN]_2[Ru_6(CO)_{18}]$[18] were prepared by published methods, respectively. Infrared spectra were obtained with a Hitachi EPI-G spectrometer. Quantitative analysis of Fe ions in solution was carried out by an atomic absorption spectrometer of Nippon Jarrell Ash, AA-825.

Synthesis of Aminated Polymers.[19] Bulk polymerization of *p*-(chloromethyl)styrene and divinylbenzene (98/2, w/w) was carried out at 80 °C using AIBN, followed by amination with *N,N*-dimethyl-1,3-propanediamine in dioxane at room temperature under a nitrogen atmosphere. The polymer was then washed with dioxane, a 50 vol % solution of acetone in H_2O, and 0.2 N NaOH, successively. Further, the polymer was repeatedly washed with a 50 vol % solution of acetone of in H_2O until the rinses became neutral and, finally, rinsed twice with acetone and dried in vacuo. Diamino-substituted **I** with C, 70.26, H, 8.74, N, 8.36, and Cl, 3.44% was obtained, which displayed a 75.5% amination degree of the chloromethyl moieties (X). Under conditions similar to those of the diamino polymer (**I**), amination with diethylamine in place of the 1,3-propanediamine was carried out to give a monosubstituted polymer (**II**) with C, 81.86, H, 9.82, N, 6.87, and Cl, 0.85% and $X = 95.3\%$. The synthesis of the two aminated polymers (**I** and **II**) is shown in Scheme 1.

General Procedures for the Preparation of Polymer-Bound Fe Complexes Using the *in Situ* Method. $Fe_3(CO)_{12}$ (0.05 mmol) and the aminated polymer (**I** or **II**; 0.5 mmol of N) were placed in 25 mL flask equipped with a reflux condenser. The reaction vessel was evacuated and flushed three times with nitrogen. A mixed solvent of methanol (10 mL) and deoxygenated water (1 mL) was added by syringe, and the mixture was stirred and heated at a desired temperature for several hours under a nitrogen atmosphere. After reaction, the mixture was cooled to room temperature, and then vacuum filtered and washed by water two times quickly in air to give a polymer-bound Fe complex. On the other hand, in the case of $Fe(CO)_5$, the aminated polymer (**I** or **II**; 0.5 mmol of N) was placed in 25 mL flask equipped with a reflux condenser. The reaction vessel was evacuated and flushed three times with nitrogen. A mixed solvent of methanol (10 mL), deoxygenated water (1 mL), and $Fe(CO)_5$ (0.15 mmol) was

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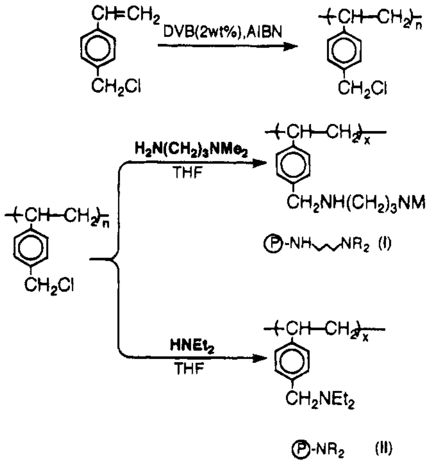
Scheme 1. Synthetic Method of Diaminated and Monoaminated Polystyrenes (I and II)



successively added by syringe, and the mixture was stirred and heated at a desired temperature for several hours under a nitrogen atmosphere. The following workup procedure is the same as that of $Fe_3(CO)_{12}$. IR spectra of the polymer-bound Fe complexes were measured and were compared with those of homogeneous Fe complexes, which are summarized in Table1 and Figures 1−4. Quantitative analysis of the Fe ion in the above filtrates showed that almost all of the charged Fe (>98%) remained in the polymer matrices, respectively.

Trapping the Intermediate Polymer-Bound $[HFe(CO)_4]^-$ Complex. In order to trap intermediate species formed during the conversion of $Fe(CO)_5$ to the polymer-bound $[HFe_3(CO)_{11}]^-$, reaction of $Fe(CO)_5$ (0.5 mmol) with the aminated polymer (**I**, 0.5 mmol of N equimolar to $Fe(CO)_5$) in the mixed solvent of methanol (10 mL) and water (1 mL) was carried out at room temperature for 2 h under a nitrogen atmosphere. An orange polymer was obtained, which was washed with MeOH under a nitrogen atmosphere to remove unreacted $Fe(CO)_5$. The following workup procedure was similar to that of the above *in situ* method. The IR spectrum of the orange polymer showed the presence of $[HFe(CO)_4]^-$ in the polymer matrix. For confirmation, the isolated polymer-bound $[HFe(CO)_4]^-$ complex was treated with $Fe(CO)_5$ under reflux and gave a mixture of $[HFe_3(CO)_{11}]^-$ and $[Fe_3(CO)_{11}]^{2-}$ species in the polymer matrix. The $[HFe(CO)_4]^-$ species was unchanged by a similar treatment of isolated polymers in the absence of $Fe(CO)_5$. Using the monoaminated polymer (**II**) in place of **I**, formation of polymer-bound Fe carbonyl complexes could not be observed at room temperature for 2 h, and then, $Fe(CO)_5$ remained almost quantitatively in solution.

Preparation of the Polymer-Bound $[HRu_3(CO)_{11}]^-$ Complex Using the *in Situ* Method. $Ru_3(CO)_{12}$ (0.02 mmol) and the aminated polymer (**I** or **II**; 0.2 mmol of N) were placed in a 25 mL flask. A mixed solvent of methanol (10 mL) and deoxygenated water (1 mL) was added by syringe, and the mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. The workup procedure is similar to that of $Fe_3(CO)_{12}$. In the case of **I**, a polymer-bound $[HRu_3(CO)_{11}]^-$ complex was selectively formed, while using **II** in place of **I** led to no polymeric Ru complexes and the starting $Ru_3(CO)_{12}$ remained almost quantitatively in solution (Table 1 and Figure 5).

Preparation of the Polymer-Bound Fe and Ru Complexes Using the Ion Exchange Method. Standard Schlenk techniques were adopted for the preparation of $K_2[Fe_3(CO)_{11}]$,[11] $K_2[Fe_4(CO)_{13}]$,[13] $[pyH][HFe_4(CO)_{13}]$,[14] $Na[HRu_3(CO)_{11}]$,[17] and $K_2[Ru_6(CO)_{18}]$[18] according to the literature procedures cited. All of the polymer-bound complexes were prepared in O_2-free inert atmosphere.

(a) Polymer-Bound $[Fe_3(CO)_{11}]^{2-}$ Complex. $Fe_3(CO)_{12}$ (0.05 mmol) was added to 1.0 mL of 0.5 N methanolic KOH. The mixture was stirred at room temperature for 2 h and then filtered through a medium-porosity Schlenk-type frit. The filtrate was added to an aminated polymer (**I** or **II**, 0.5 mmol of N) in a mixed solvent of methanol and H_2O. Within 10 min, the color of the aminated polymer changed to reddish brown. The mixture was stirred at room temperature for 2 h. The workup procedure, similar that of the above *in situ* method, gave a reddish brown polymer.

(b) Polymer-Bound $[Fe_4(CO)_{13}]^{2-}$ Complex. *From $K_2[Fe_4(CO)_{13}]$.* To $[Fe(py_6)][Fe_4(CO)_{13}]$ (0.12 mmol) was added 4 mL of acetonitrile and 0.46 mL of 0.5 N methanolic KOH, and the mixture was stirred at room temperature for 2 h. The mixture was filtered through the Schlenk-type frit, and the precipitate was washed with acetonitrile two times. The filtrate was added to an aminated polymer (**I** or **II**, 0.5 mmol of N) in a mixed solvent of methanol and H_2O, followed by stirring at room temperature for 2 h. Applying a workup procedure similar to that of the above polymer-bound $[Fe_3(CO)_{11}]^{2-}$ complex gave a reddish brown polymer.

From $[pyH][HFe_4(CO)_{13}]$. To $[Fe(py_6)][Fe_4(CO)_{13}]$ (0.595 mmol) was added 5 mL of 0.2 N KOH in H_2O. The reaction mixture was stirred at room temperature for 2 h. The filtrate from the Schlenk-type frit was added dropwise to 4 mL of 0.2 N HCl, and a black solid of $[pyH][HFe_4(CO)_{13}]$ deposited. The isolated solid was dissolved in 10 mL of methanol. Aliquots of this methanolic solution (1 mL) were mixed with an aminated polymer (**I** or **II**, 0.5 mmol of N) in a mixed solvent of methanol and H_2O and stirred at room temperature for 2 h. The workup procedure was similar to that of the above polymer-bound $[Fe_3(CO)_{11}]^{2-}$ complex. A reddish brown polymer was obtained.

(c) Polymer-Bound $[HRu_3(CO)_{11}]^-$ Complex. The mixture of $Ru_3(CO)_{12}$ (0.03 mmol) and $NaBH_4$ (0.15 mmol) was added to 3 mL of THF and stirred for over 20 min. The suspension was filtered through the Schlenk-type frit, and the filtrate was added to an aminated polymer (**I** or **II**, 0.5 mmol of N) in a mixed solvent of methanol and H_2O, followed by stirring at room temperature for 2 h. Using a workup procedure similar to that of the above polymer-bound $[Fe_3(CO)_{11}]^{2-}$ complex resulted in the isolation of a dark brown polymer.

(d) Polymer-Bound $[Ru_6(CO)_{18}]^{2-}$ Complex. To a solution of KOH (0.9 mmol) in 0.02 mL of H_2O was added 0.4 mL of THF. Then, a solution of $Ru_3(CO)_{12}$ (0.03 mmol) in 4 mL of THF was added dropwise for over 30 min to the KOH solution. The resulting deep red-brown solution was stirred for 1.5 h and was mixed with an aminated polymer (**I** or **II**, 0.5 mmol of N) in a mixed solvent of methanol and H_2O. The resulting mixture was stirred at room temperature for 2 h. Using a workup procedure similar to that of the above polymer-bound $[Fe_3(CO)_{11}]^{2-}$ complex gave a dark brown polymer. The isolated product gave infrared absorptions at 2002 (s), 1985 (s), and 1930 (m, sh) cm^{-1}. An authentic sample of $[PPN]_2[Ru_6(CO)_{18}]$ exhibited absorptions at 2000 (s), 1983 (s), and 1930 (w, br) cm^{-1}. In the preparation of polymer-bound $[HRu_3(CO)_{11}]^-$ and $[Ru_6(CO)_{18}]^{2-}$ complexes by the above ion exchange method, use of the diaminated polymer (**I**) seems to be preferable to that of the monoaminated one (**II**).

When the above prepared polymer-bound Fe and Ru complexes were stored in H_2O under a nitrogen atomsphere, IR spectra of the complexes did not change for several days. The Fe and Ru carbonyl anionic species are stabilized by the polymer matrix in aqueous medium to form ion-pair complexes. It has been reported that treatment of $[HNEt_3][HFe_3(CO)_{11}]$ complex with aqueous HCl gave $Fe_3(CO)_{12}$.[10] A similar acid treatment of the polymer-bound $[HFe_3(CO)_{11}]^-$ complex was carried out to give a pale pink solid material. The IR spectrum of the pink material had no carbonyl stretching bands in the region 1700−2200 cm^{-1}. Probably, the Fe_3 frame was decomposed into polymer-bound mononuclear Fe complexes with liberation of CO during the above acid treatment.

Results and Discussion

IR data of polymer-bound Fe, Fe_3, and Fe_4 carbonyl complexes and of the corresponding homogeneous Fe complexes are summarized in Table 1 and Figures 1−4, which will be discussed after this. Treatment of $Fe_3(CO)_{12}$ (0.05 mmol) with the monoaminated polymer (**II**,

Table 1. Stretching Frequencies in the ν_{CO} Region of Fe and Ru Carbonyl Compounds

	polymer-bound Fe & Ru complex	conditions	ν_{CO}, cm^{-1} (2200–1800 cm^{-1})				
Fig. 1a	$[HFe_3(CO)_{11}]^-$/polymer **II** (Nujol)[a]	$Fe_3(CO)_{12}$, 50 °C, 6 h	2064 (w)		1999 (s)	1970 (s)	1945 (m, sh)
Fig. 1b	$[HFe_3(CO)_{11}]^-$/polymer **II** (Nujol)	ion-exchange	2064 (w)		1999 (s)	1970 (s)	1945 (m, sh)
Fig. 1c	$[PPN][HFe_3(CO)_{11}]$ (Nujol)		2065 (w)		1999 (s)	1969 (s)	1945 (m, sh)
Fig. 2a[b]	$[Fe_3(CO)_{11}]^{2-}$/polymer **I** (Nujol)	$Fe_3(CO)_{12}$, 50 °C, 6 h	2022 (w)	1999 (m)	1946 (s)	1911 (m)	1882 (m)
Fig. 2b[b]	$[Fe_3(CO)_{11}]^{2-}$/polymer **I** (Nujol)	ion exchange	2022 (w)	1999 (m)	1946 (s)	1911 (m)	1882 (m)
Fig. 2c	$[PPN]_2[Fe_3(CO)_{11}]$ (MeCN)				1947 (s)	1912 (m)	
Fig. 3a	$[HFe_3(CO)_{11}]^-$/polymer **II** (Nujol)	$Fe(CO)_5$, reflux, 2 h	2065 (w)		2000 (s)	1970 (s)	1946 (m, sh)
Fig. 3b	$[HFe(CO)_4]^-$/polymer **I** (Nujol)	$Fe(CO)_5$, rt, 2 h	2002 (w)	1912 (m)	1881 (s)		
Fig. 3c	$[PPN][HFe(CO)_4]$ (Nujol)		2003 (w)	1912 (m)	1881 (s)		
Fig. 4a	$[Fe_4(CO)_{13}]^{2-}$/polymer **I** (Nujol)	$Fe_3(CO)_{12}$, reflux, 6 h	2021 (w)		1950 (s)		
Fig. 4b[c]	$[Fe_4(CO)_{13}]^{2-}$/polymer **I** (Nujol)	$Fe(CO)_5$, reflux, 16 h	2021 (w)	2000 (w)	1950 (s)		
Fig. 4c	$[Fe_4(CO)_{13}]^{2-}$/polymer **I** (Nujol)	ion exchange	2021 (w)		1950 (s)		
Fig. 4d	$[PPN]_2[Fe_4(CO)_{13}]$ (MeCN)		2020 (w)		1951 (s)		
Fig. 5a	$[HRu_3(CO)_{11}]^-$/polymer **I** (Nujol)	$Ru_3(CO)_{12}$, rt, 24 h	2076 (w)	2014 (s)	1988 (s)	1953 (w, sh)	
Fig. 5b	$[HRu_3(CO)_{11}]^-$/polymer **I** (Nujol)	ion exchange	2076 (w)	2014 (s)	1988 (s)	1953 (m)	
Fig. 5c	$[PPN][HRu_3(CO)_{11}]$ (CH_2Cl_2)		2076 (w)	2014 (s)	1987 (s)	1953 (m)	

[a] State of IR samples is given in parentheses. [b] These stretching frequencies of 2022, 1999, and 1882 cm^{-1} are assignable to $Fe(CO)_5$, $[HFe_3(CO)_{11}]^-$, and $[HFe(CO)_4]^-$ species, respectively. [c] A weak absorption band of 2000 cm^{-1} shows formation of a small amount of $[HFe_3(CO)_{11}]^-$ species.

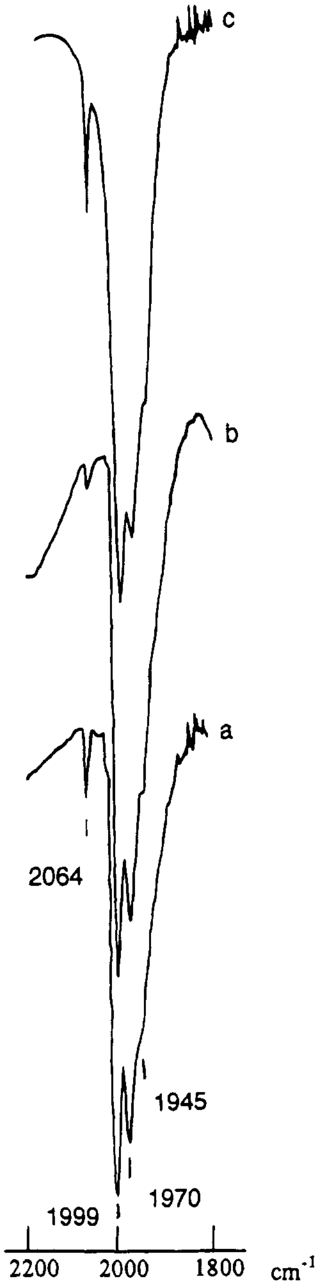
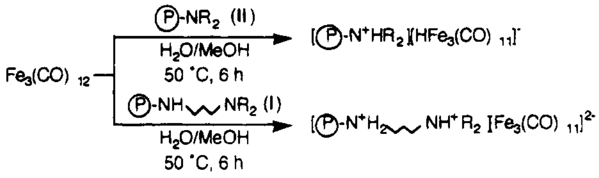


Figure 1. Polymer **II**-bound $[HFe_3(CO)_{11}]^-$ complex prepared by (a) the *in situ* method from $Fe_3(CO)_{12}$ at 50 °C for 6 h and (b) the ion exchange method. (c) $[HNEt_3][HFe_3(CO)_{11}]$.

0.5 mmol of N) in a mixed solvent of methanol and H_2O (10:1, 11 mL) at 50 °C for 6 h gave a wine red polymer as a solid material. The IR spectrum of the isolated polymer showed 2064 (w), 1999 (s), 1970 (s), and 1945 (m, sh) cm^{-1}, which was assigned to a $[HFe_3(CO)_{11}]^-$ species in Figure 1a, by comparison with the infrared spectrum of a homogeneous $[HNEt_3][HFe_3(CO)_{11}]$ complex.[20] However, under similar conditions, using **I** in place of **II** led to formation of a reddish brown polymer, with $[Fe_3(CO)_{11}]^{2-}$ as the main species (1946 (s) and 1911 (m) cm^{-1})[21] together with the $[HFe_3(CO)_{11}]^-$ (1999 (m) cm^{-1}) and $[HFe(CO)_4]^-$ species (1882 (m) cm^{-1}) in Figure 2a (eq 1). IR analysis in the course of the above



(1)

reaction with **I** revealed that two $[Fe_3(CO)_{11}]^{2-}$ and $[HFe(CO)_4]^-$ anions were formed by way of formation of the $[HFe_3(CO)_{11}]^-$ species.[22] Taking account of the homogeneous Fe chemistry,[23] formation of the above polymer-bound Fe_3 cluster complexes can be explained as follows: reaction of H_2O with an amino function in the polymers gives an ammonium ion and OH^-, followed by attack of OH^- at a carbonyl moiety of $Fe_3(CO)_{12}$ to give the $[HFe_3(CO)_{11}]^-$ species *via* a Fe hydroxycarbonyl intermediate. In the case of the diaminated polymer (**I**), another OH^- further attacks at a hydrogen of the $[HFe_3(CO)_{11}]^-$ species to form the $[Fe_3(CO)_{11}]^{2-}$ species. Such Fe carbonyl anions of the $[HFe_3(CO)_{11}]^-$ and $[Fe_3(CO)_{11}]^{2-}$ species may be stabilized by ion-pairing in the polymer matrix. Generation of Fe_3 cluster anions using solid materials has been also observed in the case of basic metal oxides as supports. Basset *et al.* have reported that Fe carbonyl complexes of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ were treated with hydrated MgO or Al_2O_3 under air-free conditions to give exclusively the $[HFe_3(CO)_{11}]^-$ species on the surface of the metal oxides without formation of the $[Fe_3(CO)_{11}]^{2-}$ species: OH^- on the metal oxides attacks $Fe_3(CO)_{12}$ to form the $[HFe_3(CO)_{11}]^-$ species, which binds to a cationic site of the metal oxides.[2]

The polymer-bound $[HFe_3(CO)_{11}]^-$ and $[Fe_3(CO)_{11}]^{2-}$ complexes could also be obtained by the ion exchange method. $K_2[Fe_3(CO)_{11}]$ formed from treatment of Fe$_3$-

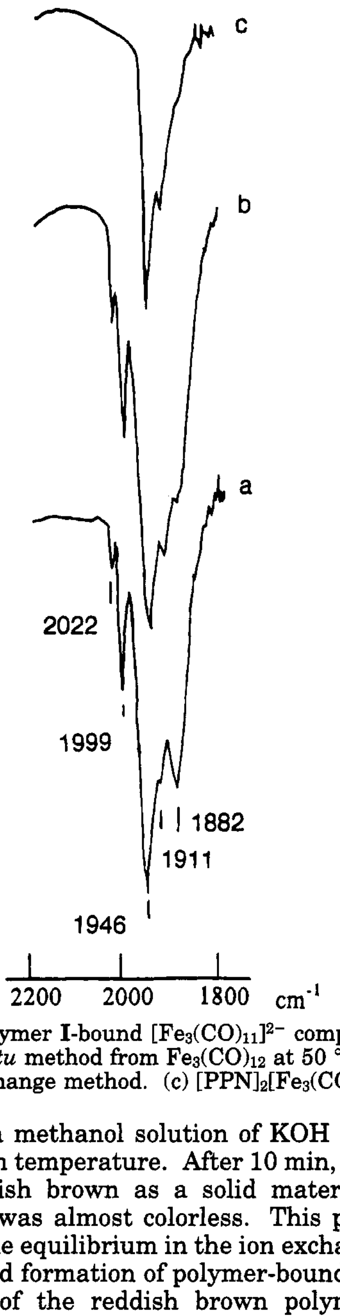


Figure 2. Polymer **I**-bound $[Fe_3(CO)_{11}]^{2-}$ complex prepared by (a) the *in situ* method from $Fe_3(CO)_{12}$ at 50 °C for 6 h and (b) the ion exchange method. (c) $[PPN]_2[Fe_3(CO)_{11}]$.

$(CO)_{12}$ with a methanol solution of KOH was reacted with **I** at room temperature. After 10 min, the polymer became reddish brown as a solid material and the supernatant was almost colorless. This phenomenon shows that the equilibrium in the ion exchange process lies far toward formation of polymer-bound Fe species. IR analysis of the reddish brown polymer showed selective formation of the $[Fe_3(CO)_{11}]^{2-}$ species (Figure 2b, eq 2). On the other hand, reaction of $K_2[Fe_3(CO)_{11}]$ with **II** in place of **I** did not afford the polymer-bound dianion $[Fe_3(CO)_{11}]^{2-}$ complex, but the polymeric monoanion $[HFe_3(CO)_{11}]^-$ complex (Figure 1b), exclusively. Addition of [PPN]Cl to the red filtrate from the reaction with **II** led to formation of $[PPN]_2[Fe_3(CO)_{11}]$ as the main precipitate. The result showed that monoaminated polymer (**II**) cannot bind to $[Fe_3(CO)_{11}]^{2-}$ in the solution, but it can bind to $[HFe_3(CO)_{11}]^-$ equilibrated with $[Fe_3(CO)_{11}]^{2-}$ (eq 3). It seems likely that the diaminated polymer (**I**) can strongly stabilize a species of $[Fe_3(CO)_{11}]^{2-}$ by a diamino chelate ligand bound to the polymer support. In the case of the monoaminated polymer (**II**), two amino moieties are unlikely to form an ion-pair complex with the Fe_3 dianionic species because of steric restrictions due to the polymer matrix, and this may result in selective formation of the polymer-bound $[HFe_3(CO)_{11}]^-$ complex. In addition, the different basicity between the two aminated polymers, **I** and **II**, might influence formation paths for the $[Fe_3(CO)_{11}]^{2-}$ and $[HFe_3(CO)_{11}]^-$ species. IR spectra of two polymer-bound Fe_3 complexes were superimposable on those of the Fe_3 complexes obtained from the above *in situ* method.

$$K_2[Fe_3(CO)_{11}] + [\textcircled{P}\text{-}N^+H_2\sim NH^+R_2\,[OH^-]_2 \longrightarrow [\textcircled{P}\text{-}N^+H_2\sim NH^+R_2\,[Fe_3(CO)_{11}]^{2-} + 2KOH \qquad (2)$$

$$[Fe_3(CO)_{11}]^{2-} + H_2O \rightleftarrows [HFe_3(CO)_{11}]^- + OH^- \qquad (3)$$

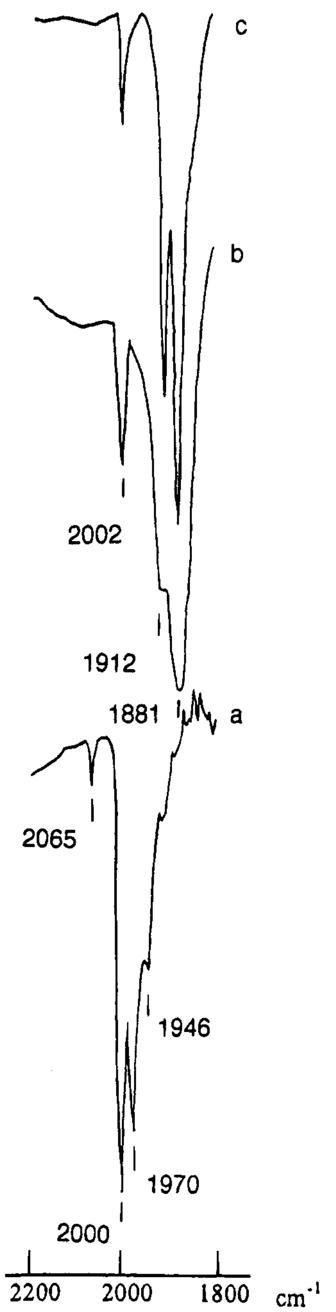


Figure 3. (a) Polymer **II**-bound $[HFe_3(CO)_{11}]^-$ complex prepared by the *in situ* method from $Fe(CO)_5$ under reflux for 2 h. (b) Polymer **I**-bound $[HFe(CO)_4]^-$ complex by the *in situ* method from $Fe(CO)_5$ at room temperature for 2 h. (c) [PPN]-$[HFe(CO)_4]$.

Treatment of $Fe(CO)_5$ (0.15 mmol) with **II** (0.5 mmol of N) in the mixed solvent of methanol and H_2O under reflux for 2 h gave a wine red polymer involving the $[HFe_3(CO)_{11}]^-$ species (Figure 3a, eq 4). Notably, in both cases of the *in situ* method using $Fe(CO)_5$ and $Fe_3(CO)_{12}$ as starting materials, the monoaminated polymer (**II**)

Scheme 2. Formation Paths of the $[\mathrm{Fe(CO)_{11}}]^{2-}$ Species from $\mathrm{Fe(CO)_5}$ as a Starting Material[26]

$$\mathrm{Fe(CO)_5} + \mathrm{OH^-} \longrightarrow [\mathrm{HFe(CO)_4}]^- + \mathrm{CO_2} \qquad (1)$$

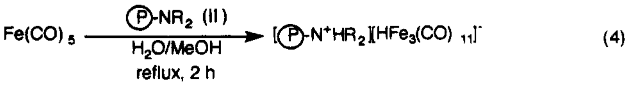
$$[\mathrm{HFe(CO)_4}]^- + \mathrm{H_2O} \longrightarrow \mathrm{H_2Fe(CO)_4} + \mathrm{OH^-} \qquad (2)$$

$$[\mathrm{HFe(CO)_4}]^- + \mathrm{H_2Fe(CO)_4} \longrightarrow [\mathrm{HFe_2(CO)_8}]^- + \mathrm{H_2} \qquad (3)$$

$$[\mathrm{HFe_2(CO)_8}]^- + \mathrm{H_2Fe(CO)_4} \longrightarrow [\mathrm{HFe_3(CO)_{11}}]^- + \mathrm{CO} + \mathrm{H_2} \qquad (4)$$

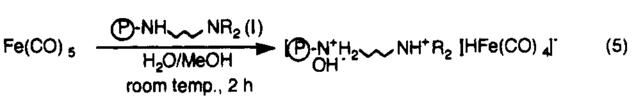
$$[\mathrm{HFe_3(CO)_{11}}]^- + \mathrm{OH^-} \longrightarrow [\mathrm{Fe_3(CO)_{11}}]^{2-} + \mathrm{H_2O} \qquad (5)$$

can generate selectively a monoanionic species of $[\mathrm{HFe_3(CO)_{11}}]^-$ in the polymer matrix. On the other



$$\mathrm{Fe(CO)_5} \xrightarrow[\text{H}_2\text{O/MeOH, reflux, 2 h}]{\text{Ⓟ-NR}_2\text{ (II)}} [\text{Ⓟ-N}^+\mathrm{HR_2}][\mathrm{HFe_3(CO)_{11}}]^- \qquad (4)$$

hand, reaction of $\mathrm{Fe(CO)_5}$ (0.5 mmol) with the diaminated polymer (**I**) in the mixed solvent of methanol and $\mathrm{H_2O}$, carried out at room temperature for 2 h, gave an orange polymer. Its IR spectrum showed 2002 (w), 1912 (m, sh), and 1881 (s) $\mathrm{cm^{-1}}$ due to the $[\mathrm{HFe(CO)_4}]^-$ species (Figure 3b, eq 5), which is similar to that of

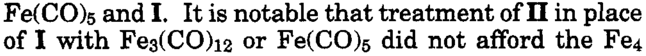


$$\mathrm{Fe(CO)_5} \xrightarrow[\text{H}_2\text{O/MeOH, room temp., 2 h}]{\text{Ⓟ-NH}\sim\sim\text{NR}_2\text{ (I)}} [\underset{\mathrm{OH^-}}{\text{Ⓟ-N}^+}\mathrm{H_2}\sim\sim\mathrm{NH^+R_2}][\mathrm{HFe(CO)_4}]^- \qquad (5)$$

$[\mathrm{PPN}][\mathrm{HFe(CO)_4}]$ (Figure 3c).[24] Using the monoaminated polymer (**II**) in place of **I**, formation of polymer-bound Fe carbonyl complexes could not be observed at room temperature for 2 h and $\mathrm{Fe(CO)_5}$ remained almost quantitatively in solution. The high basicity of the diaminated polymer (**I**) may play an important role in the formation of the polymer-bound $[\mathrm{HFe(CO)_4}]^-$ complex.

It is known that the mononuclear Fe anion of $[\mathrm{HFe(CO)_4}]^-$ is one intermediate in the formation of the $[\mathrm{HFe_3(CO)_{11}}]^-$ cluster from $\mathrm{Fe(CO)_5}$ in basic medium.[10,25] In our polymer system, treatment of the above polymer-bound $[\mathrm{HFe(CO)_4}]^-$ complex with $\mathrm{Fe(CO)_5}$ in the mixed solvent of methanol and $\mathrm{H_2O}$ at 50 °C could generate the $[\mathrm{HFe_3(CO)_{11}}]^-$ and $[\mathrm{Fe_3(CO)_{11}}]^{2-}$ species in the polymer matrix. Scheme 2 depicts possible formation paths for the polymer-bound $[\mathrm{Fe_3(CO)_{11}}]^{2-}$ complex according to Ford's work.[26] Attack of $\mathrm{H_2O}$ on $[\mathrm{HFe(CO)_4}]^-$ species gives $\mathrm{H_2Fe(CO)_4}$ and successive reactions of $\mathrm{H_2Fe(CO)_4}$ with $[\mathrm{HFe(CO)_4}]^-$ and $[\mathrm{HFe_2(CO)_8}]^-$ lead to formation of the polymer-bound $[\mathrm{HFe_3(CO)_{11}}]^-$ complex.

When reaction of $\mathrm{Fe_3(CO)_{12}}$ (0.05 mmol with **I** (0.5 mmol of N) in the mixed solvent of methanol and $\mathrm{H_2O}$ was carried out under reflux conditions for 6 h, a reddish brown polymer was isolated. Its IR spectrum showed 2021 (w) and 1950 (s) $\mathrm{cm^{-1}}$, which can be ascribed to a $[\mathrm{Fe_4(CO)_{13}}]^{2-}$ species by comparison with that of $[\mathrm{PPN}]_2[\mathrm{Fe_4(CO)_{13}}]$ in Figure 4 (eq 6).[27] The polymer-bound



$$\mathrm{Fe_3(CO)_{12}} \xrightarrow[\text{H}_2\text{O/MeOH, reflux, 6 h}]{\text{Ⓟ-NH}\sim\sim\text{NR}_2\text{ (I)}} [\text{Ⓟ-N}^+\mathrm{H_2}\sim\sim\mathrm{NH^+R_2}][\mathrm{Fe_4(CO)_{13}}]^{2-} \qquad (6)$$

$[\mathrm{Fe_4(CO)_{13}}]^{2-}$ complex could also be obtained by using $\mathrm{Fe(CO)_5}$ and **I**. It is notable that treatment of **II** in place of **I** with $\mathrm{Fe_3(CO)_{12}}$ or $\mathrm{Fe(CO)_5}$ did not afford the $\mathrm{Fe_4}$ cluster species but produced the $[\mathrm{HFe_3(CO)_{11}}]^-$ species in the polymer.

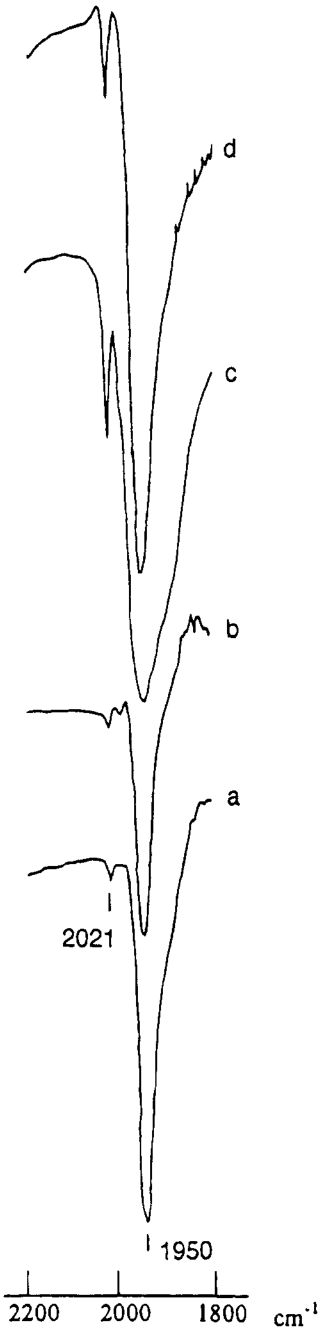
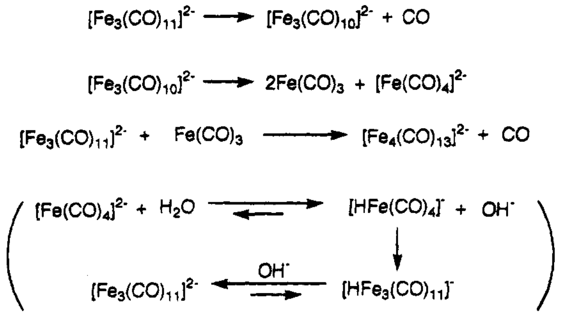


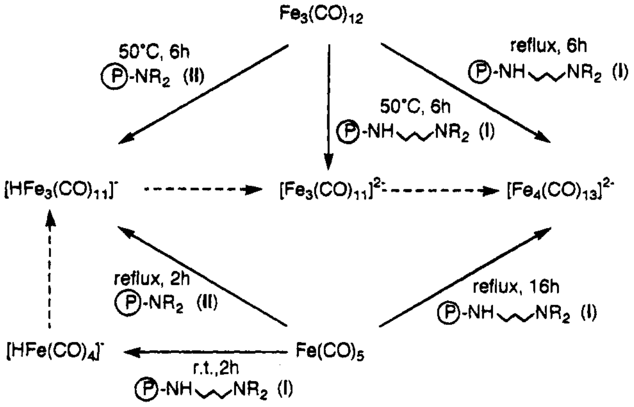
Figure 4. (a) Polymer **I**-bound $[\mathrm{Fe_4(CO)_{13}}]^{2-}$ complex prepared by the *in situ* method from $\mathrm{Fe_3(CO)_{12}}$ under reflux for 6 h. Polymer **I**-bound $[\mathrm{Fe_4(CO)_{13}}]^{2-}$ complex prepared by (b) the *in situ* method from $\mathrm{Fe(CO)_5}$ under reflux for 16 h and (c) the ion exhange methods. (d) $[\mathrm{PPN}]_2[\mathrm{Fe_4(CO)_{13}}]$.

Buskirk *et al.* have reported that refluxing THF solution of $[\mathrm{NEt_4}][\mathrm{HFe_3(CO)_{11}}]$ gave $[\mathrm{NEt_4}]_2[\mathrm{Fe_4(CO)_{13}}]$.[28] Another $\mathrm{Fe_4}$ species, $[\mathrm{Fe(py_6)}][\mathrm{Fe_4(CO)_{13}}]$, also has been prepared by use of $\mathrm{Fe(CO)_5}$ as a starting Fe compound; the process to $[\mathrm{Fe_4(CO)_{13}}]^{2-}$ from $\mathrm{Fe(CO)_5}$ contains $[\mathrm{Fe_3(CO)_{11}}]^{2-}$ as a key intermediate.[29] In our reaction of **I** with $\mathrm{Fe_3(CO)_{12}}$, the mononuclear Fe species $[\mathrm{HFe(CO)_4}]^-$ and $\mathrm{Fe(CO)_5}$ were observed as minor species accompanying $[\mathrm{Fe_3(CO)_{11}}]^{2-}$. The above observations suggest that fragmentation of the $[\mathrm{Fe_3(CO)_{11}}]^{2-}$ to mononuclear Fe species might occur in the polymer matrix under our reaction conditions. On the other hand, reaction of either $\mathrm{Fe(CO)_5}$ or $\mathrm{Fe_3(CO)_{12}}$ with the monoaminated polymer (**II**) did not give the $[\mathrm{Fe_4(CO)_{13}}]^{2-}$ species but $[\mathrm{HFe_3(CO)_{11}}]^-$ was formed selectively (*vide supra*). We have presented possible formation paths of the $[\mathrm{Fe_4(CO)_{13}}]^{2-}$ species from the $[\mathrm{Fe_3(CO)_{11}}]^{2-}$ intermediate for the diaminated polymer (**I**) in Scheme 3.[30] The $[\mathrm{Fe_3(CO)_{11}}]^{2-}$ species gives a $[\mathrm{Fe_3(CO)_{10}}]^{2-}$ species

Scheme 3. Formation Paths of the $[Fe_4(CO)_{13}]^{2-}$ Species via the $[Fe_3(CO)_{11}]^{2-}$ Intermediate[29]



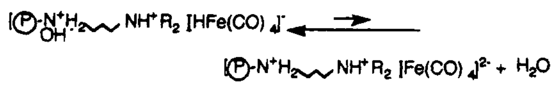
Scheme 4. Synthetic Routes for Polymer-Bound Fe_1, Fe_3, and Fe_4 Carbonyl Complexes from $Fe(CO)_5$ and $Fe_3(CO)_{12}$ Using the *in Situ* Method



A dotted line shows a possible formation route.

with loss of CO, which decomposes to the coordinatively unsaturated $Fe(CO)_3$ and $[Fe(CO)_4]^{2-}$ species. Reaction of the $[Fe_3(CO)_{11}]^{2-}$ species with $Fe(CO)_3$ leads to formation of the $[Fe_4(CO)_{13}]^{2-}$ species, while the $[Fe_3(CO)_{11}]^{2-}$ species is also generated from $[Fe(CO)_4]^{2-}$ under the aqueous basic conditions.

Ion exchange reactions of $[Fe(py_6)][Fe_4(CO)_{13}]$ with the aminated polymers of **I** and **II** were carried out. Compound **I** leads to selective formation of the polymer-bound $[Fe_4(CO)_{13}]^{2-}$ complex (Figure 4c), while reaction with **II** afforded neither the $[Fe_4(CO)_{13}]^{2-}$ nor $[HFe_4(CO)_{13}]^-$ species in the polymer. In the reaction of the diaminated polymer (**I**) with $[pyH][HFe_4(CO)_{13}]$ in the mixed solvent of methanol and H_2O, the polymer-bound $[Fe_4(CO)_{13}]^{2-}$ complex was selectively formed with no $[HFe_4(CO)_{13}]^-$. It is known that an equilibrium between the $[Fe_4(CO)_{13}]^{2-}$ and $[HFe_4(CO)_{13}]^-$ species exists: in aqueous HCl solution, the $[Fe_4(CO)_{13}]^{2-}$ species is protonated to give $[HFe_4(CO)_{13}]^-$ and, on the other hand, bases favor formation of the $[Fe_4(CO)_{13}]^{2-}$ species.[14] In our polymer systems, amino functions of the polymers act as bases to shift the equilibrium to formation of the $[Fe_4(CO)_{13}]^{2-}$ species. Ion exchange reaction of $K_2[Fe_3(CO)_{11}]$ with **I** gave the polymer-bound $[Fe_3(CO)_{11}]^{2-}$ complex, and in a similar treatment of $K_2[Fe_3(CO)_{11}]$ with **II**, $[HFe_3(CO)_{11}]^-$ was formed exclusively. From the above discussion of the equilibrium between dianionic Fe clusters and monoanionic Fe clusters, one might expect that the $[Fe(CO)_4]^{2-}$ species could be selectively formed in the case of diaminated polymer (**I**). But, as mentioned previously, reaction of $Fe(CO)_5$ with **I** did not give the $[Fe(CO)_4]^{2-}$ species, but the $[HFe(CO)_4]^-$ species. This can be explained by the high proton affinity of $[Fe(CO)_4]^{2-}$, which results in formation of the $[HFe(CO)_4]^-$ species when water is present.[26] The above formation paths for various polymer-bound Fe carbonyl complexes are summarized in Scheme 4. Use of aminated polymers causes selective formation of Fe clusters in the polymer matrix, which can mimic the behavior of homogeneous Fe clusters.



(7)

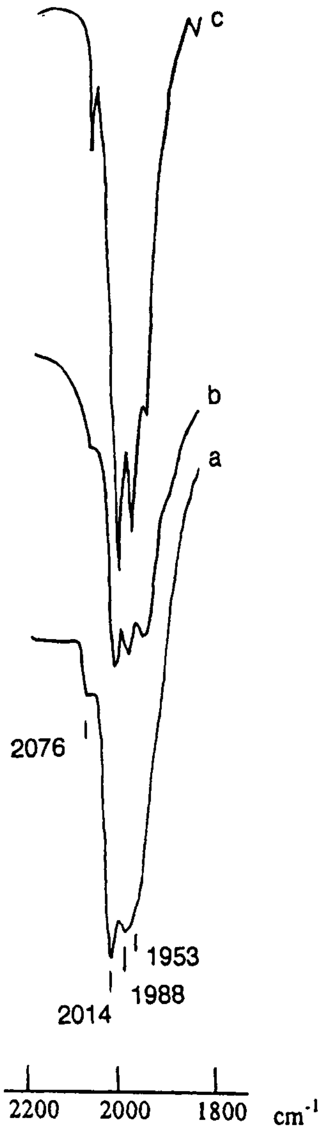


Figure 5. Polymer **I**-bound $[HRu_3(CO)_{11}]^-$ complex prepared by (a) the *in situ* method from $Ru_3(CO)_{12}$ at room temperature for 24 h and (b) the ion exchange method. (c) $[PPN][HRu_3(CO)_{11}]$.

In order to apply this synthetic method of the polymer-bound Fe complexes to other transition metals, the reaction of $Ru_3(CO)_{12}$ (0.03 mmol) with the diaminated polymer (**I**) (0.3 mmol of N) was carried out at room temperature for 24 h. As expected, a polymer-bound $[HRu_3(CO)_{11}]^-$ complex was obtained exclusively (Figure 5a). Ion exchange reactions of **I** with $Na[HRu_3(CO)_{11}]$ and $K_2[Ru_6(CO)_{18}]$ gave the corresponding polymer-bound $[HRu_3(CO)_{11}]^-$ and $[Ru_6(CO)_{18}]^{2-}$ complexes, respectively.[17,18] Compared with the Fe cluster anions, these Ru clusters were more stabilized in the aminated polymers. IR spectra of the Ru_3 cluster complexes are summarized in Figure 5.

In conclusion, Fe, Fe_3, and Fe_4 carbonyl cluster anions are formed by treatment of neutral Fe carbonyl complexes with aminated polymers in the presence of H_2O. The polymer-bound Fe cluster complexes can be also obtained by ion exchange with the aminated polymers. The functions of polymeric amines are to generate OH^- in the aqueous media, which yields the Fe cluster anions, and to stabilize the Fe cluster anions by forming ion pairs.

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