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Intramolecular Donor–Acceptor Interaction in Stilbene and Styrene π-Complexes with Tricarbonylchromium. Observation in the IR Spectra

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Abstract—The IR spectra of complexes derived from conjugated arylalkenes and tricarbonylchromium, namely (stilbene)tricarbonylchromium and (styrene)tricarbonylchromium, displayed three absorption bands instead of two expected in the region of carbonyl stretching vibrations (1800–2000 cm^{-1}). Additional absorption bands also appeared in the region corresponding to metal–π-fragment stretching vibrations (250–400 cm^{-1}). These findings indicated additional interaction involving the central metal atom, carbonyl ligands, and aromatic π-system. Such interaction increases mobility of the tricarbonylchromium fragment which may become capable of readily migrating from one π-fragment to another under certain conditions.

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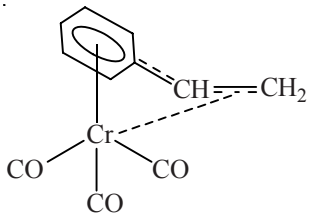
It is generally accepted that tricarbonylchromium complexes with π-systems are formed mainly via donor–acceptor interaction between the metal atom (electron-acceptor center) with the π-fragment (electron-donor center) directly attached thereto [1]. Using IR spectroscopy we found that tricarbonylchromium complexes with aromatic ligands having conjugated side-chain double bonds, such as (stilbene)tricarbonylchromium and (styrene)tricarbonylchromium, give rise to additional interaction between the tricarbonylvhromium fragment and other π-fragments of the complex (double bond or aromatic ring).

It is known that the tricarbonylchromium fragment belongs to the C_{3v} point group symmetry, for which two carbonyl stretching vibrations should be active in the IR spectra [2]. The IR spectrum of (styrene)tricarbonylchromium contained two expected carbonyl stretching vibration bands at 1920 and 1980 cm^{-1}, which were displaced to higher frequencies relative to the corresponding bands of (benzene)tricarbonylchromium [3]. In the IR spectrum of (stilbene)-tricarbonyl chromium we observed three absorption bands at 1850, 1890, and 1950 cm^{-1} (see figure).

These data suggest that the molecule of (stilbene)-tricarbonylchromium contains three nonequivalent carbonyl groups. A probable reason is direct donor–acceptor interaction between the carbonyl groups with the stilbene conjugated π-system (see scheme below). An analogous pattern was observed for the π-complex of triphenylstibine with tricarbonylchromium, which also showed in the IR spectrum three carbonyl absorption bands at 1860, 1900, and 1960 cm^{-1} (see figure). On the other hand, the IR spectrum of (stilbene)bis(tricarbonylchromium) contains only two carbonyl stretching vibration bands at 1905 and 1950 cm^{-1}.

The assumed donor–acceptor interaction is also reflected in the IR region corresponding stretching vibrations of the olefinic double bond (1500–1640 cm^{-1}). Styrene and stilbene give rise to absorption bands at 1630 and 1570 cm^{-1}, respectively. In the IR spectra of their complexes with tricarbonylchromium these bands are displaced toward lower frequencies (1560 and 1510 cm^{-1}, respectively. The observed low-frequency shift results not only from conjugation of the double bond with the aromatic ring (as in molecules of the free ligands) but also from direct donor–acceptor interaction between the exocyclic double bond in arylalkenes with tricarbonylchromium. The presence of three absorption bands in the region of chromium–olefin stretching vibrations (250–400 cm^{-1}), namely at 290, 310, and 350 cm^{-1} for (styrene)tricarbonylchromium and at 300, 320, and 360 cm^{-1} for (stilbene)-tricarbonylchromium, instead of the expected one

strong band [2, 3] should also be regarded as response to additional interaction between the tricarbonylchromium fragment and olefinic π-bond in the aromatic ligand (see scheme).



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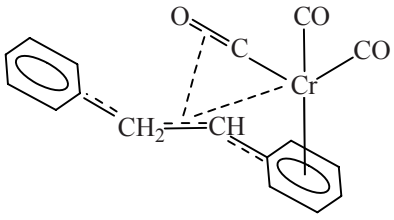

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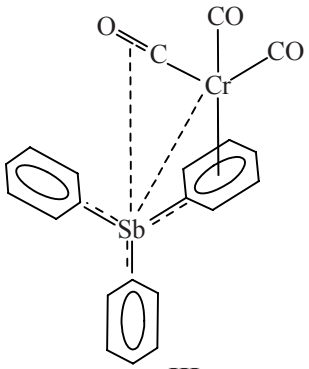
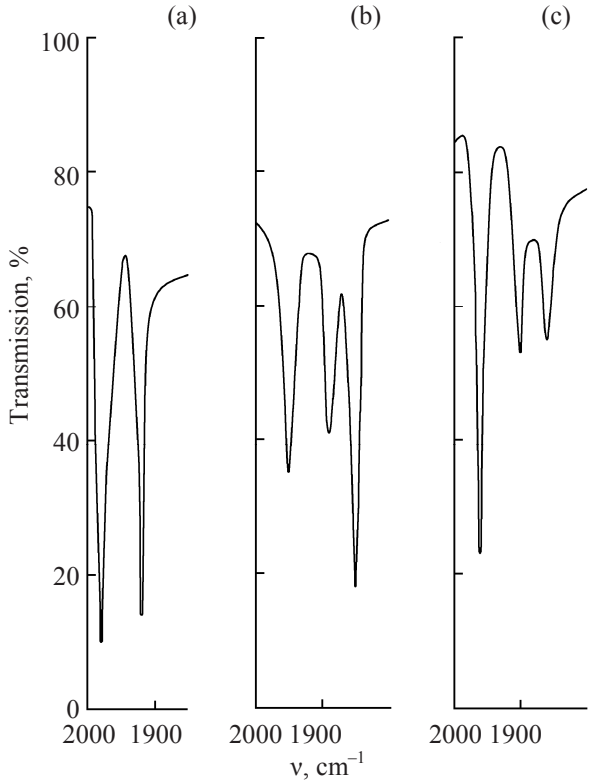


III



IR spectra in the region of carbonyl stretching vibrations of (a) (styrene)tricarbonylchromium, (b) (stilbene)tricarbonylchromium, and (c) (triphenylstibine)tricarbonylchromium.

Thus the above findings indicate that tricarbonylchromium complexes with conjugated arylalkenes are characterized by additional donor–acceptor π-type interaction involving the chromium atom, conjugated π-system, and carbonyl group. Such interaction should increase mobility of the tricarbonylchromium group, so that it may become capable of readily migrating from one π-fragment to another under certain conditions [4].

EXPERIMENTAL

Syntheses of organometallic compounds and all subsequent operations were carried out under argon. (Styrene)tricarbonylchromium was synthesized and purified according to Rausch [5], (stilbene)tricarbonylchromium was obtained as described in [6], and (stilbene)bis(tricarbonylchromium) was prepared as reported in [7]. (Triphenylstibine)tricarbonylchromium was synthesized as purified according to the procedure described in [8]. The purity of the tricarbonylchromium complexes was checked by liquid chromatography using a Knauer Smart Line instrument equipped with a UV-Vis diode matrix detector and a 8×250-mm column packed with Diasfer-110-S16 (5 μm); acetonitrile–water (84:16) was used as eluent.

The IR spectra were measured in the range from 200 to 4000 cm^{-1} on a Perkin–Elmer spectro-

photometer from samples dispersed in mineral oil and placed between cesium iodide plates.

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