HYDROGEN BONDS INVOLVING CO BRIDGING GROUPS IN CYCLOPENTADIENYL IRON DICARBONYL DIMER

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We have shown previously, by IR spectroscopy [1, 2], that carbonyl ligands in metal car- bonyls can function as proton acceptors in hydrogen bonds of the type M-CO...HX. It is known from the results of [3] that bridging CO groups have a higher basicity than terminal groups and one can suppose from this that they must also be able to participate in H-bonding. The formation of such bonds with bridging CO groups has been suggested in a study of the IR spectra of a series of bridging carbonyl complexes in solution in alcohols [4].

In the present work, we have shown, by determining the IR spectra in solution in lique- fied inert gases [1], that it is possible to form H-bonds with bridging CO groups in the reaction of the complex \([\text{CpFe(CO)}_2]_2\) (I) (Cp = \(\eta^5-\text{C}_5\text{H}_5\)) with perfluoro-t-butanol (PFTB) and HCl in solution in liquid xenon.

EXPERIMENTAL

The technique for obtaining spectra in solution in liquefied inert gases was detailed in [5, 6]. Liquid xenon was used as the solvent in the present work. A cryostat with a hori- zontal optical axis with path length 7.5 cm and windows of BaF\(_2\) was employed. The concentra- tion of the solutions amounted to 10\(^{-4}\) to 10\(^{-5}\) mole/liter. The IR spectra were run on a Bruker IFS-113 Fourier spectrometer in the 4000-800 cm\(^{-1}\) region with a resolution of 2 cm\(^{-1}\). The com- plex (I) was prepared by the method of [7].

RESULTS AND DISCUSSION

The study of the IR spectra of the \(\eta\)-complex (I) has been the subject of several arti- cles [4, 8-10]. This attention to (I) arises from the possibility of its existing in different forms: as a bridged structure in cis- and trans-forms (Ia and Ib respectively) and as the unbridged structure (Ic) for which, in its turn, different rotational isomers can exist as a re- sult of rotation round the M-M bond.

At the present time, it is taken as established that (I) exists in solution in the form of a mixture of two bridged isomers and the amount of the unbridged form is extremely small: from the results of [8] its concentration is \(<1\%\) at 30°C and \(<0.1\%\) at -30°C. The IR spectrum of (I) in solution in liquid xenon in the CO absorption region is shown in Fig. 1; it appears as a superposition of the spectra of (Ia) and (Ib). The band at 1794 cm\(^{-1}\) belongs to the anti- symmetrical stretching vibrations of the bridging CO group the frequency of which practically coincides in the two isomers. The symmetrical vibration band does not appear in the IR spectra since in the present case the selection rules are determined not by the symmetry of the molecule as a whole but by the local symmetry of the Fe(CO)\(_3\)Fe fragment (D\(_{3h}\)). The vibrations of the terminal CO groups for (Ia) have frequencies of 2007 and 1962 cm\(^{-1}\). For the (Ib) isomer, the high-frequency symmetrical vibration is forbidden in the IR spectrum and the


Fig. 1. IR spectra: a) [CpFe(CO)$_2$]$_2$ in liq. Xe, 200 K; b), c), d) mixture of [CpFe(CO)$_2$]$_2$ and PFTB in liq. Xe at 200, 170, and 165 K respectively.

antisymmetrical has a frequency which coincides with that of the antisymmetrical vibration of the cis-isomer. Naturally, the coincidence of the frequencies of bridging and terminal groups in (Ia) and (Ib) makes it difficult to study the geometrical isomers and the mutual transitions of the isomers. In solution in liquid xenon, very weak bands are also observed at 2016, 1973, and 1944 cm$^{-1}$ which can be assigned to the nonbridged form in accordance with the results of [8] and their proximity to the frequencies of the nonbridged isomer of the complex [CpRu(CO)$_2$]$_2$.

Several changes are observed in the IR spectrum on addition of PFTB to the solution of (I) in liquid xenon. Firstly, in addition to a band due to free PFTB in the OH absorption region (3590 cm$^{-1}$) a new band appears in the spectrum at ~3400 cm$^{-1}$, shifted into a lower frequency region. Since PFTB itself does not associate under these conditions, the 3400 cm$^{-1}$ band is assigned to PFTB bonded to (I) by an intermolecular hydrogen bond. Examination of the spectrum in the region of CO stretching vibrations shows that the bridging CO groups in the complex (I) participate in the formation of the H-bond. On reducing the temperature from 200 to 170 K an increase in the intensity of the 1733 cm$^{-1}$ band is observed, shifted by 60 cm$^{-1}$ into the lower frequency region relative to the vCO band of the bridging group of free (I) (Fig. 1). Simultaneously, bands at 2015, 1973, and 1817 cm$^{-1}$ appear, shifted into a higher frequency region from the corresponding bands of (I). The low-frequency shift of the bridging carbonyl band shows that formation of a hydrogen bond takes place at the oxygen atom of the bridging carbonyl group. As would be expected, the high symmetry of the molecule of (I) is disturbed and the symmetrical vibration of the bridging CO groups becomes active in the IR spectrum at 1817 cm$^{-1}$. A small high-frequency shift (8-11 cm$^{-1}$) of vCO for the terminal CO groups simultaneously occurs which also would be expected as a result of drawing-away of electron density from the metal atoms and an increase in the order of the CO bond for the terminal groups. On further increasing the temperature, the intensity of the band at 1733 cm$^{-1}$ continues to increase, new bands appear at 2022 and 1983 cm$^{-1}$, and the intensity of the 1817 cm$^{-1}$ band decreases. Changes of this type in the spectrum point to the involvement of a second bridging CO group in hydrogen bonding to PFTB (H-complex of composition 1:2). In the formation of the second H-bond, the local D$_{2h}$ symmetry of the Fe(CO)$_2$Fe fragment is restored and the symmetrical vibration of the bridging CO groups is again made inactive. The drawing-away of electron density from the metal atom increases and this leads to an additional shift of the terminal CO band by up to 15-21 cm$^{-1}$ relative to the free complex (I). Thus, in addition to the formation of a 1:1 complex a 1:2 complex is also formed with two molecules of PFTB with the participation of both bridging CO groups of the complex (I).

It should be noted that the observed changes in the spectra in the vCO region of (I) when it reacts with PFTB are similar to those observed on reaction of (I) with Lewis acids [10] where adducts are also detected with one and with both CO groups. The basicity of the bridging carbonyls proves to be considerably higher than that of the terminal carbonyls: in (I) only the bridging groups take part in H-bonding with PFTB. A high-frequency shift of the bridging carbonyl band of complex (I) has been observed [4] in solutions in alcohol in comparison with solutions in solvents without OH groups. However, because of the considerable breadth of the CO group band at ordinary temperatures in alcoholic solvents these workers did not succeed in recording the changes in the terminal CO bands. They were also unable to register the presence of the two forms of H-bonded complex and the equilibrium between them and the