Applied Organometallic Chemistry (1990) 4 35–42
0268-2605/90/010035-08/$05.00

Preparation and properties of surface-active organocobalt complexes having long-chain alkyl groups

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Received 22 September 1989 *Accepted 4 November 1989*

New types of surface-active organocobaltocenium(I) complexes, η-$C_nH_{2n+1}X$-$C_5H_4(\eta C_5H_5)_2Co^+Y^-$ and (η-$C_nH_{2n+1}X$-$C_5H_4)Co^+Y^-$ (n = 6–16; X not present, NHCO or OCO; Y = Cl or PF_6) were prepared and their surface character studied. (1) The critical micelle concentrations of the cobaltocenium chlorides were much lower than those of corresponding trimethylammonium-type cationic surfactants. (2) The surface-active character of the cobaltocenium chlorides in aqueous solution (and the redox potentials of the hexafluorophosphates in acetonitrile) were affected by the substituents (X) in the cyclopentadienyl groups. (3) The surface activities of the cobaltocenium salts were lost on reduction with $NaBH_4$ to afford (alkyl-substituted cyclopentadiene)cyclopentadienylcobalt(0) complexes which were surface-inactive but could be re-oxidized to afford the surface-active cobaltoceium(I) salts. The cobalt complexes mentioned above may be the first examples of redox-responsive surfactants.

Keywords: Cobalt complex, surfactant, surface-active organometallics, redox surfactant, micelle, cobaltocenium salt, redox potential

INTRODUCTION

The great advances of using organotransition metals for preparative and coordination chemistry have now stimulated their applications to materials science. For example, simple organotransition metallics such as ferrocene derivatives were investigated as electromagnetic materials.[1,2] However, long-chain alkyl substituted organotransition metal complexes, especially cationic complexes, are usually unstable and are assumed to be merely reaction intermediates in the catalysis of, for example, the oxo- (or hydroformylation) reaction of long-chain alkenes. Therefore, little attention has been paid to their isolation and application to develop new functionallized materials. Saji *et al.* reported the preparation of ω-ferrocenyl substituted alkylammonium or non-ionic surfactants and their application to form electrochemically thin film by micelle disruption by control of the redox state of the ferrocenyl moiety. Nakahara and Fukuda prepared Langmuir–Blodgett aggregates of charge-neutral ferrocene derivatives of long-chain alkyls,[4] and Fujihira *et al.* studied the photosensitive accumulated molecular assembly of a long-chain alkyl substituted ferrocene, a viologen derivative, and pyrene.[5] The reported studies such as cited herein were concerned only with charge-neutral ferrocene derivatives, because of their stable structures. In our previous paper, a new type of the stable organoiron cationic complexes with long-chain alkyl groups (**1**) were prepared and their surface activities and electrochemical properties were studied.[6]

In this paper we report some long-chain alkyl substituted cobaltocenium cationic complexes (**2a–c** and **3b–c**) as examples of stable organotransition metal surfactants with redox-responsive character.

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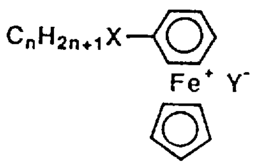

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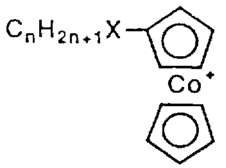

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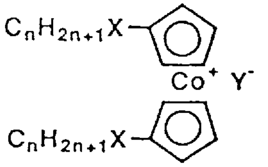

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a;X=none, b;X=NHCO, c;X=OCO

Y=Cl, PF_6^-

EXPERIMENTAL

Analysis

Melting points were measured by a Yanaco melting point apparatus and are uncorrected. Infrared spectra were obtained with a Shimazu IR-410 spectrometer as a solution in $CHCl_3$. ^1H NMR spectra were measured by a Hitachi R24 spectrometer. Elemental analyses were performed by the Microanalysis Centre of Kyoto University. Cyclic voltammographs were measured 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 concentration (cobaltocenium hexafluorophosphates) was 1×10^{-3} mol dm^{-3}, $(C_2H_5)_4N^+PF_6^-$ as supporting electrode 0.1 mol dm^{-3}, vs Ag/AgCl]. Surface or interface tension of the corresponding cobaltocenium chlorides was measured by Wilhelmy's method at room temperature (about 20 °C) by using a Kyowa surface tension meter, model CBVP-A3.

Chemicals

6-Alkylfulvenes were prepared from cyclopentadiene and aldehydes by Little's method[7] and used immediately thereafter. Cyclopentadienylcobalt dicarbonyl was synthesized from dicobalt octocarbonyl ($Co_2(CO)_8$) and cyclopentadiene.[8] 1-Carboxycobaltocenium hexafluorophosphate was obtained by the reaction of anhydrous cobalt (II) bromide ($CoBr_2$) with an equimolar mixture of cyclopentadiene and methylcyclopentadiene, followed by oxidation using potassium permangonate ($KMnO_4$) in an alkali medium according to the reported method.[9] 1,1′-Dicarboxy cobaltocenium salt was prepared from two equivalents of methylcyclopentadiene by the same methods. Alkyl amines and alcohols (more than 99% pure) were commercially available.

Preparation of 1-(long-chain alkyl) cobaltocenium hexafluorophosphates (Method A)

The reported ligand-exchange reaction of η-$C_5H_5Co(CO)_2$ with simple substituted fulvenes[10] was applied to the reaction with long-chain alkyl substituted fulvenes. For example, 6-heptylfulvene (4.7 g, 27 mmol) and η-$C_5H_5Co(CO)_2$ (4.9 g, 27 mmol) were refluxed in deoxygenated xylene (50 cm^3) for 15 h under a nitrogen atmosphere, treated with hydrochloric acid (3 mol dm^{-3}) at 60 °C to form 1-octylcobaltocenium hexafluorophosphate (**2a**; $n = 8$) in 7% yield (yellow solid); m.p. 113.0–114.0 °C. IR: 820 cm^{-1} (ν_{PF_6}). ^1H NMR($CDCl_3$): δ 5.17–5.68 (m, 9H, Cp-ring), 2.45 (m, 2H, $=C-CH_2$), 1.83–0.88 (15H, C_7H_{15}). Calcd for $C_{18}H_{26}F_6PCo$: C, 48.44; H, 5.48. Found: C, 48.62; H, 5.87%.

Other monoalkylcobaltocenium salts (**2a**) were also prepared and the results are summarized in Table 1.

Preparation of 1-(long-chain alkylaminocarbonyl)cobaltocenium hexafluorophosphate (Method B)

1-Chlorocarbonylcobaltocenium hexafluorophosphate, prepared *in situ* from the 1-carboxycobaltocenium salt (2.0 g, 5.3 mmol) and excess of thionyl chloride ($SOCl_2$), was allowed to react with octylamine (0.8 g, 6 mmol) in the presence of triethylamine (0.6 g) in $CHCl_3$(60 cm^3) at room temperature overnight. The solution was separated, washed with water, and dried over magnesium sulphate ($MgSO_4$). By the addition of diethyl ether to the solution, octyl aminocarbonylcobaltocenium hexafluorophosphate (**2b**; $n = 8$) was separated as a yellow powder (yield 85%), m.p. 135.0–136.0 °C. IR($CHCl_3$): 1640 cm^{-1} (ν_{CO}). ^1H NMR($CDCl_3$): δ 5.91(br.s, 5H,

Table 1 Preparation and properties of long-chain alkyl substituted cobaltocenium salts $(C_nH_{2n+1}{-}X{-}C_5H_4)_i(C_5H_5)_{2-i}Co^+PF_6^-$

No.	Compound *i*	X	*n*	Prepn method[a] (Compd. no.)	Yield (%)	M.p. (°C)	CMC[b] (mmol dm^{-3})	Redox potential (V)[c]
1	1	—	4	A (**2a**)	16	—	nd	−0.82
2	1	—	6	A	9	93.5–5.0	nd	—
3	1	—	8	A	7	113.0–4.0	1.3	−0.82
4	1	—	10	A	1	111.0–3.0	0.48	−0.81
5	1	—	12	A	tr.	126.0–30.0	0.24	—
6	1	NHCO	8	B (**2b**)	85	135.0–6.0	nd (137)[d]	−0.57
7	1	NHCO	12	B	85	140.5–2.5	0.15(16)	−0.57
8	1	NHCO	16	B	64	144.0–6.5	0.1 (1.0)	−0.57
9	1	OCO	8	B (**2c**)	57	116.0–7.0	nd	−0.48
10	1	OCO	12	B	55	118.0–21.0	0.14	−0.47
11	2	NHCO	8	C (**3b**)	21	121.5–31.0	nd	−0.40
12	2	NHCO	10	C	23	127.0–8.5	0.02	−0.39
13	2	NHCO	12	C	40	135.0–7.5	0.1	−0.40
14	2	NHCO	14	C	10	98.0–100.0	—	−0.40
15	2	NHCO	16	C	8	78.0–9.0	0.27	−0.40
16	2	OCO	8	C (**3c**)	13	55.0–5.5	nd	−0.26
17	2	OCO	12	C	27	82.0–3.0	0.14	−0.26

Abbreviations: tr, trace; nd, not determined. [a] See text. [b] Critical micelle concentration of the cobaltocenium chloride. [c] Volts vs Ag/AgCl. [d] CMC for $C_nH_{2n+1}N(CH_3)_3{}^+Br^-$.

C_5H_5), 6.40–5.99 (m, 4H, C_5H_4), 3.28 (m, 3H, $NHCH_2$), 1.27–0.83 (15H, C_7H_{15}). Calcd for $C_{19}H_{27}NF_6PCo$: C, 46.47; H, 5.56; N, 2.86. Found: C, 46.56; H, 5.65; N, 2.83%.

Other 1-(long-chain alkylaminocarbonyl)cobaltocenium salts (**2b**) were prepared by the same route (Table 1).

Preparation of 1-(long-chain alkyloxycarbonyl)cobaltocenium hexafluorophosphates (Method B)

1-Octyloxycarbonylcobaltocenium hexafluorophosphate (**2c**; *n* = 8) was prepared from the chlorocarbonylcobaltocenium salt and sodium octanoate by the method described above. A yellow solid resulted, yield 57%, m.p. 116.0–117.0 °C. IR($CHCl_3$): 1713 cm^{-1} (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 5.89 (s, 5H, C_5H_5), 6.28–6.08 (m, 4H, C_5H_4), 4.41 (t, J = 6 Hz, 2H, OCH_2), 1.35–0.88 (15H, C_7H_{15}). Calcd for $C_{19}H_{26}OF_6PCo$: C, 46.54; H, 5.34. Found: C, 46.62; H, 5.32%.

1-Dodecyloxycarbonylcobaltocenium hexafluorophosphate was also prepared (Table 1).

Preparation of 1,1′-bis(long-chain alkylaminocarbonyl)cobaltocenium hexafluorophosphate (Method C)

1,1′-Bis(chlorocarbonyl)cobaltocenium hexafluorophosphate was prepared *in situ* by the reaction of η-$(HOCOC_5H_4)_2Co^+PF_6^-$ (2.09 g, 5.5 mmol) with $SOCl_2$ (80 cm^3) at reflux for 48 h, followed by addition of potassium hexafluorophosphate (KPF_6) (1.0 g, 5.5 mmol), distillation of excess $SOCl_2$ and filtration to isolate the solid salt. Then the solution of dodecylamine (2.10 g, 11.0 mmol) and triethylamine (1.11 g, 11.0 mmol) in $CHCl_3$ (70 cm^3) was added to the salt mentioned above, and stirred for 4 h at room temperature. The reaction mixture was washed with water, dried over $MgSO_4$, and filtered. Chloroform was evaporated to afford crude 1,1′-bis(dodecylaminocarbonyl)cobaltocenium hexafluorophosphate (**3b**; *n* = 12), which was recrystallized from diethyl ether/pentane (1:1). The yield was 40% (1.63 g, 2.2 mmol); m.p. 135.0–137.5 °C. IR: 1652 cm^{-1} (ν_{CO}); ^{1}H NMR: δ 5.68–6.00 (m, 8H, C_5H_4), 2.93–3.55 (m, 6H, $NHCH_2$), 1.02–1.68 (br.s, 40H, $C_{10}H_{20}$), 0.85 (br.t, 6H, CH_3).

Other salts (**3b**; *n* = 8–16) were obtained in the same manner and the results are summarized in Table 1.

Preparation of 1,1′-bis(long-chain alkyloxycarbonyl)cobaltocenium hexafluorophosphate

The same preparative method as for **3b** was applied to the reaction with sodium dodecanoate to afford 1,1′-bis(dodecyloxycarbonyl)cobaltocenium hexafluorophosphate (**3c**). The yield was 27%; m.p. 82.0–83.0 °C. IR 1710 cm^{-1} (ν_{CO}); ^1H NMR δ 6.05 (m, 8H, C_5H_4), 4.35 (br.t, 4H, OCH_2), 1.0–2.0 (br., 40H, $C_{10}H_{20}$), 0.85 (br.s, 6H, CH_3).

Preparation of the cobaltocenium chlorides by anion exchange

The water-soluble cobaltocenium chlorides were prepared by using an anion-exchange resin and used in surface-tension measurements: the cobaltocenium hexafluorophosphate was passed through an anion-exchange column (Amberlite IRA-400), eluted with hydrochloric acid in methanol, and washed with methanol. The eluent was evaporated to dryness *in vacuo* to give the corresponding cobaltocenium chloride, in which the characteristic band of the PF_6^- salt at 820 cm^{-1} was not observed.

Preparation of cyclopentadienyl (3-dodecylaminocarbonylcyclopenta-1, 4-diene)cobalt (4)

1-Dodecylaminocarbonylcobaltocenium hexafluorophosphate (**3b**; 0.55 g, 1 mmol) was reduced by excess of sodium borohydride ($NaBH_4$) in methanol at room temperature to give a reddish violet solution of the title compound **4** (see Scheme 3), which was extracted with chloroform, washed with water, and dried to form a reddish violet oil of the titled compounds (**4**; 0.39 g, 1 mmol). ^1H NMR (CCl_4): δ 5.90–5.00 (m, 4H, CH=CH), 4.56 (s, 5H, C_5H_5), 3.21 (m, 3H, $NHCH_2$), 2.6 (m, 1H, =C—CH), 1.28–0.83 (23H, $C_{11}H_{23}$).

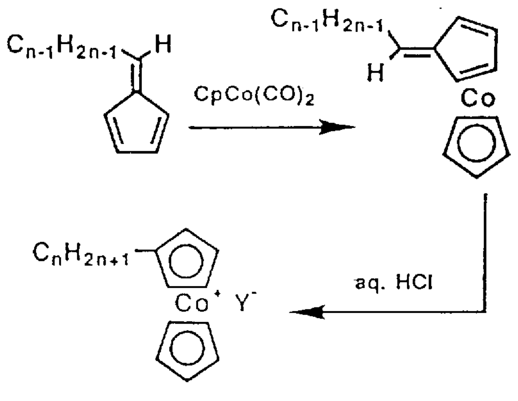
RESULTS AND DISCUSSION

Preparation of long-chain alkyl substituted cobaltocenium salts

Direct Ligand-exchange reactions of organometallic complexes with long-chain organic compounds are generally difficult. For example, in the oxo reaction, long-chain alkenes poorly coordinate onto the cobalt catalyst and yields of long-chain aldehydes are low. This may be explained by steric hindrance of long-chain alkenes. Several attempts to prepare long-chain alkylcobaltocenium salts by electrophilic substitution reaction on the cyclopentadienyl ring have been made, but the introduction of long-chain alkyl groups into cyclopentadienyl ligands was not successful. For example, acylation of cobaltocene(0) with acyl halides followed by hydrogenolysis was not successful because of fast oxidation during the acylation reaction to form an unsubstituted cobaltocenium salt. We found that the ligand-exchange reaction of carbonyls in cyclopentadienylcobalt dicarbonyl with 6-alkylfulvenes under neutral reaction conditions, followed by treatment with hydrochloric acid andpotassium hexafluorophosphate (Method A) was able to afford alkylcobaltocenium salts **2a** (Scheme 1).

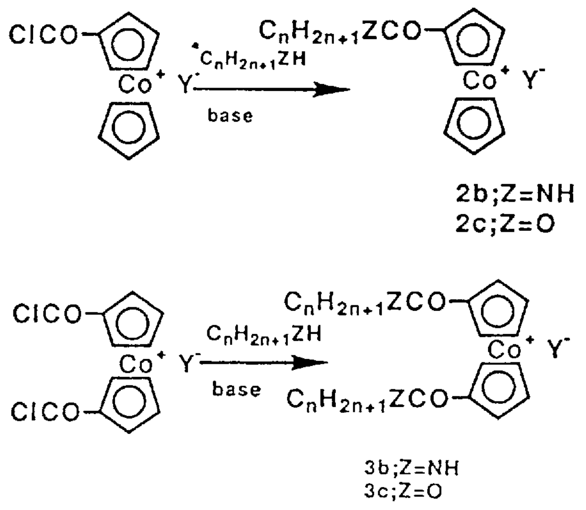
As shown in Table 1 (nos 1–5), the effect of the alkyl chain-length of fulvenes on the yields of the complexes was critical in the reaction of Scheme 1, and cobaltocenium salts with alkyl groups greater than C_{12} were not obtained.

The second method of introducing long-chain alkyl



2a (Y=Cl)

Scheme 1 Method A



Scheme 2 Methods B (above) and C (below)

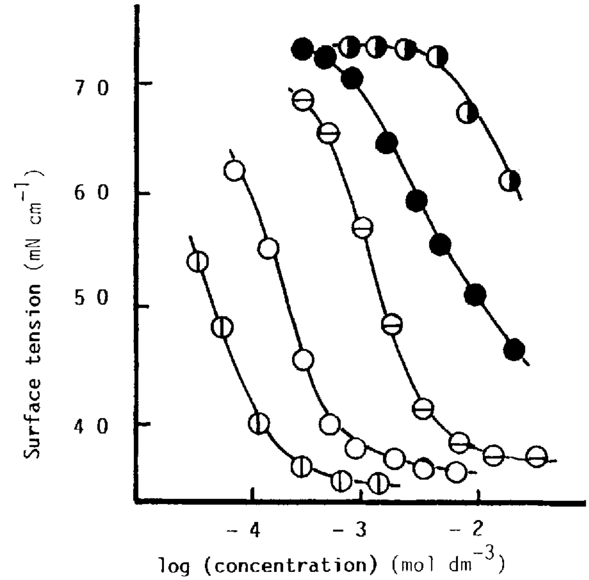


Figure 1 Effect of concentration of $C_nH_{2n+1}C_5H_4$ (η-C_5H_5)Co^+Cl^- (**2a**; Y = Cl) on surface tension in aqueous solution. ◑, n = 0; ●, n = 4; ⊖, n = 6; ○, n = 8; ⦶, n = 10.

groups into cobaltcenium salts was the reaction of long-chain organic compounds with reactive substituents of ligands in a cobalt complex. Schotten–Baumann-type reactions of the (acid chloride) complex with amines or alcohols in basic media were performed smoothly and (long-chain alkyl-amino- or oxy-carbonyl)cobaltocenium hexafluorophosphates (*2b* or **2c**) were obtained in good yields (Method B; nos 6–10 in Table 1). Long-chain distributed complexes, bis(alkyl-amino- or oxy-carbonyl)cobaltocenium salts (**3b** or **3c**) were also obtained in moderate yields by Schotten–Baumann reactions (Method C; nos 11–17 in Table 1).

Surface activities

Cobaltocenium hexafluorophosphates were soluble in chloroform but insoluble in water. To solubilize the complexes in water at room temperature for surface-tension measurements, they were converted to the corresponding chlorides by using an anion-exchange resin column.

From the surface tension–concentration curves, the critical micelle concentrations (CMC) of the cobaltocenium chlorides were estimated and they are summarized in Table 1.

Surface tension–concentration curves for the various alkylcobaltocenium chlorides are shown in Fig. 1. Three characteristic features were observed:

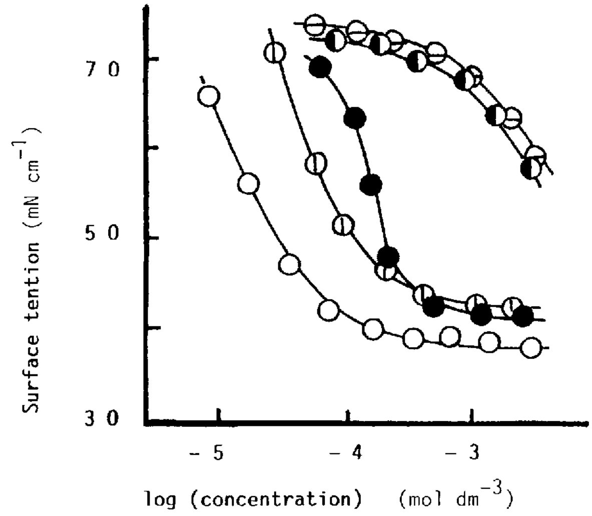


Figure 2 Surface tension–concentration curves for ${}_nH_{2n+1}X$—COC_5H_4(η-C_5H_5)Co^+Cl^- (**2b**; Y = Cl).
X = NH: ⊖, n = 8; ⦶, n = 12; ○, n = 16; X = O: ◑, n = 8; ●, n = 12.

(1) Micelle formation was found even in the medium-length alkylcobaltocenium chloride (n = 6 or 8 in **2a**).

(2) The critical micelle concentrations (CMC) of the cobaltocenium chlorides were much lower than those of the corresponding alkylammonium halides as discussed below.

(3) The longer the length of the alkyl chains in the complex salts were, the lower were the CMC values.

Alkyl-amino- (**2b**) and -oxy-carbonylcobaltocenium chlorides (**2c**) showed almost the same surface-active behavior as the alkylcobaltocenium salts (**2a**) as long as the alkyl chain-lengths were sufficiently large (n = 12–16). However, for the medium-length chains in **2b** and **2c** (n = 8) these did not show CMC points (Fig. 2), although one appeared in the case of **2a** (n = 8). This fact indicated that the electron-withdrawing substituent (X) affected the hydrophilicity of the cobaltocenium moiety.

The most important feature of the organocobalt complexes (**2a–c**) is that the critical micelle concentration is as abnormally low as those of ionic surfactants having only one long-chain alkyl group [polymer-type surfactants such as $RO(C_2H_4)_nOH$ have much lower CMC values (0.003–0.05 mmol dm^{-3}), because of their polymeric structures in aqueous solution]. CMC values of **2a–c** (n = 12) were less than *ca* 0.2 mmol dm^{-3}, while that of $C_{12}H_{25}N(CH_3)_3{}^+Br^-$ is 16 mmol dm^{-3}. [The extreme molecular areas of organotransition metal surfactants measured by Langmuir–Blodgett's method were less than 100 Å^2, which was comparable with the values of alkylammonium salts and five times that of fatty acids (unpublished data).] Similarly, low CMC values were reported for (long-chain alkyl substituted benzene)cyclopentadienyliron cationic complexes (0.9–5 mmol dm^{-3}),[6] for [N-(long-chain alkyl)ethylenediamine] complexes (n = 12; 0.02 mmol dm^{-3}),[11] and for complexes formed with N-dodecyl-β-alanine in aqueous solution.[12]

The reason why organotransition complexes show abnormally low CMC values is not yet clear. The size of the cobaltocenium moiety is roughly estimated as a sphere having a 5 Å diameter by comparing crystallographic data for simple cobaltocenium(1+) cations, which are similar sizes, with those of aromatic-plane rings.

Figures 3 and 4 show how the surface-tension

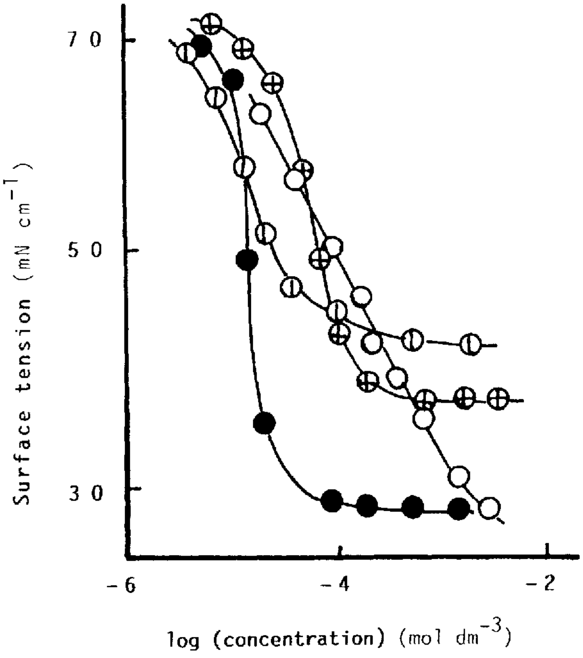


Figure 3 Surface tension–concentration curves for $(C_nH_{2n+1}NH{-}COC_5H_4)_2Co^+Cl^-$ (**3b**; Y = Cl). ●, n = 8; ○, n = 10; ⦶, n = 12; ⊕, n = 16.

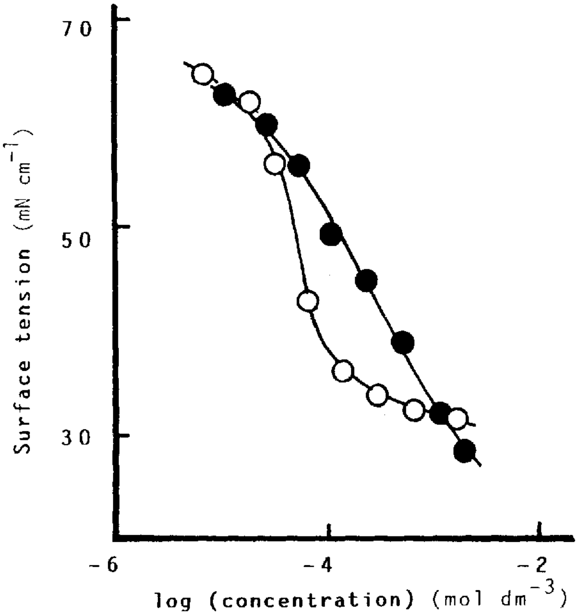


Figure 4 Surface tension–concentration curves for $(C_nH_{2n+1}O{-}COC_5H_4)_2Co^+Cl^-$ (**3c**; Y = Cl). ●, n = 8; ○, n = 12.

behavior of bis(alkyl chain) surfactants, 1,1′-bis(alkyl-amino- (**3b**) and -oxo-carbonyl)cobaltocenium chlorides (**3c**) are different from monoalkyl chain surfactants:

(1) Surface tention is low even in the case of shorter alkyl chains of **3** (n = 8), and the surface tensions at 5 mmol dm^{-3} become as low as 30 mN cm^{-1} although a CMC was not observed in this case.
(2) CMC values are lower than those of monoalkyl surfactants (nos 11–17 in Table 1), and the minimum CMC value reached 0.02 mmol dm^{-3} in the case of **3b** (n = 10).
(3) Alkyl chain-length is effective for the surface-tension behavior in aqueous solution. Complexes with an alkyl chain greater than C_{12} in the substituted salt (**3b**) showed less surface activity, as in the case of common ionic surfactants having much larger hydrophobic groups.

Redox character

The electrochemical nature of the unsubstituted or simply substituted cobaltocenium salts was studied by cyclic voltammetry, where reversible redox potentials were observed.[13,14] The cyclic voltammography of the (long-chain substituted) cobaltocenium hexafluorophosphates is shown in Fig. 5; it gave a chathodic potential and an anodic potential observed only in the first cycle. In the second cycle of the voltage scanning (−1.5 to +0.5 V), no current peak appeared, because of the formation of the thin insulating film of the long-chain alkyl complexes on the platinum (Pt) electrode surface. This type of insulation effect was not observed in cyclic voltammetry of the unsubstituted cobaltocenium salt, suggesting that long-chain alkyl groups in the cobaltocenium salt may make a monolayer molecular aggregate on the electrode. However, the oxidized form (**3b**; n = 12) and the reduced form (**4**) are stable and will be able to exist on the surface of the electrode from the fact that cathodic and anodic potentials were observed. [In the case of (alkylbenzene)cyclopentadienyliron(1+) salts (**A**),[6] only cathodic potentials appeared because of low stabilities of the reduced form which decomposed instantaneously to afford surface-inactive products. Therefore, surface activities of **A** were essentially lost by reduction.] The reduced form **4b** (n = 12) was isolated from the reaction of **3b** with $NaBH_4$ (Scheme 3).

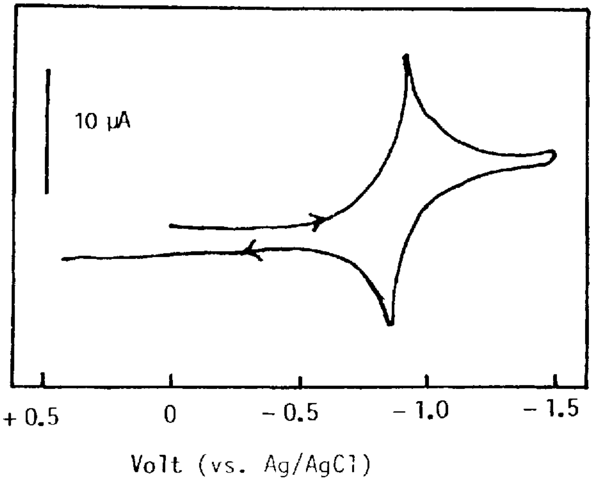
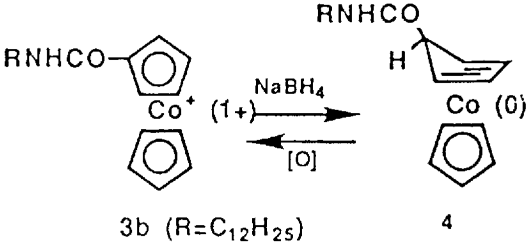


Figure 5 Cyclic voltammogram of 1-dodecylaminocarbonylcobaltocenium hexafluorophosphate (**2b**; n = 12, Y = PF_6). Conditions: see text.



Scheme 3

The reduced compound **4** as isolated shows a low interface tension (3 mN cm^{-1}) in the interface between aqueous 2% H_2O_2 solution and $CHCl_3$, which was the same as the value for the interface between water and the solution of **3b** in $CHCl_3$, suggesting the *in-situ* formation of the oxidized form (**3b**). The compound **3b** did not decrease the interface tensions of aqueous $NaBH_4$ solution/$CHCl_3$, which was 32 mN cm^{-1}, which is the same as for the water/$CHCl_3$ interface in the absence of the surfactant, suggesting the formation of **4**. These results implied that the alkyl substituted cobaltocenium salt **3b** is the first example of a redox-reversible or -responsive surfactant. Reversible control of the surface activities was performed chemically but not electrochemically, because of thin-film formation on the electrode.

The second point of interest for cobaltocenium surfactants is that the substituent (X) in **3a** and **3b** affects the surface-active properties; for example, the CMC values (and redox potentials) of **3a**, **3b** and **3c** were 0.24 (−0.82), 0.15 (−0.57), and 0.14 mmol dm^{-3} (−0.48 V), respectively. The CMC and redox potential of dodecyltrimethylammonium salts were 16 mmol dm^{-3} and *ca* −2.6 V. The effect of redox potentials of the complexes on their CMC values was apparently observed, but the meaning of their relationship is not clear and further investigations are required.

CONCLUSION

Direct ligand-exchange reactions of 6-alkylfulvenes with carbonyl ligands in η-$C_5H_5Co(CO)_2$ was able to afford 1-(long-chain alkyl)cobaltocenium hexafluorophosphates in only low yields. However, in the reactions of long-chain amines or alcohols with reactive substituents (chlorocarbonyl) of the cyclopentadienyl ligands in cobaltocenium salts, long-chain substituted organocobalt cationic complexes were obtained as oil-soluble hexafluorophosphates in good yields. They were converted to the water-soluble cobaltocenium chlorides for measurements of surface activities. The characteristic features of the cobaltocenium chlorides, η-$(C_nH_{2n+1}XC_5H_4)$ (η-C_5H_5)Co^+Cl^- (**2**) and η-$(C_nH_{2n+1}XC_5H_4)_2Co^+Cl^-$ (**3**), are as follows:

(1) Critical micelle concentrations are much lower than the corresponding trimethyalkylammonium-type surfactants.

(2) Surface-active behavior of the cobaltocenium chlorides in aqueous solution (and redox potentials of the cobaltocenium hexafluorophosphates in organic solvents) were affected by substituent (X) in the cyclopentadienyl ligand.

(3) Critical micelle concentrations of the bis(long-chain substituted)cobaltocenium salts (**3**) were lower than those of the monosubstituted ones (**2**).

(4) Surface activities of the cobaltocenium salts (**2**) were lost by reduction with $NaBH_4$ to give (alkyl substituted cyclopentadiene)cyclopentadienyl-cobalt(0) complexes, which were surface-inactive but which were re-oxidized chemically to afford the surface-active cobaltocenium(1+) salts. These cobalt complexes mentioned above may be the first examples of 'redox-responsive' surfactants.

Acknowledgement This work has been partially supported by a Grant-in-Aid from the Ministry of Education, Science and Culture (no. 61550570).

REFERENCES

1. Dong, T Y, Kambara, T and Hendrickson, D N *J. Am. Chem. Soc.*, 1986, 108: 5857
2. Tredgld, R H, Young, M C J, Hodge, P and Hoorfar, A *IEEE Proc.*, 1985, 132: 151
3. Hoshino, K and Saji, T *J. Am. Chem. Soc.*, 1987, 109: 5881; *Chem. Lett.*, 1987: 1439; *ibid.*, 1988: 693
4. Nakahara, H and Rukuda, K *Thin Solid Films*, 1985, 133: 1
5. Fujihira, H, Nisiyama, K and Yamada, H *Thin Solid Films*, 1985, 132: 77 and 1988, 160: 125
6. Sakai, S, Kozawa, H, Yoshinaga, Y, Kosugi, K, Fukuzawa, S and Fujinami, T *J. Chem. Soc., Chem. Commun.*, 1988: 663
7. Stone, K J and Little, R D *J. Org. Chem.*, 1984, 49: 1849
8. Raush, M D and Genetti, R A *J. Org. Chem.*, 1970, 35: 3888
9. Sheate, J E and Raush, M D *J. Org. Chem.*, 1970, 35: 3245
10. Sheate, J E, Miller, W and Krisch, K *J. Organomet. Chem.*, 1975, 91: 97
11. Yashiro, M, Matsumoto, K and Yoshikawa, S *Chem. Lett.*, 1989: 986
12. Nakamura, A and Tajima, K *Bull. Chem. Soc. Jpn*, 1988, 61: 3807
13. Geiger, W E, Bogden, W L and Murr, N E *Inorg. Chem.*, 1979, 18: 2358
14. Simon, R A, Mallouk, T E, Daube, K A and Wrington, M S *Inorg. Chem.*, 1986, 24: 3119