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Abstract

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ISOTOPIC EXCHANGE OF HYDROGEN ATOMS IN THE CYCLOPENTADIENYL RINGS OF COBALTICINIUM COMPOUNDS

Dicyclopentadienylcobalticinium compounds (I) were first obtained by Wilkinson in 1952 ([1]). However, up to the present time the properties of these compounds, especially substitution reactions of hydrogen atoms, have still been insufficiently studied ([2]). According to the data of Wilkinson ([3]), Fischer ([4]), and Nesmeyanov ([5]), the cobalticinium cation, unlike its isoelectronic analogue—ferrocene—is not inclined toward substitution reactions, but is capable of addition reactions. Attempts to acylate, arylate, sulfonate, and nitrate cobalticinium compounds proved unsuccessful ([4,5]).

In contrast to electrophilic reagents, nucleophilic reagents ($PhLi$, $AlkMgX$, $LiAlH_4$, $LiAlD_4$) react with cobalticinium salts, forming addition products II ([3,4]). According to Fischer ([4]), these reactions correspond to the scheme*:

$$I + R^{\ominus} \longrightarrow II$$

$$R = Ph,\ Alk,\ H,\ D$$

Recently Furlani and Kollamati ([7]) reported that, upon the interaction of cobalticinium salts with phenyllithium or phenylmagnesium bromide, along with addition products, a certain amount of the phenyl-containing substitution product (III) $[Co(C_2H_5)(C_2H_4Ph)]^{\oplus}X^{\ominus}$ is formed.

It seemed important to investigate more broadly the ability of cobalticinium compounds to enter into substitution reactions, using for this purpose the method of hydrogen isotopic exchange.

We found that cobalticinium salts do not undergo hydrogen isotopic exchange in an acidic medium. However, our experiments showed that in an alkaline medium a hydrogen-exchange reaction does take place.

Thus, upon interaction of cobalticinium hydroxide with deuteriomethanol in the presence of sodium methylate and subsequent treatment of the reaction

products with chloroplatinic acid, deuterium-containing cobalticinium chloroplatinate was isolated.

* At present, compounds II are assigned the structure of Diels–Alder-type adducts with the metal in the bridge ([6]).

The kinetics of isotopic hydrogen exchange of cobalticinium hydroxide in a 10% solution of sodium methoxide in deuteromethanol at 50° was studied, and it was established that the rate constant of this reaction is $6.4 \cdot 10^{-5}$ sec^{-1}.

It should be noted that, under our conditions, ferrocene does not enter into the hydrogen-exchange reaction.

The fact that a substitution reaction, and not an addition reaction, has taken place follows from the following data:

1. The substance isolated by us after the reaction was a salt, whereas, according to the data of Wilkinson and Fischer, the addition product is a non-salt-like substance.
2. In the high-resolution NMR spectrum of both the undeuterated and the deuterated cobalticinium cation, only one singlet is observed at 5.85 ppm relative to the signal of the protons in $(CH_3)_4Si$*, which unambiguously indicates the presence in the compound under study of one kind of equivalent protons.
3. The IR spectrum of the deuterated cobalticinium cation (Fig. 1, *a*) is very similar to the spectrum of the initial cobalticinium cation (Fig. 1, *b*); however, in the frequency region characteristic of vibrations of cyclopentadienyl rings, splitting of certain absorption bands is observed. The character of this splitting is analogous to the character of the splitting of the same bands in the spectrum of monodeuteroferrocene (Fig. 1, *v*), which indicates an analogous change in the symmetry of the rings upon deuterium substitution in ferrocene and in the cobalticinium cation. The IR spectrum of the compound in question proved to differ substantially, in the number and position of many absorption bands, from the spectrum of $Co(C_5H_5)(C_5H_6)$ (compound II, where $R = H$), measured by Wilkinson et al. (3).

In the frequency region of the stretching vibrations of C–H bonds, the spectrum of the deuterated cobalticinium cation lacks the absorption bands characteristic of the vibrations of the C–H and C–D bonds of the methylene group in compound II ($R = H$), namely 2742, 2942, and 2017-2076 cm^{-1}. At the same time, bands at 3085-3095 cm^{-1} and 2314 cm^{-1} are observed, corresponding respectively to the stretching vibrations of the C–H and C–D bonds of cyclopentadienyl groups.

Fig. 1. IR spectra of crystals in Vaseline oil:
a –deuterated cobalticinium chloroplatinate;
b –cobalticinium chloroplatinate;

Fig. 1

Figure 1: Fig. 1

v –monodeuteroferrocene;
g –ferrocene

On the basis of the data obtained in the study of hydrogen exchange, it may be expected that cobalticinium compounds are also capable of entering into other base-catalyzed substitution reactions.

* The authors express their gratitude to S. L. Portnova for measuring the NMR spectrum.

Experimental Part

Cobalticinium perbromide $[Co(C_5H_5)_2]^+Br_3^-$ was obtained by the method of Titov and co-workers ([8]).

Found, %: C 27.83; H 2.34; Br 56.09
Calculated, %: C 27.97; H 2.33; Br 56.94.

Deuteromethanol (27.1 at.% D) was obtained by mixing MeOH with D_2O, followed by distillation on a column of efficiency 20 theoretical plates.

Cobalticinium hydroxide $[Co(C_5H_5)_2]^+OH^-$ was obtained by Fischer' s method ([4]) from cobalticinium perbromide and moist silver oxide.

Study of the kinetics of hydrogen exchange of cobalticinium hydroxide in deuteromethanol in the presence of MeONa. Cobalticinium hydroxide, obtained from 5 g of cobalticinium perbromide, was dissolved in 55 ml of deuteromethanol (27.1 at.% D) and added to a solution of 17.6 g of MeONa in 183 ml of deuteromethanol of the same enrichment. The reaction was carried out in a stream of dry nitrogen at 50°. The reaction was stopped by pouring the reaction mixture into water acidified with HCl to an acidic reaction. The acidified solutions of each sample were evaporated, and, in order to separate cobalticinium chloride from NaCl, the residue was extracted with absolute EtOH. Cobalticinium chloride was precipitated from the alcoholic solution with H_2PtCl_6 (0.75 g), and the cobalticinium chloroplatinate obtained was recrystallized from water. The purity of the chloroplatinate samples isolated after the experiment was checked by elemental analysis.

Table 1

Time, min	Excess density of combustion water, γ/ml, calculated for all H	Excess density of combustion water, γ/ml, found	Exchange, %	$K_{BO} \cdot 10^5$*, sec^{-1}
62	27090	6080	22.5	6.8
120	27090	9797	36.2	6.2
240	27090	14263	52.7	6.9
360	27090	15746	58.2	6.0

* K_{BO} is the rate constant of hydrogen exchange.

$C_{20}H_{20}Co_2PtCl_6$. Found, %: C 30.48; H 2.61; Cl 27.04
Calculated, %: C 30.55; H 2.55; Cl 27.14

The deuterium content in the samples was determined from the excess density of the combustion water (e.d.c.w.) by the drop method. The results of the study are given in Table 1.

When cobalticinium hydroxide was boiled with deuteromethanol in the presence of MeONa, in the same ratios as in the preceding experiment, for 13 h, the extent of exchange reached 80-90% of the equilibrium value.

Spectroscopic investigations. Infrared spectra were measured on a double-beam UR-10 infrared spectrometer in the region 400-4000 cm^{-1}, using KBr, NaCl, and LiF prisms, in crystals with vaseline oil and in KBr pellets. The results of the measurements are given in Table 2.

Table 2

Frequencies of vibrations in the infrared spectra of crystals in the region 2000-3200 cm^{-1}

$Fe(C_5H_5)_2$	$Fe(C_5D_5)_2$ (9)	$[Co(C_5H_5)_2]^+$	$Co(C_5H_5)(C_5H_6)$ (3)	$Co(C_5H_5)(C_5H_4D)$ (3)	Deuterated cobalticinium cation
–	–	–	–	2017	–
–	–	–	–	2039	–
–	–	–	–	2057	–
–	2354	–	–	–	2314
–	–	–	2742	2742	–
–	–	–	2780	–	–
–	–	–	2871	–	–
–	–	–	2942	2932	–
–	–	–	3053	3042	–
3075	–	–	3076	3068	–

$Fe(C_5H_5)_2$	$Fe(C_5D_5)_2$ (9)	$[Co(C_5H_5)_2]^+$	$Co(C_5H_5)(C_5H_6)$ (3)	$Co(C_5H_5)(C_5H_4D)$ (3)	Deuterated cobalticinium cation
3085	–	3085	–	–	3085
3105	–	3095	3096	3105	3095

The NMR spectra were measured in saturated solutions of cobalticinium chloride in D_2O, using dioxane as an internal standard, 3.70 ppm, on a JNM-C-60 NMR spectrometer.

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Note: Figure translations are in progress. See original paper for figures.