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Overcrowded Metallocenes. The Preparation of Deca-methyl Ferrocene, Ferricinium Perchlorate, and Cobalticinium Reineckate

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Chimica. — *Overcrowded Metallocenes. The Preparation of Decamethyl Ferrocene, Ferricinium Perchlorate, and Cobalticinium Reineckate* (*)(**). Nota di GABRIELLO ILLUMINATI, GIANCARLO ORTAGGI e SALVATORE SCURO, presentata (***) dal Corrisp. G. SARTORI.

RIASSUNTO. — Allo scopo di studiare la reattività di metalloceni « overcrowded » sono stati sintetizzati e caratterizzati decametilmetalloceni delle formule generali $(C_5Me_5)_2M(II)$ e $(C_5Me_5)_2M(III)^+X^-$ (M = Fe(II), Fe(III), Co(III)) a partire dal pentametilciclopentadiene come legando.

Gli spettri n.m.r., infrarossi ed elettronici sono in accordo con una struttura a sandwich. È stata inoltre considerata la reazione di ossidazione del decametilferrocene a ione decametilferricinio sia per via chimica sia per via elettrochimica.

Metallocenes are outstanding counterparts of benzene in transition metal chemistry because they possess aromatic character [1–3]. Although many derivatives of metallocenes that are analogous to mono– and poly-substituted benzenes have been reported, little attention has been given to the counterparts of such overcrowded systems as hexamethylbenzene [4].

In view of the recent report [5] on the successful synthesis of pentamethylcyclopentadiene, we have undertaken an investigation on the chemistry of overcrowded metallocenes of the types $(C_5Me_5)_2M(II)$ and $(C_5Me_5)_2M(III)^+X^-$. In this paper we wish to report on the preparation and some of the properties of the members of the series with M = Fe(II), Fe(III), and Co(III).

Decamethylferrocene (M = Fe(II)) and decamethylcobalticinium ion (M = Co(III)) were obtained by the reaction of sodium pentamethylcyclopentadienate with the corresponding metal(II) halides in liquid ammonia or tetrahydrofuran solution. Metallocene formation was found to be of more difficult occurence with the pentamethyl ligand than with the unsubstituted cyclopentadiene. This fact is to be attributed, at least in part, to the acid strength-depressing influence of the five electron-releasing alkyl groups on the ligand in the first stage of the synthesis (sodium salt formation). However, steric hindrance may also play a role in the over-all process. Decamethylferricinium perchlorate was obtained from ferrocene by anodic oxidation.

The n.m.r. spectrum of decamethylferrocene exhibits a singlet peak at 1.63 δ, tetramethylsilane being taken as the reference compound. Unlike the free, starting ligand, it shows no signals for geminal position hydrogens.

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Both members with M = Fe(II) and Co(III) show an i.r. spectrum with characteristic frequencies of the methyl group region (Fe(II): 1370, 1420, 1445, and 1470 cm^{-1}; Co(III): 1375, 1465 cm^{-1}). The electronic spectra of the members with M = Fe(II) and Fe(III) are reported in Table I and compared with those of the corresponding unsubstituted metallocenes.

TABLE I.

Electronic spectra for some ferrocenes and ferricinium salts.

Compounds	λ (mμ)	log ε
$(C_5H_5)_2$Fe(II) $^{(a)}$	325 440	1.72 1.96
$(C_5Me_5)_2$Fe(II) $^{(b)}$	220 420	4.56 2.07
$[(C_5H_5)_2$Fe(III)$]BF_4$ $^{(c)}$	250 617	4.08 2.53
$[(C_5Me_5)_2$Fe(III)$]ClO_4$ $^{(d)}$	275 315	4.07 3.82

(*a*) In 95% ethanol. Data from ref. 2. (*b*) In isoöctane. (*c*) In water. Data from ref. 2. (*d*) In 95% ethanol.

All the above spectral data are perfectly consistent with a sandwich, metallocene structure (fig. 1).

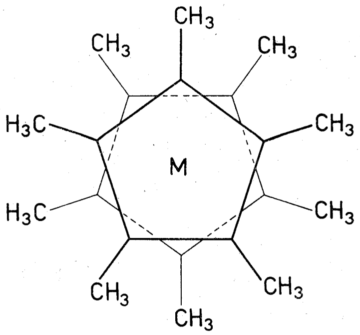

Fig. 1.

Decamethylferrocene is oxidized at a measurable rate in several solvents (ethanol, chloroform, acetonitrile) in the presence of acetic acid, and much more readily by chlorine in acetic acid solution. It also was found to give a well defined reversible anodic wave at the dropping mercury electrode, with 0.1 M sodium perchlorate supporting electrolyte in 90 % ethanol. The polarographic parameters are distinctly different from those of ferrocene [6] (given in parentheses), as follows:

$E_{1/2}$, $-0,120 \pm 0.010$ V *vs.* S.C.E. ($+0.310$);

D, $2.2 \cdot 10^{-6}$ cm·sec^2 ($4.38 \cdot 10^{-6}$);

$i_d/\mathrm{Cm}^{2/3} t^{1/6}$, 1.06 $\mu a/\mathrm{mM/lmg}^{2/3}\,\mathrm{sec}^{-1/2}$ (1.27).

The greater tendency of the decamethyl derivative toward oxidation is in line with the polar effects of the alkyl substituents.

Synthetic work is now under way dealing with other transition metals, such as Ru(II) and Hg(II). Work is also in progress to correlate the chemistry of these compounds with that of benzenoid overcrowded systems, and look for new kind of evidence for aromatic character in metallocene chemistry.

EXPERIMENTAL.

Decamethylferrocene.—In a 150 ml three-necked flask, equipped with a pressure-equalized dropping funnel and magnetic stirring under dry nitrogen atmosphere, 0.35 g of sodium was first dissolved in 100 ml of anhydrous liquid ammonia [7] and, then, 2.4 g (0.018 mole) of pentamethylcyclopentadiene [5] was added. After one hour of continuous stirring the solution became green-yellow and 5.0 g (0.039 mole) of anhydrous ferrous chloride [8] was introduced. After two additional hours, petroleum ether, b.p. 60–70°, was added and then the ammonia allowed to evaporate under dry nitrogen current. The ether solution was filtered and the solid residue was washed with petroleum ether, b.p. 60–70°, until the washings appeared colorless. On evaporation of the petroleum ether fractions yellow crystals in admixture with unreacted pentamethylcyclopentadiene were obtained as a residue. Washing with pentane and recrystallization from a petroleum ether—ethanol mixture (4 : 1, by volume) yielded 0.300 g of pure product (10.5 %). The m.p. of this material was found to be 277–278° and remained unchanged on sublimation of the crystals at 0.2 mm Hg and 100° C. The product is very soluble in organic solvents such as pentane, ether, chloroform, and scarcely so in methanol and ethanol.

Analysis: calcd. for $FeC_{20}H_{30}$: C, 73.64 %; H, 9.20 %.

Found: C, 73.57; H, 9.02.

Decamethylcobalticinium reineckate.—Sodium pentamethylcyclopentadienate was prepared by reaction of the ligand with $NaNH_2$, as decribed above. A solution of anhydrous cobaltous bromide (1.6 g, 0.008 mole) in 100 ml of anhydrous tetrahydrofuran was slowly added under stirring to a solution of the reagent in the same solvent. The resulting solution was kept for twelve hours at room temperature. The filtered solution from the reaction mixture was poured into 100 ml of 1 N HCl. The aqueous layer was then neutralized with sodium hydroxide and filtered from the precipitated hydroxides. On addition of a saturated solution of ammonium reineckate, the product was obtained as a red-orange powder. The yield was 0.480 g (10 %).

Analysis: calcd. for $CoC_{24}H_{36}CrN_6S_4$: C, 44.51 %; H, 5.56 %.

Found: C, 44.58; H, 5.05.

Decamethylferricinium perchlorate.—Decamethylferrocene (0.010 g) was dissolved in 100 ml of a 0.1 M sodium perchlorate solution in 90 % (by volume) ethanol and oxidized by the electrolytic method under a controlled potential. After the oxidation was complete, the solution was evaporated to a small volume at room temperature and then kept in a refrigerator overnight. The yellow-green needles were filtered, washed with ethanol and diethyl ether, and dried. The yield was 0.005 g (39 %).

Analysis: calcd. for $FeC_{20}H_{30}ClO_4$: C, 56.44 %; H, 7.05 %.

Found: C, 56.40; H, 7.15.

Spectral and polarographic measurements.—The infrared absorption spectra were recorded on a Beckman model IR–7 spectrophotometer equipped with sodium chloride optics. The complexes were studied as Nujol mulls in the region 650–1300 cm^{-1} and as Fluorolube mulls in the region 1300–4000 cm^{-1}. The electronic absorption spectra of the complexes in either isoöctane or 95 % ethanol were obtained with a Beckman DB spectrophotometer using 10 mm quartz cells. The nuclear magnetic resonance spectra were measured in deuterated chloroform with a Varian Associated model A–60 spectrometer. Polarograms were registered with a Radiometer model PO4 instrument, and a divided H–shaped cell with a NaCl–saturated calomel reference electrode. The solvent was degassed and all operations were carried out under a dry nitrogen atmosphere.

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Added in proof.—R. B. King. and M. B. Bisnette (J. Organometal. Chem., *8*, 287 (1967)) have just reported an independent synthesis of decamethylferrocene. Their results are in essential agreement with ours (spectral and analytical data), although we noted a somewhat lower, but sharper, m.p. value (see Experimental).

REFERENCES.

[1] M. D. RAUSCH in *Reaction of Coordinated Ligands*, « Advances in Chemistry Series N. 37 », American Chemical Society, Washington 1963.

[2] M. ROSENBLUM, *Chemistry of the Iron Group Metallocenes*, Part I, J. Wiley and Sons, New York 1965.

[3] J. P. COLLMAN in R. L. CARLIN, *Transition Metal Chemistry*, Vol. 2, Marcel Dekker, New York 1966.

[4] E. BACIOCCHI and G. ILLUMINATI in A. STREITWIESER and R. TAFT, *Progress in Physical Organic Chemistry*, Vol. 5, Interscience, New York 1967.

[5] L. DE VRIES, « J. Org. Chem. », *25*, 1838 (1960).

[6] J. A. PAGE and G. WILKINSON, « J. Am. Chem. Soc. », *74*, 6149 (1952).

[7] H. JONAS, F. MÖLLER and W. SIMMLER in HOUBEN–WEYL, *Methoden der Organischen Chemie*, Vol. 1/2, Georg Thieme Verlag, Stuttgart 1959.

[8] P. KOVACIC and N.O. BRACE, « J. Am. Chem. Soc. », *76*, 5491 (1954).