

## A New Type of Surface-active Organotransition Metal Complex: (Long-chain Alkyl Substituted Benzene) (Cyclopentadienyl) Iron(1+) Cationic Complexes

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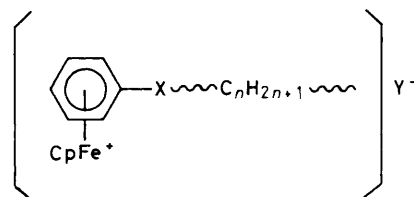
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Surface-active cationic iron complexes containing long-chain alkyl substituted benzene have been prepared.

In general, cationic organotransition metal complexes having a long-chain alkyl group are unstable and are assumed to be merely intermediates in the catalysis of, *e.g.*, the Oxo reaction of long-chain alkenes. For this reason, little attention has been given to their isolation. However, such complexes are redox sensitive cationic surfactants which can be used in the preparation of Langmuir-Blodgett films containing organotransition metal moieties<sup>1,2</sup> and in phase-transfer catalysis. We report here the preparation of the first examples, (1) and (2), of a new class of stable iron(1) complexes whose surface-active properties are sensitive to reduction.

(Long-chain alkyl substituted benzene)(cyclopentadienyl)-iron(1+) complexes (**1b–g**; Y = PF<sub>6</sub>) were obtained by (A) aromatic nucleophilic substitution<sup>3</sup> of [(ClC<sub>6</sub>H<sub>5</sub>)FeCp]<sup>+</sup> (Cp = cyclopentadienyl) complexes with long-chain alcohols or amines, (B) acylation<sup>4</sup> of long-chain compounds using [(ClOCC<sub>6</sub>H<sub>5</sub>)FeCp]<sup>+</sup>, and (C) acylation of [(HO- or H<sub>2</sub>N-C<sub>6</sub>H<sub>5</sub>)FeCp]<sup>+</sup> complexes with fatty acid chlorides at room temperature. Complex (**1a**) was obtained by the reaction<sup>5</sup> of

ferrocene with alkylbenzene catalysed by AlCl<sub>3</sub> and aluminium powder at 170°C (method D). Other long-chain



- (1) Y = PF<sub>6</sub>
- (2) Y = Cl
- a; X = CH<sub>2</sub>
- b; X = CO<sub>2</sub>
- c; X = CONH
- d; X = OCO
- e; X = NHCO
- f; X = O
- g; X = NH

**Table 1.** Preparation and properties of (1) and (2).

	<i>n</i>	Preparation of (1)			<i>E<sub>c</sub></i> <sup>b</sup> /V	C.m.c. of (2) <sup>c</sup> /mmol
		Method <sup>a</sup>	% Yield	M.p./°C		
(b)	8	B	87	Liq.		6.0(140) <sup>d</sup>
	12	B	82	59.0—60.5	−0.90	5.5(20)
	16	B	67	72.0—73.5		0.90(1.3)
(c)	12	B	82	108.5—109.5	−1.04	4.8
(d)	12	C	74	55.0—57.0	−1.09	3.0
(f)	12	A	73	53.0—55.5	−1.21	3.1
(e)	12	C	40	Liq.	−1.35	2.7
(g)	12	A	90	85.0—87.0	−1.35	5.0
(a)	12	D	65	98—101	−1.40	5.0

<sup>a</sup> See text. <sup>b</sup> Cathodic potentials measured by cyclic voltammetry of (1) in MeCN (Pt electrode, vs. Ag/AgCl, 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>, 100 mV s<sup>−1</sup>). <sup>c</sup> At room temperature. <sup>d</sup> Data for trimethylalkylammonium chloride.

compounds did not undergo ligand-exchange reactions.† The corresponding chlorides (2) were prepared from (1) by anion-exchange.

The hexafluorophosphates (1) were insoluble in water and stable in the solid state or in organic solution, whereas the chlorides (2) were fairly soluble in water and partially decomposed after a few weeks. The surface tension of aqueous solutions of (2a—g) measured by the Wilhelmy method was about 35 mN cm<sup>−1</sup> at the critical micelle concentration (c.m.c.) (Table 1). The c.m.c. values for (2b; *n* = 12) are smaller than those of the corresponding trimethylalkylammonium chlorides. The limiting molecular areas obtained by extrapolation of the condensed region in the Langmuir–Blodgett films are 75 (1c) and 100 Å<sup>2</sup> (1d), respectively, which are much larger than the molecular areas of trimethyl(hexadecyl-amino- and -oxo-carbonyl-ferrocenes) (25 Å<sup>2</sup>).<sup>6</sup> Furthermore, the cathodic potentials (*E<sub>c</sub>*) for (1) range from −0.90 to −1.40 V, but no anodic peak appears. It appears likely that iron(0) complexes are formed on the electrode and immediately decompose, suggesting that the

surface activity is affected by reduction of the cationic complexes. For instance, the interface tension (CCl<sub>4</sub>/H<sub>2</sub>O) of (2a) in CCl<sub>4</sub> was increased by addition of a reducing agent such as NaBH<sub>4</sub> to the aqueous phase.

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† Complexes (1a—g) gave satisfactory elemental analyses and <sup>1</sup>H n.m.r. data.

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