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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XXXIV *. MASS SPECTRAL INVESTIGATION OF ALKYLCOBALTICINIUM SALTS AND OF THE FRAGMENTATION OF ALKYLCOBALTOCENES BY ELECTRON IMPACT

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Summary

The mass spectrometric method was used for the investigation of cobalticinium salts and their alkyl derivatives. Metal-containing ions are formed as a result of evaporation of the cobaltocenes obtained in the thermal reduction of cobalticinium cations. It was established that the decomposition of cobalticinium tetraphenylborates at 300°C is accompanied by the formation of phenyl-substituted alkylcobaltocenes. One of the processes of the thermal conversion of alkylcobalticinium salts has been shown to be a ligand exchange reaction. The principal directions of the molecular ion fragmentation by electron impact are stipulated by rupture of the metal–ligand bond and the bonds in the alkyl substituents. The first type of process is less likely than that for analogous ferrocene derivatives. Fragmentation of the substituents occurs along an unusual path including the consecutive elimination of two radicals.

Introduction

Dicyclopentadienyl complexes of transition metals, specifically cobaltocene (Cp_2Co), were studied repeatedly by mass spectrometry. The basic fragmentation directions for Cp_2Co and the activation energies of these processes have been determined [2–5].

In the present work the mass spectra of a number of cobalticinium salts and their alkyl derivatives are studied. Di- and poly-alkyl-substituted salts were obtained by a known method [6,7]. The synthesis of monosubstituted cobalticinium salts has been described earlier by us [8].

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* For part XXXIII see ref. 1.

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Results and discussion

i Mass-spectral investigation of the thermal conversions of alkylcobalticinium salts

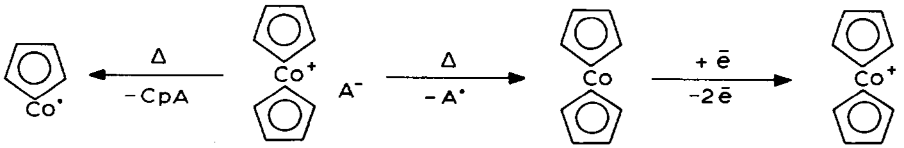
The appearance of metal-containing ions in the mass spectra of cobalticinium salts takes place at 300°C, a temperature which exceeds that of their decomposition under usual conditions. The formation of Cp_2Co^+ ions is apparently due to reduction of the cobalticinium salts by the anion to form cobaltocene, followed by evaporation of the latter with subsequent gas-phase ionization *. Inspection of the ratio of Cp_2Co^+ ion intensities and also of the decomposition products of the ions, $CpCo^+$ and Co^+, indicates an increase of some of the latter ions in the case of cobalticinium salts as compared with cobaltocene (Table 1). Taking into account the fact that the decomposition temperature for cobaltocene is essentially higher than the temperature effecting generation of Cp_2Co^+ ions from cobalticinium salts [10], one may conclude that the increase in the contribution of $CpCo^+$ and Co^+ ions is evidence of thermal destruction of the salts to their respective neutral molecules. The thermal processes discussed above are presented in Scheme 1.

In the spectra of tetraphenylborates of non-substituted and alkyl-substituted cobalticiniums, along with the molecular ions of the respective complexes, the formation of ions with m/z values exceeding the mass of the initial organometallic cation by a magnitude divisible by 76 amu is observed, with the multiplicity changing from 1 to 6 due to steric factors depending on the nature and quantity of alkyl groups in the cobalticinium molecule. Besides these ions, the tetraphenylborate spectra contain benzene ions ($m/z = 78$), biphenyl ions ($m/z = 154$) and those of triphenylborane ($m/z = 242$) which do not vanish with decreasing ionizing electron energy, thus indicating the presence of neutral molecules of these compounds. We believe that the appearance of all these ions is due to chemical conversions of the

TABLE 1

INTENSITIES OF THE MAIN METAL-CONTAINING IONS IN THE MASS SPECTRA OF $Cp_2Co^+X^-$ AND Cp_2Co

Ion	X^-				
	–	PF_6	$\frac{1}{2}CoCl_4$	I	BPh_4
	(25°C)	(340°C)	(330°C)	(305°C)	(285°C)
Cp_2Co^+	100	100	100	100	100
$CpCo^+$	36	53	56	57	46
Co^+	14	32	39	35	27



SCHEME 1

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* An analogous mechanism for the reduction of ferricinium cation to ferrocene has previously been suggested for the case of thermolysis of ferricinium salts [9].

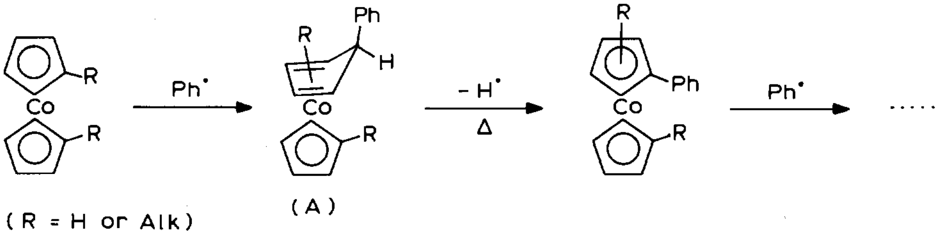
cobalticinium tetraphenylborates and their alkyl-substituted analogues at about 300°C. It is possible that the tetraphenylborate anion reduces the cobalticinium cation, the former being converted to $Ph_4B^{\cdot}$ radical. The latter then decays to form Ph_3B and $Ph^{\cdot}$. This radical reacts with cobaltocene to give a phenylated diene complex A (Scheme 2), which is unstable and dissociates at high temperatures to form a phenyl-substituted cobaltocene. Subsequent interaction with $Ph^{\cdot}$ leads to di-, tri- and poly-phenyl-substituted cobaltocenes. The $Ph^{\cdot}$ radical can also recombine, forming biphenyl or benzene.

Another type of secondary process which easily occurs in the cobalticinium salts under vacuum heating is ligand exchange. As a result of this reaction, the spectra of monoalkylcobalticinium salts contain peaks corresponding to the molecular ions of non-substituted and 1,1′-disubstituted compounds. In the study of an authentic mixture of non-substituted and 1,1′-disubstituted cobalticinium salts, $RC_5H_4CoC_5H_5^+$ molecular ion peaks were detected together with the molecular ions Cp_2Co^+ and $(RC_5H_4)_2Co^+$. The formation of the former ions is also observed with low emitter currents under field desorption conditions. The relative contribution of $RC_5H_4CoC_5H_5^+$ increases with increasing temperature.

The ligand exchange processes observed somewhat restrict the applicability of the mass-spectral method to solving structural analytical problems in the chemistry of this type of compound. So it is apparently unlikely that an unequivocal answer can be given on the presence of impurities of symmetrically substituted and non-substituted cobalticinium in the samples of monosubstituted cobalticinium salts.

ii Fragmentation of alkylcobaltocenes by electron impact

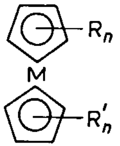
Comparison of the mass spectra of alkyl-substituted cobaltocenes formed in the thermal reduction of alkylcobalticinium cations and similar ferrocene derivatives indicates that the alkylcobaltocene molecules possess greater stability towards electron impact. In both cases the fragmentation occurs along two principal paths: elimination of the substituent or part of it and rupture of the metal–cyclopentadienyl ring bonds. The extent of effecting these processes depends essentially on the structure and quantity of the alkyl substituents, however preserving the general tendency according to which the relative contribution of the rupture products of the metal–ligand bonds is lower with cobaltocenes than with the respective alkylferrocenes. For example, the total contribution of ions with one cyclopentadienyl ligand for isopropylcobaltocene is 15.5% of the total intensity of metal-containing ions, whereas that of isopropylferrocene [11] is 31.9%. The contributions of ions with two ligands are 60.4 and 28.5%, respectively. These data are in agreement with the



SCHEME 2

TABLE 2

INTENSITIES OF THE MAIN ION PEAKS RELATIVE TO THE TOTAL INTENSITY OF METAL-CONTAINING IONS (%) IN THE MASS SPECTRA OF ALKYL-SUBSTITUTED COBALTOCENES AND THEIR FERROCENE ANALOGUES



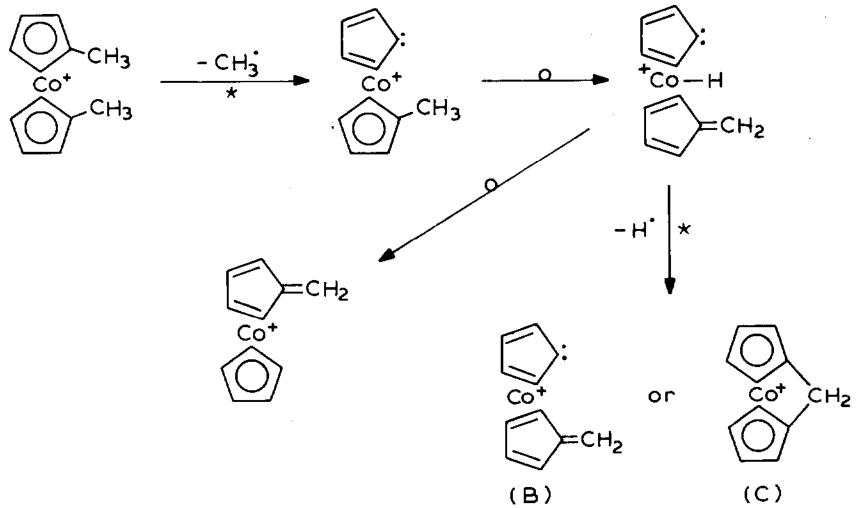
Ion	R_n,R'_n											
	H,Me	H,Me [a]	H,Et	H,i-Pr	H,t-Bu	H,C_6H_{11} [b]	Me,Me	Me,Me [a]	Et,Et [c]	H,1,3-t-Bu_2	1,3-Me_2,1,3-Me_2	1,3-t-Bu_2,1,3-t-Bu_2
P^+	25.7	28.5	24.3	17.6	21.8	30.2	26.8	31.3	16.7	26.9	41.7	50.0
$(P-H)^+$	2.1	3.0	0.8	1.2	–	0.5	1.2	2.4	1.3	–	3.5	–
$(P-H_2)^+$	0.3	0.7	3.9	4.7	1.0	1.2	1.9	0.2	3.0	–	1.5	–
$(P-CH_3)^+$	–	–	25.2	9.4	9.7	–	7.1	2.4	5.7	13.0	3.9	4.3
$(P-CH_4)^+$	–	–	–	21.4	16.4	–	4.0	–	13.0	8.4	1.0	–
$(P-C_2H_6)^+$	–	–	–	–	10.3	–	–	–	7.3	6.9	0.8	–
Cp_2M^+	–	–	2.2	6.1	8.2	–	1.9	0.5	2.2	12.8	–	–
$(R'C_5H_4M-H)^+$	–	19.7	–	–	–	5.1	22.8	14.1	1.7	–	14.1	–
$C_6H_8M^+$	–	–	2.8	2.2	2.2	1.5	–	–	0.8	–	–	0.4
$C_6H_6M^+$	4.1	(19.7)	5.6	4.7	5.6	4.6	(22.8)	(14.1)	2.5	1.7	2.8	1.1
$C_5H_6M^+$	1.8	1.4	6.2	3.1	1.1	–	0.2	–	5.2	1.5	–	1.5
CpM^+	9.5	8.3	12.5	5.5	–	7.6	5.9	5.0	5.2	1.9	–	1.1
M^+	25.0	21.8	8.6	11.4	7.5	6.6	11.4	19.9	9.7	2.7	9.2	1.1

[a] For corresponding alkylferrocenes [11]. [b] Other ions present: $P^+ - C_2H_2$ (3.8). [c] Other ions: $P^+ - C_2H_4$ (3.8), $P^+ - C_3H_7$ (3.4), $C_7H_9Co^+$ (2.2).

considerably higher stability of the 18-electron cobalticinium system against the 17-electron one of ferricinium.

Progressing from alkylferrocenes to alkylcobaltocenes also results in a decrease of some of the ions connected with the hydrogen atom migration from the substituent to the metal atom or to the other cyclopentadiene ring. In particular, this is seen from inspection of the mass spectral data of methylferrocene and methylcobaltocene listed in Table 2. Possible reasons for the difference in the degree of effecting these processes may involve an increase in the metal–ligand distance on going from ferrocene (1.66 Å [12]) to cobaltocene (1.73 Å [12]) and/or a change of the energy of hydrogen binding, which is equal to 58 and 52 kcal mol^{-1} for "naked" iron and cobalt, respectively [13].

The formation of $P^+ - H$ ions is characteristic of most of the alkylcobaltocenes studied. These fragments are absent only in the case of t-butyl derivatives, whose mass spectra exhibit intense peaks of $P^+ - CH_3$ ions. This enables us to suggest that the $P^+ - H$ and $P^+ - CH_3$ ions are formed as a result of splitting off a hydrogen atom or methyl group from the α-position of the side chain and they have a fulvenecyclopentadienylcobalt-type of cation structure. It should be pointed out that similar iron-containing ions are formed to a great extent in the mass spectra of ferrocene derivatives [11,14,15]. Further decay of Fe and Co ions of this type takes place along different paths. With the iron complexes it involves rupture of the metal–ligand bonds, whereas destruction of the cobalt-containing systems is conditioned by elimination of one more radical. The ions formed as a result of consecutive elimination of two radicals apparently have the structure of cobalticinium cations with an unsaturated substituent. Differences in the reactivity of Fe- and Co-containing ions ($P^+ - H$ or $P^+ - CH_3$) may be accounted for by the different electronic structures of the iron and cobalt atoms. The fulvenecyclopentadienyliron cations have a stable 18-electron structure with the metal atom in oxidation state (OS) + 2. In the case of Co, these ions are characterized by an unstable 17- or 19-electronic configuration. The loss of another radical from the side chain leads, in this case, to



SCHEME 3. Processes which have been confirmed by the corresponding metastable peaks are marked with asterisks.

stable cobalticinium cations (OS of the metal +3) with an unsaturated substituent. The formation of vinylferricinium cations is observed with substituted ferrocenes [15,16], with their development being stipulated, however, solely by 1,2-elimination of neutral molecules from the side chain and not leading to a change in the oxidation or electronic state of the metal atom.

Besides the molecular ions of monoalkyl-substituted cobaltocenes, the consecutive loss of two radicals takes place in the case of di- and tetra-alkyl derivatives with substituents both in one and in several cyclopentadienyl ligands. The loss of two radicals from heteroannular substituents is likely. The mass spectrum of 1,1'-dimethylcobaltocene deserves special consideration. Both this compound and the corresponding ferrocene derivative [11,17] are characterized by the formation of parent ion peaks as well as $C_6H_6M^+$, $P^+ - CH_3$ and M^+ ions. The essential difference in the mass spectral behaviour of these derivatives is the presence of intense peaks of $P^+ - CH_4$ ions which are absent in the case of similar ferrocene derivatives. With M = Co, the appearance of these ions is probably caused by elimination of the methyl substituent and the hydrogen atom from another methyl group. In considering possible structures of these ions, one may assume carbene (**B**) or bridged (**C**) ions (Scheme 3).

Experimental

Electron impact mass spectra were recorded on an AEI MS-30 mass spectrometer using a system for direct introduction of the sample into the ion source and ionizing voltages of 70 and 10 V (the intensity values at 70 V are listed in the Tables); the ionizing camera temperature was 280°C. Field desorption mass spectra were obtained on a Varian MAT III instrument with emitter currents of 0, 5, 10 and 15 A. Mixtures of non-substituted cobalticinium salts and symmetrical disubstituted derivatives were prepared by co-precipitation from water.

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