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Journal of Organometallic Chemistry 693 (2008) 1252–1260

Journal of Organometallic Chemistry

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

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Received 27 October 2007; received in revised form 11 January 2008; accepted 13 January 2008
Available online 19 January 2008

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.

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0022-328X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.01.020

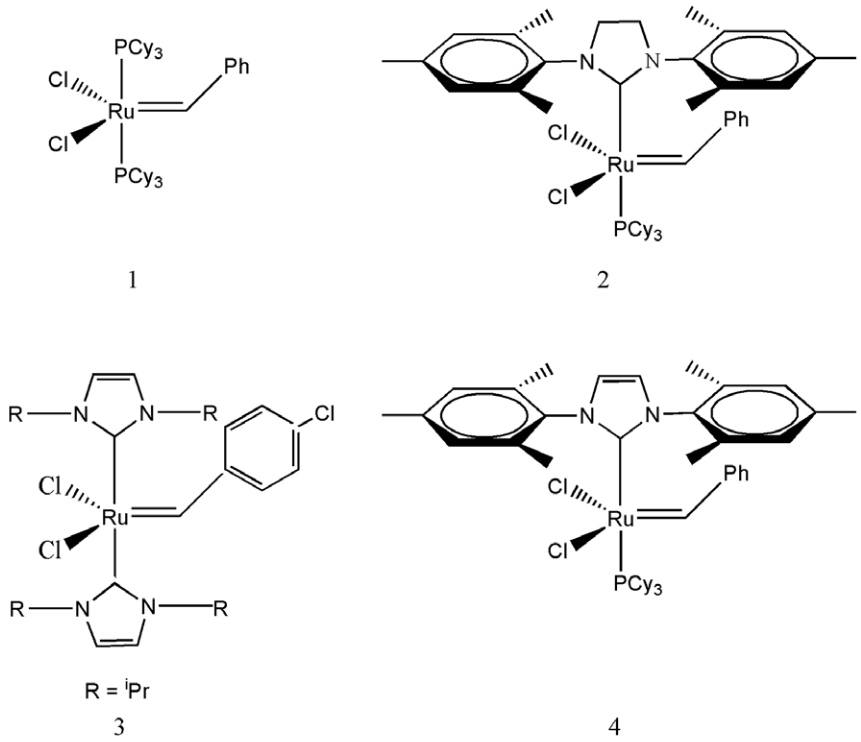

Fig. 1. Well-defined ruthenium catalysts.

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$_{\text{alkylidene}}$–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$_{\text{alkylidene}}$ 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$_6$D$_6$ and CD$_2$Cl$_2$ 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$_2$Cl$_2$ than in C$_6$D$_6$. Rotation around the C$_{\text{alkylidene}}$–Ph bond has been studied by Grubbs for **1** [9]. They determined the $\Delta G^{\pm}$ for the rotation around the C$_{\text{alkylidene}}$–Ph to be 40.8 ± 2.5 kJ mol^{-1} in CD$_2$Cl$_2$.

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.