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Academician A. N. NESMEYANOV, R. B. MATERIKOVA, N. S. KOCHETKOVA,

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Abstract

Full Text

CHEMISTRY

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SALTS OF 1,1′-DIALKYLCOBALTICINIUM

In the present work the possibility is shown of using ferrocene derivatives as starting materials for the synthesis of substituted cobalticinium salts. Apparently, this method can also be applied to the preparation of other substituted cyclopentadienylmetals, if the latter can be synthesized by the action of a metal salt on cyclopentadiene in an amine medium.

Up to the present time it has not yet been possible to carry out reactions of electrophilic substitution of hydrogen atoms in the rings of cobalticene or cobalticinium. The possibilities for synthesizing cobalticinium derivatives from substituted cyclopentadienes (^1, ^2) are limited because of the great tendency of the latter toward polymerization and the difficulty of purifying them (^3). Pauson' s method (^4, ^5) does not make it possible to obtain derivatives, for example, with normal aliphatic or aromatic radicals. The availability of a large number of diverse alkyl derivatives of ferrocene, which have been synthesized both by direct alkylation (^6, ^7) and as a result of reduction of other ferrocene derivatives (^8, ^9), makes it possible to use alkylferrocenes as starting substances.

We succeeded in carrying out the cleavage of 1,1′-dialkylferrocenes with lithium in ethylamine under conditions analogous to those first described by Treichel and Nichols (^10) for ferrocene and then applied by Pauson (^11) to N-dimethylaminomethylferrocene. The reaction mixture was then treated with a tetrahydrofuran solution of cobalt bromide. In this way salts of 1,1′-diethyl- and 1,1′-di-*n*-propylcobalticinium were obtained.

The chloroplatinates of 1,1′-dialkylcobalticinium are more soluble in water than the chloroplatinate of unsubstituted cobalticinium and have sharp melting points. The IR spectrum of 1,1′-diethylcobalticinium chloroplatinate contains a band in the region of 3104 cm^-1, characteristic of C—H stretching vibrations of the equalized cyclopentadienyl rings of ferrocene and cobalticinium; it has no absorption in the region of 1000 and 1100 cm^-1, whereas the spectrum of the chloroplatinate of unsubstituted cobalticinium contains these frequencies, which indicates the absence of unsubstituted rings in the molecule; it contains frequencies in the region of 2875 and 2970 cm^-1, characteristic of the methyl group, and a frequency characteristic of the methylene group, 2938 cm^-1. The NMR spectrum of 1,1′-diethylcobalticinium consists of three signals (on

the τ scale): $4.06 \cdot 10^{-6}$ —ring protons, $7.25 \cdot 10^{-6}$ —protons of the CH_2 group (quadruplet), and $8.72 \cdot 10^{-6}$ —protons of the CH_3 group (triplet). The data of the IR and NMR spectra make it possible to regard the substances obtained by us as cobalticinium derivatives of the structure

$$\mathrm{R} - \langle\text{cyclopentadienyl ring}\rangle$$
$$\mathrm{Co}^{+}\ \mathrm{X}^{-}$$
$$\mathrm{R} - \langle\text{cyclopentadienyl ring}\rangle$$

where $\mathrm{R} = \mathrm{C_2H_5},\ n\text{-}\mathrm{C_3H_7}$, $\mathrm{X} = \mathrm{H_2PtCl_6}^{-2},\ \mathrm{HgCl_3}^{-1}$.

The authors express their deep gratitude to G. G. Dvoryantseva for recording the IR spectra, and also to E. I. Fedin and P. V. Petrovsky for recording and discussing the NMR spectra.

Chloroplatinate of 1,1′-diethylcobalticinium. A solution of 4 g (0.017 mole) of 1,1′-diethylferrocene in 70 ml of ethylamine was added in one portion

To lithium shavings weighing 2.2 g (0.32 mol), the mixture was stirred for 10–12 min in an atmosphere of N_2 while cooling the flask with dry ice; the solution was poured into a flask cooled to −30 to −20°, equipped with a stirrer, dropping funnel, and nitrogen inlet; a solution of 2.2 g of anhydrous $CoBr_2$ in 60 ml of tetrahydrofuran was added dropwise, the reaction mixture was gradually warmed to 20°, stirred for 2 h, cooled to 3–5°, and then 80 ml of water was slowly added. The precipitate was separated by centrifugation and washed with water; the water was combined with the solution, and the solution was evaporated in the vacuum of a water-jet pump at 35–40° until water began to distill. The solution and the previously obtained precipitate were treated with heptane and filtered through a layer of Al_2O_3; the heptane was evaporated to give 0.7 g of 1,1′-diethylferrocene, n_D^{20} 1.5800, d_4^{20} 1.1787. The aqueous solution was neutralized with conc. HBr, cooled to 3–5°, and a solution of 2.5 ml of Br_2 and 30 ml of 40% HBr was added until precipitation ceased. The oily precipitate was filtered off, washed with a cooled solution of $HBr + Br_2$, and the excess bromine was removed in vacuo. The residue was dissolved in water and treated with shaking for 30 min with moist Ag_2O, obtained from 1 g of $AgNO_3$; it was filtered off, treated again with Ag_2O, the mixture was left for 12 h, and then decanted. To the solution was added 2 ml of HCl; after settling, the solution was decanted, treated with 0.4 g of H_2PtCl_6, evaporated to a volume of 2 ml, treated with 4–5 ml of absolute alcohol; the precipitate was filtered off, washed with absolute alcohol, and recrystallized from water. Weight of 1,1′-diethylcobalticinium chloroplatinate 0.37 g, mp 187–187.5°. Yield 6%.

Found, %: C 37.12; 37.23; H 3.90; 3.86; Cl 23.43; 23.13
$C_{28}H_{36}Co_2PtCl_6$. Calculated, %: C 37.4; H 4.03; Cl 23.68

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Chloroplatinate of 1,1′-di-*n*-propylcobalticinium. A solution of 5.4 g of 1,1′-di-*n*-propylferrocene in 60 ml of ethylamine was treated with 1.8 g of lithium, as described above. Reaction time 12–15 min. The solution was poured off and treated with 2 g of anhydrous $CoBr_2$ in 60 ml of abs. tetrahydrofuran, stirred for 2 h at 20°, 80 ml of water was added, the solution was centrifuged, the solvents were removed until water began to distill, the solution was extracted with heptane, the heptane was filtered through Al_2O_3, and 3.48 g of 1,1′-di-*n*-propylferrocene was recovered, n_D^{20} 1.5617, d_4^{20} 1.1240. The aqueous solution was acidified with HBr, cooled to 2–3°, and treated with bromine until precipitation ceased. The precipitate was filtered off, the excess bromine was removed in vacuo, the residue was dissolved in water and treated with moist Ag_2O; the solution was filtered, acidified with hydrochloric acid, and evaporated to a volume of 8 ml. Half of the resulting solution was treated with 0.4 g of H_2PtCl_6; 0.31 g of 1,1′-di-*n*-propylcobalticinium chloroplatinate was obtained, mp 208.5–209°, yield 18%.

Trichloromercurate of 1,1′-di-*n*-propylcobalticinium. 4 ml of the solution of 1,1′-di-*n*-propylcobalticinium chloride obtained in the preceding experiment was cooled to 2–3°, and 0.28 g of $HgCl_2$ was gradually added with stirring. The lemon-yellow precipitate was filtered off and recrystallized from nitromethane without heating; 0.12 g of 1,1′-di-*n*-propylcobalticinium trichloromercurate was obtained, mp 84.5–85°.

Found, %: *C* 33.14; *H* 3.81

$C_{16}H_{22}CoCl_3Hg$. Calculated, %: *C* 33.15; *H* 3.83

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