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Ruthenium Catalyst with a Chelating Pyridinyl-Alcoholato Ligand for Application in Linear Alkene Metathesis

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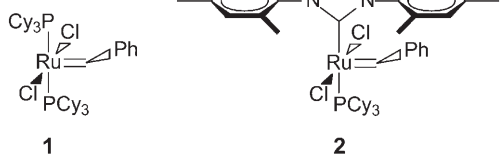
Abstract: The catalytic activity of ruthenium alkylidene complexes [RuCl(L)(ON)(=CHPh)] [L = H_2IMes and PCy_3, ON = 1-(2′-pyridinyl)cyclohexan-1-olate)], bearing a chelating pyridinyl-alcoholate ligand, was investigated for the metathesis of 1-octene in the absence of a solvent. Both systems were active for the metathesis of 1-octene yielding *trans*-7-tetradecene and ethene as the primary metathesis products. Although the activity of both systems increased with an increase in reaction temperature, the activity of [RuCl(H_2IMes)(ON)(=CHPh)] started to decrease at temperatures above 70 °C, with a simultaneous exponential increase in the secondary metathesis products due to double-bond isomerisation of the substrate. Although the initiation rates for these systems are slower compared to Grubbs 1 and Grubbs 2 for the metathesis of 1-octene at 60 °C, they have a higher activity and longer lifetime.

Keywords: alkene metathesis; chelating ligands; Grubbs-type precatalyst; 1-octene; ruthenium

Introduction

The ruthenium carbene complexes developed by the Grubbs group, $RuCl_2LL'$(=CHPh) [L, L′ = PCy_3 (**1**) and L = PCy_3, L′ = NHC (**2**)], are of interest because of their high 1-alkene metathesis activity and tolerance towards polar functional groups.[1,2] The lifetime and reactivity of the metal carbene complex **1** have been improved through the replacement of the phosphine ligand by a more bulky and basic N-heterocyclic carbene ligand.[3,4] The higher activity of **2** can also be attributed to electronic and steric effects that influence the dissociation of the phosphine ligand as well as the ratio of alkene to phosphine coordination during the mechanistic cycle.[5]



1 **2**

The chemistry of transition metal complexes with chelating ligands containing mixed functionalities is enjoying an increase in popularity, as the different features associated with each donor atom give unique reactivity to their metal complexes.[6–8] Hemilabile ligands, which are a class of chelating ligands, have the ability to place two or more donor atoms with very different electronic properties close to the metal atom (Figure 1). The relevance of these ligands is increasing in coordination and organometallic chemistry, since they can reversibly create and/or occupy a vacant coordination site at the metal, with consequent stabilisation of reactive intermediates or enhancement of reactivity in catalytic reactions.[9,10] It is presumed that these ligands act as chelating ligands at room temperature and at elevated temperatures will liberate one coordination site 'on demand' of a competing substrate, e.g., an alkene.[10,11]

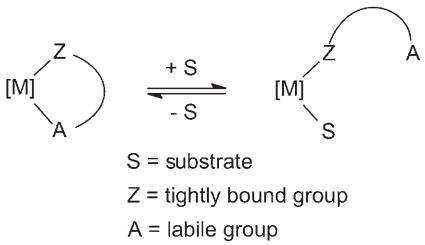


Figure 1. Schematic representation of the concept of hemilability.

A number of ruthenium carbene systems with hemilabile ligands for application in ring-opening meta-

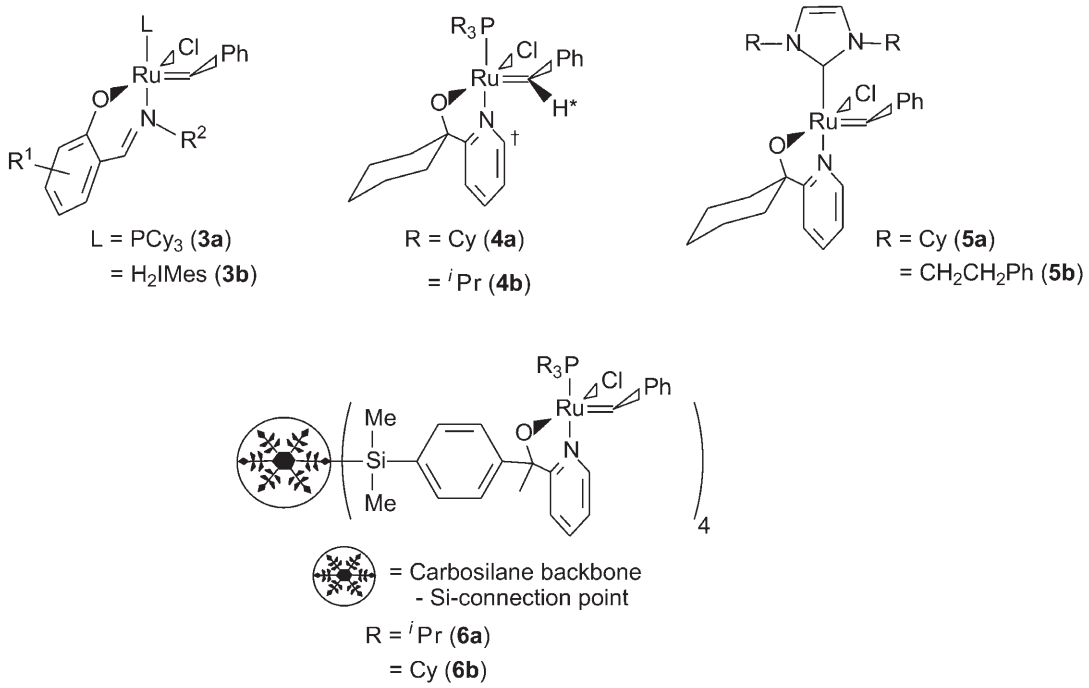
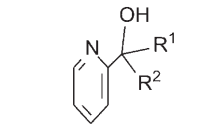


Figure 2. Chelating ruthenium catalysts for alkene metathesis.[10,12–16]

thesis polymerisation (ROMP) and ring-closing metathesis (RCM) has been published (Figure 2).[11–16] Grubbs[12] and later Verpoort[13,14] introduced bidentate O,N-chelated Schiff-base ligands on **1** and **2** to give **3a** and **3b**, respectively. The thermal stability and activity of these complexes towards ROMP and RCM were increased through the combination of the Schiff-base ligand with an NHC ligand (**3b**).[11,14,17] 2-Pyridinylcarbinol (**L1**) is another type of O,N-chelated



L1

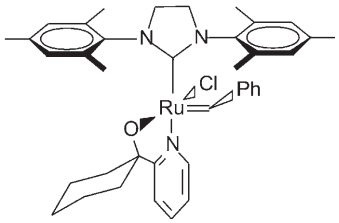
ligand, which has been well established in tungsten (VI) catalyst precursors for ROMP reactions.[18] Several groups incorporated this type of ligand into the first- and second-generation Grubbs systems to give complexes **4** to **6**, which were shown to be active for RCM and/or ROMP.[11,15,16] Although Denk et al.[11] have synthesised **4a**, they did not report on its metathesis activity. Complex **4a** was only used as an intermediate in the synthesis of **5a** and **5b**, which catalysed the ROMP of norbornene and cyclooctene, respectively, in 78 and 98% yield within 60 min. This type of ligand has also found application in the design of periphery-functionalised dendritic catalysts (**6**) for RCM reactions.[16] Van Koten et al.[16] reported a 100% conversion of diethyl diallylmalonate to diethyl 3-cyclopentenecarboxylate after 30 min at 80 °C. The 2-pyridinylcarbinol-containing ruthenium carbene catalysts are therefore very active for metathesis reactions. To our knowledge the catalytic activity of these types of systems towards the self-metathesis of linear alkenes has not been previously investigated or reported.

In this study we report on the synthesis and catalytic activity of the precatalysts [RuCl(L)(ON)(=CHPh)] [L = H_2IMes (**7**) or PCy_3 (**4a**), ON = 1-(2′-pyridinyl)cyclohexan-1-olate] for the metathesis of 1-octene at elevated temperatures. The formation and interaction of the carbene active species are illustrated with the use of ^{1}H NMR spectroscopy.

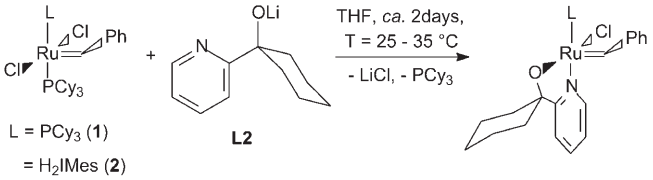
Results and Discussion

Synthesis of Complexes 4a and 7

Precatalysts **4a** and **7** were prepared by stirring **1** and **2**, respectively, with the lithium salt (**L2**) of 2-pyridi-



7



Scheme 1. Schematic representation of the synthesis of catalysts **4a** and **7**.

nylcarbinol (**L1**), which was obtained through reaction of **L1** with butyllithium (Scheme 1).[11,19] The reaction mixture was stirred for 2 days in tetrahydrofuran (THF) at room temperature for **4a** and at 35 °C for **7**. Although within 120 min a dark green solution was obtained for **7** and a brown solution for **4a**, TLC indicated that substrate was still present, and therefore the mixture was stirred for a longer period than what was reported by Denk et al.[11] The formation of LiCl drives the reaction and its high solubility in THF may be the reason why these reactions took so long. The LiCl was removed through the extraction of the product with toluene. The free phosphine was removed by sonification (10 min) of the product in pentane with subsequent removal of the pentane by syringe. The complexes were finally obtained in moderate yields as microcrystalline powders through recrystallisation from THF/pentane.

Metathesis of 1-Octene using 4a and 7

A mixture of products can form during the metathesis of 1-octene due to alkene isomerisation and the metathesis reactions (self- and cross-metathesis) that can occur simultaneously as the reaction proceeds (Table 1).[20] As a result of double-bond isomerisation occurring during the metathesis reaction secondary cross-metathesis between the various alkenes can take place yielding a range of C_2–C_{14} alkene products. Therefore three major groups of products can be identified, i.e., primary metathesis products (PMP), isomerisation products (IP) and secondary metathesis products (SMP).

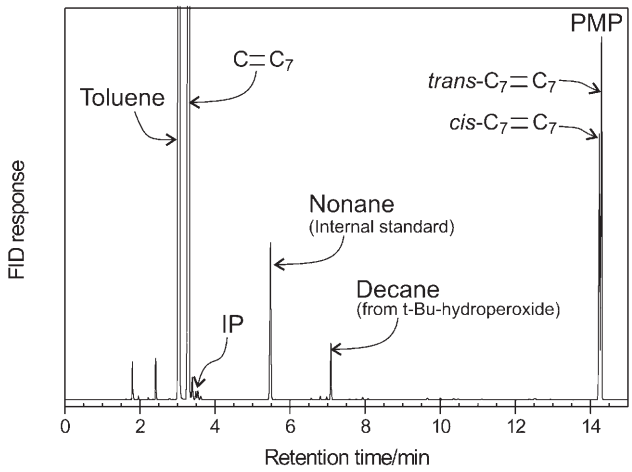


Figure 3. GC/FID chromatogram of the reaction mixture of 1-octene in the presence of **4a** at 60 °C after 60 min.

It has been reported that the phosphine-based ruthenium carbene systems with an O,N-chelating ligand are not very active for RCM and ROMP reactions at room temperature.[11,12,15] Therefore, experiments were carried out at reaction temperatures ranging from 35–80 °C to determine the effect of temperature on the metathesis activity and selectivity of **4a** and **7** at a 1-octene/Ru molar ratio of 9000. Samples (0.3 mL) were withdrawn by syringe at regular time intervals and quenched with a solution of toluene (0.3 mL) and tert-butyl hydrogen peroxide (2 drops). The reaction was monitored by GC/FID to determine the different products that form during the metathesis of 1-octene; these products were identified by GC/MSD. The self-metathesis of 1-octene typically leads to the formation of two isomers (Figure 3), *cis*- and *trans*-7-tetradecene, which combined with ethene (not observed by GC) represent the PMP of the reaction.

Table 1. Possible reactions of 1-octene in the presence of metathesis catalysts.

Reaction	Substrate[a]	Products[a]	
Primary metathesis			
- Self-metathesis	$C{=}C_7$	$C{=}C + C_7{=}C_7$	(PMP)[b]
- Isomerisation	$C{=}C_7$	$C_2{=}C_6 + C_3{=}C_5 + C_4{=}C_4$	(IP)[c]
Secondary metathesis			
- *Cross-metathesis*	$C{=}C_7 + C_2{=}C_6$	$C_2{=}C_7 + C{=}C_6 + C{=}C_2 + C_6{=}C_7$	(SMP)[d]
- *Self-metathesis*	$C_2{=}C_6$	$C_2{=}C_2 + C_6{=}C_6$	

[a] Hydrogens are omitted and geometrical isomers not shown for simplicity.
[b] Primary metathesis products (PMP) refers to the homometathesis products of 1-octene, i.e., $C_7{=}C_7$ and C=C.
[c] Isomerisation products (IP) refers to the double bond isomerisation reaction of terminal to internal alkenes.
[d] Secondary metathesis products (SMP) refers to the metathesis of the isomerisation products of 1-octene.

Table 2. Catalytic activity and selectivity of **4a** and **7** towards the metathesis of 1-octene at 35 to 80 °C (1-octene/Ru = 9000, no solvent) after 420 min.

Catalyst	T [°C]	PMP [%]	SMP [%]	IP [%]	% S[a]	k_{init} [mol s^{-1}]	TON
4a	35	10.2	0.1	0.0	98.67	5.48×10^{-8}	1143
	60	53.2	0.4	0.5	98.34	2.06×10^{-6}	5907
	70	59.6	1.2	1.5	95.97	5.55×10^{-6}	6652
	80	90.3	8.1	2.2	89.80	6.39×10^{-6}	10119
7	35	3.3	0.6	0.0	85.40	6.00×10^{-8}	379
	60	81.1	12.9	0.0	86.28	5.19×10^{-6}	9214
	70	91.8	26.1	0.0	77.83	1.35×10^{-5}	10428
	80	59.9	58.5	0.3	50.46	2.82×10^{-5}	6811

[a] Selectivity towards PMP

Table 2 summarises the catalytic activity and selectivity of **4a** and **7** towards the metathesis of 1-octene over a temperature range of 35 to 80 °C. Both **4a** and **7** showed rather low activity for the metathesis of 1-octene at 35 °C, i.e., approximately 10% and 3% PMP after 420 min, respectively. Although a linear increase in the activity of **4a** towards the formation of PMP was observed with an increase in temperature, exponential increases in IP and SMP were noted. In contrast, **7** shows a sharp increase in PMP formation up to 70 °C with an even sharper decrease in activity when the temperature increases above 70 °C with an exponential increase in SMP. It was also noted that in the presence of **7** the mol% IP increases to a maximum within the first 10 min followed by a sharp decrease to 0% within 30 min as the reaction proceeds, most probably due to cross-metathesis of the IPs to form SMPs.

The initiation rate constants (k_{init} [mol s^{-1}]) for both **4a** and **7** were determined as a function of the mol 7-tetradecene formed over time. A linear increase in k_{init} for the formation of 7-tetradecene was observed in the presence of **4a**, while k_{init} increased exponentially for **7** with an increase in temperature (Figure 4). Although a steady increase in the turnover number (TON) was observed for both **4a** and **7** at elevated temperatures, a sharp reduction in the selectivity and TON was noted for **7** at temperatures above 70 °C (Table 2). The optimum reaction temperature where both catalytic systems gave high activity while retaining a high degree of selectivity towards PMP with a limited amount of SMP and IP formation was found to be 60 °C. All reactions were further performed at 60 °C.

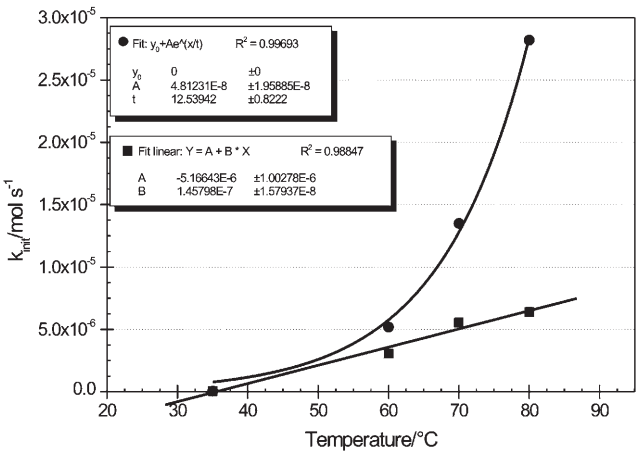


Figure 4. Initiation rate (k_{init}) as a function of temperature [■ **4a**, ● **7**]

Table 3. Catalytic activity and selectivity of **4a** towards the metathesis of 1-octene at 60 °C at different 1-octene/Ru molar ratio (no solvent) after 420 min.

1-Octene/Ru molar ratio	PMP [%]	SMP [%]	IP [%]	% S[a]	k_{init} [mol s^{-1}]	TON
2000	68.0	1.5	0.9	96.59	2.65×10^{-6}	1728
9000	53.2	0.4	0.5	98.34	2.06×10^{-6}	5907
100 000	32.0	0.2	0.5	97.86	5.52×10^{-7}	3569

[a] Selectivity towards PMP

We also investigated the influence of the 1-octene/Ru molar ratio on the performance of **4a** to determine if the catalyst will be active at lower catalyst concentrations. Table 3 summarises the catalytic activity and selectivity of **4a** towards the metathesis of 1-octene at 60 °C varying the 1-octene/Ru molar ratio from 2000 to 100,000. The activity of **4a** towards the formation of PMP increases with a decrease in the 1-octene/Ru molar ratio as illustrated in Figure 5, with a simultaneous increase in both the SMP and IP (Table 3). Although the initiation rate of **4a** increased with an increase in the catalyst concentration, a sharp decrease in the TON was observed after reaching a maximum at a 1-octene/Ru molar ratio of 9000. Therefore, in order to have a high activity and selectivity of **4a** towards PMP with limited SMP and IP formation, an 1-octene/Ru molar ratio = 9000 was used for further investigations.

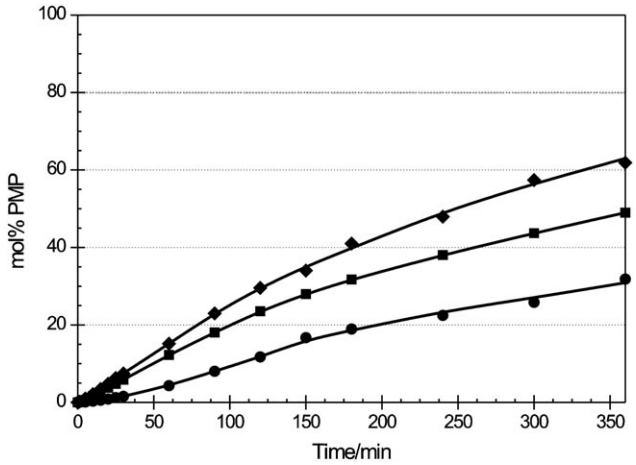


Figure 5. Influence of 1-octene/Ru molar ratio on the self-metathesis of 1-octene to 7-tetradecene and ethene (PMP) in the presence of catalyst **4a** at 60 °C [◆ 2000, ■ 9000, ● 100,000].

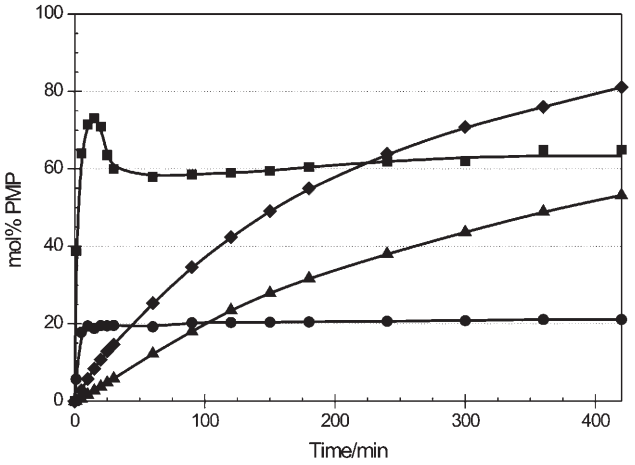


Figure 6. Self-metathesis of 1-octene to 7-tetradecene and ethene (PMP) in the presence of precatalysts **1**, **2**, **4a** and **7** at 60 °C (1-octene/Ru = 9000) [■ **2**, ● **1**, ◆ **7**, ▲ **4a**].

Subsequently a comparative study on the activity and selectivity of **1**, **2**, **4a** and **7** was performed at a 1-octene/Ru molar ratio of 9000. Table 4 summarises the catalytic activity and selectivity of the various catalysts towards the metathesis of 1-octene at 60 °C. 1-Octene was converted to approximately 15 % *trans*- and 12 % *cis*-7-tetradecene (approximately 53 % PMP) in the presence of **4a** as compared to 6 % *trans*- and 5 % *cis*-7-tetradecene (approximately 21 % PMP) for **1** after 420 in (Figure 6). In the presence of **7** 1-octene was converted to approximately 36 % *trans*- and 7 % *cis*-7-tetradecene (approximately 81 % PMP) as compared to 27 % *trans*- and 6 % *cis*-7-tetradecene (approximately 63 % PMP) for **2** after 420 min (Figure 6). SMP formation due to the double-bond isomerisation of 1-octene to mainly 2-octene and the subsequent metathesis reactions remained below 2 % for both **1** and **4a** while 13 % and 36 % SMP are observed in the presence of **7** and **2**, respectively. The selectivity towards the formation of PMP increase with 20–35 % in the presence of **4a** and **7** compared to **1** and **2**. After 18 h both **4a** and **7** still show activity, i.e., approximately 69 % and 81 % PMP, respectively, while **1** (21 % PMP) and **2** (63 % PMP) are inactive. Although the initiation rates of **4a** and **7** are slower compared to those of **1** and **2**, the TON, selectivity and lifetime of the precatalysts are improved. This indicates that the incorporation of a hemilabile ligand into the Grubbs systems improves the lifetime, activity and selectivity of the catalysts towards 1-alkene metathesis at higher temperatures. Denk et al.[11] and van Koten et al.[16] have also shown that the incorporation of a hemilabile ligand into the Grubbs system improves the activity of the catalyst for ROMP and RCM reactions.

Table 4. Catalytic activity and selectivity of catalysts **1**, **2**, **4a** and **7** towards the metathesis of 1-octene at 60 °C (1-octene/Ru = 9000, no solvent) after 420 min.

Catalyst	PMP [%]	SMP [%]	IP [%]	% S[a]	k_{init} [mol s^{-1}]	TON
1	21.1	0.2	4.8	81.16	3.78×10^{-5}	2175
2	63.4	35.8	0.4	63.73	1.36×10^{-4}	6750
4a	53.2	0.4	0.5	98.34	2.06×10^{-6}	5907
7	81.1	12.9	0.0	86.28	5.19×10^{-6}	9214

[a] Selectivity towards PMP.

In addition we investigated the metathesis of 1-octene in the presence of **4a** and **7** with ^{1}H NMR at 50 °C in $CDCl_3$, to gain some insight into the reaction mechanism.

NMR Investigation: Metathesis with 4a

The carbene α-H (denoted H* in the structures) signal of the coordinated benzylidene **4a** appears at $\delta = 17.85$ ppm, that of the heptylidene [RuCl(PCy_3)-($\widehat{ON}$)(=CHC_6H_{13})] (**4ab**) at $\delta = 17.00$ ppm and the methylidene [RuCl(PCy_3)($\widehat{ON}$)(=CH_2)] (**4ac**) at $\delta = 16.19$ ppm. The shift of the carbene α-H peak of the benzylidene to lower field to produce a triplet and doublet is due to the change in the electronic environment of the ligand attached to the carbene carbon. A shift in the pyridine α-H (denoted H† in the structures) signal was also observed during the course of the reaction, indicating that the electronic environment of the ligand is changing, most probably due to the coordination and decoordination of the N-donor atom as the reaction continues. The pyridine α-H signal of the coordinated benzylidene **4a** appears at

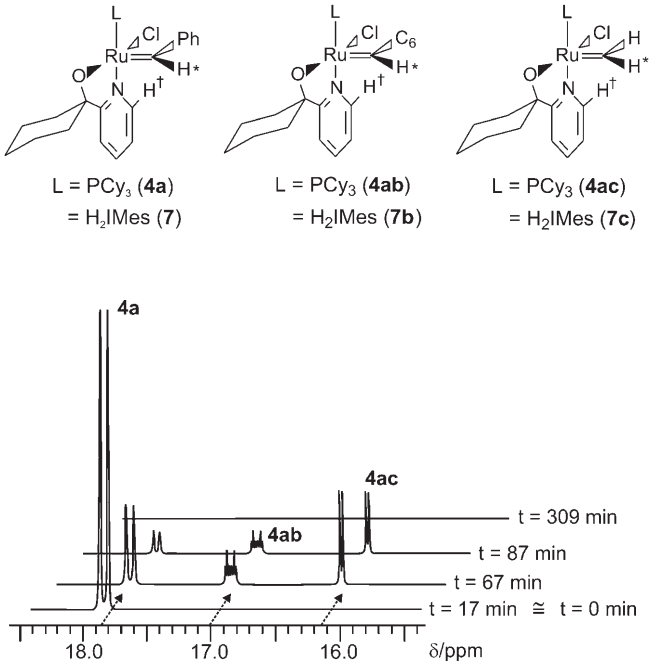


Figure 7. ^{1}H NMR spectra of the carbene proton region at different time intervals of a 1-octene/**4a** reaction mixture in $CDCl_3$ at 50 °C.

$\delta = 9.04$ ppm, but the other signals cannot be assigned with certainty to the other intermediates.

Only three carbene species were observed during the metathesis of 1-octene in the presence of **4a** (Figure 7). Theoretically six carbenes should be involved, but neither of the carbene α-H signals for the uncoordinated intermediates (**4a-open**, **4ab-open** and **4ac-open**) was observed. This may be due to the fast rate of the reaction, and the fact that approximately 13 min were needed for each NMR spectrum to be recorded over a period of 5 h. The reaction may therefore proceed at such a fast rate that some of the carbene signals are not observed within the time scale of the NMR.

Figure 8 illustrates the change in the peak integration values of the individual carbene species as a function of time. The methylidene intermediate seems to follow a different pattern than what was reported for **1**[20] in which it seems the signal increases to a maximum with a gradual decrease without it being depleted in the 5 h the reaction proceeds. The benzylidene signal gradually decreases suggesting the conversion

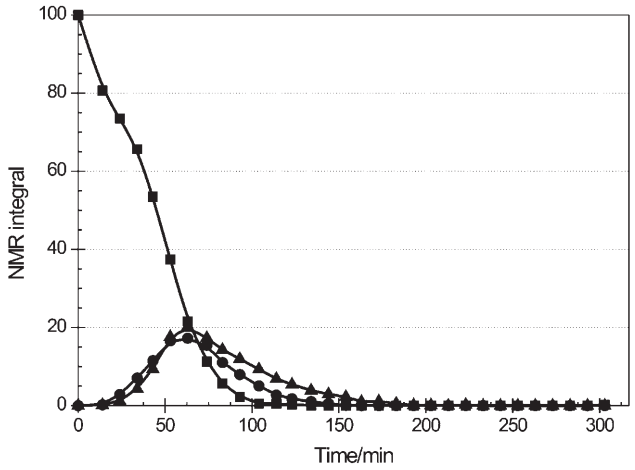


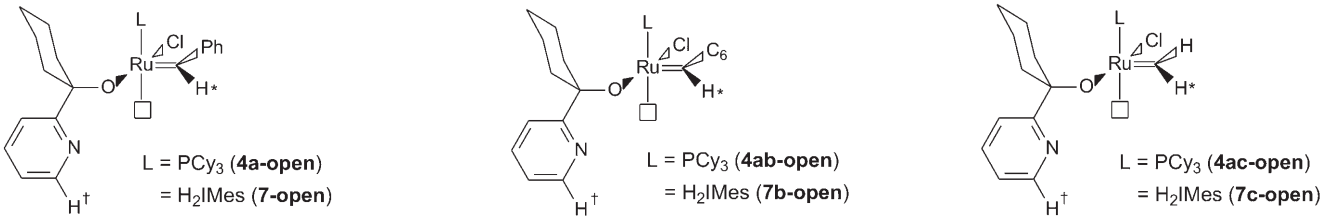
Figure 8. The ^{1}H NMR peak integration values (normalized) of the carbenes involved in the metathesis reaction of 1-octene in the presence of **4a** [■ $\delta = 17.85$ ppm, ● $\delta = 17.00$ ppm, ▲ $\delta = 16.17$ ppm].

of the benzylidene to the heptylidene and methylidene; after 200 min all of **4a** has been converted. The heptylidene and methylidene signals increase to a maximum followed by a gradual decrease to a minimum as the reaction proceeds. The simultaneous decomposition of the benzylidene to some other species cannot be ruled out. In the presence of 1-octene it seems as if the benzylidene is simultaneously converted to the heptylidene and the methylidene as the reaction proceeds.

NMR Investigation: Metathesis with 7

We also investigated the metathesis of 1-octene in the presence of **7** with ^{1}H NMR at 50 °C in $CDCl_3$. In contrast to **4a**, five carbene species were observed during the metathesis of 1-octene in the presence of **7**, which might relate to the open and coordinated intermediates as illustrated in Figure 9. The carbene α-H signal of the uncoordinated heptylidene intermediate (**7b-open**) was not observed.

The carbene α-H signal of the coordinated benzylidene **7** appears at $\delta = 18.05$ ppm, that of the heptylidene [RuCl(H_2IMes)(ÔN) (=CHC_6H_{13})] (**7b**) at $\delta = 16.71$ ppm and the methylidene [RuCl(H_2IMes)-(ÔN)(=CH_2)] (**7c**) at $\delta = 16.08$ ppm. The shift of the



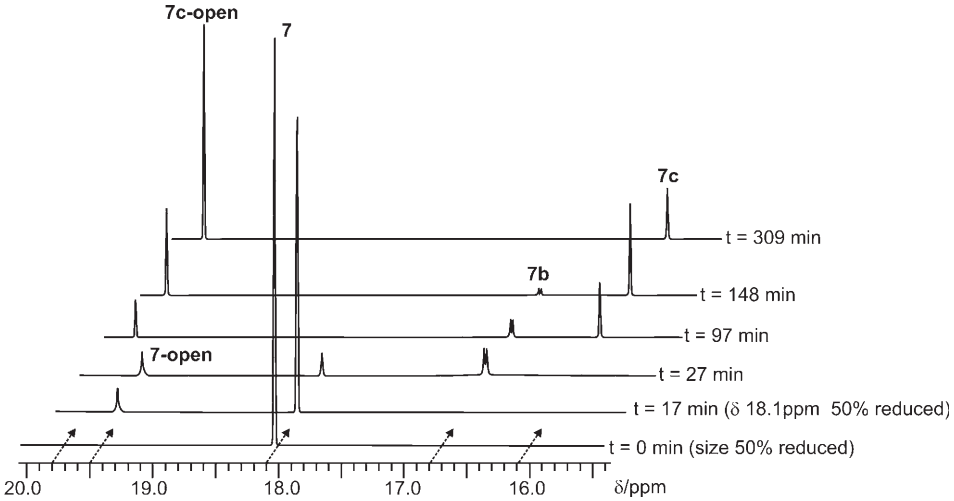


Figure 9. ^{1}H NMR spectra of the carbene proton region at different time intervals of a 1-octene/**7** reaction mixture in $CDCl_3$ at 50 °C.

carbene α-H peak of the benzylidene to lower field to produce a doublet and singlet is due to the change in the electronic environment of the ligand attached to the carbene carbon. The appearance of singlets at $\delta =$ 19.48 ppm and $\delta = 19.76$ ppm can be attributed to the decoordination of the N-donor to produce the open benzylidene (**7-open**) and methylidene (**7c-open**) intermediates. The downfield shift of the carbene signals is due to the decrease in electron density around the Ru=C moiety and therefore the carbene α-H becomes less shielded. A shift in the pyridine α-H signal was also observed during the course of the reaction, indicating that the electronic environment of the ligand is changing, most probably due to the coordination and decoordination of the N-donor atom as the reaction continues. The pyridine α-H signal of the coordinated benzylidene **7** appears at $\delta = 9.48$ ppm, but the other signals cannot be assigned with certainty to the coordinated and uncoordinated heptylidene and methylidene intermediates nor the uncoordinated benzylidene.

Figure 10 illustrates the change in the peak integration values of the individual carbene species as a function of time. The individual species seems to follow a similar pattern as was reported for **1** in which it has been shown that the heptylidene is thermodynamically and kinetically favoured above the methylidene species.[20] The sharp decrease of the benzylidene signal suggests a fast conversion of the benzylidene to either the uncoordinated benzylidene intermediate (**7-open**) or the heptylidene and methylidene; after 50 min all of **7** has been converted. The simultaneous decomposition of the benzylidene to some other species cannot be ruled out. The increase of the heptylidene signal to a maximum within 26 min is followed by a gradual decrease as the reaction proceeds while

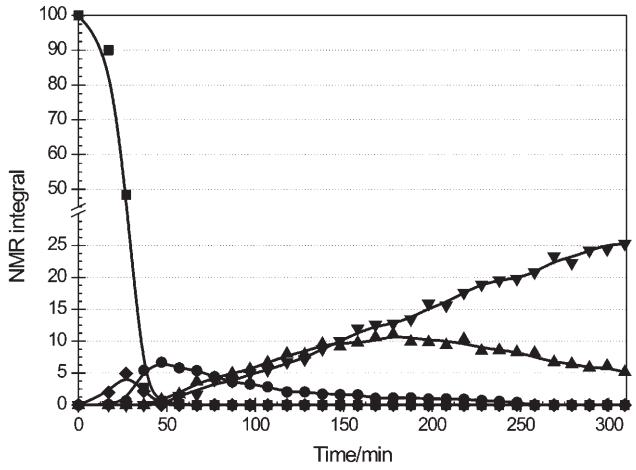


Figure 10. The ^{1}H NMR peak integration values (normalised) of the carbenes involved in the metathesis reaction of 1-octene in the presence of **7** [▼ $\delta = 19.76$ ppm, ◆ $\delta =$ 19.48 ppm, ■ $\delta = 18.05$ ppm, ● $\delta = 16.71$ ppm, ▲ $\delta =$ 16.08 ppm].

the methylidene signal gradually increases to a maximum within 3 h. This is followed by a slow decrease possibly due to catalyst decomposition or formation of the uncoordinated methylidene intermediate, which may be correlated to the gradual formation of the carbene α-H signal at $\delta = 19.76$ ppm. The form of the graph for signals $\delta = 19.48$ ppm and $\delta = 16.71$ ppm follows the same pattern, which suggests that these signals might be connected to each other in the form of the uncoordinated and coordinated heptylidene species, respectively. In the presence of 1-octene it seems as if the benzylidene is rapidly converted to the heptylidene while the formation of the methylidene proceeds at a much slower rate.

Conclusions

Complexes **4a** and **7** have been shown to be active for the self-metathesis of 1-octene. As expected, these systems show low reactivity at room temperature due to the additional stabilization of the chelating ligand. At elevated temperatures these systems show higher activity and stability towards the formation of PMP relative to **1** and **2**, since after 18 h **4a** and **7** still show activity for the metathesis of 1-octene. The SMP for both catalyst systems increases exponentially at temperatures above 70 °C with a slight decrease in the selectivity of **4a**, while a sharp decrease in selectivity and TON is observed for **7** at temperatures above 70 °C. This indicates that 60–70 °C is the optimum temperature for both **4a** and **7** to maintain high selectivity towards PMP and limit the formation of SMP and IP during the metathesis of 1-octene. The incorporation of a hemilabile ligand into the Grubbs systems therefore decreased the degree of SMP and IP formation and increased the activity and selectivity of **1** and **2**.

The NMR results indicate that the heptylidene is the catalytically active species that preferentially forms in the 1-octene metathesis reaction with **7** at 50 °C in $CDCl_3$. In contrast, both the heptylidene and methylidene species forms simultaneously during the 1-octene metathesis reaction with **4a**. Investigations are currently underway to verify the intermediate species formed during the reaction.

Experimental Section

General Procedures

Manipulations of organometallic compounds were performed using standard Schlenk techniques under an atmosphere of dry argon. All reactions were performed in oven-dried (100 °C) glassware. 1-Octene (Aldrich) was passed through a column of basic alumina and stored on molecular sieves (4 Å) under nitrogen. Solvents were dried by standard methods and distilled over 4 Å molecular sieves under nitrogen. $RuCl_2(PCy_3)L(=CHPh)$ [$L = PCy_3$ (**1**) or H_2Imes (**2**)] (Fluka) were used as received. The synthesis of ruthenium complexes **4a** and **7** was adapted from literature.[11] The ^1H NMR spectra were recorded on a Varian Gemini 300 Broadband NMR spectrometer at 300 MHz in deuterated chloroform. Gas chromatographic analyses were performed on an Agilent 6890 gas chromatograph equipped with an Agilent 7683 autoinjector, HP-5 capillary column (30 m × 320 μm × 0.25 μm) and a flame ionisation detector (FID). The following instrumental conditions were used: inlet temperature of 200 °C, oven programmed from 60 to 130 °C (hold time 16 min) and 130 to 290 °C (hold time 5 min) at 25 °C min^{-1}, N_2 carrier gas with a flow rate of 2 mL min^{-1} at 20 °C and FID temperature of 250 °C. For product identification the reaction mixtures were also analysed using an Agilent 6890 gas chromatograph equipped with an Agilent 7683 autosampler, HP-5 MS capillary column (30 m × 320 μm × 0.25 μm) and an Agilent 5973 mass selective detector (MSD). The same oven program was used as before with a 6 min solvent delay and He as carrier gas with a 1 mL min^{-1} flow rate at 20 °C.

The ^1H NMR investigations of the 1-octene metathesis reactions were performed in an NMR tube with 1-octene (0.05 mL, 0.32 mmol) mixed with a solution of the catalyst (0.032 mmol) in $CDCl_3$ (0.75 mL) at 50 °C. Spectra were recorded at approximately 13 min intervals.

Complex 4a

A solution of lithium alcoholate (0.650 mmol, 0.120 g) in THF (5 mL) was added dropwise to a solution of **1** (0.580 mmol, 0.479 g) in THF (5–10 mL). The reaction mixture was stirred at room temperature for 60 min with a colour change of dark purple to brown. The progress of the reaction was monitored by TLC to determine if the starting complex was being consumed. The reaction mixture was stirred until the TLC indicated that the starting complex was not present any more. After evaporation of the solvent, the residue was dissolved in a minimal amount of toluene. The lithium chloride was then removed by filtration *via* a syringe filter and the volume of the filtrate reduced to ca. 0 mL. THF (1 mL) was added to the residue and after layering 10–15 mL cold pentane onto the THF, it was placed in the refrigerator awaiting precipitation of the desired complex. After removal of the pentane *via* syringe, the desired complex was washed with cold pentane and sonificated for 10 min. The solid thus obtained was filtered and then dried under vacuum to afford **4a** as a dark brown microcrystalline powder; yield: 317.5 mg (85 %). $^{31}P(^1H)$ NMR (121 MHz, $CDCl_3$): $\delta = 41.5$ (s); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 17.85$ (d, 1H, Ru=CHPh), 7.09 (d, 2H, *ortho* H of C_6H_5), 7.38 (t, 1H, *para* H of C_6H_5), 6.97 (dd, 2H, *meta* H of C_6H_5), 8.95 (bs, 1H, *ortho* H of C_5H_4N), 6.97 (dd, 1H, *para* H of C_5H_4N), 6.90 (dd, 1H, *meta* H of C_5H_4N), 7.03 (dd, 1H, *meta* H of C_5H_4N), 0.85–2.45 (m, 43H, CH_2 of PCy_3 and C_6H_{10}); anal. calcd. for $C_{36}H_{53}ClNOPRu$ (683.76 g mol^{-1}): C 63.24, H 7.81, N 2.05; found: C 62.82, H 8.05, N 1.77.

Complex 7

A solution of lithium alcoholate (0.650 mmol, 0.120 g) in THF (5 mL) was added dropwise to a solution of **2** (0.620 mmol, 0.527 g) in THF (5–10 mL). The reaction mixture was stirred at 30–40 °C for 1 h with a colour change of brown to dark green. The progress of the reaction was monitored by TLC to determine if the starting complex was being consumed. The reaction mixture was stirred until the TLC indicated that the starting complex was not present any more. After removing the solvent under vacuum the residue was dissolved in a minimal amount of toluene. The lithium chloride was then removed by filtration *via* a syringe filter and the toluene removed under vacuum. THF (1 mL) was added to the residue. The product was precipitated by layering 10–15 mL cold pentane onto the THF and placing it in a refrigerator for 8 h. After removal of the pentane *via* syringe, the desired complex was washed with cold pentane and sonificated for 10 min. The solid thus obtained was filtered and then dried under vacuum to afford **7** as a forest green microcrystalline powder; yield: 370 mg (84 %).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 17.96$ (s, 1H, Ru=CHPh), 7.25 (d, 2H, *ortho* H of C_6H_5), 7.05–7.15 (m, 1H, *para* H of C_6H_5), 6.88 (dd, 2H, *meta* H of C_6H_5), 9.55 (d, 1H, *ortho* H of C_5H_4N), 7.05–7.15 (m, 1H, *para* H of C_5H_4N), 6.78 (dd, 1H, *meta* H of C_5H_4N), 6.60 (d, 1H, *meta* H of C_5H_4N), 6.66 and 6.88 (bs, 4H, *meta* H mesityl), 3.85 (m, 4H, CH_2 of NHC), 2.15, 2.40 and 2.55 (s, CH_3 mesityl), 1.25–1.65 (m, 10H, CH_2 of C_6H_{10}); anal. calcd. for $C_{39}H_{47}ClNOPRu$ (683.76 g mol^{-1}): C 65.94, H 6.67, N 5.92; found: C 66.45, H 6.58, N 5.29.

General Experimental Procedure for Self-Metathesis Experiments

The metathesis reactions were carried out in a 100-mL three-necked round-bottom flask fitted with a reflux condenser, thermometer and septum. 1-Octene (20 mL, 0.127 mmol) and nonane (1 mL) were transferred to the flask after flushing it for 5 min with a steady stream of Ar. Nonane served as internal standard for quantification. The solution was heated to 60 °C, and the catalyst (0.015 mmol) was added to the flask, and the reaction mixture stirred for 7 h. Samples (0.3 mL) were withdrawn by syringe at regular time intervals, quenched with a solution of toluene (0.3 mL) and tert-butyl hydrogen peroxide (2 drops) and then analysed by GC/FID. The sample collected after 3 h was also analysed by GC/MSD to characterise the mixture. Conversions are reported as the molar % 1-octene that was converted to the desired 7-tetradecene product.

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