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Preliminary Communication

Modulation of quantum mechanical exchange couplings in transition metal hydrides through hydrogen bonding

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Abstract

Addition of various proton donors (methanol, indole, phenol, *p*-I-phenol, *p*-CF_3-phenol and hexafluoroisopropanol) to solutions of $Cp^*RuH_3(PCy_3)$ (**1**) in d_8-toluene leads to an increase of the quantum mechanical exchange couplings J_{ab} between the hydride sites of **1** and to changes of the hydride chemical shifts, e.g. at 193 K the exchange couplings of **1** in d_8-toluene vary from 74 Hz in the absence of additives to 249 Hz in the presence of 3 equiv. of $(CF_3)_2CHOH$. Exchange couplings and hydride chemical shifts are non-linear functions of the number of hydrogen bond donor equivalents (R). The effect is reversed when pyridine is added and does not occur with tetrahydrofuran as solvent. These observations provide evidence for the formation of hydrogen bonded associates between **1** and the proton donors added. Linear correlations are observed between the exchange couplings and the hydride chemical shifts of hydrogen bonded complexes indicating that these parameters can be used as sensors of the hydrogen bond strength and geometry.

Keywords: Exchange couplings; Transition metal complexes; Hydride complexes; Hydrogen bonding complexes

Hydrogen bonding [1] has long been neglected in organometallic chemistry. Only recently the ability of hydrides to act as hydrogen bond acceptors has been recognized. Intramolecular hydrogen bonds to the hydride sites of transition metal complexes were observed independently by Crabtree et al. [2] and Morris and co-workers [3]; intermolecular hydrogen bonds between $ReH_5(PPh_3)_3$ and indole in the solid state by Crabtree and co-workers [4] and between a tungsten monohydride and various proton donors in solution by Shubina et al. [5]. Moreover, a recent study of solid state structures revealed hydrogen bonds in a number of other hydride derivatives [6a]. Such hydrogen bonds have been studied by theoretical calculations [2b,4,6].

The chemical and spectroscopic properties of polyhydride complexes exhibiting quantum mechanical exchange couplings J_{ab} between adjacent hydride sites a and b has attracted recently considerable interest [7–12]. The phenomenon consists in the observation of J_{ab} coupling constants which are very large and which increase strongly with increasing temperature. The quantum mechanical origin of the phenomenon was recognized by two groups [8a,b,9] but the exact mechanism at the origin of these couplings has been controversial. The fact that the magnitude of the couplings was enhanced upon complexation of Lewis acids [7d–f,12] such as Au^+ to ruthenium and niobium trihydrides, or using less electron-donating ligands in selected niobium [7], iridium [8] and ruthenium complexes [7], led us to propose that this phenomenon be associated with the formation of thermally accessible dihydrogen configurations [7h] in agreement with recent quantum chemical calculations [13]. Indeed, we have shown recently that the presence of a slow rotating dihydrogen ligand was linked to the occurrence of such couplings in tantalum dihydrogen complexes [11]. However, this may not be a necessary condition and alternative explanations based on the existence of a soft vibrational mode of the hydrides on the way to classical exchange have also been proposed [14].

The sensitivity of exchange couplings to electronic effects and the previous report of their solvent dependence [8e] led us to the idea that they should be strongly perturbed in the case of hydrogen bonding. We present in this communication preliminary results demonstrating that this is indeed the case.

For this purpose, we investigated the hydrogen bond acceptor properties of $Cp^*RuH_3(PCy_3)$ (**1**, $Cp^* \equiv C_5(CH_3)_5$,

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$Cy \equiv$ cyclohexyl, Fig. 1), the first complex reported to exhibit large anomalous temperature dependent J_{ab} values [7a,c]. Solutions of **1** (0.06 M) in d_8-toluene were prepared to which defined equivalents R of various proton donors were added. The final composition of the solutions was checked by ^1H NMR experiments (250 MHz) performed at 193 K.

The spectral changes of the high field hydride signals of **1** in the presence of proton donors AH are illustrated in Figs. 1 and 2. The spectra display typical second-order AB_2 patterns on which determination of the chemical shifts δ_a and δ_b and of the exchange coupling constants J_{ab} is straightforward [15]. In the absence of a proton donor (Fig. 1(a)) a value of $J_{ab} = 74$ Hz is obtained which increases monotonically with the series of additives: methanol (not shown), indole, phenol, p-I-phenol, p-CF_3-phenol and hexafluoroisopropanol (HIP; Fig. 1(b)–(f)), characterized respectively by pK_a values of 29.0, 20.95, 18.0, ~16.5, 15.2 and 17.9 [16]. The largest coupling constant value ($J_{ab} = 249$ Hz) was observed in the case of HIP for $R = 3$. The chemical shift of the alcohol proton varies as a function of the temperature and of the alcohol concentration; for example, in the case of HIP for $R = 3$, it is found at 4.41 ppm at 193 K. There is a correlation between J_{ab} and the pK_a values in DMSO, but not a simple one as previously observed for hydrogen bonding between organic molecules [17]. In the same series, the chemical shifts δ_a of the hydride site a move to high field whereas those of hydride site b (δ_b) slightly move to low field (see Fig. 2). All effects were partly reversed when pyridine was added and did not occur when d_8-tetrahydrofuran was used as solvent. In the latter case, the exchange couplings increase with temperature, but the chemical shifts remain constant. Addition of stronger hydrogen bond donors such as benzoic acid does not lead to any effect whereas trifluoroacetic acid protonates the complex and dihydrogen elimination is observed [18]. The absence of modification of the spectrum using benzoic acid probably results from the preferential formation in toluene of strong hydrogen bonded acid dimers. The longitudinal relaxation times T_1 of the hydride sites which exhibit minima at 250 MHz around 233 K were slightly reduced in the presence of the donor, in agreement with a supplementary loose interaction between one hydride and an external proton [1]. Finally, attempts to crystallize adducts of **1** with the above proton donors from various solvents only led to crystalline pure **1**.

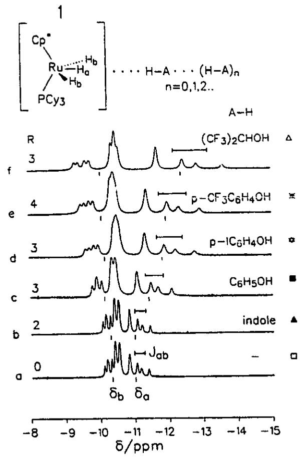

Fig. 1. Hydride regions of the ^1H NMR spectra (250 MHz) of solutions of $Cp^*RuH_3(PCy_3)$ (**1**) in d_8-toluene at 193 K in the absence (a) and the presence (b–f) of various proton donors AH. The symbols refer to the data points of Fig. 2.

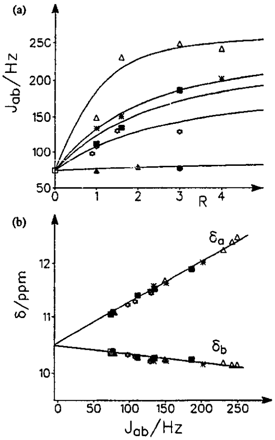

Fig. 2. Spectral ^1H NMR parameters of $Cp^*RuH_3(PCy_3)$ (**1**) in the presence of proton donors AH at 193 K using d_8-toluene as solvent. The symbols refer to the proton donors defined in Fig. 1, except the bold circle which refers to methanol. (a) Exchange couplings J_{ab} as a function of the number of equivalents R of the proton donors added. The solid curves were calculated according to Ref. [16]. (b) Correlation between the exchange couplings J_a listed in Fig. 1 and the chemical shifts δ_a and δ_b of the hydride sites of **1**.

All observations can be explained by the formation of hydrogen bonded aggregates (Fig. 1) with varying number n of proton donor molecules. The exact composition, structure and dynamics of the complexes could not be elucidated in this study. The various species formed exchange rapidly within the NMR timescale, leading to averaged values of

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[1] T_1 minimum values for $Cp^*RuH_3(PCy_3)$ (**1**) in d_8-toluene (233 K, 250 MHz): 92±2 ms; T_1 minimum values for $Cp^*RuH_3(PCy_3) \cdot 3(CF_3)_2CHOH$ in d_8-toluene (233 K, 250 MHz): 84±2 ms. A rapid calculation shows that this excess relaxation for $Cp^*RuH_3(PCy_3) \cdot 3(CF_3)_2CHOH$ would correspond in a static system to an additional proton in the vicinity of the three hydrides with a distance of ~1.92 Å from the central hydride, close to values found in intramolecular systems described by Crabtree and Morris (see Refs. [2] and [3]).

coupling constants and chemical shifts. It is understandable that the formation of these complexes is suppressed in the presence of stronger hydrogen bond acceptors such as tetrahydrofuran or pyridine.

As shown in Fig. 2(a), the values of J_{ab} are non-linear functions of the number of equivalent R of added proton donor. This dependence was modeled in terms of the simplest hydrogen bond equilibrium $AH+B \rightleftarrows AH\cdots B$ [2]. Although this association model is oversimplified, the calculated solid lines in Fig. 2(a) reproduce the experimental results fairly well within the margin of the experimental error, which mainly arises from variations in concentrations.

The variation of the average hydride chemical shifts δ_a and δ_b is proportional to that of exchange coupling constants as illustrated in Fig. 2(b). The fact that the chemical shift δ_a is more affected than δ_b could result from a preferential interaction of the central hydride with the hydrogen bond donor. All data points are located on straight lines independent of the donor type and concentrations. The concentration fluctuations of Fig. 2(a) are not apparent in this case since they apply linearly to both chemical shifts and coupling constants. It is straightforward to show that the correlations observed imply similar correlations between the intrinsic quantities $\delta_a(i)$, $\delta_b(i)$ and $J_{ab}(i)$ of the individual species i formed. Thus, with respect to the spectral changes in **1**, the various proton donors have lost their chemical identity and only the proton donating power of the OH groups, which depends on the chemical structure, is important for modulating the strength and geometry of the hydrogen bonds formed. Other specific interactions between the ligands of **1** and the residual groups of the donor would lead to a breakdown of the linear correlation of Fig. 2(b). Similar observations were made recently in the case of hydrogen bonded complexes of carboxylic acids with pyridine [1g,h], where it was also found that the proton donating power increased with the number n of donor molecules in the complexes. However, n depended on the structure of the donor. Therefore, there is no simple correlation between hydrogen bond properties and the pK_a values of the donors.

We propose that the increase of exchange couplings in **1** as a function of the strength of the hydrogen bonds formed is correlated with a partial charge transfer from the metal hydride to the hydrogen bond donor, i.e. with a decrease of the overall electron density on the metal. Such a decrease could favor the formation of dihydrogen configurations displaying very large exchange couplings. Similar effects were previously observed in the case of Lewis acid adducts [7f,12] and changes in the ligand basicity [7,8]. This proposal can seem contradictory with the observation that the central hydride is more affected by hydrogen bonding than the side ones. However, rapid transfer of hydrogen bond donor between the central and the side hydrides is to be expected or even bidentate interaction like in the rhenium complex crystallized by Crabtree and co-workers [4]. Alternatively, this effect can also arise from a modification of the vibrational potential of the central hydride, although in this case the M–H distance is expected to be reduced by hydrogen bonding as a result of the polarizability of the M–H bond which seems also in contradiction with the increase of the exchange couplings.

In conclusion, we present in this letter evidence for enhancement of exchange couplings upon formation of hydrogen bonds between a ruthenium trihydride complex (**1**) and a series of proton donors AH. Exchange couplings appear therefore as novel valuable sensors for the geometry and strength of hydrogen bonding to transition metal hydrides. In order to establish the exact structure and intramolecular dynamics of the hydrogen bonded complexes, further NMR studies at lower temperatures in the regime of slow hydrogen bond exchange [1g,h] will be necesssary. In addition it will be interesting to determine whether the classical dihydrogen exchange observed at higher temperatures and more generally the reactivity of transition metal hydrides is also affected by hydrogen bonding.

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[2] The solid lines in Fig. 2(a) were calculated in terms of the equation $J_{ab}=\Sigma_i x(i)J_{ab}(i)$ where $x(i)$ represents the mole fraction and $J_{ab}(i)$ the intrinsic exchange coupling of the species i. In particular, it was assumed that only one hydrogen bonded species is formed according to $AH+B \rightleftarrows AH\cdots B$, characterized by the equilibrium constant K. It is then straightforward to show that in this case: $J_{ab}=J_{ab}(1)+(J_{ab}(2)-J_{ab}(1))[-\sqrt{K^{-2}+(1-R)^2+2K^{-1}(1-R)}+K^{-1}+1+]/2$. For the solid curves of Fig. 2 we assumed values of K^{a} 0.1, 0.5, 0.6, 0.75, 3 and $J_{ab}(2) \approx 100, 200, 230, 250$ and 270 Hz.

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