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HYDROGEN TAUTOMERISM IN A RHENIUM CLUSTER COMPOUND

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Summary

The hydrogen tautomerism in the hydrido carbonyl cluster compound of rhenium $[H_4Re_4(CO)_{15}](NEt_4)_2$ has been studied by analysis of the PMR spectra at different temperatures.

Introduction

In spite of many studies on the polyhydrido complexes of transition metals, the interesting problem of their fluxionality has remained unsolved [1]. In principle, location of the hydrido ligands in the crystalline state is possible by means of X ray or, better, neutron diffraction techniques: however, the first method is limited by the low scattering power of the hydrogen atom bonded to a metal atom with high nuclear charge, while the second is still a long way from routine application.

PMR spectroscopy is useful in studying the symmetry of the metal hydride complexes in solution, but has failed in the case of the polyhydrido compounds of rhenium; many of the PMR studies of the latter have indicated that the non equivalent protons rapidly exchange. Thus, different protons show a single resonance frequency and in the presence of phosphine ligands, the resonance has a fine structure corresponding to a unique value of the coupling constant $J(P—H)$.

Very recently, Albano et al. [2] reported the preparation, properties and X-ray structure of the rhenium cluster compound $[H_4Re_4(CO)_{15}](NEt_4)_2$ which is a specially interesting fluxional hydride. We have determined the structure in solution and also the values of the kinetic parameters of the exchange process by means of PMR spectrum analysis at different temperatures.

Results and discussion

The PMR spectra of $[H_4Re_4(CO)_{15}](NEt_4)_2$ were recorded in acetone-d_6 solution with TMS as internal reference on a Varian NEVA NV-14 spectrometer

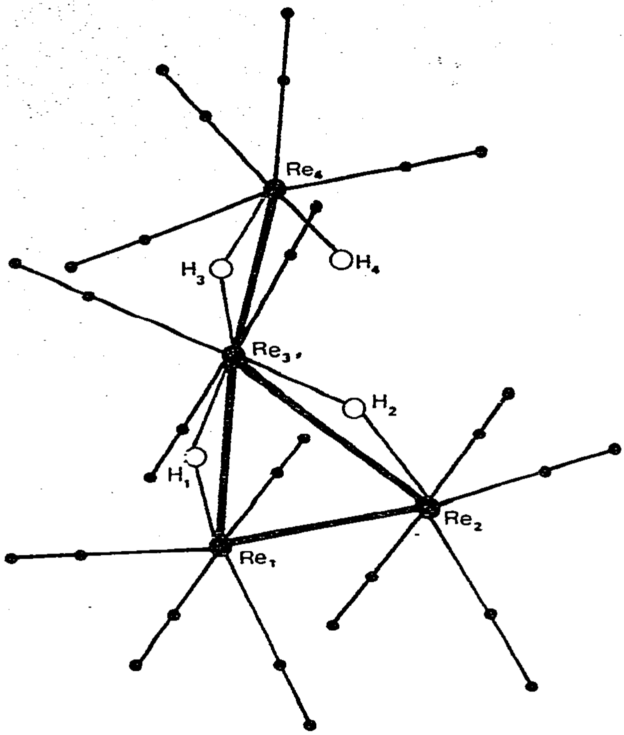

Fig. 1. Schematic structure of the cluster anion $[H_4Re_4(CO)_{15}]^{2-}$

operating at 60 MHz. The temperature range was —39° C to 46.5° C. The probe temperature was determined with a standard thermocouple apparatus and controlled by an alcohol thermometer. The temperatures are accurate to ±0.5° C. We discuss in detail only the hydrido part of the spectrum: the signals of the tetraethylammonium cation are considered only in order to confirm by integration the presence of four protons in the anion. The structure of the cluster anion is presented schematically in Fig. 1; from X-ray diffraction data [2] the presence of three types of hydrido ligands was suggested: two hydrogen atoms of bridged type lie in the plane of the Re(1)—Re(2)—Re(3) atoms and are equivalent because the anion possesses an idealized C_s symmetry; another hydrogen atom is bonded to the Re(3) and Re(4) atoms and the fourth hydrogen is bonded only to the Re(4) atom. The analysis of the PMR spectrum in solution at low temperature has confirmed this structure.

At 46.5° C, at τ values above TMS only two signals are present; they are sharp and of equal intensity, and centered at τ 26.93 and 20.57 ppm respectively. On lowering the temperature, the signal at lower field broadens and near to 0° C collapses. At lower temperatures, this signal splits into two bands, one at τ 15.04 and the other at τ 25.95 ppm. The sequence of the spectra reported in Fig. 2 clearly confirms that the exchange process involves a terminal and a bridged hydride with very different resonance frequencies (H(3) and H(4) of Fig. 1); the signal of the other two bridged protons at τ 26.93 is unaffected by temperature change. The assignement of the low frequency to the terminal

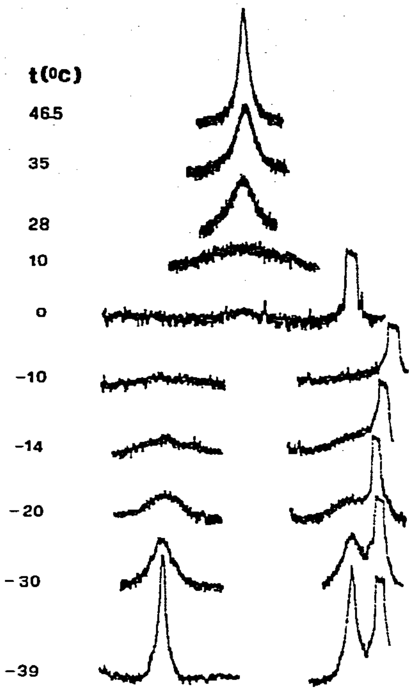

Fig. 2. Experimental PMR spectra of $[H_4Re_4(CO)_{15}]^{2-}$. The truncated band on the right is the H(1), H(2) signal. See text for the τ values.

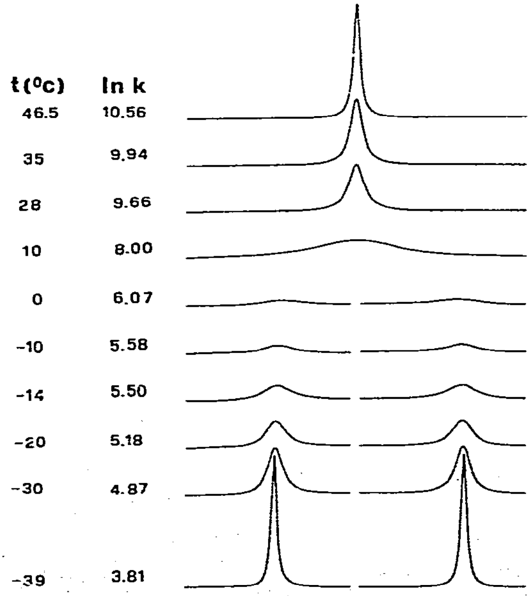

Fig. 3. Computer simulated PMR spectra of $[H_4Re_4(CO)_{15}]^{2-}$.

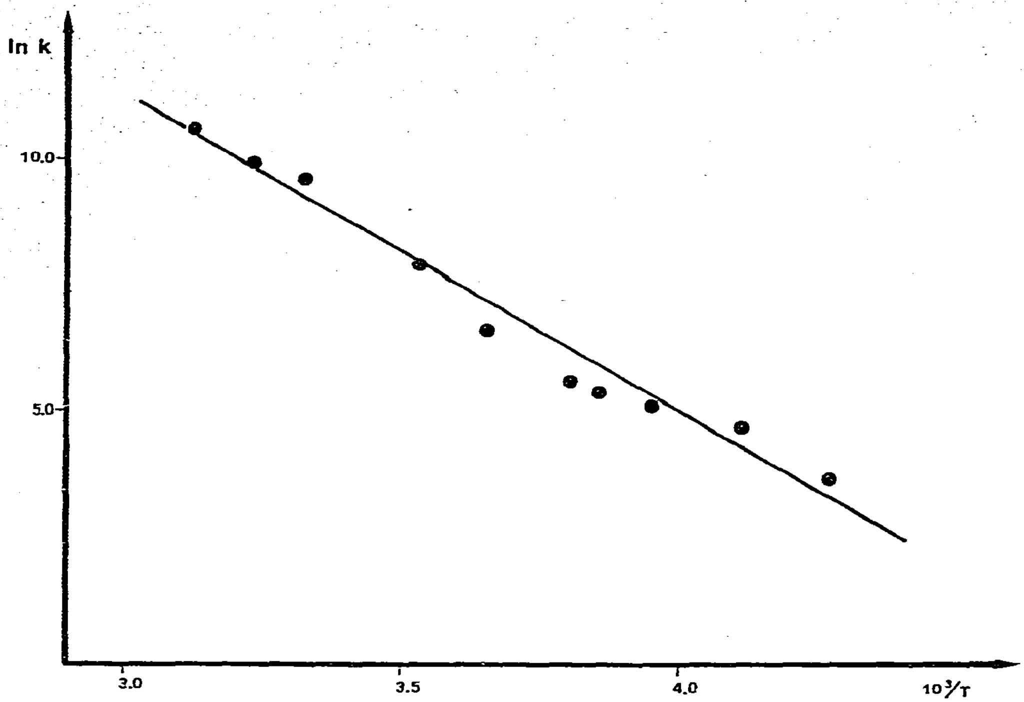

Fig. 4. Arrhenius plot for the exchange process of the H(3) and H(4) atoms (see Fig. 1).

hydride and the other to the bridged hydride is based on established practice. The exchange process was fully analysed using the method developed by Gutowsky and Holm [3], and reviewed by Johnson [4]. First of all, the H(3) and H(4) spectrum for each temperature was reconstructed as the sum of two Lorenzian functions in order to give an analytical form for the spectrum. Then these functions were fitted by least-squares method to those resulting from the exchange theory (see Fig. 3). The only variable parameter in the fitting procedure is the life-time parameter ϑ. The transverse relaxation time T_2 has been determined from the line width of the spectrum at —39° C by assuming that the exchange rate is negligible under these conditions. Small variations of the T_2 parameter do not alter significantly the best fitting ϑ values. The computer simulated spectra are reported in Fig. 3 only for H(3) and H(4) protons. Figure 4 shows the plot of the rate constant k against $1/T$, which gives values for the activation energy and the frequency factor (log A), of 12.32 ± 0.66 kcal mol^{-1} and 12.90 ± 0.53 respectively.

The Eyring equation yields the following values for the activation parameters: $\Delta H^{\neq} = 11.73 \pm 0.66$ kcal mol^{-1} and $\Delta S^{\neq} = -1.35 \pm 2.21$ e.u. The entropy term is subject to a large uncertainty which prevents even the sign determination, but the low value is consistent with an exchange process which probably involves only a partial dissociation accompanied by some variations in vibrational degrees of freedom or some variations in coordination geometry in the transition state. In fact, it is possible to suggest that the H(3)—H(4) exchange mechanism corresponds to the concerted formation of a bridged bond

(Re(3)—H(4)—Re(4)) and the breaking of the other bridged bond (Re(3)—H(3)—Re(4)). Obviously, such a mechanism can operate only between a pair of protons bonded to a common metal atom, and must be accompanied by a partial rearrangement of the carbonyl groups around the Re(3) and Re(4) atoms. This hypothesis is supported by the absence of exchange between the terminal H(4) proton and the other bridged protons H(1) or H(2). Due to the lack of data for other examples of hydrogen tautomerism in rhenium cluster compounds, very few comments are possible about the value of the activation energy. However, our value of 12.36 kcal mol^{-1} seems to be much higher than that found by Kaesz [5,6] in the series of ruthenium clusters $H_4Ru_4(CO)_{12-x}$-$[P(OMe)_3]_x$ ($x = 1,2,3,4$), where the exchange between non equivalent bridged protons is fully hindered only at very low temperature (lower than —120°C) and is controlled by an activation energy of only 3—4 kcal mol^{-1}. Such behaviour may be related mainly to the fact that in ruthenium clusters the exchange process involves a highly symmetric transition state in which each hydrogen atom is face-bridged on the Ru(4) tetrahedron. Moreover, in the latter case the exchange between hydrogen nuclei, which are not very different magnetically, does not involve any dissociation. The rhenium cluster is very different: the exchange between the non-equivalent bridged protons H(3)—H(1) or H(3)—H(2) would occur only with complete dissociation; the observed H(3)—H(4) exchange is accompanied by a partial dissociation, and the transition state is always characterized by a low symmetry.

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