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Preparation and Properties of (η^5-Pentamethylcyclopentadienyl)iron Cationic Complexes with Long-Chain Alkyl Groups

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Synopsis. Organo-transition metal surfactants, (η^5-pentamethylcyclopentadienyl)iron cationic complexes with long-chain alkyl groups were prepared and their characteristics such as surface tension, redox, and photo-decomposition are discussed.

In general, modifications of lipophilic groups of surfactants have been widely investigated,[1] while hydrophilic groups of cationic surfactants still had been limited to cationic species of main-group elements such as trimethylammonium ion. We reported organo-transition metal surfactants in which cyclopentadienyl-iron, -cobalt, and -manganese cationic moieties play the role of a hydrophilic group.[2] These organo-transition metal surfactants formed micelles in water, and their critical micelle concentration (cmc) values were much smaller than those of the corresponding trimethylammonium surfactants. In addition, organo-transition metal surfactants have redox properties, and are useful in the preparation of LB films containing orogano-transition metal moieties[3] and in phase-transfer catalysis.[4]

Ferrocenium cation complexes have been known to be photosensitive,[5] so (η^5-cyclopentadienyl)iron cationic surfactants are anticipated to decompose even under daylight. Here, we wish to report the preparation and properties of stable (η^5-pentamethylcyclopentadienyl)iron cationic complexes with long-chain alkyl groups, and discuss the effects of electron-donating and lipophilic methyl groups on redox properties, surface activity, and photodecomposition characteristics under UV-vis irradiation.

Experimental

General. Melting points were measured by a Yanaco melting point apparatus and are uncorrected. Infrared spectra were obtained with a Shimadzu IR-410 spectrometer as a solution in $CHCl_3$. ^1H NMR spectra were measured by a Hitachi R24 spectrometer. Elemental analyses were done by the Microanalysis Center of Kyoto University. Cyclic voltammographs were obtained using a Yanaco cyclic voltammetric analyzer, model FG-121, with a Watanabe WX-4401-LO recorder [Pt electrode, 100 mV s^{-1}, in acetonitrile, sample (ferrocenium hexafluorophosphates): 1×10^{-3} mol dm^{-3}, $(C_2H_5)_4N^+PF_6^-$ as a supporting electrode: 0.1 mol dm^{-3}, vs. Ag/AgCl]. The chloride complexes (**b**) were prepared from the corresponding hexafluorophosphates (**a**) by anion exchange on a resin column, and their surface tensions were measured by Wilhelmy's method at room temperature (about 20 °C) using a Kyowa surface-tension meter, model CBVP-A3. Photo-decomposition of the surfactants at about cmc was done by irradiation with a Hg-lamp (120W) with thermo-cut water filter, and was estimated by the decrease of the surface tension. Long-chain alkanoyl chlorides and amines were commercially available and their purities were over 95%. (η^6-Chlorobenzene)(η^5-pentamethylcyclopentadienyl)iron(1+) (**2**), (η^6-*p*-dichlorobenzene)(η^5-pentamethylcyclopentadienyl)iron(1+) (**3**), and (η^6-aniline)(η^5-pentamethylcyclopentadienyl)iron(1+) hexafluorophosphates (**4**) were prepared in the usual ways.[6]

Preparation of (η^6-Dodecylbenzene)(η^5-pentamethylcyclopentadienyl)iron(1+) Hexafluorophosphate (5a: n=12). Dicarbonyl(η^5-pentamethylcyclopentadienyl)iron(1+) bromide (0.64 g, 2 mmol), dodecylbenzene (1.6 g, 6 mmol), aluminium trichloride (2.1 g, 15 mmol), and metallic aluminium powder (0.48 g, 6 mmol) were stirred under N_2 and heated at 180 °C for 12 h in 50 ml of decalin. After hydrolysis at 0 °C, 100 ml of aqueous ammonia (pH=8) was added to the aqueous phase to remove Al^{3+}, and then aqueous KPF_6 (2 mmol) was added to the filtrate to precipitate the desired complex salt. Hexafluorophosphates were dissolved in CH_2Cl_2, dried by anhydrous magnesium sulfate, and then concentrated using a rotary evaporator. Reprecipitation by the addition of excess dry pentane to a CH_2Cl_2 solution provided crude crystals. Recrystallization from hot ethanol gave 1.0 g (90% yield) of yellow-brown solid. Mp 62—64 °C. IR 840 (νPF_6), 1380, 1460, and 2950 (νCH_3), 1492 and 1595 (νAr) cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.87 (3H, br, CH_3), 1.18 (22H, br, CH_2), 1.82 (15H, s, Cp*), 5.64 (5H, m, Ar).

Calcd for $C_{28}H_{45}F_6PFe$: C, 57.74; H, 7.78%. Found: C, 57.86; H, 7.63%.

Other (η^6-alkylbenzene)iron(1+) complexes were also prepared by the same method, and identified by IR, ^1H NMR, and elemental analyses; their results are summarized in Table 1.

Preparation of (η^6-Dodecylaminobenzene)(η^5-pentamethylcyclopentadienyl)iron(1+) Hexafluorophosphate (6a: n=12). (η^6-Chlorobenzene)(η^5-pentamethylcyclopentadienyl)iron(1+) hexafluorophosphates (0.22 g, 0.5 mmol) and dodecylamine (0.93 g, 5 mmol) were stirred for 24 h at room temperature in 40 ml of CH_2Cl_2 under an argon atmosphere, followed by addition of saturated aqueous KPF_6 solution (30 ml). The organic layer was separated, dried by anhydrous magnesium sulfate, concentrated using a rotary evaporator, and mixed with a large amount of dry hexane to precipitate crude crystals which was recrystallized from methanol–hexane (1 : 1) to afford (dodecylaminobenzene)(pentamethylcyclopentadienyl)iron(1+) hexafluorophosphate (n=12) in 63% yield as a yellow-brown solid. Mp 66—67 °C. IR 840 (νPF_6), 1380, 1460, and 2900 (νCH_3), 1500—1600 (νAr) 3300 (νNH) cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.79 (3H, br,

Table 1. Comparison of Cp*- with Cp-Complexes

$X^{a)}$	n	Cp*-complexes				Cp-complexes$^{d)}$	
		Yield%	Mp/°C	cmc/mmol dm^{-3} $^{b)}$	E_c/V$^{c)}$	cmc/mmol dm^{-3}	E_c/V
				Single chain alkyl type			
NH	8	43	114—118	2.51	−1.65	8.0 (140)$^{e)}$	—
	12	63	66—67	0.25	−1.66	5.0 (20)	−1.37
	16	96	66—69	0.25	−1.66	0.85 (1.3)	—
None	8	50	85—86	0.80	−1.69	—	—
	12	90	62—64	0.70	−1.66	5.0	−1.40
	16	33	83—85	0.30	−1.72	0.63	—
NHCO	8	97	92—95	1.58	−1.78	5.6	—
	12	35	48—51	0.90	−1.68	2.7	−1.35
	16	51	50—51	0.76	−1.76	1.97	—
				Double chain alkyl type			
NH-p	8	48	60—61	0.04	−1.81	1.3	−1.47
	12	66	49—51	0.02	−1.78	—	—
	16	25	54—55	0.01	−1.80	—	—

a) X is a connection group between benzene ring and a long-chain alkyl group. b) Chlorides used, at room temperature. c) Cathodic potentials measured by cyclic voltammetry of hexafluorophosphates in MeCN (Pt electrode, vs. Ag/AgCl, 0.1 M Bu_4NClO_4, 100 mV s^{-1}). Cp*-complexes showed reversible behavior in CV, while Cp-complexes afforded only a cathodic peak. d) S. Sakai et al., *J. Chem. Soc., Chem. Commun.*, **1988**, 663. e) The cmc values for $C_nH_{2n+1}N^+(CH_3)_3Cl^-$ are shown in parentheses.

CH_3), 1.12 (22H, br, CH_2), 1.83 (15H, s, Cp*), 2.95 (3H, m, CH_2NH), 6.00 (5H, m, Ar).

[η^6-Bis(*p*-alkylamino)benzene]iron(1+) hexafluorophosphates (**7a**) were prepared from (η^6-*p*-dichlorobenzene)iron(1+) hexafluorophosphates (**4**) and alkylamine in the same manner, and identified by IR, NMR, and elemental analyses. Other (η^6-alkylaminobenzene)iron(1+) complexes were prepared and identified by the same methods. The results are presented in Table 1.

Preparation of (η^6-Dodecanoylaminobenzene)(η^5-pentamethylcyclopentadienyl)iron(1+) Hexafluorophosphate (8a: n=12). (η^6-Aniline)(η^5-pentamethylcyclopentadienyl)iron(1+) hexafluorophosphates (0.20 g, 0.4 mmol), dodecanoyl chloride (0.44 g, 2 mmol) and pyridine (0.16 g, 2 mmol) were stirred for 48 h at room temperature in 30 ml of CH_2Cl_2 under an argon atmosphere, followed by addition of aqueous HCl solution (pH=4, 20 ml), and then saturated aqueous KPF_6 solution (20 ml). The organic layer was separated, dried by anhydrous magnesium sulfate, concentrated using a rotary evaporator, and mixed with a large excess of dry diethyl ether to precipitate crude crystals. The crude product was recrystallized from methanol–ether (1 : 1) to afford (η^6-dodecanoylaminobenzene)(η^5-pentamethylcyclopentadienyl)iron(1+) hexafluorophosphate (n=12) in 35% yield as an orange-yellow solid, mp 48—51 °C. IR 830 (νPF_6), 1380, 1460, and 2950 (νCH_3), 1550 (νAr) 1700 (νCO), 3350 (νNH) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.80 (3H, br, CH_3), 1.12 (20H, br, CH_2), 1.73 (15H, s, Cp*), 5.40 (5H, m, Ar).

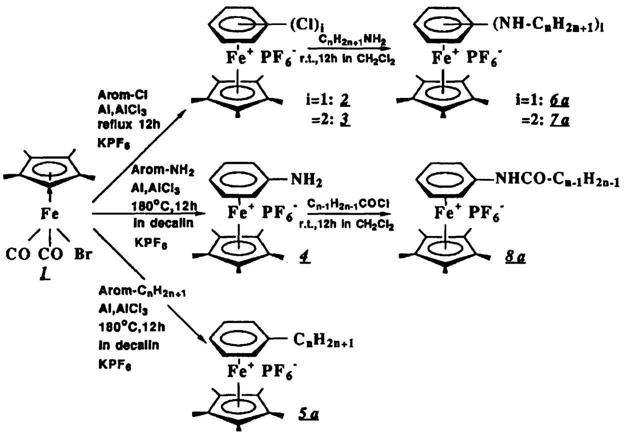
Calcd for $C_{28}H_{43}NOF_6PFe$: C, 55.00; H, 7.25%. Found: C, 54.48; H, 7.45%.

Other (η^6- alkanoylaminobenzene)iron(1+) complexes were prepared and identified in the same manner. The results are presented in Table 1.

Results and Discussion

The (η^5-cyclopentadienyl)iron cationic complexes with long-chain alkyl group (Cp-complexes) were prepared by the ligand-exchange reaction of ferrocene with aromatic compounds.[2] However, the corresponding (η^5-pentamethylcyclopentadienyl)iron complexes with long-chain alkyl group (Cp*-complexes) were not obtained by the ligand-exchange reaction from decamethylferrocene. Hamon reported the preparation of (η^6-benzene)(η^5-pentamethylcyclopentadienyl)iron(1+) hexafluorophosphate by using dicarbonyl(η^5-pentamethylcyclopentadienyl)iron(1+) bromide (**1**),[6] and we obtained (η^6-chloro-, dichoro-, amino-, and long-chain alkylarene)(η^5-pentamethylcyclopentadienyl)iron cationic complexes (**2**, **3**, **4**, and **5a**) by the similar reaction of **1** with aromatic compounds. Complexes (**6a**, **7a**, and **8a**) were prepared by aromatic nucleophilic substitution reaction (S_N reaction) of **2** and **3** with long-chain amines, and by acylation of **4** with fatty acyl chlorides at room temperature, respectively (Scheme 1).

As to Cp*-complexes with double chain alkyl groups, we prepared [η^6-*p*-bis(alkylamino)benzene](η^5-pentamethylcyclopentadienyl)iron(1+) hexafluorophosphates (**7a**) by aromatic S_N reaction of $[(p\text{-}Cl_2C_6H_4)\text{-}FeCp^*]^+$ complexes with long-chain amines. However, *o*- and *m*-disubstituted complexes could not be obtained. Pearson suggested that (η^6-*m*-diaminobenzene)iron complexes were not obtained from (η^6-dichlorobenzene)iron complexes.[7] Moreover, it seems likely that introduction of long-chain amines by the S_N reaction of (η^6-*o*-dichlorobenzene)iron complex is very difficult because of steric hindrance between each of the long-chain



Scheme 1.

alkyl groups.

The hexafluorophosphates (**5**—**8a**) were insoluble in water. However, the corresponding chlorides (**5**—**8b**) prepared by anion exchange of **5**—**8a** were soluble in water. The surface tensions of aqueous solution of **5**—**8b** measured by the Wilhelmy method were about 30—35 mN m^{-1} at cmc (Fig. 1). In Table 1, we show the comparison of Cp*-complexes with Cp-complexes. The cmc values for Cp*-complex chlorides (**5**—**8b**) were smaller than those of the corresponding Cp-complex salts. The hydrophobicity of Cp*-complex is larger than that of the corresponding Cp-complex, because 1) electron density of the central metal is increased by the electron-donating effect of methyl groups to decrease the hydrophilicity of the cationic moiety, and 2) lipophilicity is increased by substitution with five hydophobic methyl groups on the Cp ring in the complexes.

In addition, we measured the cathodic potentials (E_c) of Cp*-complex hexafluorophosphates (**5**—**8a**), which were more negative than those of the corresponding Cp-complexes. Each methyl group introduced onto the Cp ring can be expected to make the E_c value more negative by 0.05 V,[6,8] and therefore it is reasonable that E_c values of **5a**, **6a**, and **8a** are negatively shifted by about 0.25 V.[9] These data show that the electron density of the central metal atom enhanced by Cp* ligand weakens the cationic property of the surfactants to reduce the hydrophilicity. The cmc value of a cationic surfactant such as quarternary ammonium salt becomes larger as increasing hydrophilicity or as decreasing lipophilicity.[10] From these viewpoints, the cmc values for **5b**, **6b**, and **8b** should be smaller than those of the corresponding Cp-complexes. In fact, we observed a lower cmc of Cp*-complexes, therefore we suggest that the cmc values correlate to their E_c values.

The (η^5-cyclopentadienyl)iron cationic complexes were known to decompose under daylight,[5] so we suppose that surface activity of organo-iron surfactants are diminished by irradiation. Surface tension of Cp-complex at cmc was measured under medium-pressure Hg-light (120 W) irradiation and it increased rapidly with irradiation time, followed by deposition of orange ferrocene crystals. On the other hand, surface tension of Cp*-complex did not change even after 24 hour under UV-vis light irradiation. From these results, the Cp*-complex is photochemically stable, because 1) the enhanced electron density of the central iron atom effects on the electron back donation from occupied d orbitals of metal atom to antibonding π orbitals of arene[11] and 2) the attack of solvent or oxygen dissolved in water on the central iron atom is prevented by the steric effect of five methyl groups. (Fig. 2)

In conclusions, we prepared new organoiron cationic surfactants, (η^5-pentamethylcyclopentadienyl)iron cationic complexes with long-chain alkyl groups. These cmc and E_c values were smaller than those of the cor-

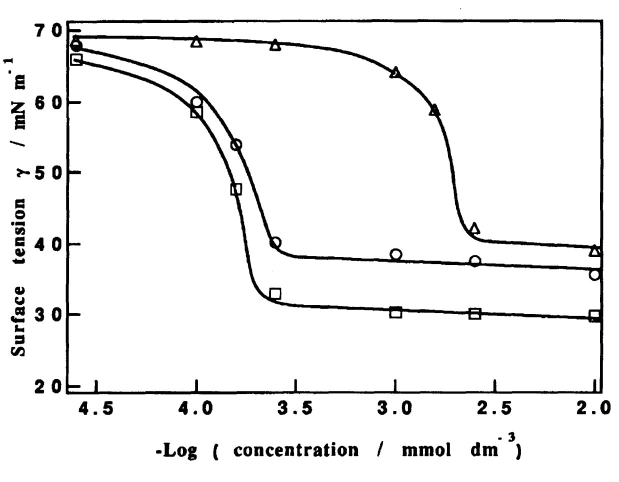


Fig. 1. Surface tension of Cp*($C_nH_{2n+1}NHC_6H_5$)-Fe^+Cl^- (**6b**) vs. concentration in water at 20 °C under air. △, n=8; ○, n=12; □, n=16.

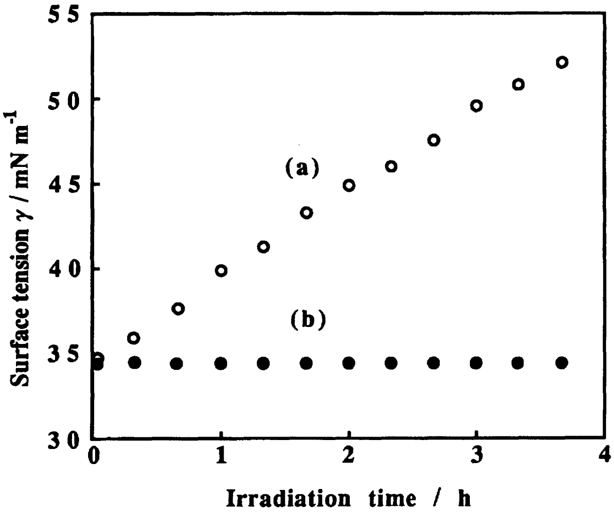


Fig. 2. Surface tension of Cp($C_{12}H_{25}C_6H_5$)Fe^+Cl^- (a) and Cp*($C_{12}H_{25}C_6H_5$)Fe^+Cl^- (b) at cmc under Hg-lamp (120 W) irradiation at 20 °C.

responding (η^5-cyclopentadienyl)iron cationic surfactants. Moreover, (η^5-pentamethylcyclopentadienyl)iron surfactant was stable even under UV-vis light irradiation in water for a day or more.

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