FAST MOTIONS OF AN IRIDIUM DIHYDRIDE COMPLEX IN AN AQUEOUS MEDIUM REVEALED BY NMR RELAXOMETRY WITH HIGH RESOLUTION

A. S. Kiryutin,* N. N. Fishman, and A. V. Yurkovskaya

International Tomography Center, Siberian Branch of the Russian Academy of Sciences, ul. Institutskaya 3A, Novosibirsk, 630090 Russia

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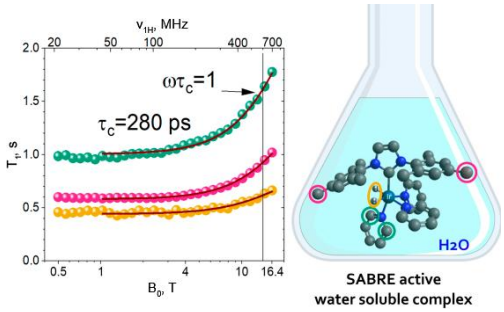
Abstract

The correlation times in iridium dihydride catalytic complex $[Ir(IMes)(Py_{eq})_2(Py_{ax})H_2]Cl$ were studied in water, where it remains stable for days. T_1 relaxation times of individual protons were measured across magnetic fields using NMR with fast field cycling. Above 4 Tesla, T_1 time increased, indicating a transition from the fast ($\omega\tau_c < 1$) to slow motion ($\omega\tau_c > 1$) regime. Fitting the experimental data to a local magnetic field fluctuation model provided the site-specific rotational correlation times with an average of 280 ps for the whole molecule.



Key words: NMR, relaxation dispersion, correlation time, SABRE complex.

Introduction

Molecular mobility, namely, the correlation times of rotational motions in solution is a very useful characteristic of substances, which depends on the size of a molecule, temperature, and solvent properties. This parameter often affects spin relaxation time as it determines the mode of motion of the molecule slow or fast compared to the Larmor frequency [1]. Field-cycling nuclear magnetic resonance (NMR) relaxometry is a versatile technique for studying molecular mobility and is suitable for a wide variety of systems: molecules in solutions, polymers, molecular and liquid crystals, as well as biomolecules [2, 3]. Previously, our group determined the correlation times of neutral iridium complex [Ir(IMes)(COD)Cl] in methanol (see Fig. 1) [4]. This is the most popular pre-catalyst for the SABRE (signal amplification by reversible exchange) method, which has become very efficient and convenient way to enhance the NMR signal of some molecules capable of non-covalent reversible binding to an iridium hydride complex that constantly exchanges hydrogen atoms with dissolved para-hydrogen [5, 6].

Results and discussion

In this work, we found that bubbling pre-catalyst [Ir(IMes)(COD)Cl] with para-hydrogen in an aqueous solution in the presence of 1% pyridine produced stable positively charged iridium dihydride $[Ir(IMes)(Py_{eq})_2(Py_{ax})H_2]Cl$ with three pyridine ligands and IMes carbene. Previously, the crystal structure of the complex was studied by XRD for crystals obtained from organic solvents [7]. Moreover, the activation of the pre-catalyst in the presence of pyridine and nicotinamide was studied by the indirect detection using para-hydrogen [8]. The SABRE experiments were performed in a strong magnetic field [9], and the NMR parameters of the complex in methanol-d_4 were obtained [10].

Here, we report the results of the proton T_1 relaxation time measurements over a wide range of magnetic fields from 0.5 T to 16.4 T using a home-built fast magnetic field cycling setup based on a high-resolution 700 MHz NMR spectrometer [11].

A sample containing 1.1 mg of the pre-catalyst (synthesized according to the published procedure [12]), 6 μL of pyridine, 30 μL of D_2O, and 589 μL of H_2O was bubbled with hydrogen at 4 atm and 45 °C in an NMR tube for 15 min. The color change from yellow to colorless indicated the end of the hydrogenation of cyclooctadiene and the formation of a stable iridium dihydride stabilized by three pyridine molecules and IMes. The ^1H NMR spectrum of the resulting solution is shown in Fig. 1. The suppression during FID accumulation was applied to suppress the ^{13}C satellites.

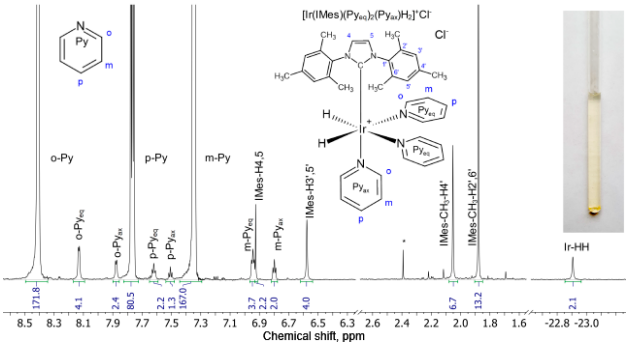


Figure 1. 700 MHz $^1H\{^{13}C\}$ NMR spectrum of $[Ir(IMes)(Py_{eq})_2(Py_{ax})H_2]Cl$ detected in an aqueous solution at 25 °C. Molecular structure and atom numbering is shown in the inset. Signal from an impurity is marked by an asterisk. The relative integrals of signals are shown under the signals.

The measurements of T_1 relaxation times were carried out by the recovery inversion method on a specially designed setup

for rapid displacement of the sample along the vertical axis of a cryomagnet. The magnetic field for relaxation was determined by the position of the sample from the center of the cryomagnet bore. The experimental protocol was as follows: (1) relaxation in a 16.4 T field for 15 s to create the initial Boltzmann polarization; (2) application of a 180-degree hard pulse to invert the magnetization of all protons; (3) moving the sample into the selected magnetic field (faster than 290 ms); (4) holding the sample in B_0 field for a varying time from 0.01 to 10 s for relaxation; (5) returning the sample to the detection field; (6) delay 150 ms to calm down the vibration of the sample; (7) recording the NMR spectrum using excitation sculpting [13] sequences to avoid the excitation of the large H_2O solvent signal and using the suppression of the ^{13}C interactions to get rid of satellites from the pyridine signals.

Each relaxation kinetics containing 16 time points was modeled by a decreasing exponent, and a set of T_1 for each signal in the NMR spectra was obtained. The dependence of the relaxation time on the magnetic field was then plotted and fitted using equation (1), derived from the model of nuclear relaxation due to fluctuations of the local magnetic fields (Fig. 2). As a result, the rotational correlation times τ_c for the protons of the complex were obtained that are summarized in Table 1.

$$\frac{1}{T_1(B_0)} = \frac{1}{T_1^{inf}} + \frac{A}{(1+(\gamma_H B_0 \tau_c)^2)}, \quad (1)$$

where T_1^{inf}, A, τ_c are the fitting parameters, γ_H is the ^1H gyromagnetic ratio.

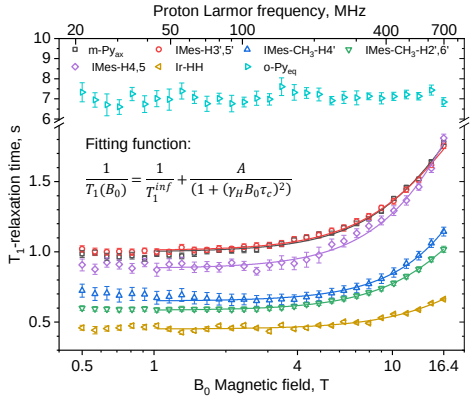


Figure 2. Proton relaxation dispersion data. (symbols) T_1 relaxation times of individual protons, (lines) fitting curve using function (1) and the correlation times from Table 1.

Table 1. Site-specific rotational correlation times (τ_c) for $[Ir(IMes)(Py_{eq})_2(Py_{ax})H_2]Cl$ in an aqueous solution at 25 °C

Proton	τ_c, ps	Proton	τ_c, ps
m-Py$_{ax}$	294 ± 13	IMes-CH$_3$-H4'	217 ± 16
IMes-H4,5	394 ± 119	IMes-CH$_3$-H2',6'	259 ± 6
IMes-H3',5'	303 ± 10	Ir-HH	208 ± 28
Common 280 ± 7			

Conclusions

This work presented the site-specific measurements of rotational correlation times for complex $[Ir(IMes)(Py_{eq})_2(Py_{ax})H_2]Cl$, revealing significantly shorter times than those previously reported for precursor [Ir(IMes)(COD)Cl] in methanol [4], despite the larger size of the iridium hydride and the higher viscosity of the solvent (water). Variations in the correlation times among protons indicated that the molecule is not rigid. The marked independence of T_1 relaxation times for equatorial pyridine (Py_{eq}) protons is attributed to chemical exchange with free pyridine in solution, with the exchange rate exceeding the nuclear relaxation rate, which is consistent with the data in methanol [14]. In contrast, for the protons of the axial pyridine ligand, T_1 relaxation times were much shorter and exhibited a strong magnetic field dependence similar to that of the protons of the tightly bound IMes ligand.

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Corresponding author

* E-mail: kalex@tomo.nsc.ru. Tel: +7(383)330-3959 (A. S. Kiryutin).

Electronic supplementary information

Electronic supplementary information (ESI) available online: the sample preparation procedure, HSQC spectra with signal assignments, DOSY spectrum, temperature dependence, and the ^{15}N SABRE spectrum for the studied complex. For ESI, see DOI: 10.32931/io2547a.

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