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Cis—trans ISOMERISM OF PROTONATED FORMS OF π-CYCLOPENTADIENYLRHENIUM DICARBONYL TRIPHENYLPHOSPHINE

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Summary

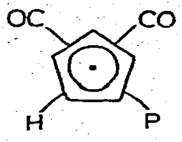
The protonation of π-cyclopentadienylrhenium dicarbonyl triphenylphosphine, π-CpRe$(CO)_2PPh_3$ at the metal, which affords *cis* and *trans* isomers, in the mixture $CHCl_3$: CF_3COOH : BF_3 · H_2O 1 : 1 : 0.5 has been demonstrated by the PMR method. The study of the temperature dependence of *cis—trans* interconversions has been conducted, and effective values of the energy parameters of the processes have been calculated.

Introduction

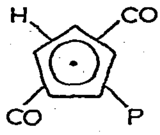
A region of particular interest in the study of the reactivity of π-complexes of transition metals is the data characterizing the behaviour of these compounds in media with different acidities, in particular, the hydrogen isotopic exchange (HIE) and protonation reactions as the first stage of this process. HIE with acids is the model of a highly important group of electrophilic substitution reactions in π-aromatic ligands of transition metal π-complexes.

Discussion

Recently, while studying the interaction of π-CpRe$(CO)_2PPh_3$ with acids we found a reversible equilibrium addition of hydrogen to the rhenium occurred [1]. Protonation at the metal atom in acidic media has been noted by other workers for π-complexes of transition metals [2-6]. However, in contrast to the previously known cases, we succeeded in observing the simultaneous formation of two, *cis* (A) and *trans* (B), isomers of the protonated form of the rhenium complex. In addition, we observed mutual transformations of the isomers with changes in temperature.



(A)



(B)

The PMR spectrum at room temperature of π-CpRe(CO)$_2$PPh$_3$ in the solvent mixture CHCl$_3$: CF$_3$COOH : BF$_3$ · H$_2$O 1 : 1 : 0.5 (*a*) exhibits two signals due to the protons of the cyclopentadienyl rings in isomers A and B with chemical shifts of 5.46 and 5.63 ppm respectively (chemical shift of protons of the cyclopentadienyl ring in CHCl$_3$ is 4.82 ppm) and with relative integral intensities of 4 : 1. The PMR spectrum also has two doublet signals in the strong field due to protons directly bound to the rhenium; the signals were characterized by chemical shifts —8.70 and —7.54 ppm and by the $J(^1\text{H}—^{31}\text{P})$ spin—spin interaction constants of 15 and 39 Hz, with relative integral intensities of the signals 4 : 1 for B and A respectively (see Fig. 1). The assignment of PMR signals for *cis* and *trans* isomers was made by reference to the literature [6,7] which dealt with analogous Mn and Mo complexes and demonstrated that the spin—spin interaction constant $J(^{31}\text{P}—^1\text{H})$ in *trans* isomers is 2.5—3 times smaller than in the corresponding *cis* isomers. For this reason we assigned the doublet signal with lower $J(^{31}\text{P}—^1\text{H})$ constant to the *trans* isomer and that with the higher constant to the *cis* isomer. Therefore, mixture *a* reveals a practically complete protonation of π-CpRe(CO)$_2$PPh$_3$ with the formation of *cis* and *trans* isomers, the *trans* isomer being the preferred protonated form.

In the mixture CHCl$_3$: CF$_3$COOH 1 : 1 (*b*) a partial protonation of π-CpRe(CO)$_2$PPh$_3$ with formation of only the *cis* isomer is observed (Fig. 2). These facts allow us to conclude that the formation of a certain isomer is mainly determined by the acidity of the medium.

The behaviour of π-CpRe(CO)$_2$PPh$_3$ · H with change in temperature, at constant acidity of the medium, was also of interest. Fig. 3 shows the PMR spectra due to protons of the cyclopentadienyl ring in π-CpRe(CO)$_2$PPh$_3$ in the mixture *a* at various temperatures, which demonstrate that interconversions of *cis* and *trans* isomers occur. Applying the method of total analysis to the line shape we evaluated energy parameters for these interconversions. For activation energy, enthalpy and entropy changes we obtained effective values of 20 kcal, —20 kcal, and +10 kcal/°C, respectively.

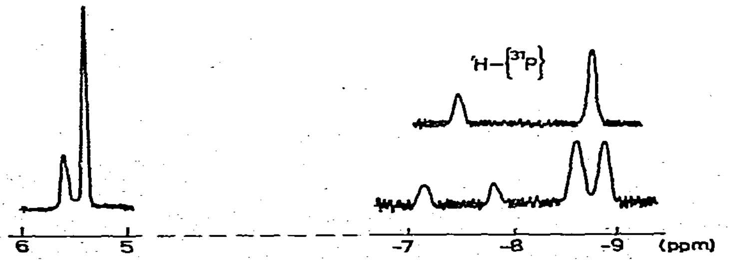
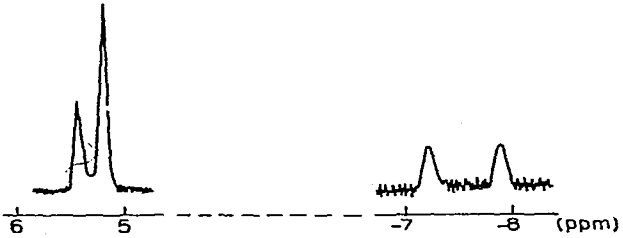


Fig. 1. PMR spectra of π-CpRe(CO)$_2$PPh$_3$ in the mixture CHCl$_3$: CF$_3$COOH : BF$_3$ · H$_2$O 1 : 1 : 0.5 (*a*).



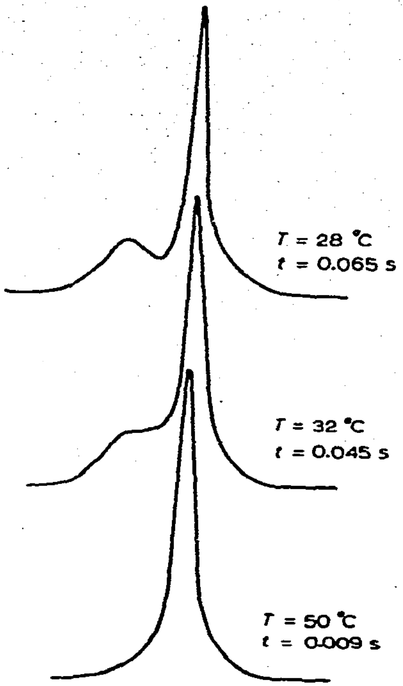


Fig. 2. PMR spectra of π-CpRe(CO)$_2$PPh$_3$ in the mixture CHCl$_3$: CF$_3$COOH 1 : 1 (*b*).

Fig. 3. The cyclopentadienyl region in the PMR spectra of π-CpRe(CO)$_2$PPh$_3$ in the mixture CHCl$_3$: CF$_3$COOH : BF$_3$ · H$_2$O 1 : 1 : 0.5 (*a*) at different temperatures.

Thus, we have succeeded in detecting the simultaneous presence of *cis* and *trans* isomers of the protonated form of π-CpRe(CO)$_2$PPh$_3$ and in evaluating the energy parameters of their mutual transformation. It was revealed that these values are noticeably higher than those of similar transformations in neutral molybdenum complexes [7].

Experimental

The PMR spectra of π-CpRe(CO)$_2$PPh$_3$ in *a* and *b* solutions were taken at a working frequency of 60 MHz by means of a RYa-2305 spectrometer equipped with a temperature cabinet. The temperature was varied in the range —10—+60° C. Energy parameters were calculated by simulating the shape of the line on a PDP-12 computer.

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