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Variable temperature ^{1}H NMR studies on Grubbs catalysts

Margaret M. Gallagher, A. Denise Rooney *, John J. Rooney

Department of Chemistry, National University of Ireland Maynooth, Maynooth, Co. Kildare, Ireland

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Abstract

Variable temperature ^{1}H NMR studies were conducted to investigate whether steric congestion is influencing the structural rigidity of $(IMesH_2)(PCy_3)(Cl)_2Ru{=}CHPh$ ($IMesH_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) in solution. It was shown that both mesityl ligands rotate at about the same rate around the N-Mesityl bonds in the $IMesH_2$ ligand and that changing the solvent does not significantly alter this rotation. It was found that the increased steric congestion in $(IMesH_2)(PCy_3)(Cl)_2Ru{=}CHPh$ compared to $(PCy_3)_2(Cl)_2Ru{=}CHPh$ does affect the rates of rotation around the $C_{alkylidene}$–Ph bonds. Unusual chemical shift positions were also observed in the low temperature ^{1}H NMR spectrum for the aromatic proton signals for $(IMesH_2)(PCy_3)(Cl)_2Ru{=}CHPh$ and $(PCy_3)_2(Cl)_2Ru{=}CHPh$.

Keywords: Grubbs catalysts; Variable temperature NMR; Rotamers

1. Introduction

There have been extensive studies carried out to determine the reactivity and properties of the Grubbs ruthenium based metathesis catalysts **1** and **2** (Fig. 1). One factor about their relative reactivities that has emerged is that **1** undergoes phosphine exchange two orders of magnitudes faster than **2** [1]. This means that although **2** shows higher metathesis activity than **1** it is a slower initiator [2]. This is surprising since the catalyst was originally designed to undergo phosphine dissociation more rapidly by substituting the sterically bulky and highly basic $IMesH_2$ ligand for one of the PCy_3 ligands. The lower ability of **2** to initiate compared to **1** has been observed in several studies. For example, although **2** has been shown to have better activity than **1** it has been found that this activity is very temperature dependent. Wagener has reported that when the two catalysts are compared, **2** promotes acyclic diene metathesis (ADMET) at a significantly greater rate than **1** at temperatures of 45–75 °C. However, at 30 °C this trend is reversed [3]. They also noted that at all temperatures **2** is slower to reach the maximum rate of metathesis compared to **1**. We noted that at a temperature of 0 °C, **2** would not catalyse ring opening metathesis polymerisation of norbornene, whereas **1** gave quantitative amounts of polymer. At room temperature they both yielded 100% polymer [4].

Cavallo has carried out an extensive theoretical analysis of the Grubbs catalysts [5]. He reported that in **2** the molecule is sterically crowded compared to **1**. This steric crowding influences the rates of initiation and propagation with this catalyst. In initiation, when the phosphine ligand is dissociated, the Ru–C bond of the $IMesH_2$ ligand becomes shorter creating steric hindrance between the mesityl ligands and the alkylidene group and chlorine atoms in the 14-electron intermediate. This steric pressure is relieved when either an incoming olefin or a phosphine is coordinated in the vacant site and the $IMesH_2$ ligand is then further away from the Ru centre. Cavallo states that the 'greatest affect of the Mes ring is to exert steric hindrance on the alkylidene ligand'. Hence, due to the steric pressure, catalysts of the type of **2** do not promote initiation, but they promote metathesis reactions and stabilise the metallacycle intermediate.

* Corresponding author. Tel.: +353 1 7083616; fax: +353 1 7083815.
E-mail address: ad.rooney@nuim.ie (A.D. Rooney).

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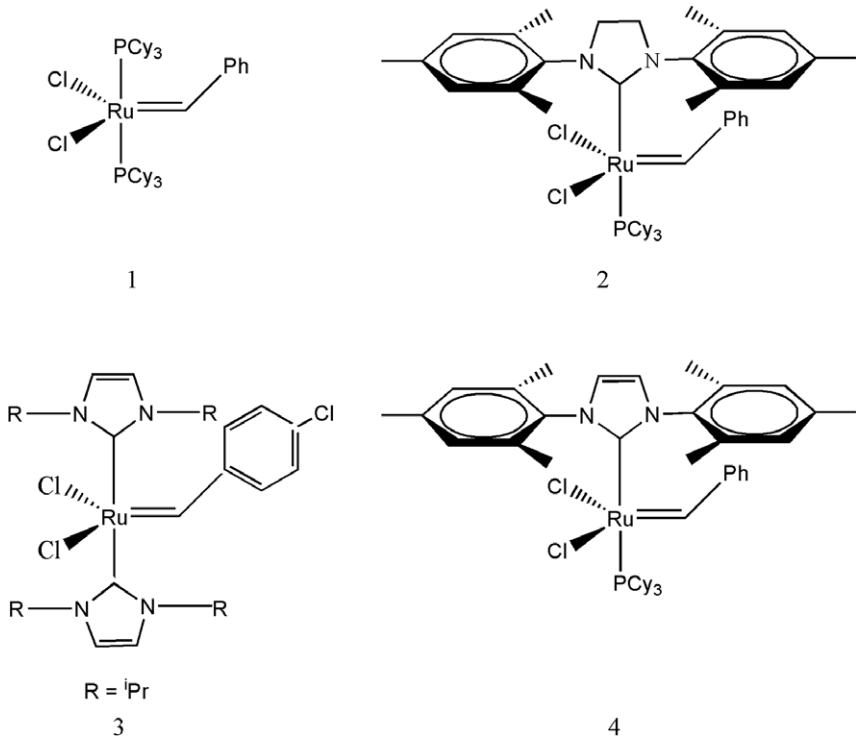

Fig. 1. Well-defined ruthenium catalysts.

In the current study, we set out to investigate what effect lowering the temperature had with regard to the conformers of the catalysts and to measure the barriers to conformational change in **2** using ^{1}H NMR spectroscopy. In detail we set out to investigate whether the activation barriers for rotation around the N-Mes bonds on the $IMesH_2$ ligand are different, as this would be an indication of steric hindrance between the Mes group and the alkylidene ligand, the influence of solvent on this rotation and a comparative study of the activation barrier to the rotation around the $C_{alkylidene}$–Ph bond for catalysts **1** and **2**. We also looked for evidence of π–π stacking between the benzylidene carbene unit and the Mes substituent on the $IMesH_2$ for **1** in solution which has been observed in the X-ray structures of these complexes [6].

There have been some previous studies carried out using NMR spectroscopy to investigate the barriers to rotation in this class of molecule. Herrmann and co-workers studied complexes of the type **3** shown in Fig. 1 [7]. They proposed that there was free rotation around the Ru–$C_{alkylidene}$ bond at room temperature while there was hindered rotation of the Ru–C bond of the $IMesH_2$ ligand. As this difference in barrier to rotation is not reflected in the bond lengths for complex **3** shown in Fig. 1 (the Ru–C bond lengths for the alkylidene is 1.821(3) Å and for the *N*-heterocyclic carbene is 2.107(3) Å) they suggested that steric hindrance is the only reasonable explanation for this phenomenon. Further studies carried out by Fürstner and co-workers looking at the line shape of the signals in the room temperature ^{1}H NMR spectra associated with the mesityl groups of complex **4** (Fig. 1) recorded in C_6D_6 and CD_2Cl_2 also found that there was restricted rotation of the IMes ligand around the C–Ru bond and interestingly that there was also restricted rotation of the mesityl groups around the N-Mes bond [8]. They determined that the barrier to the latter rotation was approximately 3.5 kJ mol^{-1} higher in CD_2Cl_2 than in C_6D_6. Rotation around the $C_{alkylidene}$–Ph bond has been studied by Grubbs for **1** [9]. They determined the $\Delta G^{\pm}$ for the rotation around the $C_{alkylidene}$–Ph to be 40.8 ± 2.5 kJ mol^{-1} in CD_2Cl_2.

2. Experimental

Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (**1**), and benzylidene-[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-dichloro-(tricyclohexylphosphine)-ruthenium (**2**), were purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker Avance 300 spectrometer that operated at 300 MHz for ^{1}H. Low temperature NMR experiments were carried out by cooling the probe with liquid nitrogen blow off. For the variable temperature studies the sample was placed in the probe and allowed to equilibrate to the required temperature for 20 min prior to shimming. The chemical shift was standardised using the residual protonated signal of the solvent or to the signal for tetramethylsilane. The spectra were processed using Bruker Xwin NMR software.

3. Results and discussion

3.1. ^1H NMR investigations of the barriers to rotation in 1 and 2

There are a variety of ways in which **2** can rotate to produce different conformers Fig. 2. The groups on **2** are denoted in this paper as shown in Fig. 3. An identical notation is used to identify the hydrogen atoms on the phenyl ring of **1**.

It should be stated for clarity that the variable temperature spectra for both complexes exhibited evidence for fluxionality associated with the phosphine ligands, however, the ^1H NMR signals associated with these moieties were broad and were too complex to interpret.

3.2. Assignment of the methyl and H signals for the Mes rings of 2 in $CDCl_3$ as the temperature is varied

Assignments of the signals for the room temperature ^1H NMR spectra of **2** and **1** in CD_2Cl_2 have been made previously by Grubbs and co-workers [10,11]. We based our assignments of the signals in the spectra recorded at high and low temperature on these assignments and on the chemical shifts of the signals and also on which signals coalesced to form an averaged signal in the high temperature spectra.

At low temperatures, −50 °C in $CDCl_3$, the complex is 'frozen' into one conformer in which the mesityl rings are held in a fixed geometry. In the ^1H NMR recorded at −50 °C (Fig. 4) six singlet signals which each integrate as 3H's are observed in the region 1.90–2.81 ppm. These are assigned as arising from the Me signals on the Mes rings. The proposed assignment for each Me is given in Table 1. It is suggested that in the spectrum recorded at −50 °C that the signals due to the methyl groups on the ring which lies over the alkylidene ligand come at slightly lower chemical shift than the signals for the corresponding methyl groups on the other ring. This occurs because of the interaction between the π systems of the Mes ring with the alkylidenes phenyl ring. This interaction has been shown in the X-ray crystal structure of this compound as the two rings are nearly co-planar in the solid state structure [6].

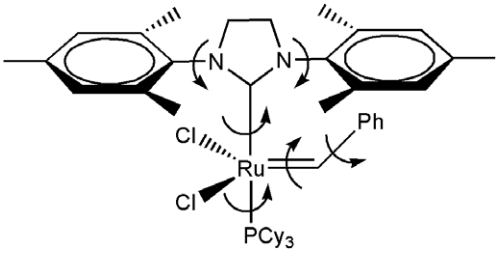

Fig. 2. Illustration of the possible rotations within **2**

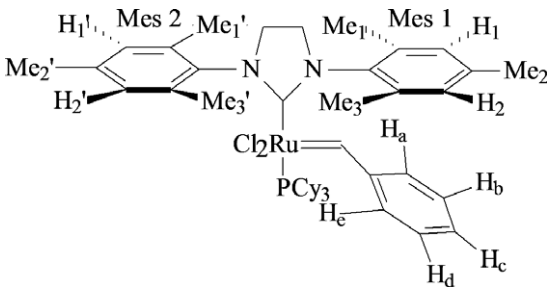

Fig. 3. Denotation of protons and methyl groups for the mesitylene rings and the phenyl ring of **2**.

The signals due to Me_2 and Me_2' appear as sharp singlets at all temperatures. This occurs because the associated methyl groups do not change position upon the rotation around the N-Mes bond. Moreover, the fact that no broadening is observed in these signals for any of the solvents at the temperature ranges studied indicates that no rotation around the Ru–$IMesH_2$ bond is observed in these experiments. The other methyl signals broaden as the temperature is increased from −50 to 10 °C. The signals due to the Me_1' and Me_3' groups start to coalesce into a broad singlet at 30 °C. This signal sharpens as the temperature is further increased resulting in a singlet signal at 2.66 ppm which integrates as 6H in the spectrum recorded at 60 °C. Similar temperature dependent behaviour is observed for the signals due to the Me_1 and Me_3 groups, although it is difficult to distinguish the peak due to the coalescence of their signals in the spectrum recorded in $CDCl_3$ at 60 °C as it overlaps with the signal due to the Me_2' group. Similar results are observed for these two sets of signals in the other solvents studied. Taking these observations, in conjunction with the observation that the signals due to Me_2 and Me_2' do not change appreciably as a function of temperature, it is deduced that at high temperatures the N-Mes rings are rotating around the N-Mes bond as found for related complexes [8]. This rotation becomes sufficiently fast in $CDCl_3$, so that at >30 °C the Me_1' and Me_3' groups and then at >60 °C the Me_1 and Me_3 groups cannot be distinguished on the NMR timescale.

If one of the factors causing the variations in the ^1H NMR spectra of **2** as a function of temperature is the rotation around the N-Mes bonds then similar behaviour should be observed in the signals due to the aromatic hydrogens on the mesitylene rings. In the spectrum recorded at −50 °C in $CDCl_3$ four singlet signals are observed at 5.80, 6.78, 7.07 and 7.12 ppm which each integrate to 1H (Fig. 5). These are assigned as arising from the aromatic hydrogens on the mesitylene groups. The proposed assignments of these signals are as given in Table 1. We propose that the signals due to the H atoms on the Mes ring that lies over the alkylidene phenyl group come at lower chemical shift than those on the other Mes ring due to the π stacking interaction that occurs between the two rings. It is well-documented that the interaction of a

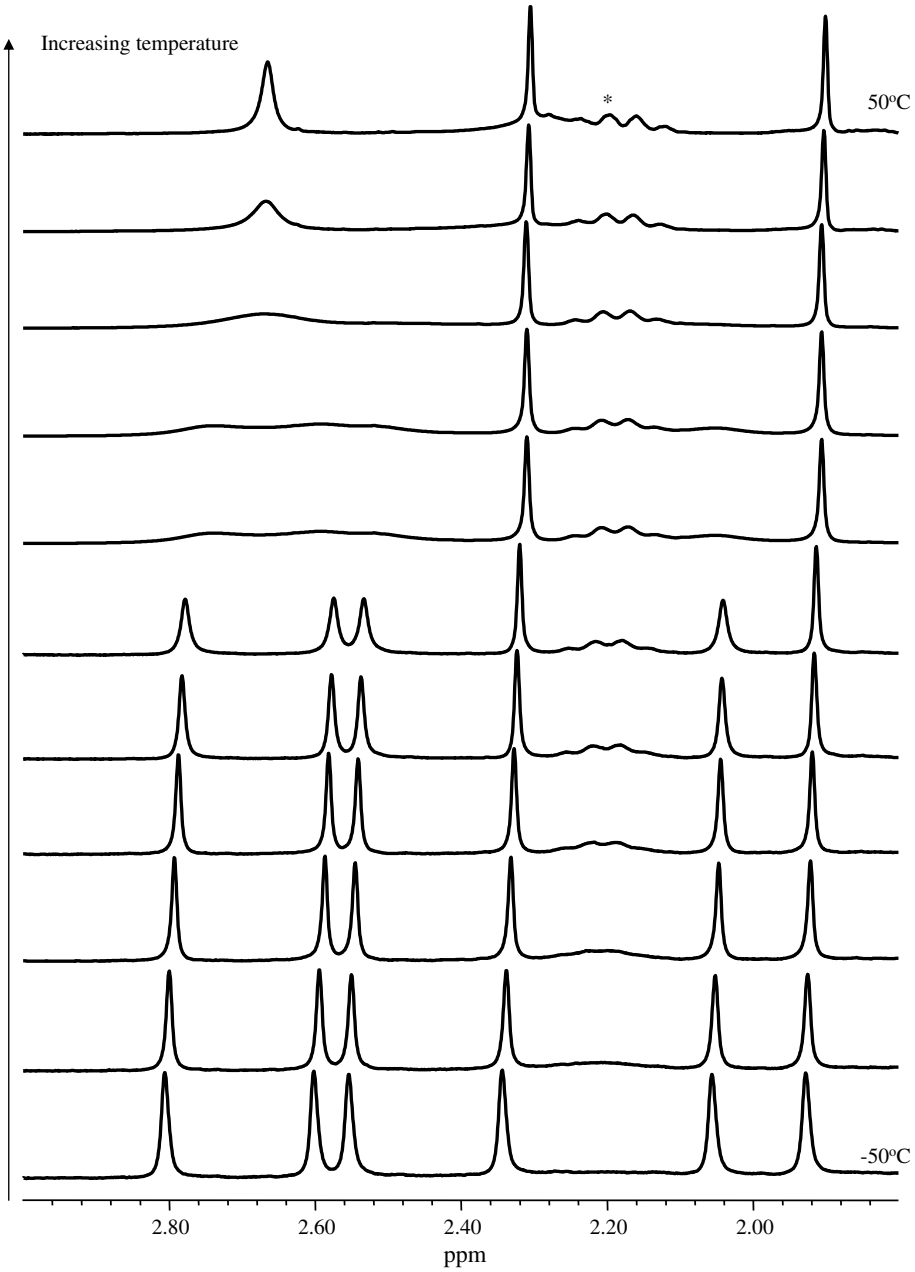

Fig. 4. ^{1}H NMR signals for the methyl groups on the mesitylene rings of **2** in $CDCl_3$ recorded as a function of temperature at 10 °C intervals. *Signals due to cyclohexyl groups on the phosphine ligand.

H with the π system of an aromatic ring will lower its chemical shift [12,13]. This is especially true for the signal due to H_2. Inspection of the X-ray crystal structure of the complex shows that this hydrogen lies directly over the π ring system of the phenyl ring and its resulting ^{1}H signal should be significantly shielded for this reason [6]. Therefore, the signal which appears at 5.80 ppm in the spectrum recorded at −50 °C is assigned to H_2.

As the temperature is raised from −50 to 0 °C the signals broaden and then at 10 °C the signals due to H_1' and H_2' coalesce into a single broad signal at 7.01 ppm which then sharpens to a narrow singlet between 20 and 60 °C. Up to a temperature of 20 °C the signals due to H_1 and H_2 broaden. Between 30 and 40 °C no signals can be observed in the ^{1}H NMR spectra which can be assigned to these atoms, presumably because the signals are now so broad that they cannot be resolved from the baseline. At 60 °C a broad signal is observed at 6.28 ppm which integrates to 2 H and is assigned as the coalesced signal of H_1 and H_2. Again, these observations indicate that at low temperatures the mesityl rings are being held in a fixed geometry and then as the temperature is raised the rings are rotating until at high temperature it is no longer possible on the NMR timescale to distinguish H_1' from H_2' or H_1 from H_2 and two 'averaged' signals are observed for the two sets of protons in the spectrum recorded at 60 °C.

Table 1
Proposed assignments of ^{1}H NMR Me and H signals on the Mes rings for **2** in $CDCl_3$

Signal position at −50 °C δ (integration) ppm	Signal position at 60 °C δ (integration) ppm	Assignment
1.93 (s, 3H)	1.90 (s, 3H)	Me_2
2.34 (s, 3H)	2.30 (s)[a]	Me'_2
2.81 (s, 3H) and 2.6 (s, 3H)	2.66 (s, 6H)	Me'_1 and Me'_3
2.56 (s, 3H) and 2.06 (s, 3H)	2.28 (s)[a,b]	Me_1 and Me_3
7.07 (s) (1H) and 7.12 (s) (1H)	7.01 (s) (2H)	H'_1 and H'_2
5.80 (s)(1H) and 6.78 (s) (1H)	6.28 (s) (2H)	H_2 and H_1

[a] The two signals together integrate as 9H.
[b] The signal is sharpening at this temperature and is not sufficiently shifted from the signal for Me'_2 to integrate them individually.

3.3. $\Delta G^{\ddagger}$ for the rotation of the Mes rings in a range of solvents as determined by the coalescence of the signals due to the H and Me groups on the ring

For simple rotations, Gutowsky showed that the rate of rotation k_c, at the temperature of coalescence, T_c is given by

$$k_c = \frac{\pi \Delta v}{\sqrt{2}} \quad (1)$$

where Δv is the chemical shift difference (in Hertz) between the two separate signals [14]. Then using Eyring equation (Eq. (2)) an approximate value for the free energy of activation for many exchange processes can be determined [14].

$$\Delta G^{\ddagger} = 19.12 T_c (10.32 + \log T_c - \log k_c) \quad (2)$$

$\Delta G^{\ddagger}$ values for the rotation of the rings for **2** in a range of solvents are given in Table 2. These values indicate that the rings are both rotating at very similar rates, as within the experimental error, there is no significant difference between the values of $\Delta G^{\ddagger}$determined for the rotation of the two rings. This indicates that there is no significant difference in the amount of steric hindrance encountered by the two Mes rings. Moreover, it would appear that if the solvent does have an influence on the rate of rotation of the Mes rings that it is quite small and cannot be determined using the experimental procedure employed in this study. We observed no evidence that the barrier to rotation about the N-Mes rings was lower in the aromatic solvent as was observed by Fürstner and co-workers for the structurally similar complex **4** (Fig. 1) [8].

Two factors are important in causing the barriers to rotation around the M-Mes bonds. The first is that due to a resonance contribution the N-Mes bond has appreciable double bond character. In fact the $\Delta G^{\ddagger}$ for the barrier to rotation around the C–N bond in simple *N*,*N*-dimethylaniline has been calculated to be 21.3 ± 4.2 kJ mol^{-1} (at 133 K) [15]. The second arises from the steric hindrance that occurs within the $IMesH_2$ ligand and between this and other ligands on the metal. As the temperature increases **2** receives sufficient energy so that the barrier to rotation can be overcome and there is rapid rotation around the N-Mes bond. In addition, fluxional processes associated with the other ligands (for example a fluxional process associated with the phosphine ligand) may reduce the degree of steric congestion in **2** at higher temperatures and thus lower the barrier to rotation around the N-Mes bond at this temperature range. As stated earlier the variable temperature NMR experiments clearly show that there are fluxional processes associated with the phosphine ligand that were too complicated to interpret.

3.4. Assignment of the signals due to the H Atoms on the phenyl ring of the alkylidene ligand of **1** and **2** at low temperatures in $CDCl_3$ and CD_2Cl_2

Grubbs and co-workers have previously assigned the signals for the protons on the alkylidene phenyl rings of **1** and **2** at room temperature [10,11]. In the ^{1}H NMR in $CDCl_3$, recorded of **2** at −50 °C five signals which each integrate as 1H are observed in the aromatic region of the spectrum between 6.9 and 8.9 ppm (Fig. 5). These signals correspond to two signals (the signal due to the *ortho* hydrogens is not observed at this temperature) which are observed between 7.1 and 7.4 ppm in the spectrum recorded at 60 °C (Fig. 5). The proposed assignments of these signals are as given in Table 3. Similar signals are observed when the spectra are recorded in CD_2Cl_2.

It is proposed that the signal due to the *ortho*-H, H_a, which lies directly under the Mes ring on the $IMesH_2$ ligand comes at a slightly lower chemical shift than the other aromatic signals. This occurs because of the interaction between this atom and the π system of the Mes ring. The signal for H_e, appearing at 8.88 ppm, is shifted further downfield than the other aromatic signals. It is possible that this unusual chemical shift arises due to H-bonding between this aromatic proton and the Cl atom bonded to the Ru atom which lies *cis* to the proton. It is evident from studying the X-ray crystal structure of the compound that these two atoms lie relatively close to each other in space, so it is reasonable to assume that a H-bonding interaction could take place [6]. In order to ensure that the signal does not arise from the other *ortho* hydrogen, H_a, and is due to a through space interaction with the alkylidene H (chemical shift 19.01 ppm at −50 °C in $CDCl_3$), a NOE study was carried out on the compound at −50 °C in $CDCl_3$. This experiment showed that there was no through space interaction between the alkylidene H and either of the *ortho*-H's. The coalesced signal for H_a and H_e is not observed over the temperature range studied indicating that over this range these atoms have not become equivalent on a NMR timescale.

The signal due to the *para*-H, H_c, comes at 7.40 ppm. This signal is a *pseudo* triplet and is not affected by warming the complex. The signals due to the two *meta*-H's, H_b and H_d, broaden as the temperature is increased from −50 °C to 0 °C. The signals coalesce into a single broad signal at 20 °C. This signal sharpens as the temperature is fur-

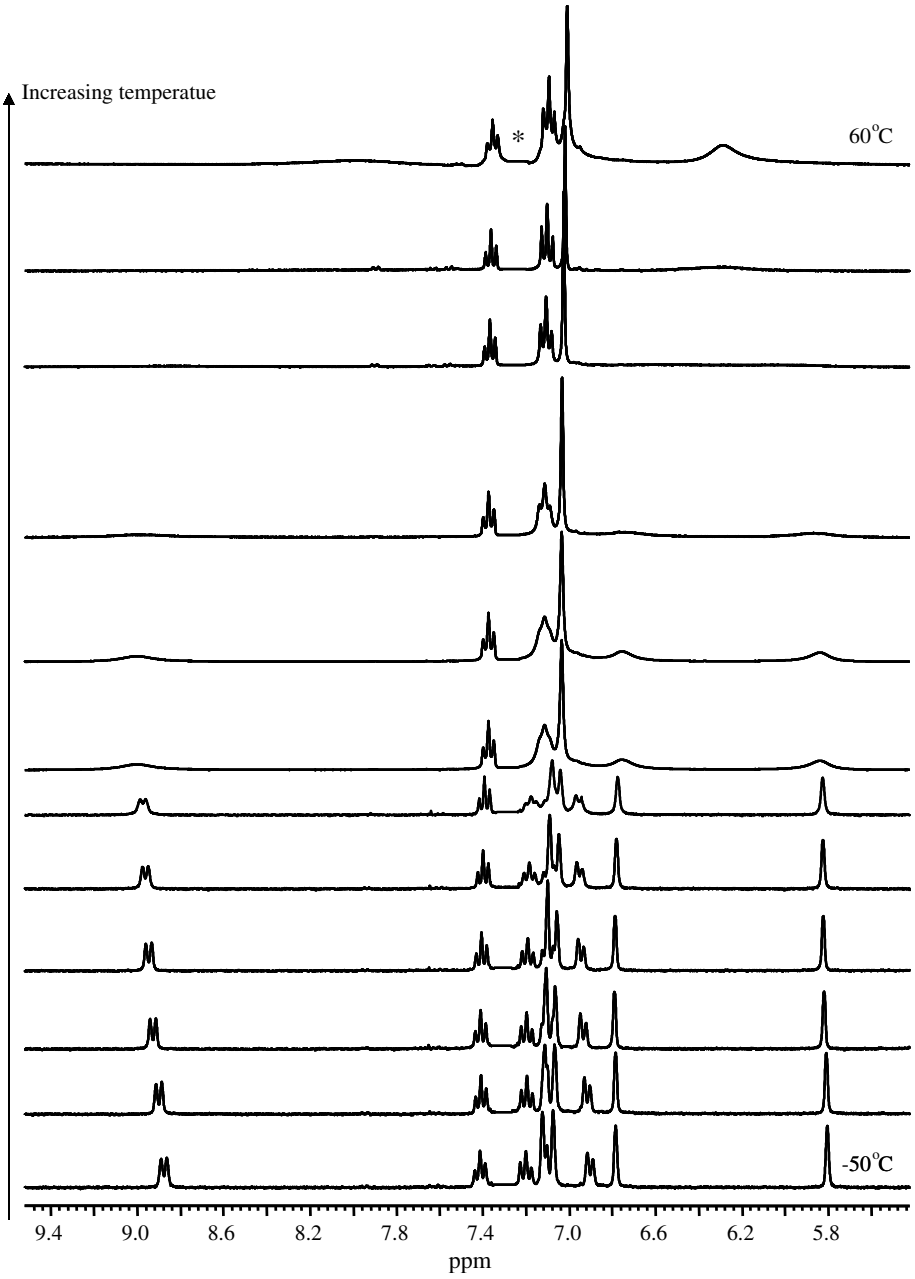

Fig. 5. ^{1}H NMR signals for the aromatic hydrogens of **2** in $CDCl_3$ recorded as a function of temperature at 10 °C intervals. *Signal due to the residual protonated solvent is removed for clarity.

ther increased resulting in a sharp *pseudo* triplet signal at 7.10 ppm which integrates as 2H in the spectrum recorded at 60 °C.

In the ^{1}H NMR spectrum of **1** in CD_2Cl_2 recorded at −90 °C four signals, three of which integrate as 1H and one which integrates as 2H, are observed in the aromatic region between 7.30 and 8.90 ppm. These signals correspond to three signals which are observed between 7.30 and 8.50 ppm in the spectrum recorded at 25 °C. The proposed assignments of these signals are given in Table 3. The signal at 8.87 ppm in the spectrum recorded at −90 °C is assigned as arising from the *ortho*-H, H_e. This signal is shifted downfield from all the other aromatic protons, like the corresponding signal for H_e in **2**. It is proposed that this downfield shift is due to H-bonding between this proton and one of the chloride ligands. This signal coalesces with the signal for H_a (7.75 ppm at −90 °C) to give a doublet signal at 8.42 ppm in the spectrum recorded at 0 °C (Fig. 6). The signal due to the *para*-H, H_c, comes at 7.51 ppm and is not affected by warming the complex. The signal due to the two *meta*-H's appears as a broad multiplet at −90 °C. Upon warming the complex this signal sharpens, appearing as a *pseudo* triplet at 7.30 ppm at 25 °C.

Table 2
$\Delta G^{\ddagger}$ for the rotation of the Mes rings in various solvents

Solvent	Signals used to determine $\Delta G^{\ddagger}$ for rotation of Mes **1** (Hz)	Signals used to determine $\Delta G^{\ddagger}$ for rotation of Mes 2 (Hz)	$\Delta G^{\ddagger}$ for rotation of Mes **1** (kJ mol^{-1})	$\Delta G^{\ddagger}$ for rotation of Mes **2** (kJ mol^{-1})
$CDCl_3$	H_1 (1741.80) and H_2 (2036.06)	H'_1 (2137.96) and H'_2 (2123.04)	62.7 ± 2.0	60.9 ± 2.0
	Me_1 (766.69) and Me_3(617.33)	Me'_1 (842.37) and Me'_3 (781.05)	64.7 ± 2.0	61.8 ± 2.0
C_6D_6	H_1 (1741.33) and H_2 (1985.49)	[a]	63.4 ± 2.0	[b]
C_6D_{12}	H_1 (1719.29) and H_2 (1995.96)	[a]	62.0 ± 2.0	[b]
CD_2Cl_2	[c]	Me'_1 (805.42) and Me'_3 (742.76)	[b]	61.7 ± 2.0
	[c]	H'_1 (2100.5) and H'_2 (2082.74)	[b]	60.5 ± 2.0

[a] Signals have not resolved into separate signals.
[b] Cannot be calculated.
[c] Signals have not coalesced at the temperature limits of the experiment.

Table 3
Proposed assignments for the ^{1}H NMR signals for the hydrogens on the phenyl ring of **2** and **1**

Complex	Signal at −50 °C δ (ppm)	Assignment	Signal at 60 °C δ (ppm)	Assignment
2 in $CDCl_3$	6.90 (d, $J = 7.7$ Hz) (1 H)	H_a	[a]	
	7.10[b] (1H)	H_b or H_d		
	7.20 (*p*t) (1H)	H_b or H_d	7.10 (*p*t) (2H)	H_b and H_d
	7.40 (*p*t) (1H)	H_c	7.34 (*p*t) (1H)	H_c
	8.88 (d, $J = 7.7$ Hz) (1H)	H_e	[a]	
	Signal at −90 °C δ (ppm)		Signal at 30 °C δ (ppm)	
1 in CD_2Cl_2	7.75 (d, $J = 6.3$ Hz) (1H)	H_a		
	7.30 (m) (2H)	H_b and H_d	7.30 (*p*t) (2H)	H_b and H_d
	7.51 (*p*t) (1H)	H_c	7.53 (t, $J = 7.3$ Hz) (1 H)	H_c
	8.87 (d, $J = 7.6$ Hz) (1H)	H_e	8.42 (d, $J = 7.6$ Hz) (2H)	H_e and H_a

[a] Signal for H_a and H_e are not observed at this temperature.
[b] Signal overlaps with signal of one of the aromatic hydrogens on Mes 2.

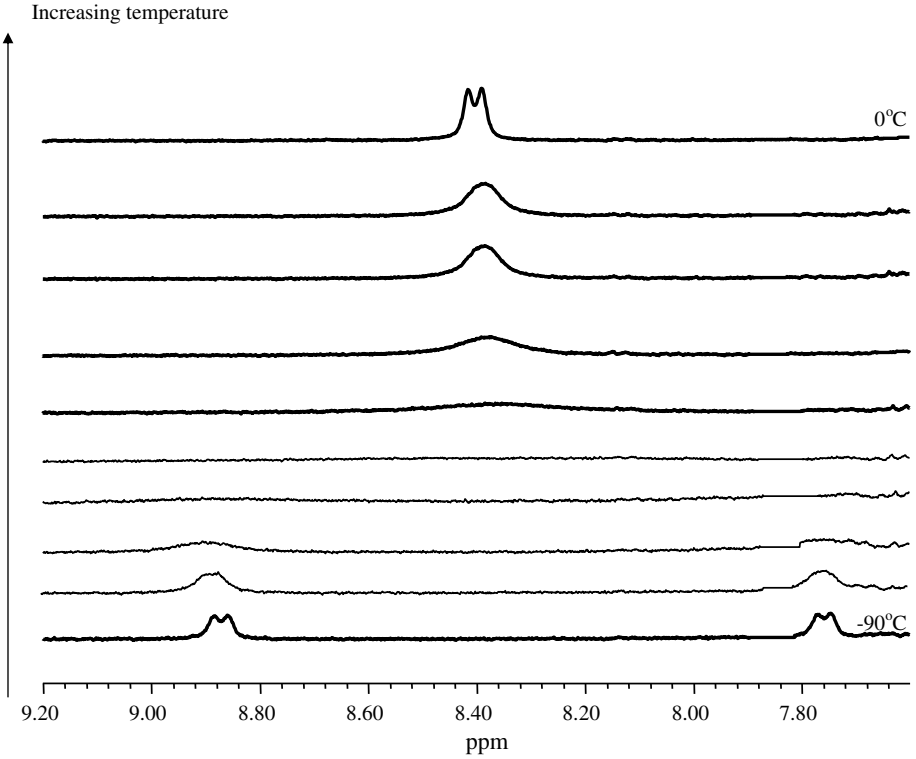

Fig. 6. ^{1}H NMR signals for the *ortho* hydrogens on the alkylidene phenyl group of **1** in CD_2Cl_2 recorded as a function of temperature at 10 °C intervals.

3.5. $\Delta G^{\ddagger}$ for the rotation of the phenyl ring in CD_2Cl_2 as determined by the coalescence of the signals due to the aromatic proton signals

Using Eq. (2) the value of $\Delta G^{\ddagger}$ for the rotation around the $C_{alkylidene}$–Ph bond of **2** in CD_2Cl_2 was determined, using the *meta* hydrogen signals (7.20 and 7.10 ppm at −50 °C and coalescence temperature 283 K), to be 61.5 ± 2.0 kJ mol^{-1}.

Grubbs and co-workers have previously calculated the $\Delta G^{\ddagger}$ for the rotation of the phenyl ring in Grubbs **1** in CD_2Cl_2 [9] and we have simply repeated this to check the accuracy of our methods and assignments. In the ^{1}H NMR spectrum recorded of **1** in CD_2Cl_2 at −90 °C (Fig. 6) the *ortho* hydrogens on the phenyl ring appear as two doublets at 8.87 and 7.75 ppm. Using Eq. (2) the value of $\Delta G^{\ddagger}$ for the rotation around the $C_{alkylidene}$–Ph bond was determined, using the *ortho* hydrogen signals (8.87 and 7.75 ppm at −90 °C, coalescence temperature 228 K), to be 42.7 ± 2.0 kJ mol^{-1}. This value corresponds well with that previously determined by Grubbs and co-workers for this complex [9].

The X-ray crystallographic data on **1** determines the $C_{alkylidene}$–Ph bond length to be 1.470(3) Å [10], while it is 1.475(5) Å for **2** [6]. These values indicate that there is no significant difference in the intrinsic strength of this bond in the two complexes. The higher barrier to rotation around the $C_{alkylidene}$–Ph bond for **2** must reflect the higher steric hindrance in this molecule and/or the stronger stabilising interactions holding the phenyl group in the plane of the Ru–$C_{alkylidene}$ bond in this molecule.

3.6. Rotation around the Ru–$C_{alkylidene}$ bonds

It has been observed that there is free rotation about the Ru–$C_{alkylidene}$ bond in a related complex [7]. The ^{1}H NMR signal which arises from the H on the alkylidene group of **1** and **2** is a sharp singlet at all temperatures and in all solvents studied. At low temperature it is likely that there is no rotation about the Ru–$C_{alkylidene}$ bond. At higher temperature there is apparent symmetry in these molecules along the Ru–$C_{alkylidene}$ plane as the groups associated with the mesityl rings are now identical on the NMR timescale. Assuming that the rotation around the Ru–$C_{alkylidene}$ bond is slower than the rotation around the N-Mes bond then, in this situation the rotation around this bond would result in two identical conformers. Therefore, our ^{1}H NMR data gives no information about the ease of rotation around this bond.

4. Conclusions

Our studies investigated the ease of rotation around the Ru=$IMesH_2$, N-Mes bonds for complex **1** and around the $C_{alkylidene}$–Ph bond in complex **1** and **2** in solution. Although our studies revealed no simple changes in the structural rigidity of complex **2** as a function of altering solvent we did obtain some interesting findings concerning the interactions in this molecule at low temperatures in solution. A summary of our main findings are as follows.

1. The Mes rings of the $IMesH_2$ ligand in **2** rotate rapidly on the NMR timescale around the N-Mes bond at high temperatures but at low temperatures no rotation is observed.
2. $\Delta G^{\ddagger}$ values for the rotation of the two Mes rings indicate that the barrier to rotation for both rings is approximately the same. Therefore, the effect of the π–π interaction between the Mes 1 and phenyl ring must be quite small and there is no significant difference in the amount of steric hindrance which each Mes ring must be exposed to.
3. The choice of solvent does not have an appreciable affect on the rate of rotation of the Mes rings. It would appear that an alteration in the structural rigidity of **2** is not a factor in the increased rate of initiation of **2** upon changing the solvent from toluene to CH_2Cl_2 [16].
4. No evidence for rotation about the Ru–$C_{N\text{-heterocycle}}$ is observed at any temperature and in any solvent.
5. Due to the symmetry of **1** and **2** variable temperature NMR does not give any information about rotation around the Ru–$C_{alkylidene}$ bond.
6. $\Delta G^{\ddagger}$ values for the rotation of the phenyl ring on the alkylidene ligand of **1** and **2** were determined. The significantly lower barrier to this rotation in the case of **1** is a clear indication of the increased steric congestion in **2** and that this congestion does have a marked influence on the structural rigidity of this molecule in solution.
7. The unusual chemical shifts of some of the signals associated with Mes 1 and the phenyl ring indicate that the interaction between the aromatic rings that is observed in the X-ray crystal structure of **2** is still observable in solution up to a temperature of 0 °C in $CDCl_3$.
8. The unusual chemical shift of the signal due to the H_e atom of both **1** and **2** led us to propose that there is a hydrogen bonding interaction between this atom and the nearest chloride ligand. This is the first report of such an interaction in these extensively studied complexes.

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