

The metathesis of 1-octene with the $W(O-2,6-C_6H_3X_2)_2Cl_4/R_4Sn$ catalytic system

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Abstract

The tungsten(VI) complexes $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ and $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ are active catalysts for the metathesis of 1-octene in the presence of R_4Sn ($R = Bu, Me$) compounds as cocatalysts. Optimum metathesis conditions are an interaction time of ≥ 10 min, interaction and reaction temperatures $> 65^\circ C$, Sn/W molar ratio = 3. Slow isomerisation (followed by secondary metathesis reactions) and dimerisation occur in parallel with the primary metathesis reaction i.e. the formation of 7-tetradecene and ethene. No metathesis is observed using $W(O-2,6-C_6H_3Me_2)_2Cl_4$ and $W(O-2,6-C_6H_3Bu'_2)_2Cl_4$ as catalysts under the same conditions. Deactivation of the catalytic systems are observed in the presence of added oxygenates. The $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system showed less deactivation than the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalytic system. The catalytic systems are also active in an air atmosphere.

Keywords: Alkene metathesis; 1-octene; Tungsten(VI)oxyaryl derivatives; Oxygenates; Deactivation

1. Introduction

The search for the ideal homogeneous catalytic system for the metathesis of alkenes has led to inter alia the discovery of the particular catalytic activity of tungsten(VI)aryloxy complexes of the type $W(OAr)_nCl_{6-n}$ ($OAr =$ unsubstituted or substituted phenoxides; $n = 1-4, 6$) [1–7]. These complexes are known to provide very active metathesis catalysts for linear, cyclic and functionalised alkenes in the presence of a cocatalyst like R_xAlCl_{3-x} , R_4M ($M = Sn, Pb$) or R_3SnH . Metathesis activity was also observed in the absence of a cocatalyst i.e. ROMP of dicyclopentadiene with $W(OAr)Cl_5$ [7].

Of these complexes $W(OAr)_2Cl_4$ seems par-

ticularly active for the metathesis of terminal and internal alkenes, as well as co-metathesis reactions and olefinic esters [2,4]. Factors influencing the metathesis activity of these complexes include the nature and position of substituents on the aryloxy ligand, the nature and content of the cocatalyst, interaction time and temperature, and the reaction temperature. Of special significance is the increase in metathesis activity observed with an increase in the electron-withdrawing properties of the aryloxy ligand [4]. No side-reactions i.e. isomerisation, solvent alkylation or dimerisation were observed with the alkenes or olefinic esters used. Alkenes that were investigated were *cis*- and *trans*-2-pentene, and for the co-metathesis reaction 1-tetradecene and 1-decene [4].

In this paper we report on the reactions of 1-octene in the presence of the $W(O-2,6-$

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$C_6H_3X_2)_2Cl_4/R_4Sn$ catalytic systems ($X = Cl, Ph, Me, Bu^t$; $R = Bu, Me$) and the deactivation in the presence of added oxygenates.

2. Experimental

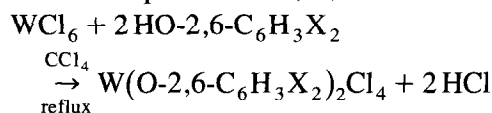
All synthesis and catalytic reactions were carried out under nitrogen using standard techniques.

2.1. Reagents

The phenolic compounds (2,6-dichlorophenol, 2,6-diphenylphenol, 2,6-dimethylphenol and 2,6-di-*tert*-butylphenol) were used as obtained from the supplier. Chlorobenzene was dried over phosphorous(V)oxide and distilled under nitrogen. CCl_4 , 1-pentene, 2-pentanone, butyl acetate, acetic acid, butanol, water and the R_4Sn ($R =$ butyl and methyl) compounds were degassed and stored under nitrogen. WCl_6 was purified by sublimation and stored under nitrogen. Only Merck reagents were used.

2.2. Synthesis of $W(O-2,6-C_6H_3X_2)_2Cl_4$

The synthesis method of Quignard et al. [5] was used to synthesise the 2,6-disubstituted aryloxide complexes of W(VI):



with $X = Cl, Ph, Me, Bu^t$. The synthesis reactions were performed under nitrogen and additions were made using gastight syringes. A solution of $HO-2,6-C_6H_3X_2$ (2.5×10^{-3} mol) in CCl_4 (20 cm^3) was added to a suspension of WCl_6 (5.0×10^{-3} mol) in CCl_4 (20 cm^3). The reaction mixture was stirred under reflux for 4 h. The complex was then filtered and dried under a constant stream of nitrogen. A percentage yield of approximately 80% was obtained in each case.

2.3. Catalytic reaction

All catalytic reactions were performed in Supelco glass reaction vials fitted with Mininert

valves and additions were made using gastight syringes. The tungsten catalyst (5×10^{-5} mol) was placed in the reaction vial under nitrogen, sealed and the solvent chlorobenzene (2.5 cm^3) added. The mixture was then heated to 85°C after which the cocatalyst (1.5×10^{-4} mol) was added. 1-octene (2.5×10^{-3} mol) was added to the reaction mixture after an activation period of 20 min at 85°C and the reaction mixture was stirred for 5 h. The addition of an excess amount of water (0.5 cm^3) terminated the reaction and an internal standard for GC analysis i.e. 1,2-dichlorobenzene was added to the reaction mixture.

For the deactivation studies the oxygenates were mixed with 1-octene to ensure that both entered the reaction vial at the same time.

2.4. Analysis

Gas chromatographic analyses were performed on a Varian Series 2400 gas chromatograph linked to an IBM computer with the DAPA integration software. The following conditions were used:

column: Perkin-Elmer OV1 stainless steel capillary column ($50 \text{ in.} \times 0.020 \text{ in.}$)

temperature program: $120-220^\circ\text{C}$ ($10^\circ\text{C min}^{-1}$)

carrier gas: N_2 ($23 \text{ cm}^3 \text{ min}^{-1}$ at 20°C)

detector: FID at 350°C .

The internal standard method (with 1,2-dichlorobenzene) was used to calculate the mol% 1-octene and products. Peak identification was performed using GC/MS and spiking with authentic samples.

3. Results and discussion

3.1. Product spectrum

Gas chromatographic analyses of the reaction mixtures after 5 h indicated the formation of a number of products i.e. C_9 to C_{16} alkenes (Fig. 1). Only products with carbon chain lengths greater than 7 were clearly distinguishable on the gas chromatograms. The major product be-

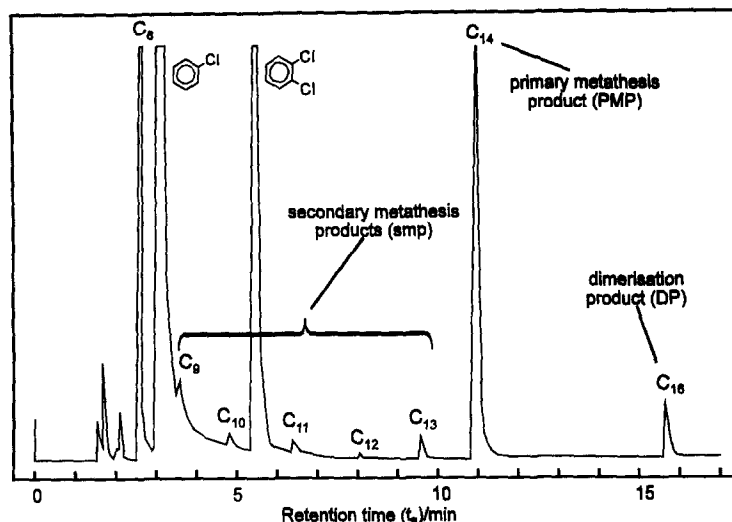


Fig. 1. Gas chromatogram of a typical reaction run after 5 h.

ing 7-tetradecene the desired metathesis product. By-products included the C_9 – C_{13} alkenes due to double bond isomerisation of 1-octene followed by metathesis and a C_{16} alkene due to dimerisation.

Although no 2-octene was observed the appearance of the C_9 – C_{13} alkenes is indicative of an isomerisation process. A summary of the

different reactions and the way in which the different products are formed, is given in Table I. In this scheme a distinction is made between the major metathesis reaction i.e. the primary metathesis reaction being the homo-metathesis reaction of 1-octene leading to 7-tetradecene and ethene, and the metathesis side-reactions due to isomerisation (secondary metathesis reac-

Table I
W(O-2,6- $C_6H_3X_2$) $_2Cl_4/R_4Sn$ catalysed reactions of 1-octene

	Reaction	Substrate	Products
1a	Primary metathesis	$C_7=C$	$C_7=C_7 + C=C$
1b	Isomerisation	$C_7=C$	$C_6=C_2$
1c	Secondary metathesis		
	Cross-metathesis	$C_7=C + C_6=C_2$	$C_7=C_6 + C_2=C + C_7=C_2 + C_6=C$
	Homo-metathesis	$C_6=C_2$	$C_6=C_6 + C_2=C_2$
1d	Dimerisation	$C_7=C$	$C_8=C_8$
2a	Isomerisation	$C_6=C$	$C_5=C_2$
2b	Secondary metathesis		
	Cross-metathesis	$C_6=C + C_5=C_2$	$C_6=C_5 + C_2=C + C_6=C_2 + C_5=C$
	Homo-metathesis	$C_5=C_2$	$C_5=C_5 + C_2=C_2$
3a	Isomerisation	$C_5=C$	$C_4=C_2$
3b	Secondary metathesis		
	Cross-metathesis	$C_5=C + C_4=C_2$	$C_5=C_4 + C_2=C + C_5=C_2 + C_4=C$
	Homo-metathesis	$C_4=C_2$	$C_4=C_4 + C_2=C_2$

Primary metathesis refers to the major metathesis reaction.

Secondary metathesis refers to the metathesis side-reactions due to isomerisation.

Scheme 2 refers to reactions due to $C_6=C$ formed in 1c.

Scheme 3 refers to reactions due to $C_5=C$ formed in 2c.

Cross-metathesis refers to the metathesis reaction between different alkenes.

Homo-metathesis refers to the metathesis reaction between the same alkenes.

Table 2
Influence of WCl_6 and derivatives on the reactions of 1-octene (Bu_4Sn/W molar ratio = 3)

Catalyst	1-octene (%)	PMP (%)	SMP (%)	DP
$W(O-2,6-C_6H_3Cl_2)_2Cl_4$	36.6	52.1	9.0	2.1
$W(O-2,6-C_6H_3Ph_2)_2Cl_4$	40.7	45.0	11.8	2.5
WCl_6	75.5	6.9	12.6	5.1
$W(O-2,6-C_6H_3Me_2)_2Cl_4$	85.1	–	–	14.9
$W(O-2,6-C_6H_3Bu^t)_2Cl_4$	90.0	–	–	10.2

PMP: primary metathesis products.

SMP: secondary metathesis products.

DP: dimerisation products.

tions). The secondary metathesis reactions consist of cross-metathesis reactions between terminal and internal alkenes, and homo-metathesis reactions between identical olefins. In each cross-metathesis reaction a terminal alkene is produced that subsequently undergoes isomerisation followed by a secondary metathesis reaction.

3.2. Catalytic activity of WCl_6 and derivatives

Results obtained in the presence of $W(O-2,6-C_6H_3X_2)_2Cl_4$ ($X = Cl, Ph, Me, Bu^t$) and Bu_4Sn indicate that an increase in the electron-withdrawing properties of the substituent on the oxyaryl ligand causes an increase in the metathesis activity (Table 2). This is in general agreement with results obtained for the metathesis of *cis*-2-pentene with the same catalysts [4]. However, in the absence of any electron-withdrawing substituents, i.e. Me and Bu^t , no metathesis is observed for 1-octene only dimerisation. Even an increase in the steric effects on the *ortho*-positions, i.e. Bu^t , did not activate the system for metathesis [1]. Under the same conditions WCl_6 seems to be relatively inactive towards metathesis, although an increase in isomerisation, as seen in the increase of the secondary metathesis products, and dimerisation are observed.

Using these results as a basis it was decided to optimise the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$

catalytic system for the primary metathesis of 1-octene.

3.3. Optimisation of metathesis activity of $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$

Various cocatalysts and cocatalyst/W molar ratios are known to be effective with $W(O-2,6-C_6H_3X_2)_2Cl_4$ complexes for the metathesis of alkenes [2,4]. The results of the investigation with the cocatalysts Me_4Sn and Bu_4Sn at different Sn/W molar ratios are given in Fig. 2.

In both cases a drastic increase in primary metathesis product yield are observed with an increase in the Sn/W molar ratio. The Bu_4Sn system reaches a maximum yield at a Sn/W molar ratio of about 3 and decreases rapidly at higher molar ratios. Initially a similar trend is observed with Me_4Sn which reaches a maximum yield at a molar ratio of about 2.5, decreases slightly and then remains constant up to a molar ratio of about 6.5. Above a molar ratio of about 6.5 the yield decreases rapidly. From these results, and because of better reproducibility of results, it was decided to use Bu_4Sn and a Sn/W molar ratio of 3 for further investigations.

To determine the optimum interaction time [3], 18°C and 85°C were first investigated as interaction temperatures at interaction times of 20 min. Interaction time is defined as the period before the 1-octene is added to a mixture of the

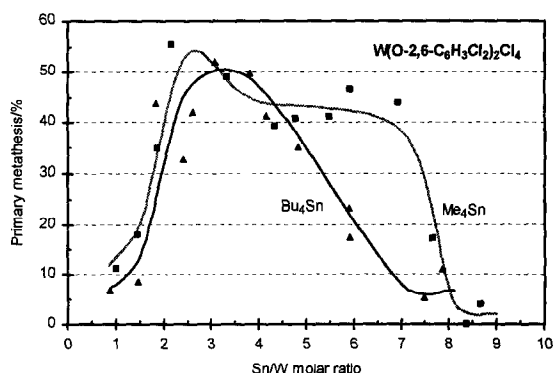


Fig. 2. Influence of the Sn/W molar ratio on the metathesis activity of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/R_4Sn$ ($R = Bu, Me$) catalytic system.

catalyst and cocatalyst in chlorobenzene, and the interaction temperature the temperature during this period. Less than 30% primary metathesis products was observed at 18°C and the higher temperature of 85°C was selected for optimising the interaction time. The composition of the reaction mixture at various interaction times ranging from 0 to 40 min is given in Fig. 3.

From these results it is evident that only a slight increase is observed with an increase in interaction time from 0 to 10 min. A constant yield of about 50% primary metathesis products is found at interaction times greater than about 10 min. No decrease is observed above 30 min as was reported for *cis*-2-pentene [4].

The influence of the reaction temperature on the yield of primary metathesis products indicates that temperatures greater than about 65°C are needed to activate the system (Fig. 4). Very little primary metathesis is observed below 55°C.

The ratios of the different reactions of 1-octene catalysed by the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalytic system are illustrated in Fig. 5.

It is evident from these results that the metathesis equilibrium is reached within 50 min and that the equilibrium is truly established after 5 h. Furthermore it is also clear that the secondary metathesis reactions (and isomerisation reactions) are much slower with constant values being reached only after 200 min. The dimerisa-

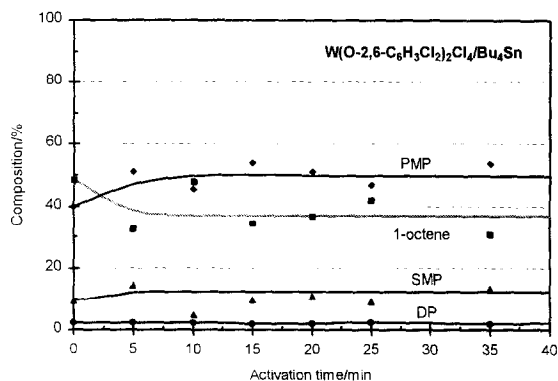


Fig. 3. Influence of the interaction time on the metathesis activity of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ (Sn/W molar ratio = 3) catalytic system.

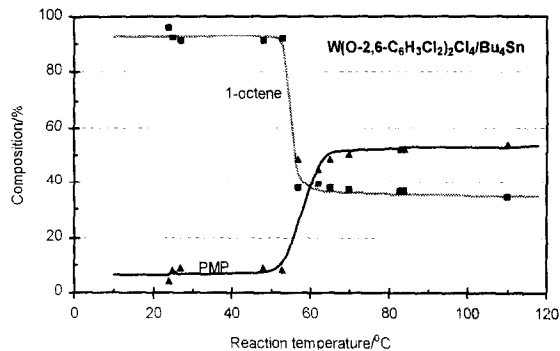


Fig. 4. Influence of the reaction temperature on the metathesis activity of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ (Sn/W molar ratio = 3) catalytic system.

tion reaction follows a similar trend than the primary metathesis reaction although it is not that evident because of the low dimer yield.

3.4. Deactivation

It is known that catalytic systems derived from $W(O-2,6-C_6H_3X_2)_2Cl_4$ complexes are also active for the metathesis of olefinic esters [4]. In this study oxygenates (oxygenate/W molar ratio = 0.75) with similar boiling points than 1-octene (b.p. 122–123°C) were added to the reaction mixtures to investigate the deactivation, if any, of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ catalytic systems ($X = Cl, Ph$). Oxygenates used include butyl acetate (b.p. 126.1°C), 1-butanol (b.p. 117.7°C), acetic acid (b.p. 117.9°C), 2-pentanone (102.3°C) and water (b.p. 100°C). These

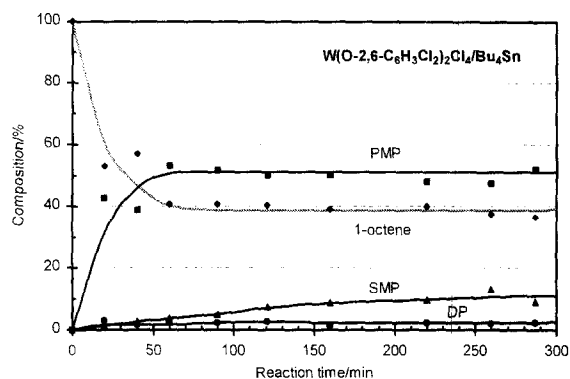


Fig. 5. Time run of the reactions of 1-octene in the presence of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ (Sn/W molar ratio = 3) catalytic system.

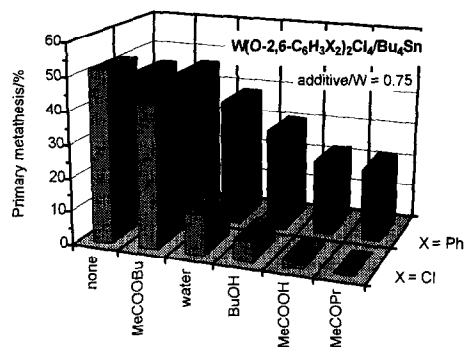


Fig. 6. Influence of oxygenates on the metathesis activity of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ (Sn/W molar ratio = 3) catalytic system.

results are illustrated in Fig. 6.

It is interesting to note that similar deactivation trends (butyl acetate > water > 1-butanol > acetic acid > 2-pentanone) are observed for both the catalysts with the $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ catalyst being more susceptible to deactivation by the oxygenates. Exactly what the reason is for this behaviour is uncertain at this stage and is currently under further investigation.

The metathesis activity of both the catalytic systems were also investigated in an air atmosphere (Table 3). Very little deactivation was found in the case of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ system, while an increase in metathesis activity was observed for the $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ catalytic system.

4. Conclusions

From the results it is clear that the $W(O-2,6-C_6H_3X_2)_2Cl_4/R_4Sn$ catalytic systems with $X = Cl, Ph$ and $R = Bu, Me$ are highly active for

Table 3

Influence of an air atmosphere on the reactions of 1-octene in the presence of $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ catalytic systems (Sn/W molar ratio = 3)

Catalyst	1-octene (%)	PMP (%)	SMP (%)	DP (%)
$W(O-2,6-C_6H_3Cl_2)_2Cl_4$	44.8	44.1	8.6	2.5
$W(O-2,6-C_6H_3Ph_2)_2Cl_4$	31.2	53.4	13.7	1.7

PMP: primary metathesis products.

SMP: secondary metathesis products.

DP: dimerisation products.

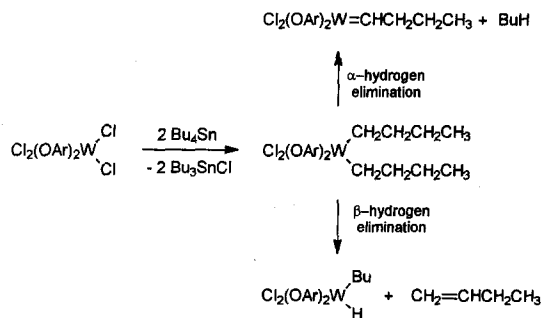
the metathesis of 1-octene. Although not absent, side-reactions like isomerisation, secondary metathesis and dimerisation are limited to a minimum. Optimum conditions for the metathesis of 1-octene with the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ catalytic system can be summarised as follows:

1. Interaction time ≥ 10 min at a temperature of $85^\circ C$.
2. Sn/W molar ratio = 3 and reaction temperature $> 60^\circ C$.

The mechanism for metathesis requires a metal carbene as active species [8]. The metal carbene for the $W(O-2,6-C_6H_3X_2)_2Cl_4/R_4Sn$ catalytic systems can be obtained from the double alkylation of the tungsten atom [4]. The mechanisms for alkene isomerisation and dimerisation require a metal hydride [9,10] that can also be obtained from the alkylated tungsten complex. The formation of the metal carbene and metal hydride can be envisaged as given in Scheme 1.

The metal carbene can then react with 1-octene to yield the primary metathesis products via a metallacyclobutane intermediate [8]. Likewise the metal hydride can give isomers via the alkyl mechanism [11] and dimers via the insertion mechanism [12].

In the presence of an oxygenate clearly the $W(O-2,6-C_6H_3X_2)_2Cl_4/Bu_4Sn$ catalytic systems show a higher stability if $X = Ph$. If $X = Cl$ the oxyaryl ligand becomes more electron-withdrawing and the tungsten atom obtains a partial positive charge that causes electron-rich compounds, i.e., oxygenates, to co-ordinate



Scheme 1.

more easily. The phenyl substituent is relatively much less electron-withdrawing and the alkene is thus in a more favourable position to compete for the co-ordination position on the tungsten atom. There are also steric effects that may play a role in the deactivation of the catalytic systems. Further investigations are therefore necessary to study the effects of electronic and steric properties on these catalytic systems.

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