

# Karakterisering van Grubbs-tipe prekatalisatore met behulp van kernmagnetiese resonansspektroskopie

**C de Lange**  
**20256353**

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van die Noordwes-Universiteit

Studieleier: Dr JHL Jordaan  
Medestudieleier: Prof HCM Vosloo

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**BEDANKINGS**

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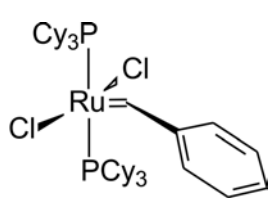
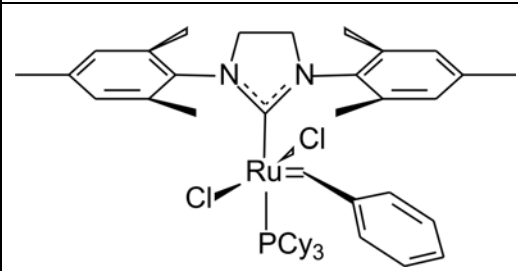
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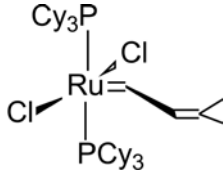
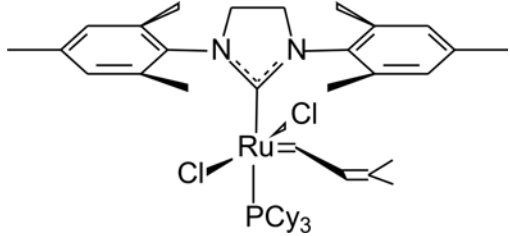
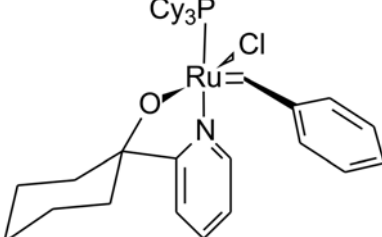
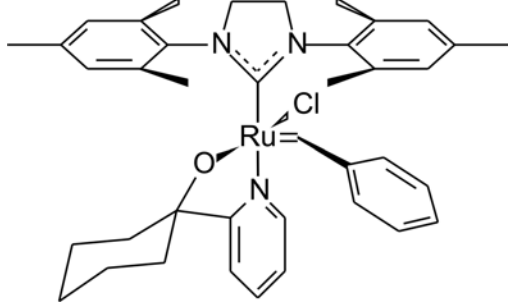
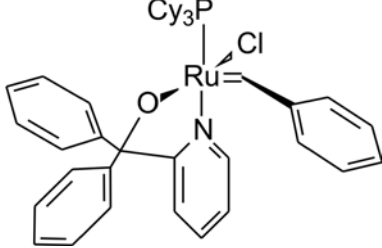
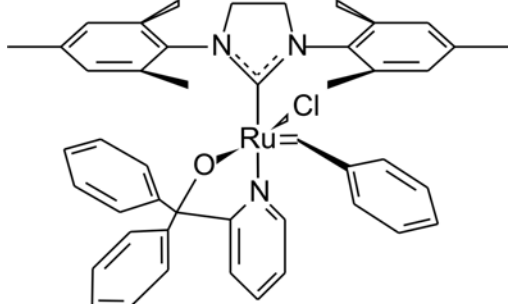
## Algemeen

$^1\text{H}$	: Protonresonansspektroskopie
$^{13}\text{C}$	: Koolstofresonansspektroskopie
$^{31}\text{P}$	: Fosforresonansspektroskopie
APCI	: Atmosferiesedruk chemiese ionisering
$\text{C}_6\text{D}_6$	: Gedeutereerde benseen
$\text{CDCl}_3$	: Gedeutereerde chloroform
COSY	: Korrelasiespektroskopie ( $^1\text{H}$ - $^1\text{H}$ )
DEPT	: Distorsielose versterking deur polarisasie-oordrag
ESI	: Elektron-sproeiionisasie
GC	: Gaschromatografie
HMBC	: Heterokernige veelvoudigebindingskorrelasie ( $^1\text{H}$ - $^{13}\text{C}$ )
HSQC	: Heterokernige enkelkwantumkorrelasie ( $^1\text{H}$ - $^{13}\text{C}$ )
IR	: Infrarooispektroskopie
KMR	: Kernmagnetiese resonansspektroskopie
MALDI TOF	: Matriks-ondersteunde laser desorpsie/ioniserings vlugtyd
MS	: Massaspektroskopie
RF	: Radiofrekwensie
$T_1$	: Longitudinale ontspanning van die spin magnetiese moment

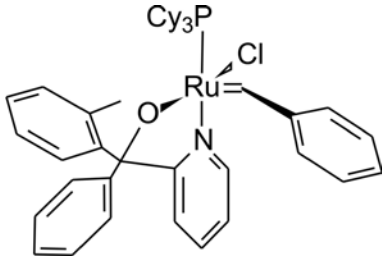
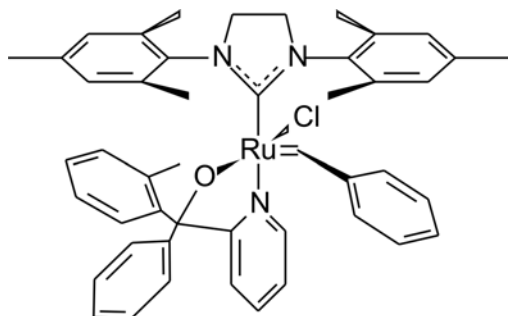

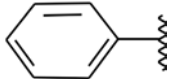
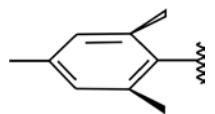
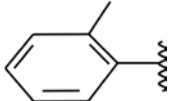
## Strukture

<b>1</b>	Bensilideen- dichloor(bis(trisikloheksielfosfien))- rutenium(II) of Grubbs1	
<b>2</b>	Bensilideen- dichloor(trisikloheksielfosfien)(1,3-bis- (2,4,6-trimetieflfeniel)-2- imidasolidinilideen)rutenium(II) of Grubbs2	

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3	Dichloor(bis(trisikloheksielfosfien))3-metiel-2-butenilideenrutenium(II)	
4	Dichloor[1,3-bis-(2,4,6-trimetielfeniel)-2-imidasolidinilideen](3-metiel-2-butenilideen) trisikloheksielfosfienrutenium(II)	
5	Bensilideen-chloor(trisikloheksielfosfien)-(1(2-piridiniel)sikloheksan-1-olato)rutenium(II)	
6	Bensilideen-chloor[1,3-bis-(2,4,6-trimetielfeniel)-2-imidasolidinilideen]-(1(2-piridiniel)sikloheksan-1-olato)rutenium(II)	
7	Bensilideen-chloor(trisikloheksielfosfien)-(1-(2-piridiniel)-1,1-difeniel-metanolato)rutenium(II)	
8	Bensilideen-chloor[1,3-bis-(2,4,6-trimetielfeniel)-2-imidasolidinilideen]-(1-(2-piridiniel)-1,1-difeniel-metanolato)rutenium(II)	

**LYS VAN AFKORTINGS**

<p><b>9</b></p>	<p>Bensilideen-chloor(trisikloheksieľfosfien)-[1-(2-piridiniel)1-feniel-o-tolielmetanolato]rutenium(II)</p>	
<p><b>10</b></p>	<p>Bensilideen-chloor[1,3-bis-(2,4,6-trimetieľfeniel)-2-imidasolidinilideen]-[1-(2-piridiniel)-1-feniel-1-o-tolielmetanolato]rutenium(II)</p>	
<p><b>Cy</b></p>	<p>Sikloheksiel</p>	
<p><b>Ph</b></p>	<p>Feniel</p>	
<p><b>Mes</b></p>	<p>Mesitiel</p>	
<p><b>Tol</b></p>	<p>o-Toliel</p>	



# OPSOMMING

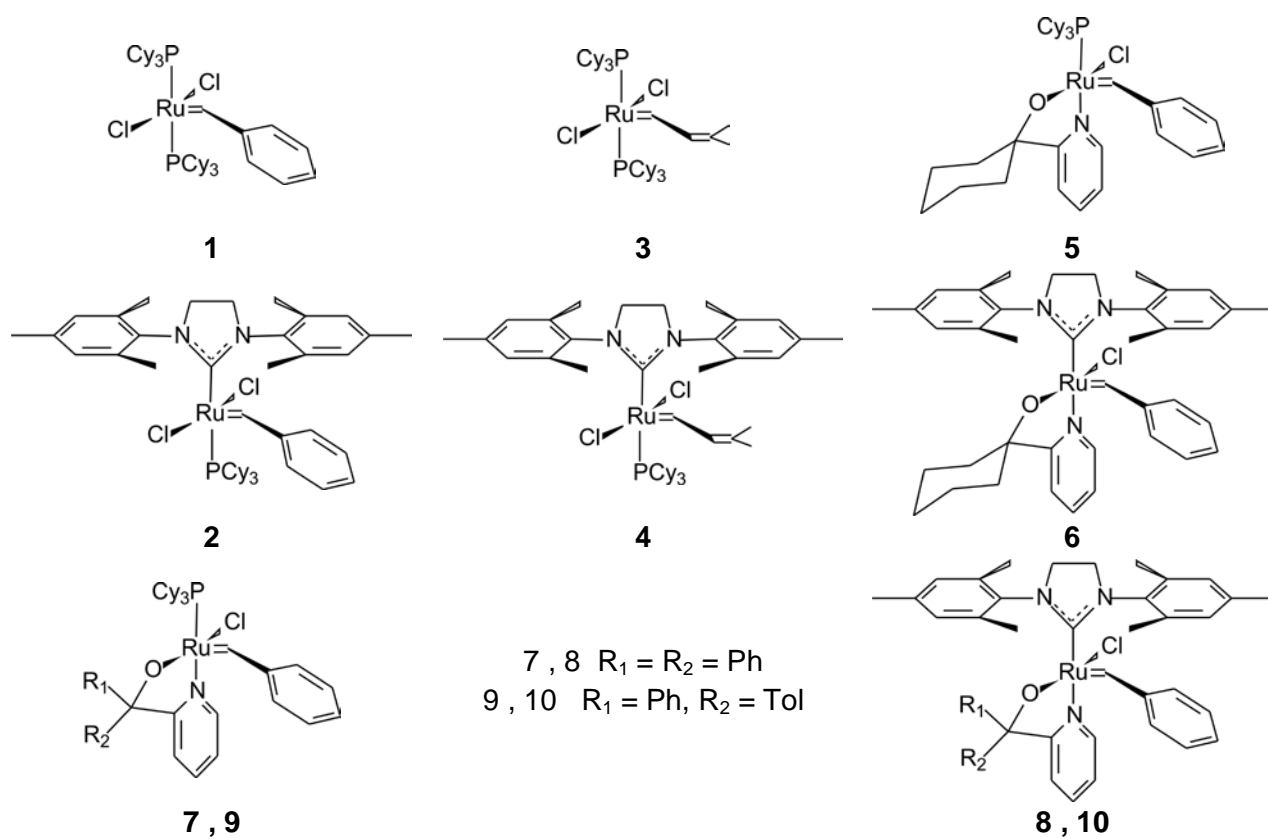
**Sleutelwoorde: KMR, KMR-parameters, KMR-karakterisering,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , COSY, HMBC, HSQC en Grubbs-tipe prekatalisatore.**

Sedert die ontwikkeling van die rutenium bevattende prekatalisatore, Grubbs 1 (**1**) en Grubbs 2 (**2**), was daar 'n toename in die ontwikkeling van nuwe prekatalisatore. Die KMR-karakterisering kon egter nie hiermee tred hou nie. Hoofsaaklik het die KMR-karakterisering bestaan uit  $^1\text{H}$ ,  $^{31}\text{P}$ , COSY en selde  $^{13}\text{C}$ . Weens die hoë natuurlike voorkoms van  $^1\text{H}$  en  $^{31}\text{P}$  (99.98 % en 100 %) kan hierdie eksperimente vinnig en eenvoudig uitgevoer word. Die enigste verandering wat aangebring moet word, is die spektraalwydte van die karbeensein (Ru=CH) wat tussen  $\delta$  20.02 en  $\delta$  17.32 dpm (resoneer) moet akkommodeer. Die tekort aan  $^{13}\text{C}$ -karakterisering word toegeskryf aan die lae natuurlike voorkoms van hierdie kerne wat slegs 1.10 % is sowel as die tekort aan gepubliseerde parameters. Verder word hierdie eksperimente bemoeilik deur die breë spektraalwydte van 300 dpm. Die aantal skanderings moet dus verhoog word om die sensitiwiteit van die spektra te verhoog om sodoende bruikbare data te verkry.

In hierdie studie is prekatalisator **1** gebruik om die KMR-tegniek aan te leer sowel as om die KMR-parameters vas te stel. **2** en twee ander kommersiële Grubbs-tipe prekatalisatore **3** en **4** het hierdie KMR-karakterisering ondergaan sodat die verkreeë waardes met die literatuur vergelyk kon word. Verder is ses ander nie-komersiële Grubbs-tipe prekatalisatore **5-10** gesintetiseer sowel as gekarakteriseer.

Weens die onstabiliteit van die prekatalisatore en met inagneming van die tydsduur van die eksperimente moes die karakterisering in drie stappe plaasvind. Die eerste stap was om die volgende eksperimente te doen:  $^1\text{H}$ , COSY, HSQC en HMBC wat vier ure duur. Die volgende stap is die DEPT135-eksperiment van drie ure lank en laastens was die  $^{13}\text{C}$ -eksperiment van sewe ure gedoen. Die maksimale hoeveelheid inligting kon op hierdie wyse bekom word.

Die saamgestelde KMR-parameters wat gedurende hierdie studie verkry is kon gebruik word om die Grubbs-tipe prekatalisatore **5-10** gedeeltelik te karakteriseer. Weens die groot aantal oorvleuelende pieke in die aromatiëse en alkaan gebiede was die resolusie nie voldoende vir volledige karakterisering nie.



**Figuur 1** Grubbs-tipe prekatalisatore gebruik gedurende die studie

# SUMMARY

## Characterization of Grubbs-type precatalysts with the aid of nuclear magnetic resonance spectroscopy

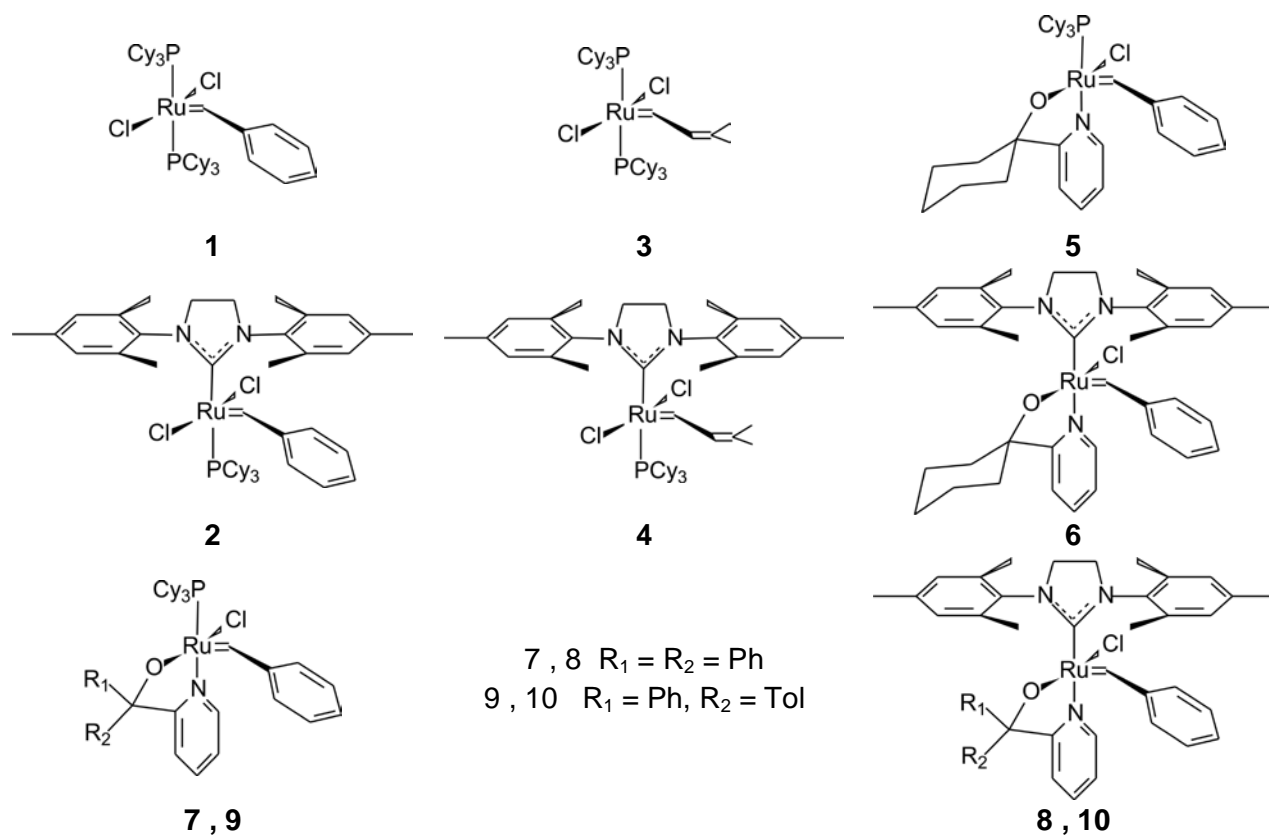
**Keywords:** NMR, NMR-parameters, NMR-characterisation,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , COSY, HMBC, HSQC and Grubbs-type precatalysts.

Since the development of the ruthenium containing precatalysts Grubbs 1 (**1**) and Grubbs 2 (**2**), there was an increase in the development of new precatalysts. The NMR characterization could not cope with this. The NMR characterization mainly consists of  $^1\text{H}$ ,  $^{31}\text{P}$ , COSY and rarely  $^{13}\text{C}$ . Due to the high natural abundance of  $^1\text{H}$  and  $^{31}\text{P}$  (99.98% and 100%), these experiments could be carried out quickly and easily. The only change that had to be made was to the spectral width, to accommodate the carbene signal ( $\text{Ru}=\text{CH}$ ) between  $\delta$  20.02 and  $\delta$  17.32 ppm. The lack of  $^{13}\text{C}$  characterization is attributed to the low natural abundance of these nuclei that is only 1.10% and the lack of published parameters. Furthermore, the broad spectral width of 300 ppm increases the difficulty because the number of scans has to be increased to increase the sensitivity of the spectra and obtain useful data.

In this study the precatalyst **1** was used to learn the NMR technique as well as to acquire the NMR parameters. **2** and two other commercial Grubbs-type precatalysts **3** and **4** underwent NMR characterization so that acquired values could be compared with the literature. Six other non-commercial Grubbs-type precatalysts **5-10** were synthesized and characterized.

Due to the instability of the precatalysts and taking into account the duration of these experiments, the characterization was done over three steps. The first step was to do the following experiments:  $^1\text{H}$ , COSY, HSQC and HMBC, which took four hours. The next step was the DEPT135 experiment of three hours, and finally the  $^{13}\text{C}$  experiment of seven hours. The maximum amount of information could be obtained in this way.

The combined NMR parameters for this study was obtained and used to characterize the Grubbs-type precatalysts **5-10** partially. Due to the large amount of overlapping peaks in the aromatic and alkane areas the resolution was not sufficient for full characterization.



**Figure 1** Grubbs-type precatalysts used during the study