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Infrared spectra of $[CpRu(CO)_2]_2$ in liquid xenon solution in the presence of proton donors

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Abstract

Using IR spectroscopy the interaction of the π-complex $[CpRu(CO)_2]_2$ with perfluorinated alcohol and HCl in liquid Xe solution has been studied. Protonation of the π-complex at the Ru–Ru bond has been observed. It is shown that the bridged carbonyl groups are able to form hydrogen bonds.

Introduction

We have shown [1,2] that carbonyl ligands in metal carbonyls can be proton acceptors for the formation of hydrogen bonds of the type $M{-}CO \cdots HX$. The bridging carbonyl ligands are stronger proton acceptors than the terminal ones; this has been demonstrated using the complex $[CpFe(CO)_2]_2$ (I) as an example [2]. The formation of such bonds had been proposed previously in a study of the IR spectra of bridged metal carbonyls in alcohol solutions [3], but in Ref. [2] conclusive evidence for the interaction of I with proton donors in liquid Xe solution was obtained. Practically all the molecules of I exist in solution in the bridged forms (*cis* or *trans*). The ruthenium analog of I, the complex $[CpRu(CO)_2]_2$ (II), exists in solution as a mixture of the bridged (IIa, b) and "open" (IIc) forms [4–6]. It seemed of interest to compare the behavior of the complexes I and II in the presence of proton donors under the same conditions. Perfluorinated alcohol, $(C_3H_7)(CF_3)_2COH$ (PFA), and HCl were used as proton donors because neither is associated in liquid xenon solutions.

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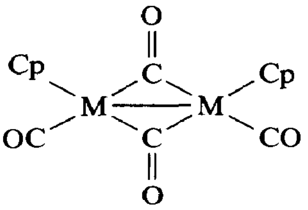
Experimental

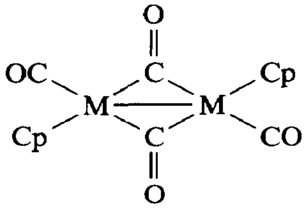
The procedure used to record IR spectra in solutions of liquid inert gases has been described previously [1,7]. The cryostat used in our experiments had a horizontal optical axis and BaF_2 windows. Its path length was 7.5 cm. The concentrations used were about 10^{-4}–10^{-5} mol/1. IR spectra were measured on a Bruker IFS-113v FT-IR spectrometer in the region 4000–800 cm^{-1} with a resolution of 2 and 0.5 cm^{-1}. The synthesis of $[CpRu(CO)_2]_2$ and its purification were carried out according to Ref. [8].

Results and discussion

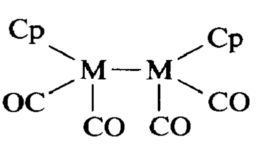
Several studies dedicated to the structure of the complexes I and II in solution and in the solid state have been published [2–6]. It has been shown that I and II can exist in different forms, with bridging CO groups (a, b) and without them (c). For the "open" form (c) rotational isomerism due to rotation around the M–M bond is possible.



(a: *cis*)



(b: *trans*)



(c: *open*)

It has been shown [2] that I in liquid Xe solution exists as a mixture of *cis*- and *trans*-bridged forms (Ia, Ib), and the content of the Ic form is very small. In contrast, in inert solvents II predominantly has the non-bridged form IIc and its content increases with an increase in the inertness of the solvent [4].

The IR spectrum of II in liquid Xe solution in the region of the stretching CO vibrations is presented in Fig. 1a. Comparing this spectrum with those obtained in solutions of heptane, CS_2 etc. [4] it is not difficult to make assignments of the bands

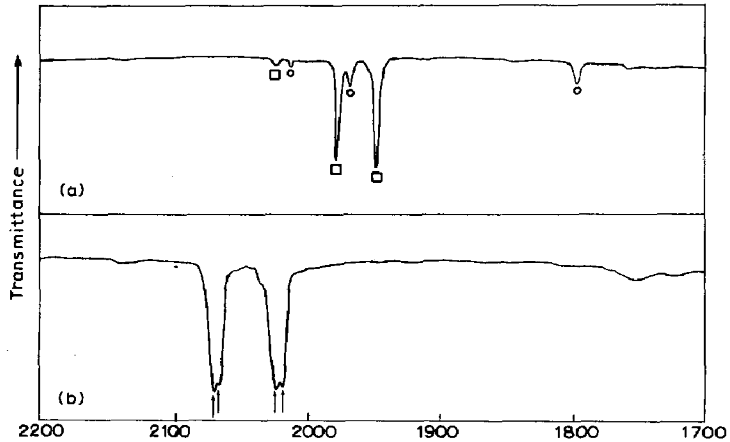


Fig. 1. IR spectra in liquid xenon solution in the ν(CO) region of $[CpRu(CO)_2]_2$ at 165 K (a) and $[CpRu(CO)_2]_2$ + HCl at 185 K (b) (○-bridged form, □-"open" form, ↑-protonated form).

that are present. The bands at 2024, 1977 and 1948 cm^{-1} belong to the CO stretching modes of the non-bridged form IIc. The frequencies of the asymmetric stretch of CO bridging groups of both the IIa and IIb isomers coincide and lie at 1797 cm^{-1}. The symmetrical CO stretch of the bridging groups does not appear in the IR spectrum because the selection rules in this case correspond to the local symmetry D_{2h} of the $Ru(CO)_2Ru$ fragment rather than the molecular symmetry as a whole.

The frequencies of vibration of the terminal CO groups are 2013 and 1968 cm^{-1}. For IIb the high-frequency symmetrical mode is forbidden in the IR spectra by symmetry and the asymmetrical mode has a frequency coinciding with that of the asymmetric CO vibration of the *cis*-isomer IIa.

Comparison of the relative intensities shows that the content of the bridged form of II in liquid Xe solution is much less than the content of the "open" form, and the relative concentration of the bridged forms of II in liquid Xe is less than in heptane [4]; this shows that liquid Xe is a more inert solvent.

When HCl is added to a solution of II in liquid Xe the following changes take place (Fig. 1). New bands 2018 and 2065 cm^{-1} shifted to the high-frequency region appear at 220 K. Taking into consideration the previous data concerning the spectra of I [2,9], the new bands can be attributed to molecules of II that have been protonated at the metal–metal bond to form a $Ru \cdots H \cdots Ru$ bridge. On lowering the temperature the intensities of these bands decrease and new bands shifted 3–5 cm^{-1} to higher wavenumber (2023 and 2068 cm^{-1}) appear. The process is reversible, i.e. when the temperature increases the previous picture is restored. Thus an equilibrium exists between the two forms in solution, and it is suggested that there are two rotamers present owing to rotation around the $Ru \cdots H \cdots Ru$ bond. The possibility of such isomerism was proposed previously [9]. We obtained the first experimental evidence of this fact [2] for the complex I under the conditions of a large excess of proton donors. It is interesting to note that under the same conditions only partial protonation of I takes place, but in the presence of HCl (Fig. 1b) in liquid Xe the complete protonation of II was observed (the bands of the initial compound disappear). This can explained by the higher basicity of Ru in comparison with Fe and by the higher content of the "open" form for II, which aids protonation at the Ru–Ru bond.

More complicated changes occur in the spectrum of II in the presence of PFA. In this case new higher-frequency bands at 2020 and 2065 cm^{-1} (at 220 K) and 2026 and 2071 cm^{-1} (at 170 K) also appear, due to the $\nu(CO)$ stretching vibrations of the protonated form of the $[Cp(CO)_2Ru \cdots H \cdots Ru(CO)_2Cp]^+$ rotamers. The small difference between the frequencies of the protonated forms in the case of HCl and PFA is explained by the influence of the anion in contact ion pairs, since the appearance of solvent-separated ion pairs in liquid Xe is less probable.

The changes in the bands of the non-protonated form of II on lowering the temperature are more interesting (Fig. 2). An analysis of the spectra in the $\nu(CO)$ region shows that at lower temperatures H-bond formation with the oxygen atoms of the bridging CO groups occurs in the case of IIa and IIb. When the temperature decreases from 220 to 175 K a new band at 1734 cm^{-1} appears in the spectrum and gradually increases in intensity. This band is shifted by 63 cm^{-1} to lower frequency as compared to the $\nu(CO)$ frequency of the bridging CO group of IIa and IIb. During H-bond formation the high local symmetry of the $M(CO)_2M$ fragment is

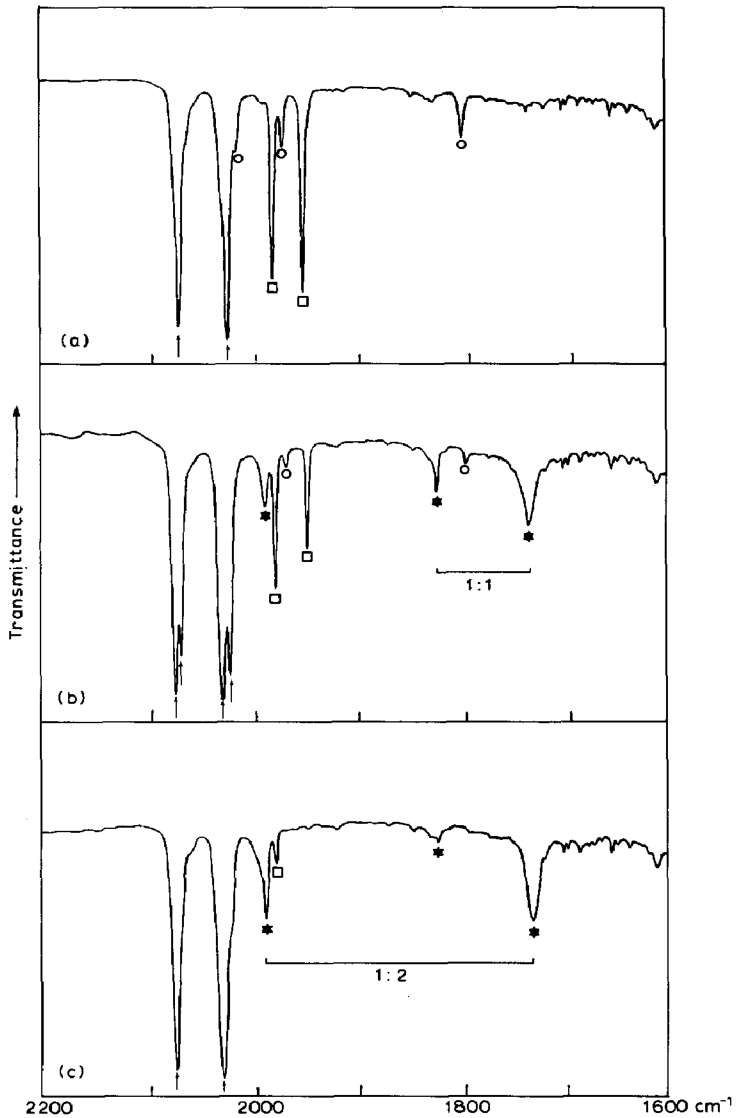
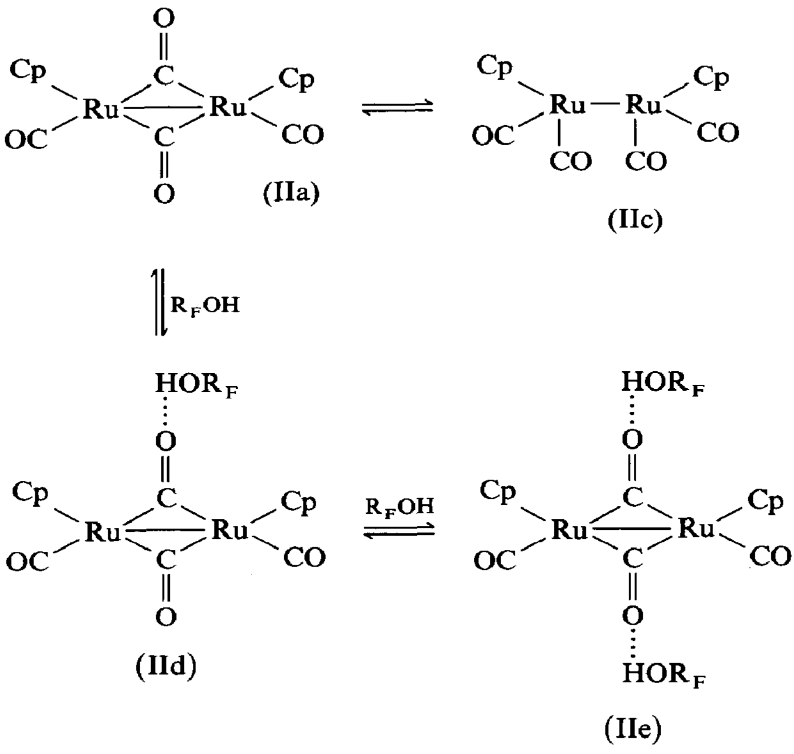


Fig. 2. IR spectra of $[CpRu(CO)_2]_2$ in liquid xenon solution in the presence of PFA at 220 K (a), 200 K (b) and 165 K (c) (○-bridged form, □-"open" form, ★-hydrogen bonded form, ↑-protonated form).

destroyed for both IIa and IIb, and the symmetrical mode of the bridged CO groups becomes IR-active and appears at 1823 cm^{-1} in the IR spectra. On H-bond formation electron density is withdrawn from the metal atoms, the bond order of the CO groups increases and the ν(CO) frequencies must also increase. However, for the terminal CO groups of II, in contrast to I, bands undergoing such shifts to high frequency were not observed. It is more probable that in the case of the band at 2013 cm^{-1} for II, the shifted band is overlapped by the strong band at 2020 cm^{-1} of the protonated form, and that the band at 1968 cm^{-1} is overlapped by the 1977 cm^{-1} band of the non-bridged form.

On lowering the temperature further the intensity of the band at 1734 cm^{-1} continues to increase, a new band at 1986 cm^{-1} appears, and the band 1823 cm^{-1}

decreases in intensity and then practically disappears. Such spectral changes provide evidence that the second bridged CO group also forms a H-bond with PFA to give a 1 : 2 H-complex. The D_{2h} symmetry of the $Ru(CO)_2Ru$ fragment is restored and the ν(CO) symmetrical mode immediately becomes forbidden. A band at 1986 cm^{-1} also appears in the spectrum, belonging to the terminal CO ligands of the 1 : 2 complex. The spectrum of Fig. 2c obtained at 165 K shows that at this temperature the bands of the "open" form are practically absent. At the same time the bands 1986 and 1731 cm^{-1} belonging to the H-bonded bridged form with two H-bonds with PFA molecules are quite intense. It is reasonable to suppose that in this case conversion of the terminal CO groups to bridging ones under interaction with the proton donor (PFA) takes place according to the following schemes:



The reversibility of the spectral changes with temperature confirms the supposition that the disappearance of the bands of the non-bridged form IIc is connected with such a process, rather than with the conversion of IIc into the protonated form. On increasing the temperature the bands of IIe and IId disappear and the initial spectrum, with intense bands at 1977 and 1948 cm^{-1} corresponding to the non-bridged structure IIc, are restored. Such a conversion of the terminal carbonyls to bridging ones was seen by Alich et al. [10] in the reaction with Lewis acids. In our case the reaction takes place due to H-bond formation in an inert solvent. All the spectral changes described above are summarized in Table 1.

Thus, $[CpRu(CO)_2]_2$ in liquid Xe solution is almost completely protonated by HCl at the Ru–Ru bond. A temperature-dependent equilibrium between two

Table 1

Stretching frequencies (cm^{-1}) of terminal and bridging carbonyl groups in liquid Xe solution $[CpM(CO)_2]_2$ (M = Fe, Ru) and of their H-bonded and protonated derivatives formed by interaction with perfluorinated alcohol

	$[CpFe(CO)_2]_2$		$[CpRu(CO)_2]_2$	
	terminal	bridging	terminal	bridging
Open form	2016, 1973, 1944		2024, 1977, 1948	
Bridged form	2007, 1962	1794	2013, 1968	1797
H-bonded form				
1:1	2015, 1973	1817, 1733	(2020), (1977)	1823, 1734
1:2	2022, 1983	1733	(2026), 1986	1731
Protonated form				
High-temperature	2064, 2023		2065, 2020	
Low-temperature	2069, 2029		2071, 2026	

isomers due to rotation around the Ru···H···Ru bond of the protonated molecule takes place in solution .

In the presence of perfluorinated alcohol $(C_3F_7)(CF_3)_2COH$ not only protonation, but also the formation of 1 : 1 and 1 : 2 H-complexes with the oxygen atoms of the bridging CO ligands, occurs. As a consequence the content of the non-bridged form of II in solution falls.

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