

P.M.S. Hendrickx<sup>1</sup>, E. De Canck<sup>2</sup>, R. Drozdak<sup>2</sup>, S. Monsaert<sup>2</sup>, J.C. Martins<sup>1</sup> and F. Verpoort<sup>2</sup>

<sup>1</sup>NMR and Structure Analysis Unit, Department of Organic Chemistry, Ghent University, Krijgslaan 281 54 B-9000 Gent, Belgium

<sup>2</sup>Centre for Ordered Materials, Organometallics and Catalysis, Department of Inorganic Chemistry, Ghent University, Krijgslaan 281 53 B-9000 Gent, Belgium

Contact: [Pieter.Hendrickx@UGent.be](mailto:Pieter.Hendrickx@UGent.be)

## Introduction

Multiple complexes catalyzing ring-opening and ring-closing metathesis reactions have been reported over the years in literature<sup>[1]</sup>. A breakthrough was achieved in 1992 when Grubbs published the structure of a 16 electron ruthenium-carbene complex (PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=CH-CHCPh<sub>2</sub><sup>[2]</sup> displaying superior stability and moderate catalytic properties. Further modifications improving the catalytic activity involved replacing the benzylidene ligand with vinylidene, allenylidene or indenylidene ligands<sup>[3]</sup> as well as introducing heterocyclic carbene ligands (NHC's)<sup>[4]</sup>.

Our research is based on the ruthenium-indenylidene class of molecules which, in contrast to benzylidene complexes, do not easily form single crystals necessary for XRD structure analysis. Only one X-Ray structure has been published by Jafarpour *et al.* in 1999 (Figure 1) indicating a slightly distorted octahedral coordination of the ruthenium atom<sup>[5]</sup>. Therefore we resorted to NMR for structure validation and conformational analysis of these complexes. Furthermore dynamic processes in the solution state were monitored and quantified using NMR spectroscopy, thereby providing additional information not available from X-Ray diffraction.

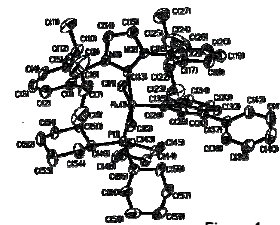


Figure 1.

## Dynamics

Following their nearly complete assignment, a series of 6 Ru(II) complexes was analyzed using off-resonance ROESY spectroscopy to reveal exchange processes that are slow on the NMR timescale (Table 1). Hindered rotations around the Ru-SiMes and the N-Phenyl bond could be observed for the pyridine-based complexes (left). Complexes based on PPh<sub>3</sub> and PPY<sub>3</sub> only show exchange correlations related to the rotation around the Ru-SiMes bond (right).

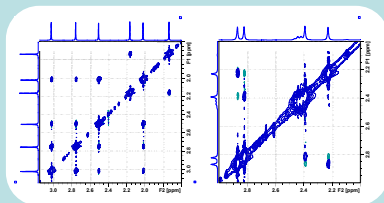


Figure 2. Off-resonance ROESY spectra of compound 2 and 4. Exchange cross-peaks between the methyl groups have the same sign as the diagonal peaks; genuine nOe interactions have opposite sign.

Besides a qualitative interpretation of the dynamics of the complex, the peak volumes can be measured to extract exchange rates<sup>[6]</sup>. Such calculations using a matrix inversion method were first presented by Perrin and Gipe<sup>[7]</sup>. The preliminary results of these calculations are presented in Table 1.

Only pyridine-based complexes show a hindered rotation around the N-Phenyl bond. This can be explained by steric effects of the L<sub>2</sub> ligand as large ligands will push the indenylidene ring and chlorine atoms closer to the phenyl rings, thus hindering the rotation of the phenyl groups.

Hindered rotation around the Ru-C bond is observed for 4-6 although it happens at the limit of detection for 4 and 6, indicating increasing steric effects. Furthermore introducing para-methyl groups on the phenyl rings (L<sub>1</sub>) further inhibits this rotation for all three sets of complexes.

L1	L2	k(Ru-C) (s <sup>-1</sup> )	k(N-Ph) (s <sup>-1</sup> )
1 CH <sub>3</sub>	PCy <sub>3</sub>	<a	<a
2 CH <sub>3</sub>	Py	0.26	0.79
3 CH <sub>3</sub>	PPh <sub>3</sub>	<b	<b
4 H	PCy <sub>3</sub>	0.05	<a
5 H	Py	4.70	0.09
6 H	PPh <sub>3</sub>	0.02	<a

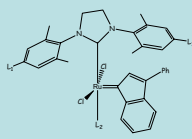


Table 1. Calculated exchange rates from 200ms off-resonance ROESY spectra at 25°C. a) no cross-peaks were observed for this rotation; b) no data due to spectral quality.

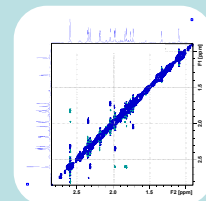
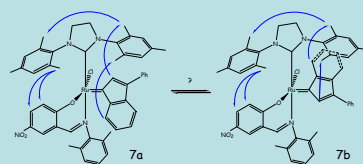
It should be noted that these dynamic processes do not interfere with the catalytic activity of these complexes as chemical reactions happen on the picosecond timescale.

## Conclusions

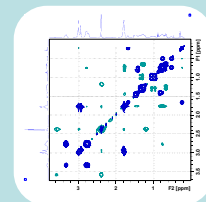
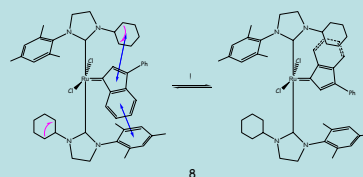
A series of 8 complexes has been studied by standard 2D NMR techniques at (1H) 500 MHz. A 'complete' assignment could be performed for all compounds. Off-resonance ROESY spectra have been used to study the dynamic properties of compounds 1-6 revealing exchange phenomena with rates ranging from 0.02 Hz to 4.70 Hz thus not interfering with the catalytic process. A thorough investigation of compound 7 made it possible to stereospecifically assign both isomers present in solution. A fast exchange process has been detected in complex 8 originating from rotations around the Ru-NHC bonds.

It can thus be concluded that NMR is an appropriate technique to validate and analyze the structure of non-rigid ruthenium-indenylidene complexes.

## Conformational Analysis



Besides studies of exchange phenomena, NMR is an appropriate tool to derive molecular conformations. Complex 7, featuring a bidentate ligand, shows two species of almost equal population in solution which could not be separated by standard chromatography. An integrated analysis of 2D homonuclear and heteronuclear NMR techniques lead to an unambiguous assignment of all <sup>1</sup>H and most <sup>13</sup>C atoms in both species. Chemical shift differences between the two species led to the hypothesis of a possible 180° flip of the indenylidene ligand. This was further investigated using nOe correlations; 156 resolved cross-peaks were assigned resulting in 39 inter-ligand spatial connections of which the most important are shown on the molecular structures. The two species could hereby be unambiguously assigned to the two rotameric/isomeric forms 7a and 7b. Furthermore the investigation of chemical shifts of two indenylidene protons in compounds 1-6 validates this assignment. No evidence could be found for the interconversion of these two conformations as no exchange correlations were observed.



One dimensional proton NMR of compound 8 at 25°C shows a mixture of sharp and broad resonances. These broad resonances, originating from the NHC ligands, split up into two sharper resonances when the temperature is lowered to 12°C indicating a coalescence phenomenon. The two NHC ligands must thus experience different magnetic environments. Analyzing nOe data, correlations to indenylidene protons were found from aromatic and methyl protons from one NHC ligand, while the other NHC ligand was interacting with its cyclohexyl ring. This means that a relatively fast rotation around both Ru-NHC bonds can occur compared to compounds 1-7. In addition to this exchange phenomenon, exchange cross-peaks between C<sub>2</sub>-protons belonging to the same cyclohexyl ring are present. These can only be related to a 180° flip of the indenylidene ligand.

## References

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## Acknowledgement

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