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Preparation of amphiphilic organoiron(1+) complexes having two long-chain alkyl groups and their molecular assemblage characteristics

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[*o*-, *m*- and *p*-Bis(alkylamino or alkyloxy)benzene](cyclopentadienyl)iron(1+) hexafluorophosphates {2 and 4; $[(C_nH_{2n+1}X)_2C_6H_4](C_5H_5)Fe^+PF_6^-$, X = NH or O} were prepared by aromatic nucleophilic substitution of the (dichlorobenzene)iron cationic complexes (1). Critical micelle concentrations of the complex chlorides (3), prepared from 2 ($n=8$, X = NH) by anion exchange and soluble in water, gave much smaller values than those of bis(long-chain alkyl)dimethylammonium surfactants. Furthermore, the substitution positions scarcely affected their surface activities. However, the surface pressure–molecular area isotherm of the hexafluorophosphates (2 and 4, $n=18$, X = NH; insoluble in water) were severely transformed by change in the substitution position of the long-chain alkyl groups on the benzene ligand in the iron cationic complexes: the *o*-substituted complex gave a molecularly assembled film by the Langmuir–Blodgett (LB) method, but the *p*-substituted one did not.

Keywords: Organoiron complex, organometallic surfactant, molecular assembly, Langmuir–Blodgett (LB) film

INTRODUCTION

Long-chain alkyl-substituted organotransition metal complexes are usually unstable and therefore little attention has been paid to their application to the development of new functionalized materials. In recent years, however, charge-neutral and relatively stable organotransition metal complexes such as ferrocene and porphyrin derivatives having long-chain alkyl groups have become the object of research efforts to prepare characteristic molecular assemblies in the fields of surfactants,[1-4] liquid crystals,[5-10] and optoelectric,[11] redox,[12] electroconductive,[13,14] photoimaging[15,16] and electromagnetic materials,[17-19] etc.

In contrast to the charge-neutral complexes, studies of ionic organotransition metal complexes having long-chain alkyl groups, and their molecular assemblies,[20] are quite rare, because of instability of the ionic complexes. We have already reported that cationic organo-manganese, -iron or -cobalt complexes *mono-substituted* with long-chain alkyl groups can act as surfactants.[21-23]

In this paper, we describe the preparation of some primary-examples of [*o*-, *m*- or *p*-bis(long-chain)-substituted benzene]iron cationic complexes and the effect of the substitution position on molecular assemblage ($n=18$) by Langmuir–Blodgett methods and surface character ($n=8$ in Scheme 1).

2 EXPERIMENTAL

2.1 Analysis

Melting points were measured using a Yanaco melting-point apparatus and are uncorrected. ^1H NMR spectra were measured using a Hitachi R24 spectrometer. Elemental analyses of the cationic organoiron hexafluorophosphates were performed by the Microanalysis Center of Kyoto University. Surface pressure versus surface area curves were obtained by Langmuir–Blodgett methjods using the hexafluorophosphate in distilled water as the subphase at 20 °C to estimate the mean molecular areas. The surface tension of the chloride complexes prepared from the corresponding hexafluorophosphates by anion exchange on a resin column, was measured by Wilhelmy's method at room temperature (about 20 °C) using a Kyowa surface-tension meter, model CBVP-A3.

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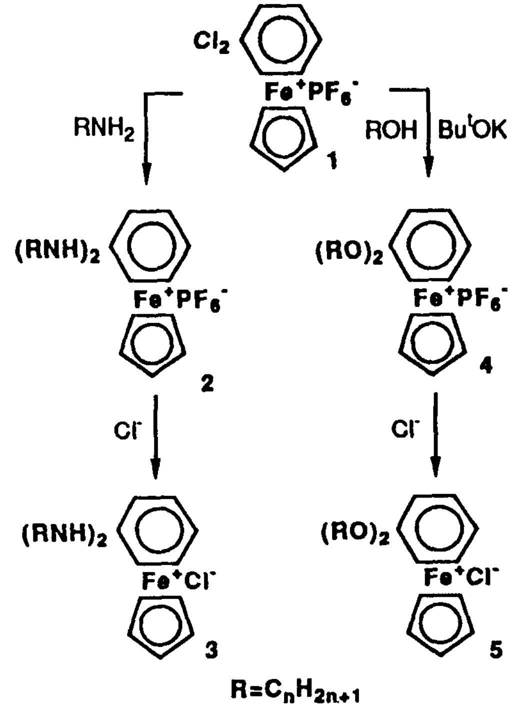


Scheme 1

2.2 Chemicals

Long-chain alcohols and amines were commercially available, more than 95% pure. (*o*-, *m*- or *p*-Dichlorobenzene)(cyclopentadienyl)iron(1+) hexafluorophosphate (**1**) was prepared from ferrocene and the corresponding dichlorobenzene using aluminum trichloride, metallic aluminum powder and a trace of ascorbic acid as catalysts and additive.[24, 25] Melting points (with decomposition) for the (*o*-, *m*-, and *p*-dichlorobenzene)iron complexes were 207–210, 168–170 and 186–189 °C respectively.

2.3 Preparation of [bis(octadecylamino)benzene] (cyclopentadienyl)iron(1+) hexafluorophosphates (2; *n*=18)

The *ortho*-derivative was prepared as follows. (*o*-Dichlorobenzene)(cyclopentadienyl)iron(1+) hexafluorophosphate (**1**; 0.41 g, 1 mmol) and 1-amino-octadecane (2.7 g, 10 mmol) were stirred for 24 h at room temperature in CH_2Cl_2 (40 ml^3) under an argon atmosphere, followed by addition of saturated aqueous KPF_6 solution (50 ml^3). The organic layer which separated was dried by anhydrous magnesium sulfate, concentrated using a rotary evaporator, and mixed with a large amount of dry hexane to precipitate crude crystals. The crude product was recrystallized from acetonitrile–hexane (1 : 1) to afford [*o*-bis(octadecylamino)benzene](cyclopentadienyl) iron(1+) hexafluorophosphate (**2**, $n = 18$; 18N in Table 1) in 96% yield as a yellow solid, m.p. 65.5–67.0 °C. IR: 3670 cm^{-1} (νNH). ^{1}H NMR($CDCl_3$): δ 0.85 (br.t, 6H, CH_3), 1.22 (br.s, 64H, CH_2), 3.18 (m, 6H, CH_2NH), 4.89 (s, 5H, Cp), 6.1 (m, 4H, aromatic). Calcd for $C_{47}H_{85}N_2F_6PFe$: C, 64.22; H, 9.75. Found: C, 64.57: H, 10.03%.

[*m*- and *p*-Bis(octadecylamino)benzene](cyclopentadienyl)iron(1+) hexafluorophosphates (m18N and p18N) were also prepared by the same methods, and identified by IR, ^{1}H NMR, and elemental analyses; their results are summarized in Table 1.

Table 1 Preparation and properties of bis(long-chain alkyl)-substituted organoiron complexes $[(C_nH_{2n+1}X)_2C_6H_4](C_5H_5)Fe^+PF_6^-$

Complex							
No.	X	*n*	Substn position	Yield (%)[a]	M.p. (°C)[a]	Molecular area (Å^2/molecule)[a]	CMC[c] (mmol dm^{-3})[b]
o18N	NH	18	*ortho*	96	65.5–67.0	53	—
m18N	NH	18	*meta*	74	56.0–57.5	(60)	—
p18N	NH	18	*para*	83	61.0–63.0	nd	—
o18O	O	18	*ortho*	31	49.0–50.5	49	—
m18O	O	18	*meta*	57	46.0–48.5	(54)	—
p18O	O	18	*para*	46	47.0–48.5	nd	—
o08N	NH	8	*ortho*	70	Oil	—	0.78
m08N	NH	8	*meta*	54	Oil	—	0.90
po8N	NH	8	*para*	64	Oil	—	1.34

[a] Data for PF_6^- salts. [b] Data for Cl^- salts. [c] Critical micelle concentration. [d] Abbreviation: nd, not determined.

2.4 Preparation of [bis(octadecanoxy)benzene] (cyclopentadienyl)iron(1+) hexafluorophosphates (4; *n*=18)

Preparation of the [*o*-bis(octadecanoxy) benzene]iron(1+) complex (**4**, $n=18$; o18O) was performed in the same manner (*o*-dimethoxy benzene)(cyclopentadienyl)iron(1+) complex.[26] Octadecanol (2.7 g, 10 mmol) and potassium 2,2-dimethylethoxide powder (0.5 g, 4 mmol) were mixed and stirred for 2 h in tetrahydrofuran (40 $cm^3 dm^{-3}$) under an argon atmosphere in a flask equipped with a Dimroch condenser. Thereafter, the (*o*-dichlorobenzene)iron complex (**1**; 0.41 g, 1 mmol) was added and refluxed for 12 h, followed by evaporation. The residue was dissolved in $CHCl_3$ and filtered. The filtrate was concentrated and recrystallized from acetonitrile–hexane (1:1), to afford [*o*-bis(octadecanoxy) benzene](cyclopentadienyl)iron(1+) hexafluorophosphate (**4**; o18O) in 31% yield as a deep yellow solid, m.p. 49.0–50.5 °C. ^{1}H NMR($CDCl_3$): δ 0.85 (br. t, 6H, CH_3), 1.21 (br.s, 64H, CH_2), 3.35 (m, 4H, CH_2O), 5.12 (s, 5H, Cp), 6.4 (m, 4H, aromatic). Calcd for $C_{47}H_{83}O_2F_6PFe$: C, 64.08; H, 9.50. Found: C, 63.80; H, 9.98%.

m- and *p*-Bis(octadecanoxy)benzene] (cyclopentadienyl)iron(1+) hexafluorophosphates (m18N and p18N) were prepared and identified in the same manner. The results are presented in Table 1.

2.5 Preparation of [bis(octylamino)benzene] (cyclopentadienyl)iron(1+) hexafluorophosphates (2; *n*=8)

o-Dichlorobenzene) (cyclopentadienyl) iron (1+) hexafluorophosphate (**1**; 0.41 g, 1 mmol) and 1-amino-octane (1.3 g, 10 mmol) were stirred for 24 h at room temperature in dichloromethane (40 cm^3) under an argon atmosphere, followed by addition of saturated aqueous KPF_6 solution (50 cm^3). The organic layer was separated, dried using anhydrous magnesium sulfate and evaporated, followed by addition of large amounts of hexane to separate the crude product. Its chloroform solution was filtered using diatomaceous earth and dried *in vacuo*. The oily product was purified by passing it through a silica column using acetonitrile–hexane (1:1) mixture as eluent to give pure **2** in 70% yield as a yellow oil. IR: 3660 cm^{-1} (νNH). ^{1}H NMR ($CDCl_3$): δ 0.83 (br.s, 6H, CH_3), 1.20 (br.s, 24H, CH_2), 3.16 (m, 6H, CH_2NH), 4.75 (s, 5H, Cp), 5.8 (m, 4H, aromatic). Calcd for $C_{27}H_{45}N_2F_6PFe$: C, 54.19; H, 7.58. Found: C, 53.71; H, 8.02%.

m- and *p*-Bis(octylamino)benzene] (cyclopentadienyl)iron(1+) hexafluorophosphates (**3**; m18O and p18O) were prepared and identified in a similar manner. The results are summarized in Table 1.

3 RESULTS AND DISCUSSION

3.1 Preparation of [*o*-, *m*-, and *p*-bis(long-chain alkyl-substituted) benzene](cyclopentadienyl)iron(1+) complexes

(*o*-, *m*-, and *p*-Dichlorobenzene)(cyclopentadienyl)iron(1+) hexafluorophosphates (**1**) reacted with an excess of 1-aminoalkane ($n=8$ or 18) in dichloromethane at room temperature and the products were purified by chromatography or by recrystallization to afford [*o*-, *m*-, *p*-bis(octylamino- or octadecylamino-)benzene]-(cyclopentadienyl)iron(1+) hexafluorophosphates (**2**; $n=8$ and 18 in Scheme 1). These complexes were identified by IR, ^{1}H NMR, and elemental analyses. The results are summarized in Table 1.

[*o*-*m*-, and *p*-Bis(octadecanoxy)benzene] (cyclopentadienyl)iron(1+) hexafluorophosphates (**4**; $n=18$ in Scheme 1) were also prepared by aromatic nuceophilic substitution of **1** with octadecanoxide formed, *in situ*, from octadecanol and *tert*-butoxide in refluxing tetrahydrofuran and purified by recrystallization. The results are presented in Table 1.

3.2 Surface activities

The bis(long-chain alkyl-substituted)organoiron(1+) complex hexafluorophosphates (**2** and **4**; $n=8$ and 18) were soluble in organic solvents such as chloroform but insoluble in water at room temperature, and were converted to the corresponding chlorides (**3** and **5**) by using an anion-exchange resin column; the latter (chlorides) were less stable than the former (hexafluorophosphates), and decomposed after a week under light, in the presence of air.

From the plots of surface tension versus concentration (Fig. 1), the critical micelle concentra-

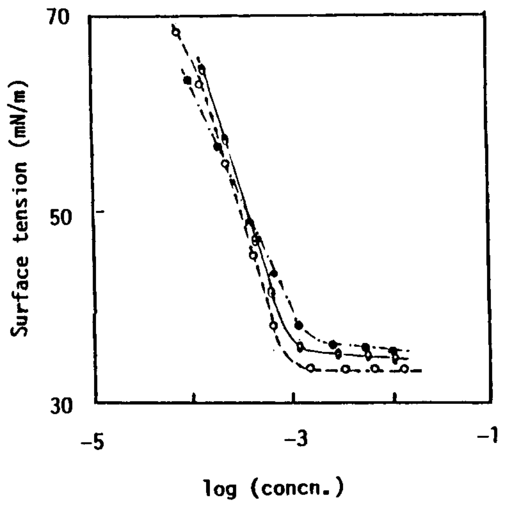


Figure 1 Surface tension–concentration curves for $[(C_8H_{17}O)_2C_6H_4](C_5H_5)Fe^+Cl^-$. – – –, o8N; ——, m8N; –·–·–, p8N.

tions (CMC) of [*o*-, *m*- and *p*-dioctylaminobenzene](cyclopentadienyl)iron(1+) chlorides (**3**; $n = 8$) were estimated and are summarized in Table 1. The CMC values of (monoalkyl-substituted benzene)(cyclopentadienyl)iron(1+) chlorides were found to be in the range of 3–6 mmol dm^{-3}.[21] Therefore, the CMC values of the [bis(octyl-substituted benzene] iron cationic chlorides shown in Table 1 were about one-fifth of those of mono-substituted ones. Such a difference between mono and bis-substitution in cationic surfactants is well known for ammonium-type cationics. The effect of the substitution position (e.g. *o*-, *m*-, or *p*-substitution) by long-chain alkyl groups on the benzene ligand in the complex is not clear, but the CMC value of *o*- (o8N) and the *m*-substituted complex salt (m8m) were estimated to be less than that of the *p*-substituted one (p8N), suggesting that the *o*- or *m*-substituted organotransition metal cationic surfactant is more associated in water than the *p*-substituted one. Secondly, this type of iron(1+) cationic surfactants is spontaneously reduced by the addition of aqueous sodium tetrahydroborate to form the charge-neutral complex (**6**), which decomposes in a few minutes, formation of **6** being detected by the ^{1}H NMR spectrum of the extract from the reduced surfactant solution by deuteriochloroform (Scheme 2).

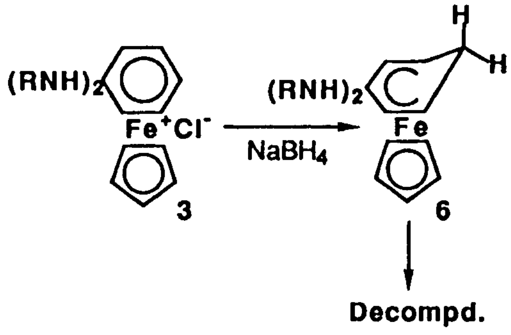
The decane-in-water emulsion prepared using the organoiron cationic surfactant (o8N in Table 1) was de-emusified by the addition of a water-soluble reductant such as sodium tetrahydroborate, to separate the oil layer of decane. This phenomenon is originally the same as the case reported by Julio *et al.*, where some vesicles were formed using a hydrophobic ferrocene derivative under redox conditions.[4] The [bis(octadecanoxy- and octadecanamino-substituted)benzene]iron complex chlorides were insoluble in water and their surface tension could not be measured.

3.3 Molecular assembly by LB methods

As already reported, the (monoalkoxybenzene)(cyclopentadienyl)iron(1+) complex does not form a closely packed molecular assembly but rather an expanded film using Langmuir–Blodgett methods and the apparent mean molecular area was estimated to be 100 Å^2 (1 nm^2) per molecule.

Bis(octadecanoxy- and octadecanyl amino-substituted benzene) (cyclopentadienyl)iron(1+) hexafluorophosphates were insoluble in water and were solid. To estimate molecular assemblage characteristics of the *o*-, *m*-, or *p*-substituted complex hexafluorophosphate (**2** or **4**; $n = 18$), a spreading solution consisting of a 1.0 mmol dm^{-3} solution of the complex in extra-pure chloroform was applied dropwise onto a pure water subphase (pH 6.3) at 20 °C, and, after solvent evaporation, the resulting layer was compressed at a rate of 0.3 mm^2 s^{-1}. The surface pressure (Π) versus mean molecular area (A) curves are shown in Figs 2 and 3.

Comparing Figs 2 and 3, the patterns of the Π–A curves of the [*o*-, *m*- and *p*-bis(octadecanylamino)benzene] complexes (**2**) are similar to those of the corresponding [*o*-, *m*- and *p*-bis(alkoxy)benzene complexes (**4**), respectively. However, the effects of the substitution position on the pattern of the Π–A curves were clearly observed. In the case of the *p*-substituted



Scheme 2

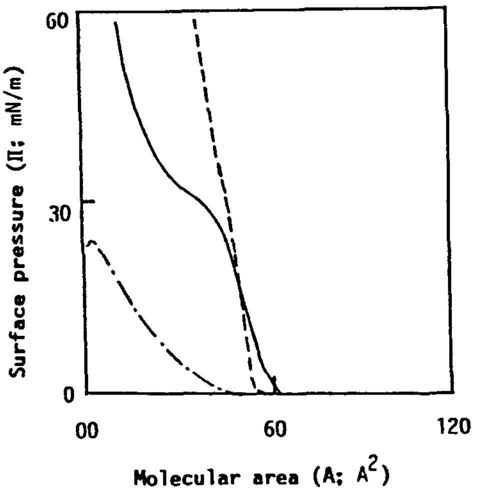


Figure 2 Π–A isotherm for $[(C_{18}H_{37}NH)_2C_6H_4](C_5H_5)Fe^+PF_6^-$. – – –, o18N; ——, m18N; –·–·–, p18N.

complexes (p18N and p18O in Table 1), the surface pressure was gradually increased by compression but the assemblage formed collapsed at less than 30 mN m^{-1}. The Π–A isotherm of the *o*-substituted complexes (o18N and o18O) indicated that the two-dimensional molecular assemblage would form easily and the molecular area was estimated at about 53 Å^2 and 49 Å^2 per molecule, respectively, which were reasonable values generally for amphiphiles having two long-chain alkyl groups (about 20 Å^2 per chain × 2 chains per molecule was predicted on inspection of a space-filled molecular model). In the case of *m*-substituted complexes (m18N and m18O), the surface pressure change in two steps, with the mean molecular areas estimated at about 60 Å^2 and 54 Å^2 per molecule respectively, from extrapolaration of Π–A curves for the first stage ($\Pi <$ *ca* 30 mN m^{-1}). In the latter stage ($\Pi >$ *ca* 40 mN m^{-1}), the apparent mean molecular areas fell to less than 20 Å^2 per molecule, suggesting that local collapse had occurred. As a result, the meta substituted positions of the two long-chain alkyl groups on the benzene ligand in the organoiron cationic complexes **2** and **4** strongly caused molecular assemblage.

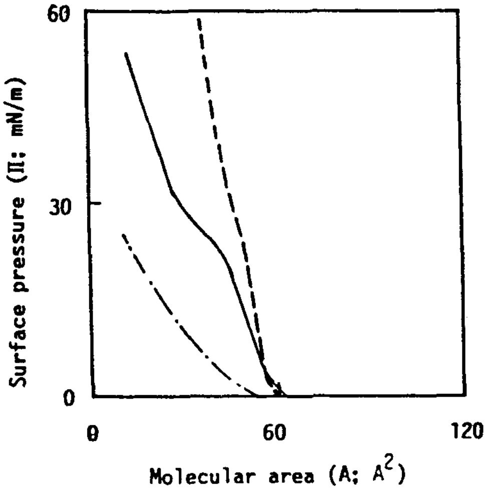


Figure 3 Π–A isotherm for $[(C_{18}H_{37}O)_2C_6H_4](C_5H_5)Fe^+PF_6^-$. – – –, o18O; ——, m18O; –·–·–, p18O.

We note that Y-type deposition onto a glass plate of the organoiron complexes o18N and o18O was attempted at a constant surface pressure of 25 mN m^{-1} and films up to 15 layers thick were obtained. However, the films did not show any X-ray diffraction patterns except the first-order reflection, suggesting incomplete molecular assemblage.

4 CONCLUSIONS

Aromatic nucleophilic substitution reactions of (*o*-, *m*- and *p*-dichlorobenzene)(cyclopentadienyl)iron(1+) hexafluorophosphates with octylamines or octadecylamines, and sodium octadecanoxide afforded new types of amphiphiles, [*s*-, *m* and *p*-bis(alkylamino- and alkoxy)benzene](cyclopentadienyl)iron(1+) hexafluorophosphates (**2** and **4**), which were soluble in organic solvents and insoluble in water. These amines could be converted to water-soluble chlorides in the case of the [*o*-, *m*- and *p*-bis(octylamino-substituted benzene]iron(1+) cationic surfactants (**5**). The characteristic features of the complexes are as follows.

(1) Critical micelle concentrations of the cationic complex chlorides (**5**) having two octyl groups are about one-fifth of those of the corresponding mono-octyl-substituted organoiron(1+) surfactants previously reported, and are much lower than that of dimethyldioctylammonium chloride. Furthermore, the effects of the substitution position on surface activities are small and CMC values trend in the order *p*- > *m*-, *o*-substituted for the complex chlorides.

(2) Surface activities of chlorides **5** are lost by reduction and by irradiation of light leading to their decomposition.

(3) From the surface pressure (Π) versus molecular area (*A*) isotherms of [*o*-, *m*- and *p*-bis(octadecylamino- and octadecyl oxy-benzene)](cyclopentadienyl)iron(1+) hexafluorophosphates (**2** and **4**; $n = 18$), molecular assembling ability trends in the order $o\text{-} > m\text{-} \gg p$ in the complexes, and the mean molecular areas of *o*-substituted **2** and **4** ($n = 18$) are about 50 Å^2, which are reasonable values, based on full-packed molecular models.

(4) The Y-type deposition of the *o*-bis(octadecyl)-substituted complexes (**2** and **4**; $n = 18$) gave LB films of up to 15 layers, but the films prepared did not show any clear X-ray diffraction patterns. Furthermore, the *m*- or *p*-bis(octadecyl)-substituted complexes did not afford any LB-type films.

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