

A Comparison of the Activity of Homogeneous Tungsten and Ruthenium Catalysts for the Metathesis of 1-Octene

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Abstract: The $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ catalytic systems ($X = Ph, F, Cl, Br$) have a high activity for the metathesis of terminal alkenes and a high selectivity towards primary metathesis products. Tungsten(VI) alkoxide complexes are not nearly as active as the tungsten(VI) aryloxy complexes. Brønsted acids such as HOAc, BuOH and H_2O deactivate both the $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ ($X = Cl$ and Ph) catalytic systems. The Lewis base (BuOAc) showed no deactivation of the catalytic systems. The Grubbs catalyst, $RuCl_2(PCy_3)_2(=CHPh)$, is very active for the metathesis of 1-alkenes, even at an alkene/Ru molar

ratio = 100,000. Selectivities > 93% were generally obtained. The ruthenium catalyst is active at low temperatures (25 °C) and high temperatures (130 °C). It shows a high tolerance towards oxygen-containing additives. The polarity of the solvent plays a major role in the activity and also the selectivity of especially the $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ catalytic systems.

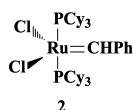
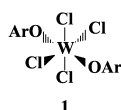
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Introduction

A large number of catalysts and catalytic systems initiate the alkene metathesis reaction.^[1] However, most of the early work on alkene metathesis was done using ill-defined multi-component catalytic systems that were furthermore easily poisoned by especially oxygen-containing additives. In our research we are interested in finding a catalytic system with a high activity towards longer chain terminal alkenes, with a high tolerance towards oxygen-containing additives and a high selectivity for the primary metathesis products (PMP) that can also be used in an industrial environment.^[2,3] Other general aspects of interest for industrial applications include the complexity of the catalytic system or catalyst, ease of synthesis, cost, etc.

Of interest in this study is the two-component tungsten catalytic system based on the precatalyst **1** and the one-component first generation Grubbs catalyst **2**.^[4,5]

It is well known that the two-component system containing a tungsten(VI) aryloxy complex of the type

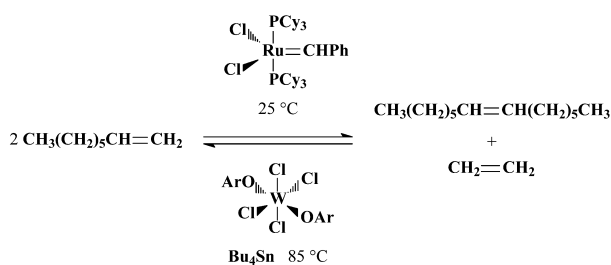


$W(OAr)_nCl_{6-n}$ (OAr = phenoxide or substituted phenoxide) and a tetraalkyltin (R_4Sn , $R = Me, Bu$) compound is very effective in alkene metathesis reactions, also with regard to functionalised alkenes.^[1,4,6]

Due to the versatility of the electronic and steric properties of the various aryloxy ligands, it is possible to control the activity and sometimes the stereoselectivity of the metathesis reaction.^[4,6] If the electron-withdrawing properties of the aryloxy ligands are increased an increase in the metathesis activity were observed.^[6] Another factor influencing the metathesis reaction is the position of the substituent on the aryloxy ligands. Complexes with substituents on positions 2 and 6 of the aryloxy ligands were found to be more active catalysts for the metathesis of 1-alkenes.^[4,7-9]

It is only in recent years that well-defined catalytic systems were developed. The Grubbs ruthenium carbene system **2** is an excellent example of this new generation catalyst.^[5] Unlike the early metathesis catalytic systems these catalysts do not require Lewis acid cocatalysts or promoters.

The ruthenium carbene systems have drawn a lot of attention, not only do they exhibit high reactivity in a variety of ROMP, RCM, and cross-metathesis reactions under mild conditions, but also because of their remarkable tolerance towards many different organic functional groups.^[1,5] Catalytic activity is not reduced



Scheme 1.

Table 1. Formation of the different metathesis products during the metathesis of 1-octene.

Reactions	Substrates	Products
1a Primary metathesis reaction		
Homometathesis	2 C ₇ =C	C ₇ =C ₇ + C=C
1b Isomerisation	C ₇ =C	C ₆ =C ₂
1c Secondary metathesis reactions		
Cross metathesis	C ₇ =C + C ₆ =C ₂	C ₇ =C ₆ + C ₂ =C C ₇ =C ₂ + C ₆ =C C ₆ =C ₆ + C ₂ =C ₂
Homometathesis	2 C ₆ =C ₂	

significantly in air, moisture or due to minor impurities in solvents.

In this study, the activity and influence of solvents and additives were investigated on the metathesis of 1-octene in the presence of the RuCl₂(PCy₃)₂(=CHPh) catalyst and the results compared to those obtained in the presence of the W(O-2,6-C₆H₃X₂)₂Cl₄/Bu₄Sn (X = F, Cl, Br, Ph) catalytic systems (Scheme 1).

Results and Discussion

Reaction Products

Gas chromatographic analyses of the reaction mixtures indicated the formation of primary (PMP) and secondary (SMP) metathesis products. In the case of the W catalytic systems the formation of Bu₃SnCl was also observed. The formation of some of the different metathesis products is illustrated in Table 1. Reactions 1b and 1c are repeated with the 1-heptene, 1-pentene, etc., formed during the secondary cross metathesis reactions to give alkenes ranging from C₃ to C₁₃.^[8,9] The selectivity of the reaction is defined as the % PMP of the total amount of metathesis products.

Catalytic Activity of the W Systems

In previous studies we found that the optimum reaction conditions for the W(O-2,6-C₆H₃X₂)₂Cl₄/Bu₄Sn catalytic systems are a reaction temperature of *ca.* 85 °C, Sn/W

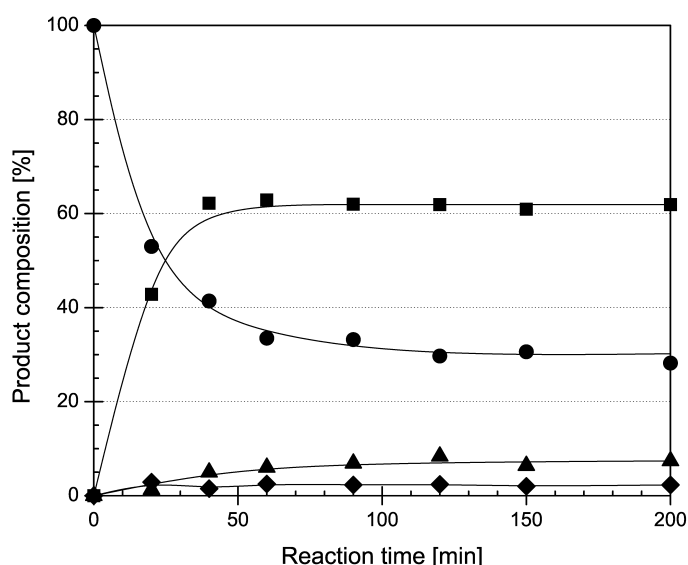


Figure 1. Kinetics of the metathesis reaction of 1-octene in the presence of the W(O-2,6-C₆H₃Cl₂)₂Cl₄/Bu₄Sn catalytic system (temp. = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; solvent = PhCl). [● 1-octene; ■ PMP; ▲ SMP; ◆ Bu₃SnCl].

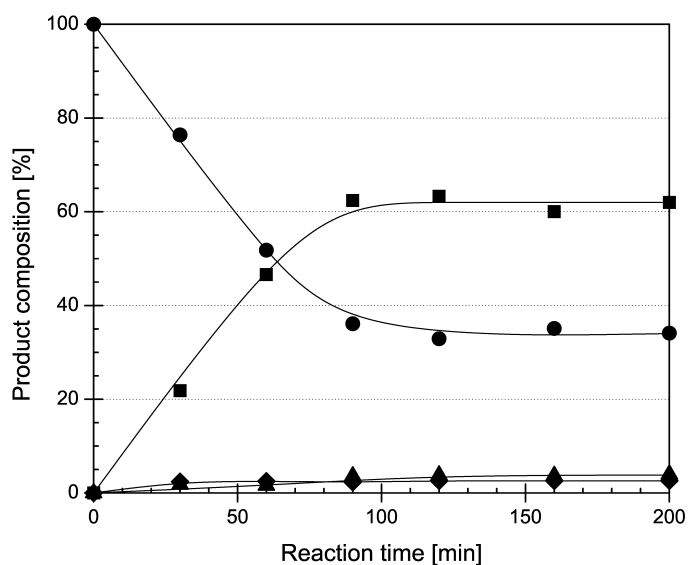


Figure 2. Kinetics of the metathesis reaction of 1-octene in the presence of the W(O-2,6-C₆H₃Ph₂)₂Cl₄/Bu₄Sn catalytic system (temp. = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; solvent = PhCl). [● 1-octene; ■ PMP; ▲ SMP; ◆ Bu₃SnCl].

molar ratio = 3 and an activation time of 20 min.^[8,9] Under these optimum conditions the kinetic profiles of the reactions of 1-octene in the presence of the W(O-2,6-C₆H₃X₂)₂Cl₄/Bu₄Sn systems, X = Ph and Cl, are illustrated in Figures 1 and 2. Similar results were obtained for the two systems with regard to the primary metathesis products and Bu₃SnCl, i.e., yields 61–64% and *ca.* 3% respectively. With the Ph-substituted system

a higher selectivity (94% vs. 88%) was obtained than with the Cl-substituted system, albeit at a slower reaction rate (completion after *ca.* 90 min vs. *ca.* 40 min).

Quignard et al. found that the electronic and steric properties of the aryloxide ligands play a role in the activity and sometimes the stereoselectivity of the metathesis reaction.^[1,4,6,7] In this study we investigated a number of aryloxide and alkoxide ligands. The same reaction conditions as mentioned before were used for both the tungsten(VI) aryloxide and tungsten(VI) alkoxide derivatives.

For the metathesis of 1-octene the $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ catalytic system with $X = F, Cl, Br$ were used to determine the electronic influence of the ligands on the metathesis activity and selectivity. The results of the aryloxide derivatives of the tungsten precatalyst are given in Table 2. In all three cases a yield of *ca.* 60% PMP and selectivities > 85% were obtained. The $W(O-2,6-C_6H_3F_2)_2Cl_4/Bu_4Sn$ catalytic system gives a slightly higher yield of SMP's than the other two systems. Similar results were obtained if the aryloxide ligand of

the $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ complex was modified with an additional fluorine atom on position 4.

With the more steric and less electron-withdrawing ligand ($X = Ph$) a yield of *ca.* 63% PMP were obtained with the SMP yield dropping by about half to *ca.* 4%. This resulted in an increase in the selectivity to above 94% which is higher than the catalytic systems with more electron-withdrawing groups.

The tungsten(VI) alkoxide complexes were prepared in the same way as the tungsten(VI) aryloxide derivative.^[6] The results of these complexes with Bu_4Sn as cocatalyst are shown Table 3.

The alkoxide ligands of both the $W(OCH(C_6H_5)_2)_2Cl_4$ and $W(OC(C_6H_5)_3)_2Cl_4$ complexes are bulky groups and can be compared with the steric effect of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system. Both these complexes were insoluble in almost all the solvents and no activity was observed. The alkoxide ligands of the $W(OC(CH_3)(CF_3)_2)_2Cl_4/Bu_4Sn$ catalytic system is more electron-withdrawing. This catalytic system gave a yield of about 28% PMP and 13% C_{16} -dimers at a reaction temperature of 25 °C. The same catalytic system is less active at a reaction temperature of 85 °C. The yield of SMP at both temperatures is < 1%.

The influence of the alkene/W molar ratio on the activity of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ catalytic systems ($X = Ph, Cl$) were also investigated and the results are illustrated in Table 4. A rapid decrease in PMP to below 12% with an increase in alkene/W molar ratio was observed. The decrease in selectivity of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalytic system was far greater than in the case of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ system, i.e., a decrease of *ca.* 25% and *ca.* 10% respectively.

Table 2. Influence of different OAr ligands on the metathesis activity of the $W(OAr)_2Cl_4/Bu_4Sn$ catalytic systems with 1-octene (temp. = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; reaction time = 2 h; solvent = PhCl).

-OAr	PMP [%]	SMP [%]	Selectivity [%]
-O-2,6- $C_6H_3Ph_2$	63.3	3.8	94.3
-O-2,6- $C_6H_3F_2$	57.5	9.5	85.7
-O-2,6- $C_6H_3Cl_2$	61.9	8.4	88.0
-O-2,6- $C_6H_3Br_2$	61.5	7.2	89.5
-O-2,6- Cl_2 -4-F- C_6H_3	59.9	7.1	89.4

Table 3. Influence of different OR ligands on the metathesis activity of the $W(OR)_2Cl_4/Bu_4Sn$ catalytic systems with 1-octene (temp. = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; reaction time = 2 h; solvent = PhCl).

-OR	PMP [%]	SMP [%]	C_{16} -dimers [%]
-OCH(C_6H_5) ₂		No reaction	
-OC(C_6H_5) ₃		No reaction	
-OC(CH ₃)(CF ₃) ₂ (Temp. = 25 °C)	27.7	1.0	12.9
-OC(CH ₃)(CF ₃) ₂	7.0	0.7	0.0

Table 4. Influence of the alkene/W molar ratio on the metathesis activity of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ catalytic systems with 1-octene (temp. = 85 °C; Sn/W molar ratio = 3; activation time = 20 min; reaction time = 2 h; solvent = PhCl).

$W(O-2,6-C_6H_3X_2)_2Cl_4$	Alkene/W molar ratio	PMP [%]	SMP [%]	Selectivity [%]
$W(O-2,6-C_6H_3Ph_2)_2Cl_4$	100	63.3	3.8	94.6
	500	26.4	2.8	93.6
	1000	11.6	1.0	85.2
$W(O-2,6-C_6H_3Cl_2)_2Cl_4$	100	61.9	8.4	88.0
	1000	9.4	5.6	62.6

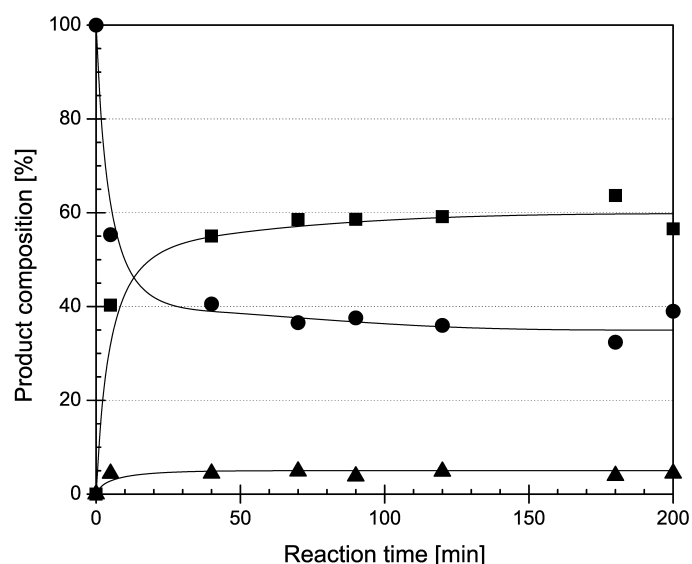


Figure 3. Kinetics of the metathesis reaction of 1-octene in the presence of the $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ complex (temp. = 25 °C; alkene/Ru molar ratio = 100; solvent = PhCl). [● 1-octene; ■ PMP; ▲ SMP].

Catalytic Activity of the Ru Catalyst

We compared the tungsten catalytic systems with the well-defined first generation Grubbs catalyst, $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$. The reaction conditions were the same as for the tungsten catalytic systems except that no cocatalyst was added and the reactions were generally performed at 25 °C. The kinetic profile of the metathesis reactions of 1-octene is illustrated in Figure 3. The primary metathesis reaction is initially very rapid reaching ca. 40% PMP within 10 min and finally ca. 60% PMP after 80 min. The formation of SMP were below 5% resulting in a high selectivity of ca. 93%.

We also investigated the metathesis activity at reaction temperatures of 85 and 130 °C (Table 5). No significant difference in metathesis activity was observed, although a decrease in PMP and SMP were evident. The selectivity was not influenced by the increase in temperature and remained high (> 92%).

Contrary to the $\text{W}(\text{O}-2,6-\text{C}_6\text{H}_3\text{X}_2)_2\text{Cl}_4/\text{Bu}_4\text{Sn}$ catalytic systems $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ remained active at very high alkene/Ru molar ratios (Table 6). It is only above

Table 5. Influence of the reaction temperature on the metathesis activity of the $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ complex with 1-octene (alkene/Ru molar ratio = 100; reaction time = 2 h; solvent = PhCl).

Temperature [°C]	PMP [%]	SMP [%]	Selectivity [%]
25	59.2	4.8	92.5
85	62.2	4.4	93.4
130	51.4	3.6	93.5

Table 6. Influence of the alkene/Ru molar ratio on the metathesis activity of the $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ complex with 1-octene (temp. = 25 °C; reaction time = 2 h; solvent = PhCl).

Alkene/Ru molar ratio	PMP [%]	SMP [%]	Selectivity [%]
100	59.1	4.3	93.1
650	60.0	2.0	96.7
1,000	57.8	1.6	97.3
10,000	56.7	0.5	99.0
40,000	51.6	0.6	98.9
100,000	48.7	0.5	99.0
200,000	33.7	0.3	98.9

an alkene/Ru molar ratio of 100,000 that a significant decrease in PMP was observed. Of interest is the increase in selectivity to ca. 99% with the increase in the alkene/Ru molar ratio.

Solvents

The influence of solvents on the metathesis activity of the $\text{W}(\text{O}-2,6-\text{C}_6\text{H}_3\text{X}_2)_2\text{Cl}_4/\text{Bu}_4\text{Sn}$ (X = Ph, Cl) catalytic systems and $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ were investigated to optimise the reaction conditions.^[9] The solvents, cyclohexane, toluene, benzene, diethyl ether, chlorobenzene, nitrobenzene, 2-propanol, butanol, ethanol, methanol and water were used. The yield of metathesis products and the selectivity were compared to the polarity of each solvent according to the E_T polarity scale of Reichardt.^[10] The results of the $\text{W}(\text{O}-2,6-\text{C}_6\text{H}_3\text{X}_2)_2\text{Cl}_4/\text{Bu}_4\text{Sn}$ systems are illustrated in Figure 4.

In toluene, benzene, diethyl ether and chlorobenzene relatively high PMP yields (> 45%) were obtained. These solvents are all in the polarity range of 0.08–0.2. In chlorobenzene the highest yields of PMP of ca. 60% were obtained. An increase in SMP was observed in toluene, benzene and diethyl ether. The highest selectivities were observed in chlorobenzene followed by an estimated steady decline in solvents of higher polarities.

Cyclohexane is a non-polar solvent and yields of ca. 32% PMP and 4% SMP were obtained. If water, the most polar solvent, were used with the $\text{W}(\text{O}-2,6-\text{C}_6\text{H}_3\text{X}_2)_2\text{Cl}_4/\text{Bu}_4\text{Sn}$ catalytic systems no metathesis was observed.

The results with $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ are illustrated in Figure 5. For both diethyl ether and chlorobenzene high yields of PMP (ca. 62 and 60% respectively) and low yields of SMP (ca. 4% for both) were obtained. In toluene the yields were ca. 50% PMP and 3% SMP. If cyclohexane is used as the solvent, 30% PMP and 2% SMP were obtained, while in the case of the alcohols and water the yields were ca. 35% and 4%, respectively. A steady decrease in selectivity from ca. 95% to ca. 88% was observed with an increase in the polarity of the solvent.

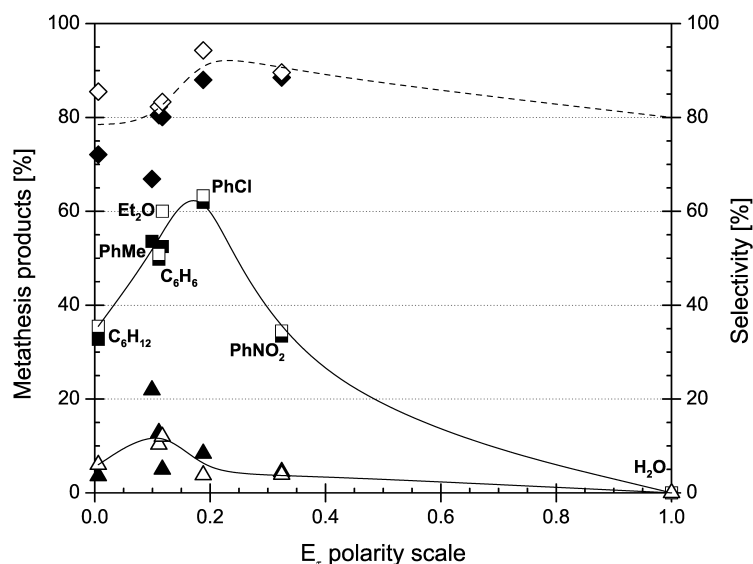


Figure 4. Influence of the solvent on the metathesis activity of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ catalytic systems with 1-octene (temp. = 85 °C; Sn/W molar ratio = 3; activation time = 20 min; reaction time = 2 h; solvent = PhCl). [closed markers: X = Cl, open markers: X = Ph; ■, □ PMP; ▲, △ SMP; ◆, ◇ selectivity]

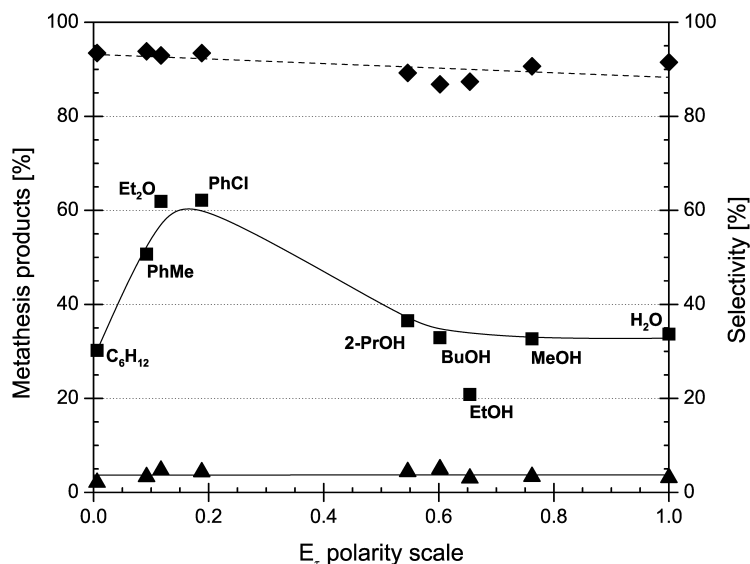


Figure 5. Influence of the solvent on the metathesis activity of the $RuCl_2(PCy_3)_2(=CHPh)$ complex with 1-octene (temp. = 25 °C; alkene/Ru molar ratio = 100; reaction time = 2 h; solvent = PhCl). [■ PMP; ▲ SMP; ◆ selectivity].

Additives

The influence of different additives with similar boiling points than 1-octene (bp 121.3 °C), i.e., water (bp 100 °C), butanol (BuOH; bp 117.3 °C), acetic acid (MeCOOH; bp 117.9 °C) and butyl acetate (MeCOOBu; bp 126.5 °C) on the activity of the $W(O-2,6-C_6H_3X_2)_2Cl_4/SnBu_4$ catalytic systems were investigated. The results are shown in Table 7.

The $W(O-2,6-C_6H_3Ph_2)_2Cl_4/SnBu_4$ catalytic system showed less deactivation in the presence of additives than the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/SnBu_4$ catalytic system.

The addition of MeCOOBu showed no deactivation of both catalytic systems, but the hydrogen-containing additives BuOH, H₂O and MeCOOH led to the deactivation of both systems with only 1% additives added.

The influence of the additives water, BuOH, MeCOOH, acetic anhydride [(MeCO)₂O; bp 139.6 °C], 2-pentanone (MeCOPr; bp 102 °C) and butyl acetate (MeCOOBu) were also investigated on the metathesis activity of the $RuCl_2(PCy_3)_2(=CHPh)$ catalyst. The results are illustrated in Table 8.

Generally the $RuCl_2(PCy_3)_2(=CHPh)$ catalyst showed the same or a slight increase in PMP yield in the presence

Table 7. Influence of additives on the PMP yield of the $W(OAr)_2Cl_4/Bu_4Sn$ catalytic systems with 1-octene (temp. = 85 °C; Sn/W molar ratio = 3; alkene/W molar ratio = 100; activation time = 20 min; reaction time = 2 h; solvent = PhCl).

Additive/W molar ratio	Additives [PMP yield (%)]			
	H ₂ O	BuOH	MeCOOH	MeCOOBu
$W(O-2,6-C_6H_3Cl_2)_2Cl_4$				
0.0	61.9	61.9	61.9	61.9
1.0	5.4	2.0	1.0	68.0
2.0	0.0	0.0	0.0	65.2
$W(O-2,6-C_6H_3Ph_2)_2Cl_4$				
0.0	63.3	63.3	63.3	63.3
1.0	26.8	20.0	16.4	62.2
2.0	10.0	4.0	0.0	58.4

Table 8. Influence of additives on the metathesis activity of the $RuCl_2(PCy_3)_2(=CHPh)$ complex with 1-octene (temp. = 25 °C; alkene/Ru molar ratio = 100; reaction time = 2 h; solvent = PhCl).

Additive	Additive/Ru molar ratio	PMP [%]	SMP [%]	Selectivity [%]
H ₂ O	0	59.2	4.8	92.5
	2	70.9	0.0	100.0
	5	70.4	0.0	100.0
	10	35.7	3.3	91.4
BuOH	2	65.1	1.4	97.8
	5	61.0	1.5	97.5
	10	49.8	1.0	95.3
MeCOOH	2	63.3	1.2	98.0
	5	62.6	0.9	98.4
	10	61.2	0.4	99.2
MeCOPr	2	61.5	4.0	93.8
	5	57.0	2.7	95.4
	10	61.0	2.0	95.2
MeCOOBu	2	61.9	3.8	94.0
	5	62.6	2.6	95.8
	10	62.0	2.8	95.6
(MeCO) ₂ O	2	66.5	2.8	95.8
	5	54.9	2.0	96.4
	10	52.3	3.2	94.1

of 2 and 5% additives. This is also true for the addition of 10% MeCOOH, MeCOPr and MeCOOBu. A significant decrease is observed when 10% BuOH and (MeCO)₂O (also true for the addition of 5% of the latter) are added. A decrease in SMP and an increase in selectivities were observed with the addition of all the additives.

Conclusion

The $W(O-2,6-C_6H_3X_2)_2Cl_4$ complexes (X = Ph, F, Cl, Br), in the presence of Bu_4Sn , have a high activity for the metathesis of long chain terminal alkenes and a high selectivity towards primary metathesis products. The $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system has the highest activity and also the highest selectivity. The tungsten(VI) alkoxide complexes are not nearly as

active as the aryloxide complexes. It seems as if a phenyl group is necessary for the activity and also the stability of the catalyst.

The catalytic activity and selectivity of the $RuCl_2(PCy_3)_2(=CHPh)$ catalyst are comparable to those of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system but with a reaction rate *ca.* 2-fold faster. It remains active even at alkene/Ru molar ratio = 10,000. With an increase in the alkene/Ru molar ratio a higher selectivity towards the primary metathesis products were obtained. The ruthenium catalyst is active at low (25 °C) and high temperatures (130 °C). It is also active in the absence of a solvent and in air.

The tolerance of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ (X = Cl and Ph) catalytic system to oxygen-containing additives is much lower than the $RuCl_2(PCy_3)_2(=CHPh)$ catalyst, with $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ the best of the two W precatalysts. Brønsted acids such as MeCOOH,

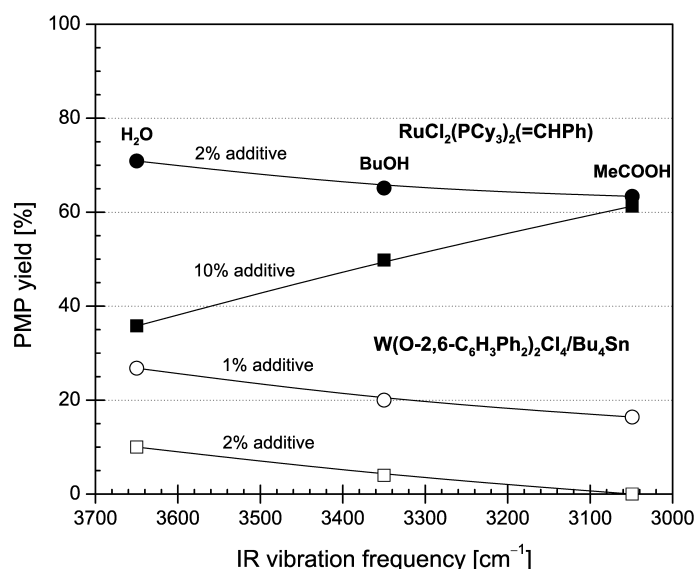


Figure 6. Relation between the OH stretching IR vibration frequency of the additive and the PMP yield. [closed: $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$; open: $\text{W}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Ph}_2)_2\text{Cl}_4/\text{Bu}_4\text{Sn}$].

BuOH , and H_2O deactivate both the $\text{W}(\text{O}-2,6\text{-C}_6\text{H}_3\text{X}_2)_2\text{Cl}_4/\text{Bu}_4\text{Sn}$ ($\text{X} = \text{Cl}$ and Ph) catalytic systems. This is most probably because they have a hydrogen to donate, which could react with the catalyst. H_2O have the strongest OH bond of the Brønsted acids investigated (based on the OH stretching IR vibration frequencies).^[11] It is therefore the weakest Brønsted acid in the series, thus it will be the last to donate its hydrogen. This could explain why the stronger Brønsted acids have a bigger deactivation influence. This is confirmed if the PMP yield is plotted against the frequencies of the OH stretching vibrations (Figure 6). A slight, but similar, decrease in PMP yield is observed for both $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ and $\text{W}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Ph}_2)_2\text{Cl}_4$ with a decrease in OH bond strength at 1–2% additive additions. If however the amount of additive is increased to 10% in the case of the $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ catalyst the reverse is true. Generally the Lewis bases did not deactivate the catalytic systems with the exception of $(\text{MeCO})_2\text{O}$.

Different solvents were used for the metathesis reaction of the $\text{W}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Ph}_2)_2\text{Cl}_4/\text{Bu}_4\text{Sn}$ catalytic system and the $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ catalyst. In this study it is clear that the polarity of the solvent plays a major role in the activity and also the selectivity of especially the $\text{W}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Ph}_2)_2\text{Cl}_4/\text{Bu}_4\text{Sn}$ catalytic system. A polarity of about 0.08–0.2 is necessary for a high metathesis activity and at a polarity of 0.11–0.2 for high selectivity. For the $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ catalyst the polarity only plays a role in determining the activity and not so much the selectivity of the reaction. A polarity of 0.08–0.2 is necessary for a high activity of the catalyst.

Experimental Section

Reagents and Synthesis of W Complexes

The tungsten precatalysts were synthesised using the method of Quignard et al.^[6,8,9] WCl_6 (Merck), phenolic compounds [2,6-difluorophenol, 2,6-dichlorophenol, 2,6-dibromophenol, 2,6-diphenylphenol, and 2,6-dichloro-4-fluorophenol (Aldrich)] and alcohols [triphenylcarbinol, diphenylmethanol (Aldrich)] were used as obtained from the supplier. The alkylating reagent (Bu_4Sn) is a commercial product obtained from Aldrich and was used as received.

The solvents, cyclohexane, toluene, diethyl ether, chlorobenzene, 2-propanol, butanol, ethanol methanol (Merck), and benzene (Holpro), were dried using 4 Å molecular sieves and stored under nitrogen over 4 Å molecular sieves. 1-Octene (Aldrich), was degassed and stored under a nitrogen atmosphere. The additives, 2-pentanone, butanol, acetic acid, butyl acetate and acetic anhydride (Merck), were also dried and stored like the solvents.

For the synthesis of $\text{W}(\text{OAr})_2\text{Cl}_4$ and $\text{W}(\text{OR})_2\text{Cl}_4$ a solution of the phenol or alcohol (5×10^{-3} mol) in CCl_4 (20 cm^3) was added to a solution of WCl_6 (2.5×10^{-3} mol) in CCl_4 (20 cm^3). The mixture was refluxed with continuous stirring for 4 h. The resulting complex was filtered, dried and stored under nitrogen.

The $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ catalyst were used as obtained from the supplier (Strem).

Catalytic Reactions

All catalytic reactions were carried out under nitrogen using standard techniques and all additions of liquids were made using gas-tight syringes. The W precatalyst (5×10^{-5} mol) was placed in a mini-reactor filled with nitrogen. This was followed by the addition of the solvent (2.5 cm^3) and Bu_4Sn (1.5×10^{-4} mol). The catalyst mixture was then heated to 85 °C. An activation period of 20 min was allowed before the alkene (5×10^{-3} mol) was added to the mixture. The progress of the reaction was followed by gas chromatographic analysis at regular intervals. For both the influence of solvents and additives the reaction was terminated after 2 h with an excess amount of water (ca. 0.5 cm^3). 1,2-Dichlorobenzene was used as the internal standard for GC analyses.

The reaction conditions was the same for the $\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})$ complex except that no cocatalyst was used.

These reaction conditions were used throughout unless otherwise indicated.

Analysis

Reaction mixtures were analysed on a Carlo Erba HRGC 5300 gas chromatograph equipped with an Alltech SE-30 capillary column (30 m \times 0.32 mm \times 0.25 μm) and flame ionisation detector (FID). The following instrument conditions were used: inlet temperature = 300 °C; injection volume = 0.2 μL , oven programme = 70–250 °C at 10 °C min^{-1} , N_2 carrier gas with a flow rate = 2 $\text{cm}^3 \text{min}^{-1}$ at 20 °C and FID temperature = 350 °C.

The internal standard method was used to calculate the % mol 1-alkene and metathesis products formed.

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