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Intramolecular CO···H Interaction in Arene(tricarbonyl)-chromium Complexes

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Abstract—Unlike benzene(tricarbonyl)chromium which displays two carbonyl stretching vibrations bands in the IR spectrum, analogous tricarbonylchromium complexes of the general formula $(C_6H_5ZMe)Cr(CO)_3$ [Z = O, CH(OH), N(Pr), CH=CH] are characterized by three carbonyl bands, one of which is displaced to the low-frequency region. The appearance of that band was rationalized in terms of intramolecular interaction between hydrogen atoms in the substituent on the benzene ring and carbonyl groups.

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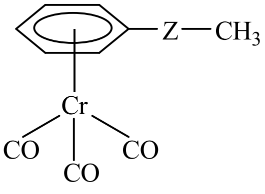
The formation of donor–acceptor complexes of transition metals with π-electron systems is usually attributed to interaction between π-bond electrons and low-lying vacant orbitals of the metal atom and possible back donation of electron density [1]. Coordination compounds possessing several donor centers could give rise to additional interactions between particular fragments. For instance, attractive interaction between substituents in the aromatic ring and carbonyl groups or metal atom in the tricarbonylchromium fragment is strongly probable [2, 3].

In the present work we made an attempt to reveal by IR spectroscopy intramolecular H-bonding in tricarbonylchromium complexes **I**–**IV** with substituted benzenes.



I–**IV**

I, Z = O; **II**, Z = CH(OH); **III**, Z = NPr; **IV**, Z = CH=CH.

Substituents in the aromatic rings in the examined compounds possess heteroatoms with lone electron pairs or π-electrons separated from the aromatic ring by one single bond, which ensures electron density transfer to the acceptor center via π–*p*, π–π, or π–σ conjugation [4]. As a result, hydrogen atoms in the substituents become activated as protons. Appropriate mutual arrangement of fragments in multidentate complexes **I**–**IV** gives rise to intramolecular H-bonding. This interaction is reflected in the IR spectra as a shift of absorption bands or appearance of new bands due to stretching vibrations of carbonyl groups involved in such interaction [5].

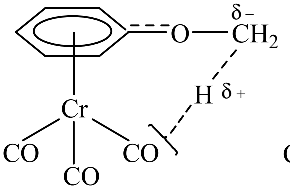
Benzene(tricarbonyl)chromium shows in the IR spectrum two absorption bands in the region 1800–2000 cm^{-1} due to stretching vibrations of carbonyl groups [6] (C_{3v} local symmetry; see table). Introduction of a substituent (ZMe) into the benzene considerably changes the IR spectral pattern. The most important is appearance of the third absortpion band in the region corresponding to carbonyl stretching vibrations (see table) and displacement of the C–H and O–H stretching vibrations bands belonging to the substituents to lower frequencies, 2300–2400 cm^{-1} (broad bands) for C–H and 3250 cm^{-1} for O–H.

Absorption bands in the IR spectra of arene tricarbonylchromium complexes **I**–**IV** in the region corresponding to carbonyl stretching vibrations

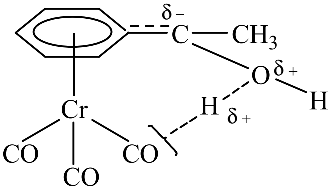
Z	ν, cm^{-1}
–	1972, 1891 [6]
O	1930, 1850, 1830
N(Pr)	1940, 1860, 1830
CH(ON)	1960, 1870, 1720
CH=CH	1980, 1910, 1725

Presumably, the observed variations in the IR spectra of complexes **I**–**IV** originate from intramolecular interaction of hydrogen atoms in the substituent on the benzene ring (assuming appropriate geometry of the substituent) with carbonyl groups in the tricarbonylchromium fragment (H-interaction). This interaction makes the carbonyl groups in the complexes nonequivalent and gives rise to a new CO stretching vibration band in a low-frequency region relative to that typical of benzene(tricarbonyl)chromium (see table).

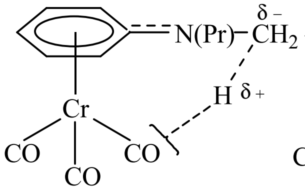
Hydrogen atoms in the substituents in the arene fragment of **I**–**IV** are activated as a result of transfer of π-electron density or lone electron pair on the heteroatom in the fragment Z toward the aromatic ring which acts here as acceptor due to coordination to metal. Electron density distribution in complexes **I**–**IV** may be represented as follows.



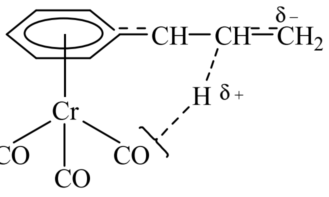
I



II



III



IV

Alternative interaction of activated hydrogen atom with chromium is excluded, for such interaction should give rise to new carbonyl stretching vibration bands at higher frequency [5].

As stated above, two carbonyl absorption bands are present in the IR spectrum of benzene(tricarbonyl) chromium [6]. Analogous pattern is observed for tricarbonyl(toluene)chromium [5]. Hydrogen atoms in the methyl group in the latter, despite proton activation via π–σ conjugation with the aromatic ring, cannot interact with carbonyl groups because of remoteness.

Arene (tricarbonyl)chromium complexes containing a hydroxy group in the α-position with respect to the aromatic ring or a methyl group at the double bond in the β-position attract specific interest. In these cases considerable shift of the carbonyl stretching vibration band (see table) is related to high acidity of hydrogens atoms in structures **II** and **IV**.

The position of the third carbonyl stretching vibration band may be used as a measure of the strength of intramolecular interaction between hydrogen and carbonyl groups. Depending on proton activity of the hydrogen atom, electron-donor center of the carbonyl group involved in H-bonding may change. Theoretically, both oxygen and carbon atoms, as well as the π-bond, can act as proton acceptor.

EXPERIMENTAL

All syntheses and operations with complexes **I**–**IV** were performed under argon. Tricarbonyl(methoxybenzene)chromium, tricarbonyl(*N*-methyl-*N*-propylaniline)chromium, and tricarbonyl(1-phenylethanol) chromium were synthesized by reaction of the corresponding aromatic compound with hexacarbonylchromium on heating in a boiling diethylene glycol dimethyl ether–octane mixture (1:1) [7]; tricarbonyl(1-phenylpropene)chromium was synthesized according to the procedure described in [8].

The purity of the products was checked by liquid chromatography on a Knauer Smart Line chromatograph equipped with a UV-Vis detector (LED matrix) and a 8×250-mm column; stationary phase Diasfer-110-S16, 5 μm; eluent acetonitrile–water (84:16). The IR spectra were measured in the range from 600 to 4000 cm^{-1} on a Perkin–Elmer spectrometer; samples were dispersed in mineral oil and placed between NaCl plates.

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