

Preliminary communication

SYNTHESIS OF *sym*-POLYMETHYLCOBALTICENIUM SALTS

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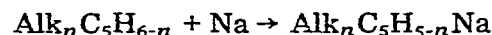
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Summary

The paper describes the synthesis of the series of *sym*-polymethylcobalticinium bromides and hexafluorophosphates of the general formula $[(Me_n C_5 H_{5-n})_2 Co]^+ X^-$ ($X^- = PF_6^-, Br^-$).

The cyclopentadienyl ligands of the cobalticinium cation, unlike those of ferrocene, cannot undergo electrophilic substitution without changes in the type of the complex molecule. For that reason, only a rather small number of substituted cobalticinium salts is known. There is as yet no example of a series of cobalticinium compounds with a successively increasing number of substituents of a certain type. The present paper describes the synthesis of one such series.

An increase in the number of electron donor substituents rapidly decreases the acidity of alkylcyclopentadienes thus hindering direct substitution of sodium for hydrogen:



The exchange reaction with RNa ($R = C_4 H_9, C_5 H_{11}$) complicates the procedure. In order to obtain the organosodium derivatives, we used freshly prepared sodium amide in liquid ammonia. All homologues of the $(CH_3)_n - C_5 H_{6-n}$ series readily undergo this reaction. Subsequent treatment of the reaction products with hexaamminocobalt(II) dichloride yields symmetrically substituted polymethylcobaltocenes. Oxidation of the latter leads to cobalticinium compounds, which can be isolated as salts containing various anions. For analytical purposes, poorly soluble hexafluorophosphates are particularly suitable.

The conditions applied in the reaction of alkylcyclopentadienylsodium derivatives with $[Co(NH_3)_6]Cl_2$, the yields and the physical constants of the products are listed in Table 1. The physico-chemical study of the compounds isolated is under way.

TABLE I
SYNTHESIS OF *sym*-POLYMETHYLCOBALTICENIUM SALTS, $[(\text{CH}_3)_n\text{C}_5\text{H}_{4-n}]_2\text{Co}^+\text{X}^-$

Ligand (CH_3) _n	Starting materials		Reaction conditions		<i>sym</i> -Polymethylcobalticentium salts		
	(CH_3) _n C ₅ H _{4-n} Na (mol)	[Co(NH ₃) ₆]Cl ₂ (mol)	THF (ml)	Temperature (°C)	Time (h)	Yield (%)	Melting point X ⁻ = Br ⁻ X ⁻ = PF ₆ ⁻
CH ₃ ^a	0.025	0.025	55	55	3	80	214 (dec.) 260 (dec.)
1,3-(CH ₃) ₂	0.020	0.025	55	55	4	73	185 (dec.) 200 (dec.)
1,2,4-(CH ₃) ₃	0.030	0.025	55	60	4.5	77	212 (dec.) 240 (dec.)
(CH ₃) ₄	0.055	0.050	80	60	4.5	70	210 (dec.) 219 (dec.)

^a 1,1'-Dimethylcobalticentium rhenate and tribromide were obtained as in [1]; the hexafluorophosphate salt is described in [2]; a mixture of mono- and 1,1'-dimethylcobalticentium salts was obtained as in [3].

References

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