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Assignment and Conformational Investigation of Asymmetric Phenylindenylidene Ruthenium Complexes Bearing N,O-Bidentate Ligands.

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Abstract: The NMR conformational study of three asymmetric phenylindenylidene Ruthenium complexes **4.1-4.3**, is presented. Complete ^{1}H and ^{13}C assignments could be obtained for **4.1-4.3** in benzene solution from multiple 2D homonuclear and heteronuclear NMR techniques. Our NMR analysis shows that each complex exists as a 55:45 mixture of two rotational isomers in slow exchange on the NMR chemical shift time scale. They are shown to be related by a 180° flip of the indenylidene ligand along the Ru=CR bond. Both rotational isomers can be discriminated by means of NOEs contacts between the various ligands coordinating to the Ru. By matching these stereospecific assignments to the chemical shift, a chemical shift based fingerprint of the isomers that may allow straightforward assignment of future asymmetric phenylindenylidene Ruthenium complexes is proposed.

Keywords:

NMR / ^{1}H / ^{13}C / ruthenium / indenylidene / complex / olefin / metathesis / chemical exchange / rotational isomerism

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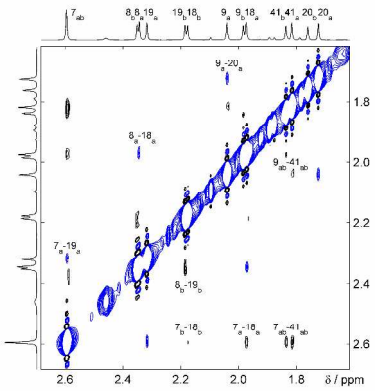
Graphical Abstract:

The conformational study of three asymmetric phenylindenylidene Ruthenium complexes in solution by NMR shows two rotational isomers in slow exchange. NOEs were successfully used to discriminate between both rotational isomers By matching these stereospecific assignments to the chemical shift, a chemical shift based fingerprint of the isomers that may allow a more straightforward assignment of future asymmetric phenylindenylidene Ruthenium complexes is proposed.



Assignment and Conformational Investigation of Asymmetric Phenylindenylidene Ruthenium Complexes Bearing N,O-Bidentate Ligands.

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Introduction

A rapidly increasing interest in olefin metathesis has been observed in recent decades as it constitutes a useful tool for the synthesis of an impressive range of molecules that required a significantly longer or tedious route before. Ruthenium catalysts that combine high activity and good stability have revolutionized the field and the development of more efficient and selective ruthenium catalysts is key to spread the application of olefin metathesis in organic chemistry[1].

Many efforts in the design of ruthenium metathesis catalysts have focused on improving both activity and latency of the Grubbs' catalyst **1**, by modifying its neutral donor ligands resulting in a wide variety of ruthenium catalysts[2,3]. This study is focused on catalysts containing a Schiff base indenylidene ligand, as these have been found to overcome stability problems common to other catalysts[4]. Furthermore, Dunbar[5] recently developed a reversible inhibition/activation protocol using N-donor ligands and H_3PO_4 for controlling ring opening metathesis polymerization (ROMP) reactions, making Schiff base phenylindenylidene ligands promising for developing latent catalysts[6]. Finally, these catalysts can be prepared safely on a large scale using only commercial reagents[7,8,9] in contrast to complexes based on the expensive Grubbs' precursor **1**.

In this study we describe the NMR characterization of three novel Ruthenium Schiff base phenylindenylidene catalysts **4.1-4.3** obtained via straightforward synthesis and purification methods. This was motivated by the fact that in spite of their importance, little information is available on the solution behaviour of such complexes[10]. In addition, the chemical shift is very sensitive to both conformational and subtle stereo electronic effects. Therefore, provided such NMR spectroscopic data is obtained from a sufficiently large collection of complexes, correlations with the catalytic activity may ultimately be inferred from analysis of the NMR spectroscopic data. Our results for **4.1-4.3** includes presented here includes complete ^{1}H and ^{13}C resonance assignments for all complexes and a qualititive description of chemical exchange processes from EXSY spectra. As each complex was present in two rotameric forms, additional analysis of NOE data was performed to unambiguously assign both conformations. Furthermore, chemical shift reference data was obtained from literature that could prove of interest for a more straightforward assignment of asymmetric Ru indenylidene catalysts.

Results and Discussion

Synthesis of Ru-indenylidene complexes bearing salicylaldimine ligands 4.1-4.3

Treatment of stoichiometric amounts of a toluene solution of dichlorido(pyridine)(3-phenyl-1*H*-inden-1-ylidene)(1,3-dimesitylimidazolidin-2-ylidene)ruthenium(II) (**2.1**)[2,8], which is a robust and versatile precursor, with thallium salts of 2-[(2,6-dimethyl-phenylimino)-methyl]-4-nitro-phenolate (**3.1**), 2-[(2,6-dimethyl-phenylimino)-methyl]-phenolate (**3.2**) or 2-[(2,6-dimethyl-phenylimino)-methyl]-4-methoxy-phenolate (**3.3**) effected complete conversion to Schiff base containing ruthenium indenylidene complexes chlorido(3-phenyl-1*H*-inden-1-ylidene)(1,3-dimesitylimidazolidin-2-ylidene)(2-[(2,6-dimethyl-phenylimino-κ*N*)-methyl]-4-nitro/H/methoxy-phenoxido)ruthenium(II) (**4.1-4.3**) after 15 min at room temperature, as judged by ^{1}H NMR analysis. Removal of the TlCl by-product was effected by filtering the reaction mixture through Celit. After evaporation of the solvent and precipitation with cold pentane, complexes were isolated as red-brown powders in high yield (98%) (Scheme 1).

>>> Scheme 1. Left: Grubbs' catalyst **1**; Right: Synthesis of phenylindenylidene-salicylaldimine complexes **4.1-4.3**. <<<

The initial analysis of the ^{1}H NMR spectra of **4.1-4.3** reveals two distinct sets of signals. Most notably, the resonance of H29 (Scheme 2) in the indenylidene moiety that is generally well recognizable as it gives rise to the only singlet devoid of small long range couplings, appears twice and with 55:45 intensity ratio in each compound investigated. In the ^{13}C NMR spectrum, low field quaternary resonances associated with the carbene atoms of the indenylidene (Ru=CR) and NHC moieties, as well as the imine and C-O of the salicylaldimine ligand, appear in pairs. (Figure 1a). As will be described in more detail below, further NMR analysis revealed that compounds **4.1-4.3** are mixtures of two rotational isomers resulting from a high barrier to the rotation of the indenylidene group around the ruthenium-carbon bond (Scheme 3).

All salicylaldimine complexes **4.1-4.3** reveal an impressive stability to air and heat. They tolerate storage for months as solids in ambient conditions, including contact with air, without suffering any degradation or change in isomer ratio. In solution, no decomposition was observed and the isomer ratio was preserved over a period of months. Unfortunately, all attempts to obtain crystals of **4.1-4.3** of sufficient quality or to separate the isomers failed, further highlighting the importance of conformational analysis by NMR.

>>> Scheme 2. Arbitrary numbering scheme of compounds **4.1-4.3** used in the NMR analysis (Table 1). <<<

>>> Scheme 3. Representation of both rotational isomers of complexes **4.1-4.3** (left) and complexes **2.1-2.6** (right) used as chemical shift references.<<<

Structure validation and conformation of 4.1-4.3

The complete ^{1}H and ^{13}C resonance assignment for each compound is collected in Table 1. It was achieved using a combination of 2D ^{1}H-{^{1}H} COSY, TOCSY, ROESY and ^{1}H-{^{13}C} HSQC, HSQC-TOCSY and HMBC spectra, complemented with 1D ^{1}H, ^{13}C and DEPT spectra[11]. In the following, only the spectral assignment of **4.1a** and **4.1b** is described in detail, as that of **4.2** and **4.3** was highly similar. The term NOE will be used for describing correlations from direct dipole couplings observed in the ROESY spectra. The presence of the diverse aromatic functionalities in addition to the use of benzene as solvent was the key in facilitating the assignment process by dispersing the ^{1}H resonances. For instance, of the 16 methyl resonances contributed by the SIMes (1,3-dimesitylimidazolidin-2-ylidene) and salicylaldimine ligand in both rotational isomers of **4.1**, only two were found to be overlapping. The arbitrary numbering scheme, depicted in Scheme 2 is used throughout.

The assignment approach initially focussed on grouping the ^{1}H and ^{13}C resonances belonging to the same ligand (SIMes, salicylaldimine and indenylidene). Next these were assembled into the rotational isomers **4.1a** and **4.1b** using the ^{1}H resonance intensity ratio (55:45) and interligand NOEs within each rotational isomer as a guide. The DEPT135 spectrum provides an unambiguous starting point for the analysis as the four methylene carbon resonances can only be contributed by the SIMes bridgehead (C10, C11) of each isomer. The associated protons are identified from the HSQC spectrum, which in turn can be linked to their respective C21 carbene atoms at 216.4 (a) and 216.8 ppm via $^{3}J_{HC}$ correlations in the HMBC. The assignment of the SIMes ligand is performed by analyzing long range correlations from the methyl ^{1}H resonances to the SIMes bridgehead and carbene carbon atoms. It is noteworthy that such contacts, while weak, can even be seen to the methyls in *para*-position. Thus the methyl signals originating from the SIMes and the Schiff base can be distinguished. NOEs linking the mesitylene *ortho* methyl groups with the bridgehead methylenes allows discriminating these from the *para* methyl groups. Furthermore, it can be deduced from a model of SIMes that a NOE contact mutually involving one *ortho* methyl group from opposing mesitylene rings can only be expected when these are not related by the local C_2 symmetry, i.e. only NOE contacts between H7-H18 and H8-H19 can be observed. Using this as a guide, the different *ortho* methyl groups of each ring can be discriminated. The complete assignment of all SIMes methyls finally allows distinguishing the bridgehead methylene functions via the $^{3}J_{HC}$ correlations mentioned above at the outset of the analysis. The assignment of the remaining aromatic SIMes protons was tackled using an integrated analysis of the TOCSY, ^{1}H-{^{13}C} HSQC and HMBC spectra (Table 1).

In the ROESY spectrum, the C_2 related methyl groups in complex **4.1** are connected by exchange cross peaks (Figure 1c). These are easily recognized as they demonstrate opposite sign with respect to the abovementioned NOEs (Figure 1c). Their observation provides independent validation of the methyl group assignment. Indeed, such exchange peaks can only arise from a hindered rotation around the Ru-C21 bond (which coincides with the C_2 symmetry axis of the SIMes ligand) that is slow on the NMR timescale. From the weak exchange cross-peak intensity, the lifetime of the rotamers can be estimated to be on the order of seconds. The weaker intensity of such exchange peaks in **4.1b** indicates a higher rotational energy barrier than for **4.1a**. (see also Supporting Information) Two other hindered rotations around N-C1 and N-C12 could not be observed in the ROESY spectrum as exchange peaks between Me7-Me8 and Me18-Me19.

>>> Figure 1. a) ^{13}C NMR spectrum of catalyst 4.1a in C_6D_6, at 22°C. Only the low field part of the spectrum is shown; b) Extract from the ^{1}H-{^{13}C} HMBC spectrum of compound 4.1. Correlations to the C22 carbene atoms in both isomers are indicated; c) Aliphatic section of the 300 ms ^{1}H Off-Resonance ROESY spectrum of 4.1. Cross-peaks arising from exchange phenomena (blue) are annotated above the diagonal, those arising from NOE interactions (black) are indicated below the diagonal. <<<

The assignment of the Schiff base *ortho*-methyl-substituted phenyl can be performed by noticing the three spin TOCSY pattern involving its aromatic protons (6.7-7.0 ppm) for each isomer. By analyzing the ROESY spectrum for contacts involving each of the *ortho*-methyls, the *meta* and *para* positions can be distinguished. The identity of the attached carbon atoms were derived either from the HSQC or HSQC-TOCSY spectra. No exchange cross-peaks are apparent between the *ortho*-methyls within the Schiff base ligand (Me41-Me42) indicating a considerable rotational energy barrier around the N-C35 bond. Long range correlations originating from the *ortho*-methyl protons to quaternary carbon atoms were used to identify the *meta*-positioned carbon atoms (129-131 ppm) and the *ipso*-atoms (150.4 ppm, 151.2 ppm). Correlations linking a CH-type (from DEPT135) carbon atom at 167.2 ppm with two resolved singlet ^{1}H resonance in the HSQC allow unambiguous assignment to the isochronous imine carbons (C_{43}) of the Schiff base of both isomers. Protons on the nitro-containing aromatic ring can be assigned from ROESY, HMBC and HSQC-TOCSY spectra. NOE contacts can be found between H45 and both methyl groups of the Schiff base ligand as well as with the imine proton. Furthermore H45 can be correlated with H47, which in turn can be linked to H48 via strong COSY/TOCSY cross-peaks, thus validating the assignment. For each isomer, long range correlations from these protons were found to quaternary carbon atoms (~173.4 ppm, ~135.6 ppm, ~116.8 ppm,) but no unambiguous assignment could be made based on the NMR data alone. Using chemical shift calculations (ChemDraw 7.0, Cambridge Soft) these resonances could be assigned to the *ortho*-, *meta*- and *ipso*-carbon atoms with respect to the imine substituent, respectively.

For the analysis of the indenylidene ligand, the quaternary carbene atom of each isomer, located at 296.8 (**4.1a**) and 295.3 (**4.1b**) ppm respectively was chosen as a starting point given the conspicuous ^{13}C frequency. Each carbene features two long-range correlations (Figure 1b) that can only arise from protons H23 (6.51 ppm, 7.71 ppm) and H29 (8.87 ppm, 7.94 ppm). As all four resonances are well-resolved, these could readily be distinguished by their multiplet fine structure. Further assignments of the H26-H29 spin system can be easily performed by analyzing the HSQC-TOCSY and ROESY spectra. Long range correlations were then used to assign the quaternary carbon atoms in the main aromatic ring system. The attached phenyl ring was characterized using ROESY spectroscopy to reveal NOE contacts between H26 and H32 for both isomers. Further analysis of the phenyl spin system was again performed by HSQC-TOCSY. As both *ortho*- and *meta*-protons are isochronous, it can be concluded that the ring flip of the phenyl ring is fast on the NMR time scale.

To complete the assignment the ligands belonging to the same isomer of **4.1** were identified from interligand NOE contacts. As all methyl groups are resolved, possible contacts of these methyls, involving two of the ligands, with the H23 and H29 of the indenylidene ligand were investigated. In each isomer, numerous contacts can be found that allow placing one mesityl moiety of the SIMes ligand over the indenylidene ligand (Scheme 4). This necessarily places the other mesityl moiety in proximity to the nitro substituted phenyl ring of the salicylaldimine ligand. This is validated by clear NOEs involving Me_8 of the SIMes and H47 and H48 of the salicylaldimine. The complete ^{1}H assignment of **4.1a** and **4.1b** together with a subsequent more in-depth analysis of the respective interligand NOE contacts, allow establishing that both isomers are indeed related by a 180 degree flip of the indenylidene ligand around the Ru=C bond (Scheme 3). First, the analysis of ^{1}H and ^{13}C chemical shift differences between both isomers shows that the SIMes mesitylene ring orientated away from the indenylidene ligand and close to the nitro-containing salicylaldimine phenyl moiety experience similar magnetic environments in both isomers. On the other hand, large differences in chemical shifts are observed for the other SIMes mesitylene ring, the indenylidene and the *ortho*-methyl phenyl of the Schiff base. These observations suggest the phenylindenylidene ligand is the source of the isomerism.

>>> Scheme 4. Schematic representations of the most important inter-ligand spatial interactions.<<<

Further proof is obtained by thorough analysis of the NOE connectivities. For **4.1a** and **4.1b** together, 156 resolved NOE cross-peaks were assigned resulting in 78 non-trivial spatial connections of which 39 are of inter-ligand nature. For both isomers, the presence of Me8-H43, Me8-H45, Me8-H47, Me9-H43 and Me9-H45 NOE contacts in addition to the absence of Me7-H43, Me7-H45 and Me7-H47 contacts, indicate that the relative position of the SIMes phenyl ring to the Cl-Ru-O plane is such that Me7 is positioned over the chlorine ligand, while Me8 is located over the Schiff base ligand. (see Supporting Information for a detailed list) NOE contacts linking Me18 and Me19 to the indenylidene ligand can be used for analysis of the indenylidene conformation. In **4.1a**, intense H23-Me19, H32-Me19, H32-H14 and H29-Me18 NOE contacts are observed. This proves the indenylidene ligand is orientated such that H23 is positioned under Me19 and H29 under Me18 as schematically shown in Scheme 4. A different set of NOE contacts is observed for the second isomer, including H23-Me18, H32-Me18, H32-H16 and H29-Me19. These correlations are clearly related to isomer **4.1b** obtained by a 180 degree rotation of the indenylidene ligand with respect to **4.1a**.

Although a thorough investigation of NOE correlation data provides the information necessary to distinguish between both different rotameric isomers present in solution, such analysis is quite tedious. To facilitate the assignment process of future asymmetric ruthenium phenylindenylidene catalysts, the potential to use ^{1}H and ^{13}C chemical shifts alone to assign the different rotamers was investigated. From Table 1, only H23, H29, C23 and C29 show significant chemical shift differences between both isomers to suit this purpose. This is even more apparent when these chemical shifts are presented in a HSQC plot (Figure 2) and compared to chemical shifts of six symmetric reference complexes **2.1-2.6** obtained from literature[10]. In these complexes, both H23 and H29 oppose a chlorine ligand (Scheme 3) whereas in **4.1a-4.3a** only H29 opposes the chlorine and H23 the Schiff base ligand. The inverse holds for **4.1b-4.3b**. This conformational difference is clearly reflected in Figure 2, as the H23-C23 resonances of **4.1b-4.3b** and the H29-C29 resonances of **4.1a-4.3a** coincide with those of **2.1-2.6**. Thus, the analysis of these resonances allows for a straightforward assignment of the different rotameric isomers.

Furthermore, no exchange cross-peaks could be identified between indenylidene resonances of the different rotamers **a** and **b** using ROESY mixing times up to 400 ms. Thus, the lifetime of the rotational isomers must exceed the second time scale. Similar arguments regarding the conformation and the identity of the rotational isomerism hold for the complexes **4.2** and **4.3**.

>>> Figure 2. Schematical representation of the H23 and H29 HSQC resonances of **4.1-4.3** in comparison with those of **2.1-2.6**.<<<

Conclusions

In this work new second-generation Ru-indenylidene complexes **4.1, 4.2** and **4.3** have been synthesized and characterized. They possess air and moisture stability allowing a shelf life time of months without any decomposition. Using NMR the presence of a 55:45 mixture of two rotational isomers **a** and **b**, related via a 180 degree flip along the Ru=C indenylidene bond and separated by a high activation barrier could be established. Rotational exchange kinetics on a second timescale around the

local C_2 axis of the Ru-C21 bond could also be established as well as a fast exchange process due to rotation around the C24-C31 bond. No exchange peaks corresponding to rotations around N-C1, N-C12 or N-C35 could be observed. (see also Supporting Information) The unambiguous full resonance assignment and NOE based structural information of each isomer could provide an avenue to future calculations of the electronic properties of these complexes. Additionally, a straightforward method based on chemical shift references was found proficient for discriminating between the rotamers present and may provide a suitable and more convenient avenue for the assignment of asymmetric indenylidene ruthenium complexes in the future.

Experimental

General remarks

All synthetic manipulations were performed under argon (oxygen free) using the Schlenk technique. Argon was dried by passage through drierite. Tetrahydrofuran (THF), toluene, dichloromethane, benzene-d6 and chloroform-d, dried by standard methods, were degassed by a standard three freeze-pump-thaw cycles. Catalyst **2.1** was prepared according to the reported methods [7,10]. ^{1}H NMR and ^{13}C spectra were recorded on a Bruker Avance 500 MHz spectrometer. Chemical shifts (δ) are given in parts per million and were referenced according to the C_6D_5H resonance. Kinetic experiments were conducted on a Varian Unity 300 MHz NMR spectrometer. Elemental analyses were performed at Chevron Technology, Ghent.

Preparation of Schiff-Base Ligands.

The condensation of an appropriate derivative of salicylaldehydes with 2,6-dimethylamine was carried out with stirring in isopropyl alcohol at 80 °C for 24 h. Upon cooling to 0 °C, a yellow solid precipitated from the reaction mixture. The solid was filtered, washed with cold ethyl alcohol, and then dried *in vacuo* to afford the desired salicylaldimine ligand in excellent yields.

Preparation of Thallium Salts **3.1-3.3**

A solution of thallium ethoxide in benzene or THF (5 mL) was added drop wise at room temperature to a solution of Schiff bases in benzene, toluene or THF (10 mL) (Note: the solution of thallium ethoxide in THF was filtered through a plug of glass wool to remove any impurities). Immediately after the addition, a pale yellow solid is formed and the reaction mixture was stirred for 2 h at room temperature. Filtration of the solid under a nitrogen or argon atmosphere yielded the thallium salts **3.1-3.3** in quantitative amounts. These salts were used in the next step without further purification.

Preparation of Schiff-Base-Substituted Ru Complexes **4.1-4.3**

To a solution of Ru complex **2.1** in THF (5 mL) was added a solution of thallium salts **3.1-3.3**. The reaction mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the residue was dissolved in a minimal amount of toluene and cooled to 0 °C. The thallium chloride (the by-product of the reaction) was removed via filtration. The filter residue was then washed with cold toluene and the filtrate was evaporated. The solid residue was recrystallized from CH_2Cl_2/pentane (-70 °C) to give the Schiff-base-substituted Ru complexes in good yields (>98 %) as brown-orange or red solids.

NMR-investigation of catalyst **4.1-4.3**

Samples are prepared using a screw-capped NMR tube, under inert Ar atmosphere using a solution of approximately 35 mM of **4.1-4.3** in benzene-d6. All experiments were performed on a Bruker DRX spectrometer equipped with a 5 mm TXI-Z probe and operating at a ^{1}H and ^{13}C frequency of 500.13 MHz and 125.77 MHz respectively. The temperature used was 298 K throughout. All 1D and 2D experiments were performed using pulse sequences available from the standard Bruker library[11]. Gradient enhanced sequences were used for the COSY and heteronuclear 2D experiments. TOCSY mixing times in the 40 to 100 ms range were used. The HMBC spectra were optimized for 3 and 8 Hz long range $^nJ_{CH}$ coupling. Off-resonance ROESY spectra with a tilt angle of 60° and 200 to 400 ms mixing time were recorded[12] to distinguish NOE and exchange correlations. Typically, 2D spectra consisted of 512 t_1 increments of 8-32 scans each, sampled with 4k points. Prior to Fourier transformation, the data was zero-filled along t_1 and suitably apodized using a squared cosine bell in both dimensions, except for the COSY and HMBC where a squared sine bell was used. ^{1}H chemical shifts were obtained using 1D proton NMR if resolved or deduced from 2D NMR cross-peaks otherwise. ^{13}C chemical shifts were obtained from the 1D ^{13}C spectrum. All processing and analysis was performed using Bruker's TopSpin 1.3 software suite.

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Atom	**4.1a**		**4.1b**		**4.2a**		**4.2b**		**4.3a**		**4.3b**	
Label	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	-	133.5	-	133.0	-	134.0	-	133.4	-	134.0	-	133.6
2	-	138.4	-	138.4	-	138.8	-	138.8	-	138.6	-	138.6
3	6.51	128.9	6.43	128.9	6.54	129.0	6.49	128.8	6.58	129.0	6.53	128.8
4	-	138.9	-	138.9	-	138.2	-	138.2	-	138.2	-	138.2
5	6.87	130.2	6.83	130.3	6.93	130.0	6.89	130.1	6.93	130.0	6.90	130.1
6	-	139.9	-	139.9	-	139.9	-	139.9	-	139.9	-	139.9
Me7	2.60	20.2	2.60	20.2	2.67	20.2	2.66	20.2	2.67	20.2	2.66	20.2
Me8	2.34	18.2	2.35	18.4	2.51	18.2	2.51	18.2	2.51	18.2	2.52	18.2
Me9	2.04	20.6	1.98	20.6	2.09	20.6	2.04	20.5	2.10	20.6	2.04	20.5
10	3.40/3.20	50.4	3.40/3.20	50.4	3.40	50.5	3.40	50.5	3.39	50.6	3.39	50.6
11	3.40/3.20	51.5	3.40/3.20	51.5	3.25	51.3	3.25	51.3	3.26	51.2	3.26	51.2
12	-	136.2	-	136.2	-	136.6	-	136.5	-	136.5	-	136.6
13	-	135.7	-	136.0	-	135.9	-	136.0	-	136.1	-	136.2
14	6.46	129.0	6.06	128.5	6.45	128.7	6.09	128.4	6.46	128.9	6.10	128.4
15	-	137.1	-	137.0	-	136.8	-	136.8	-	136.8	-	136.9
16	5.99	129.2	6.39	129.3	6.03	129.0	6.42	129.1	6.02	128.9	6.42	129.1
17	-	137.1	-	137.0	-	136.9	-	136.8	-	137.0	-	137.1
Me18	1.97	18.4	2.18	18.4	2.02	18.3	2.22	18.3	2.03	18.3	2.23	18.3
Me19	2.32	18.0	2.19	18.4	2.39	17.8	2.31	18.2	2.41	17.8	2.32	18.2
Me20	1.72	20.6	1.76	20.6	1.77	20.7	1.78	20.7	1.76	20.6	1.78	20.6
21	-	216.4	-	216.8	-	217.7	-	218.1	-	217.9	-	218.2
22	-	296.8	-	295.3	-	294.0	-	291.7	-	293.3	-	291.2
23	6.51	133.3	7.71	139.4	6.62	133.5	7.90	139.0	6.61	133.4	7.95	138.9
24	-	136.6	-	136.5	-	136.9	-	137.2	-	137.3	-	137.3
25	-	145.1	-	143.2	-	145.9	-	143.3	-	146.3	-	143.4
26	6.97	115.7	7.01	116.3	7.02	115.5	7.03	116.0	7.03	115.6	7.03	116.0
27	7.02	127.7	7.01	127.6	7.04	127.1	6.99	126.8	7.04	127.1	6.96	126.8
28	6.92	128.7	7.01	128.2	6.98	128.4	6.98	128.3	7.00	128.4	6.98	128.2
29	8.87	129.9	7.94	125.5	9.10	129.8	8.15	125.8	9.15	129.9	8.11	125.7
30	-	139.3	-	139.9	-	140.0	-	140.0	-	139.9	-	139.9
31	-	137.8	-	135.8	-	136.5	-	135.2	-	136.4	-	135.4
32	7.66	126.2	7.69	126.3	7.63	126.1	7.77	126.3	7.64	126.1	7.77	126.4
33	7.11	128.9	7.15	129.0	7.08	128.7	7.15	128.9	7.06	128.7	7.16	128.9
34	7.19	127.9	7.26	127.7	7.18	127.2	7.26	127.2	7.16	127.1	7.25	127.2
35	-	150.4	-	151.2	-	151.6	-	152.0	-	152.0	-	152.7
36	-	130.1	-	129.3	-	130.6	-	129.9	-	130.8	-	129.9
37	6.71	127.6	6.71	127.8	6.74	127.8	6.74	127.9	6.79	127.7	6.79	127.9
38	6.90	125.5	6.87	125.7	6.89	125.0	6.86	125.1	6.92	125.0	6.89	125.1
39	6.98	126.9	6.97	126.9	7.00	126.8	7.00	126.9	7.04	126.8	7.03	126.9
40	-	131.7	-	132.9	-	132.1	-	132.5	-	132.3	-	132.7
Me41	1.82	19.4	1.84	19.5	1.83	19.3	1.87	19.4	1.85	19.2	1.88	19.3
Me42	1.09	16.8	1.33	17.3	1.23	16.9	1.41	17.2	1.27	17.1	1.46	17.3
43	6.78	167.2	6.76	167.2	7.32	167.2	7.36	167.3	7.23	166.2	7.25	166.1
44	-	116.9	-	116.8	-	118.6	-	118.0	-	116.6	-	116.0
45	7.56	135.0	7.54	135.0	6.60	137.0	6.60	137.1	5.88	115.0	5.87	115.1
46	-	135.6	-	135.6	7.19	122.7	7.19	122.7	-	148.4	-	148.4
Me46	-	-	-	-	-	-	-	-	3.22	54.9	3.25	54.9
47	8.00	129.0	8.07	128.8	7.20	133.9	7.23	133.9	7.15	125.8	7.18	125.6
48	6.71	122.7	6.77	122.6	6.35	113.4	6.38	113.4	7.12	123.8	7.14	123.7
49	-	173.7	-	173.4	-	170.0	-	169.8	-	166.0	-	165.6

Table 1. ^{1}H and ^{13}C assignments of the rotational isomers of Ru-indenylidene complexes **4.1-4.3** bearing salicylaldimine ligands. Arbitrary numbering scheme is depicted in Scheme 2. Chemical shifts are quoted in ppm with respect to residual C_6D_5H as secondary internal reference.

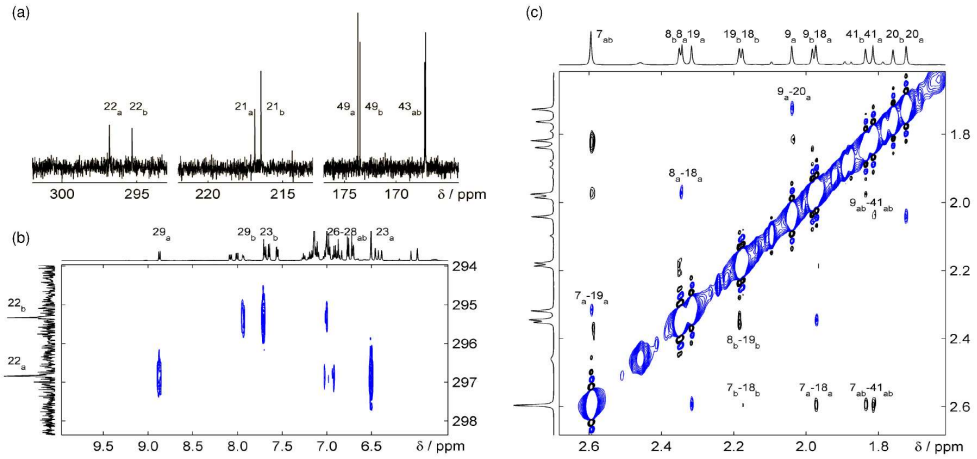
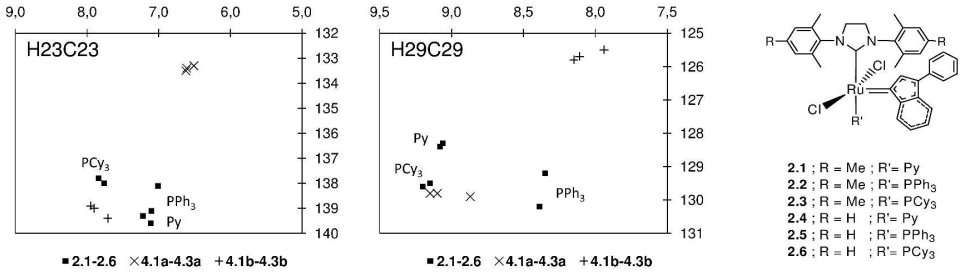
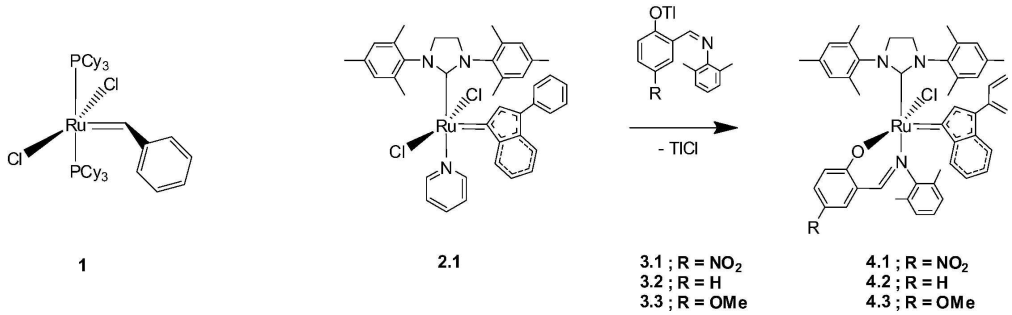


Figure 1. a) 13C NMR spectrum of catalyst 4.1a in C6D6, at 22°C. Only the low field part of the spectrum is shown; b) Extract from the 1H-{13C} HMBC spectrum of compound 4.1. Correlations to the C22 carbene atoms in both isomers are indicated; c) Aliphatic section of the 300 ms 1H Off-Resonance ROESY spectrum of 4.1. Cross-peaks arising from exchange phenomena (blue) are annotated above the diagonal, those arising from NOE interactions (black) are indicated below the diagonal.
233x116mm (600 x 600 DPI)

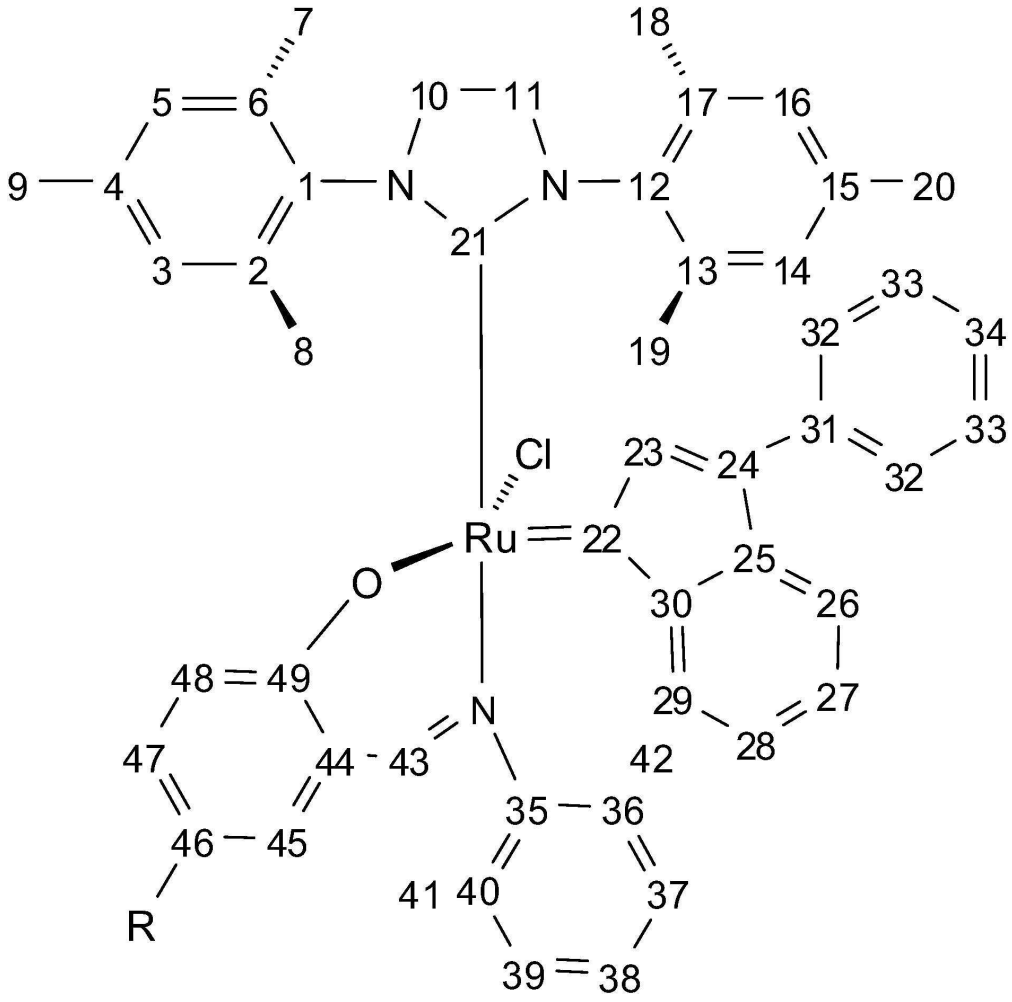


Schematical representation of the H23 and H29 HSQC resonances of 4.1-4.3 in comparison with those of 2.1-2.6.
228x71mm (600 x 600 DPI)

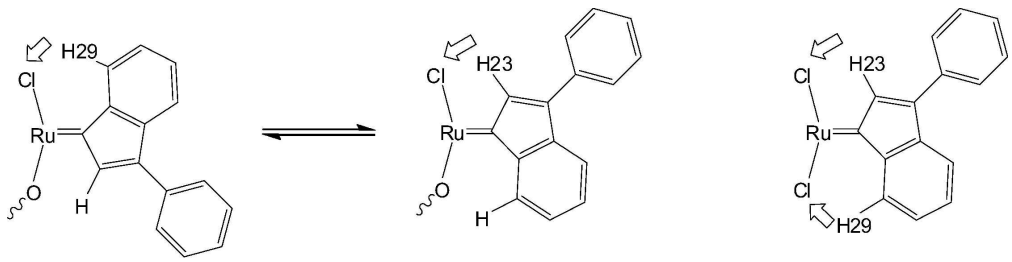


1 2.1 3.1 ; R = NO_2 3.2 ; R = H 3.3 ; R = OMe 4.1 ; R = NO_2 4.2 ; R = H 4.3 ; R = OMe

Scheme 1
189x59mm (600 x 600 DPI)

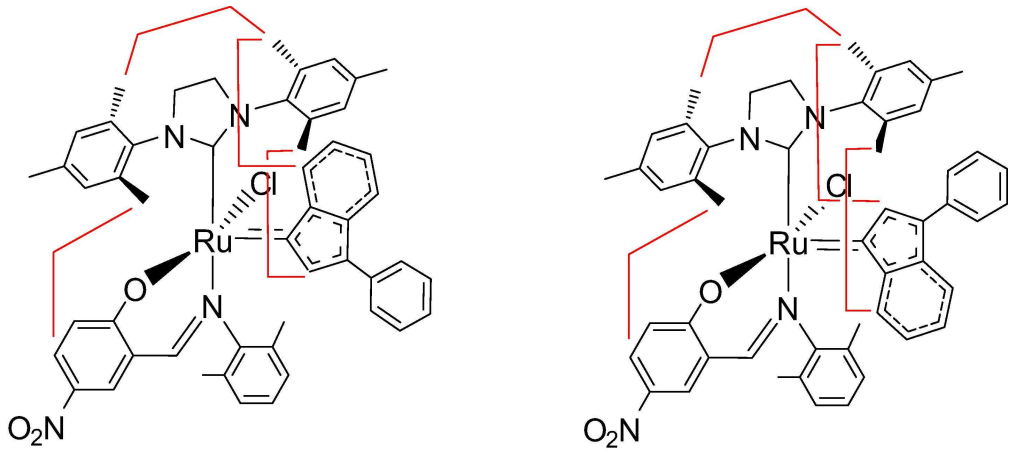


Scheme 2
79x80mm (600 x 600 DPI)



4.1a - 4.3a **4.1b - 4.3b** **2.1 - 2.6**

Scheme 3
189x62mm (600 x 600 DPI)



4.1a **4.1b**

Scheme 4
121x72mm (600 x 600 DPI)