

The metathesis of polyunsaturated fatty esters using the homogeneous $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems

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Abstract

Promoted with a small amount of Me_4Sn , $W(O-2,6-C_6H_3X_2)_2Cl_4$ ($X = Ph, Cl$) complexes are highly active metathesis catalysts for polyunsaturated fatty esters. Upon metathesis of methyl linoleate, substrate conversions of ca. 95 and 78% were obtained in 2 h with the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ and $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic systems respectively. The lower activity of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic system was attributed to the highly deactivating nature of the Cl substituents on the *o,o'*-position of the aryloxy ligand. Highly electron-withdrawing Cl substituents cause the tungsten atom to be electron-deficient and thus more susceptible to attack by the electron-rich ester groups. However, the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ system was more selective towards dicarboxylic esters. The latter are interesting starting materials for the synthesis of polyesters and polyamides. The $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems were rapidly deactivated by bromine-containing olefinic esters. Deactivation was attributed to a side reaction between the Br-group and the electron-deficient W-centre.

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1. Introduction

Tungsten(VI) aryloxy complexes were earlier reported to be useful precatalysts for the metathesis of alkenes [1–7]. These include $W(OAr)_6$ [1,2], $WO(OAr)_4$ [3] and $W(OAr)_xCl_{6-x}$ with $x = 2-4$ [2,4–7]. Aryloxy ligands offer some advantages in that their electron-withdrawing properties can be varied by changing the substituents on the ring and their steric effect on tungsten can be modified by varying the bulkiness of the substituents on the *o,o'*-position on the aryloxy [8].

Tungsten(VI) aryloxy complexes provide active metathesis precatalysts for linear, cyclic and functionalised alkenes. Quignard et al. [7] achieved metathesis of internal and terminal alkenes as well as olefinic esters using the *trans*- $W(O-2,6-C_6H_3X_2)_2Cl_4$ complexes 1 ($X = Me, Ph, Cl, F$) promoted with a R_4Sn compound. Parameters which influenced metathesis activity upon metathesis of *cis*-2-pentene were: the electron-withdrawing property of the aryloxy ligand, the nature of the cocatalyst and the interaction time between the precatalyst and the

cocatalyst. For a given cocatalyst and a given time of precatalyst–cocatalyst interaction, metathesis activity increased with the nature of the substituent in the *o,o'*-position on the aryloxy in the order: $X = CH_3 < C_6H_5 < F < Cl < Br$.

Self- and cross-metathesis of ethyl oleate, a monounsaturated fatty ester, was achieved using the $W(O-2,6-C_6H_3X_2)_2Cl_4$ ($X = Cl, Br$) complexes promoted with Me_4Sn or Bu_4Pb [7]. In most cases, the catalytic activity was better than that reported for the conventional WCl_6/R_4Sn catalyst system.

Vosloo et al. [9,10] reported the catalysed metathesis reaction of 1-alkenes using complex 1 ($X = Cl, Ph$) promoted with a R_4Sn compound. The $W(O-2,6-C_6H_3X_2)_2Cl_4$ precatalysts ($X = Cl, Ph$) works optimally at 85 °C, a Sn:W molar ratio of 3 and a precatalyst–cocatalyst interaction time of 20 min. Secondary metathesis products resulting from the double bond isomerisation of the 1-alkenes also occur [9]. The $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems deactivate in the presence of oxygenates with $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ showing more resistance to deactivation.

We have investigated the metathesis activity and selectivity of the $W(O-2,6-C_6H_3X_2)_2Cl_4$ ($X = Cl, Ph$) precatalysts promoted with Me_4Sn on the methyl ester of linoleic acid

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and a bromine-containing ester mixture. These catalytic systems were found to be active with substrate conversions exceeding 85% and high selectivity (>95%) towards the primary metathesis products (i.e. very little double bond isomerisation). A mixture of simple alkene, monoester and diester metathesis products were obtained.

2. Experimental

2.1. Materials

Chlorobenzene (Aldrich) was dried by refluxing over P_2O_5 , distilled and stored under N_2 . Methyl linoleate (99%, Aldrich) was purified from peroxides by pretreatment with calcined $SiO_2-Al_2O_3-HA$ (24.3% Al_2O_3 , AKZO) under a N_2 atmosphere. Tetramethyl tin (Me_4Sn , Aldrich), WCl_6 , CCl_4 (Merck), 2,6-dichlorophenol and 2,6-diphenylphenol (Aldrich) were used as purchased.

2.2. Precatalysts

The $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ and $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ complexes were prepared as described by Quignard et al. [8]. A solution of $HO-2,6-C_6H_3X_2$ (2.5×10^{-3} mol) in CCl_4 (20 ml) was added to a solution of WCl_6 (5.0×10^{-3} mol) in CCl_4 (20 ml). The reaction mixture was stirred for 4 h under reflux. The $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ complex was filtered off and washed with hexane to give black microcrystals (79% yield). The $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ complex was filtered off and recrystallized from ethanol to give black microcrystals with green luster (80% yield). Both complexes decompose slowly in air and were, therefore, stored under N_2 atmosphere.

2.3. Catalytic reactions

The $W(O-2,6-C_6H_3X_2)_2Cl_4$ precatalyst ($X = Cl, Ph$; 5.0×10^{-5} mol) was placed in a pear-shaped reaction flask followed by the addition of chlorobenzene (1 ml). The precatalyst mixture was heated to $85^\circ C$ after which Me_4Sn (15×10^{-5} mol) was added. After a precatalyst-cocatalyst interaction time of 20 min, the substrate (1.5×10^{-3} mol methyl linoleate or 0.3 ml brominated methyl linoleate mixture) was added. The reaction mixture was allowed to stir at $85^\circ C$. Samples for GC analysis were collected at regular intervals and a few drops of methanol were added to each sample to quench the reaction. After 4 h, the reaction mixture was quenched with methanol, cooled and analysed by GC/MS. In the case of the brominated mixture, the metathesis products were debrominated prior to analysis.

A similar procedure was used for the metathesis of methyl linoleate in the presence of the WCl_6/Me_4Sn catalytic system ($W:Sn:ester$ molar ratio = 1:1:30).

2.4. Product analysis

Samples were collected and analyzed on a GC equipped with a DB-1 capillary column and FID after quenching the reaction by adding a few drops of methanol. GC analyses were performed on a Carlo Erba 6000 Vega series 3 GC equipped with a cold on-column injector, a DB-1 fused silica capillary column (J&W Scientific, $15 m \times 0.53 mm \times 0.25 m$) and FID using the following conditions: carrier gas (He), detector temperature ($300^\circ C$), oven programmed from 100 to $150^\circ C$ at $10^\circ C/min$, $150-160^\circ C$ at $1^\circ C/min$, $160-280^\circ C$ at $15^\circ C/min$. A typical chromatogram is illustrated in Fig. 1. The substrate conversions were calculated from the peak areas of the GC analyses corrected for the molecular

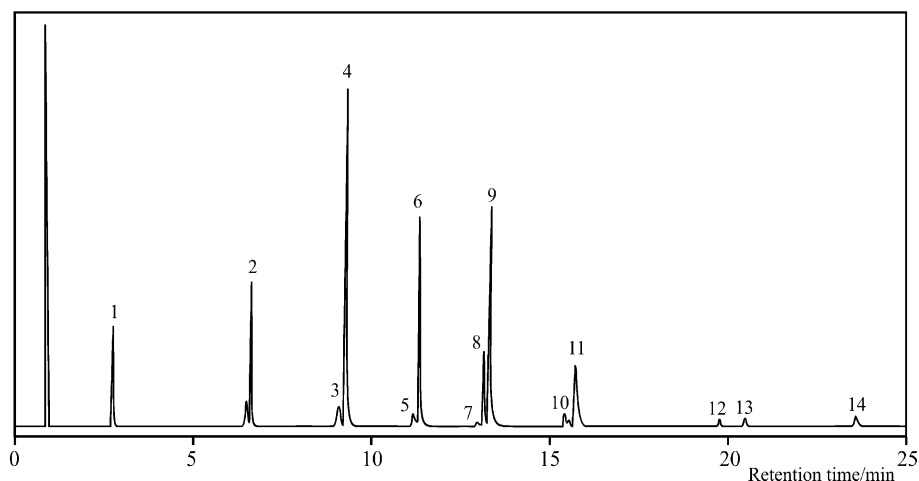


Fig. 1. Gas chromatogram of the metathesis products of methyl linoleate: simple alkenes (peaks: 1–3, 5, 7), monocarboxylic esters (peaks: 4, 6, 8, 10, 11, 13, 14) and dicarboxylic esters (peaks: 9, 11, 13, 14).

response [11,12]:

$$\text{conversion (\%)} = 1 - \frac{C_s}{\sum C_i}$$

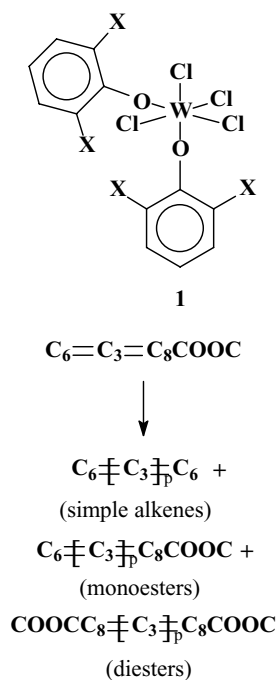
where $i = 1, 2, \dots, \xi$; C_s is the corrected peak area for the substrate ester; C_i the corrected peak area for the component i in the product mixture with ξ components.

Metathesis products were characterized on a Fisons GC/MS equipped with a DB-5 capillary column (J&W scientific, 15 m \times 0.32 mm \times 0.25 m). Similar conditions as mentioned above were used.

3. Results and discussion

3.1. Metathesis of methyl linoleate with $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ ($X = Cl, Ph$)

The metathesis activity of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ ($X = Cl, Ph$) catalytic system was investigated for polyunsaturated esters. As previously established by Quignard et al. [7] and Vosloo et al. [9,10], a Sn/W molar ratio of 3, reaction temperature of 85 °C and a precatalyst–cocatalyst interaction time of 20 min were employed. Upon activation with a small amount of Me_4Sn (substrate:W:Sn molar ratio of 30:1:3), the $W(O-2,6-C_6H_3X_2)_2Cl_4$ precatalysts were active for the metathesis of methyl linoleate giving rise to a product mixture consisting of simple alkenes, monoester and diesters (Fig. 1 and Scheme 1 (hydrogens omitted for clarity)). For both catalysts, metathesis equilibrium was attained within 2 h reaction time.



Scheme 1.

Table 1

Product spectrum resulting from the metathesis of methyl linoleate (*) in the presence of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems

Carbon no.	Product	Yield (%)	
		X = Cl	X = Ph
Simple alkenes			
C ₁₂ ¹	C ₆ =C ₆	26.64	43.62
C ₁₅ ²	C ₆ =C ₃ =C ₆	27.61	21.24
C ₁₈ ³	C ₆ =(C ₃) ₂ =C ₆	3.50	3.87
C ₂₁ ⁴	C ₆ =(C ₃) ₃ =C ₆	–	–
C ₂₄ ⁵	C ₆ =(C ₃) ₄ =C ₆	–	–
Monoesters			
C ₁₆ ¹	C ₆ =C ₈ COOC	8.91	19.10
C ₁₉ ²	C ₆ =C ₃ =C ₈ COOC*	22.46	5.37
C ₂₂ ³	C ₆ =(C ₃) ₂ =C ₈ COOC	1.60	2.72
C ₂₅ ⁴	C ₆ =(C ₃) ₃ =C ₈ COOC	0.94	0.40
C ₂₈ ⁵	C ₆ =(C ₃) ₄ =C ₈ COOC	–	–
Diesters			
C ₂₀ ¹	COOCC ₈ =C ₈ COOC	5.41	3.01
C ₂₃ ²	COOCC ₈ =C ₃ =C ₈ COOC	2.93	0.82
C ₂₆ ³	COOCC ₈ =(C ₃) ₂ =C ₈ COOC	–	–
C ₂₉ ⁴	COOCC ₈ =(C ₃) ₃ =C ₈ COOC	–	–

Reaction temp. = 85 °C. Ester:Sn:W = 30:1:3. Reaction time = 2 h.

Table 1 shows the products and the yields obtained in the presence of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems. The simple alkenes detected were the monoene compound 6-dodecene (C₁₂¹), the diene compound 6,9-pentadecadiene (C₁₅²) and the triene compound 6,9,12-octadecatriene (C₁₈³). The esters detected were the monoesters methyl 9-pentadecenoate (C₁₆¹), methyl 9,12,15-heneicosatrienoate (C₂₂³) and methyl 9,12,15,18-tetracosatetraenoate (C₂₅⁴), and the diesters dimethyl 9-octadecenoate (C₂₀¹) and dimethyl 9,12-heneicosadienoate (C₂₃²). A methyl linoleate conversion of ca. 95% to metathesis products corresponding to a turnover number (TON) of 28.4 was obtained with the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system (Fig. 2). The $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic system was slightly less active with a conversion of ca. 78% (Fig. 3). Both the catalytic systems ($X = Ph, Cl$) were very selective towards primary metathesis products (>95%) with product selectivity increasing in the order alkenes > monoesters > diesters. Figs. 2 and 3 also show the formation of the simple alkenes, monoesters and diesters, and Figs. 4 and 5 the yields of monoenes, dienes, trienes and tetraenes. In terms of unsaturation, selectivity increased in the order monoenes > dienes > trienes > tetraenes.

The $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system gave higher yields for simple alkenes than the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic system. However, the latter gave higher yields of diesters which are interesting starting materials for the synthesis of polyesters and polyamides [13]. The $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system also yielded more monoenes and trienes relative to the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic system

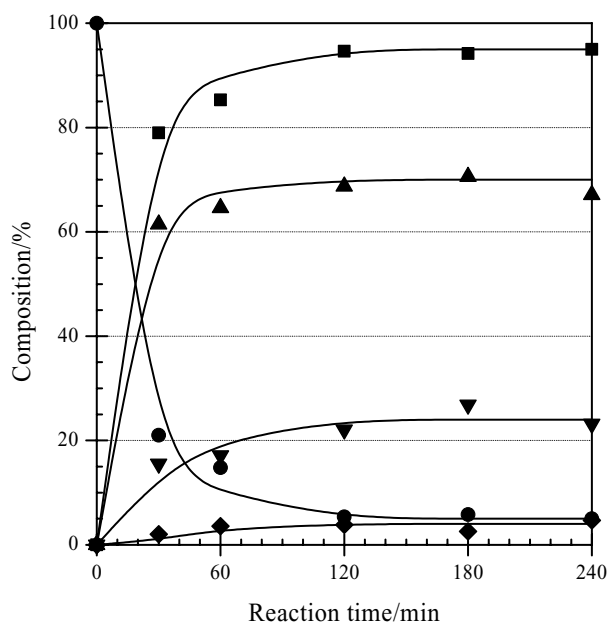


Fig. 2. The yields of alkenes resulting from the metathesis of methyl linoleate in the presence of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system. Reaction temp. = $85^\circ C$. Ester:Sn:W = 30:1:3. (●) Methyl linoleate; (■) total metathesis; (▲) simple alkenes; (▼) monoesters; (◆) diesters.

which on the other hand gave higher yields of dienes and tetraenes.

Table 2 compares the activities of the tungsten aryloxo complexes with those reported for the classi-

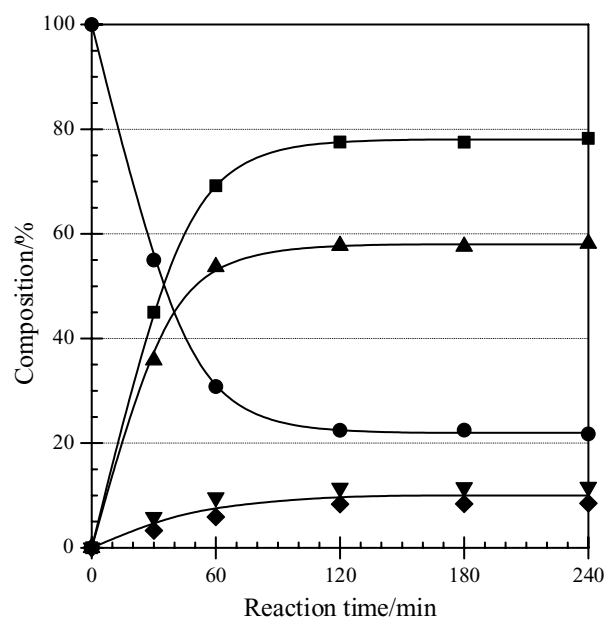


Fig. 3. The yields of alkenes resulting from the metathesis of methyl linoleate in the presence of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic system. Reaction temp. = $85^\circ C$. Ester:Sn:W = 30:1:3. (●) Methyl linoleate; (■) total metathesis; (▲) simple alkenes; (▼) monoesters; (◆) diesters.

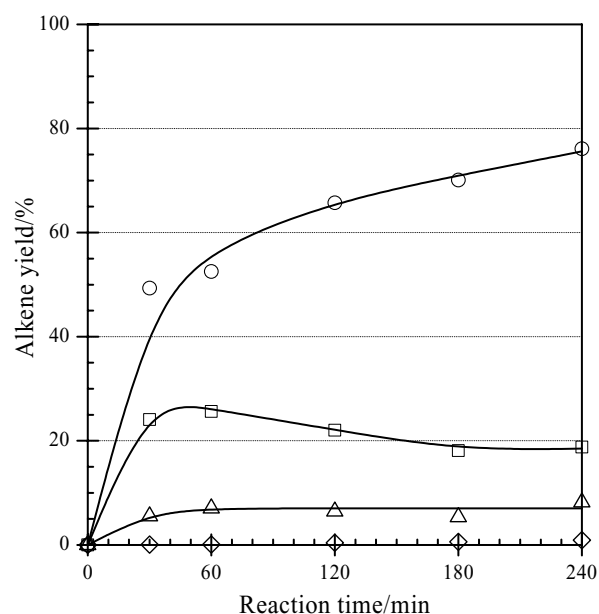


Fig. 4. The yields of alkenes resulting from the metathesis of methyl linoleate in the presence of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system. Reaction temp. = $85^\circ C$. Ester:Sn:W = 30:1:3. (○) monoenes; (□) dienes; (△) trienes; (◇) tetraenes.

cal homogeneous WCl_6/Me_4Sn catalyst [14,15]. The $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system was more active than the conventional homogeneous WCl_6/Me_4Sn catalytic system.

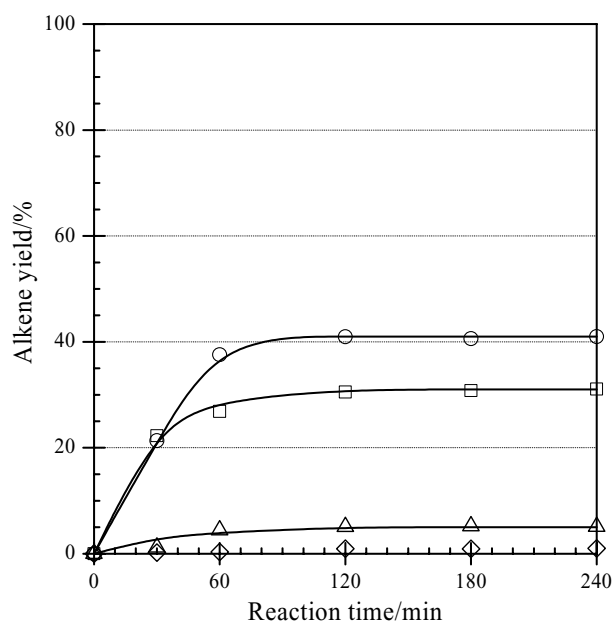


Fig. 5. The yields of alkenes resulting from the metathesis of methyl linoleate in the presence of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic system. Reaction temp. = $85^\circ C$. Ester:Sn:W = 30:1:3. (○) Monoenes; (□) dienes; (△) trienes; (◇) tetraenes.

Table 2
Metathesis activities of $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ and WCl_6/Me_4Sn catalytic systems with methyl linoleate as substrate

Catalyst	Solvent	Ester:W	Temp (°C)	Time (h)	Conversion (%)
X = Cl	PhCl	30	70	2	77.5
X = Ph	PhCl	30	70	2	94.6
WCl_6	PhCl	30	85	2	81.1
WCl_6^a	PhCl	12	60	2	83.2
WCl_6^b	None	31	80	4	84.0

^a Literature results by Ast et al. [14].

^b Literature results by Verkuijlen and Boelhouwer [15].

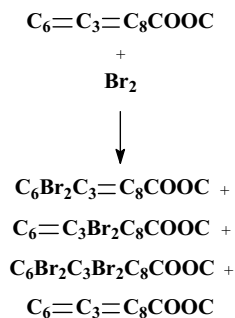
3.2. Metathesis of brominated methyl linoleate with $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$

A mixture of brominated esters resulting from a 1:1 bromination of methyl linoleate (Scheme 2 (hydrogens omitted for clarity)) was metathesized in the presence of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems (X = Ph, Cl). Although a catalytic conversion was observed, there was generally a rapid deactivation of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems. The metathesis products obtained after debromination are shown in Table 3. The selectivity for primary metathesis products was >95% and the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system had more resistance to deactivation than the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic system.

Fig. 6 compares the yields for simple alkenes, monoesters and diesters for the two systems. The $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system displayed a higher selectivity towards simple alkenes and diesters (Fig. 6), and towards monoene, diene and triene compounds (Fig. 7).

3.3. Deactivation

Previous studies have shown that systems derived from the $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ precatalyst are more resistant to deactivation by oxygenates, e.g. butyl acetate, 1-butanol, acetic acid, 2-pentanone and water, than the $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ system [9]. In an air atmosphere its metathesis activity increased, whereas the $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ precatalyst was deactivated. The



Scheme 2.

Table 3
Debrominated products resulting from the metathesis of 1:1 brominated methyl linoleate (*) with the $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems

Carbon no.	Product	Yield (%)	
		X = Cl	X = Ph
Simple alkenes			
C_{12}^1	$C_6=C_6$	5.4	9.0
C_{15}^2	$C_6=C_3=C_6$	6.9	7.1
C_{18}^3	$C_6=(C_3)_2=C_6$	3.0	3.4
C_{21}^4	$C_6=(C_3)_3=C_6$	–	–
C_{24}^5	$C_6=(C_3)_4=C_6$	–	–
Monoesters			
C_{16}^1	$C_6=C_8COOC$	11.7	8.7
C_{19}^2	$C_6=C_3=C_8COOC^*$	70.5	68.0
C_{22}^3	$C_6=(C_3)_2=C_8COOC$	0.7	0.9
C_{25}^4	$C_6=(C_3)_3=C_8COOC$	0.4	0.5
C_{28}^5	$C_6=(C_3)_4=C_8COOC$	–	–
Diesters			
C_{20}^1	$COOCC_8=C_8COOC$	1.2	1.6
C_{23}^2	$COOCC_8=C_3=C_8COOC$	0.2	0.8
C_{26}^3	$COOCC_8=(C_3)_2=C_8COOC$	–	–
C_{29}^4	$COOCC_8=(C_3)_3=C_8COOC$	–	–

Reaction temp. = 85 °C. Ester:Sn:W = 30:1:3. Reaction time = 6 h.

relatively easy deactivation of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4$ precatalyst was attributed to the high electron-withdrawing nature of the aryloxy ligand. With a more electron-withdrawing aryloxy ligand, the tungsten metal centre becomes more electrophilic and causes electron-rich oxygenates, to bind more easily with the tungsten atom [9]. However, the phenyl substituent is less electron-withdrawing thus it minimises the competition between the electron-rich

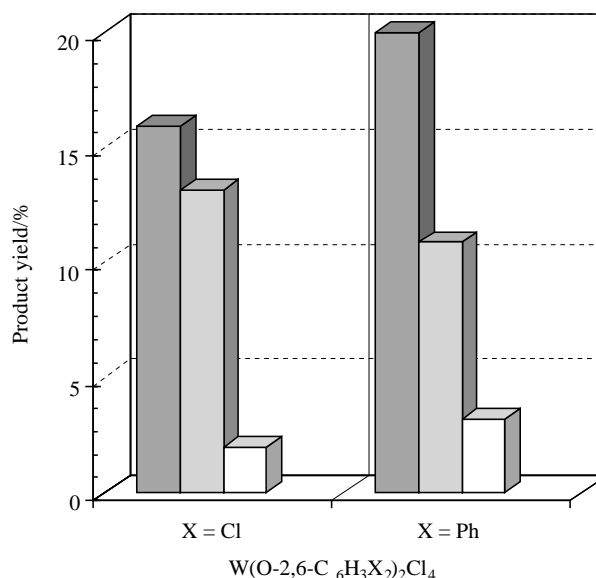


Fig. 6. The yields of alkenes resulting from the metathesis of brominated methyl linoleate in the presence of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems. Reaction temp. = 85 °C. Ester:Sn:W = 30:1:3. Reaction time = 6 h. (■) Simple alkenes; (■) monoesters; (□) diesters.

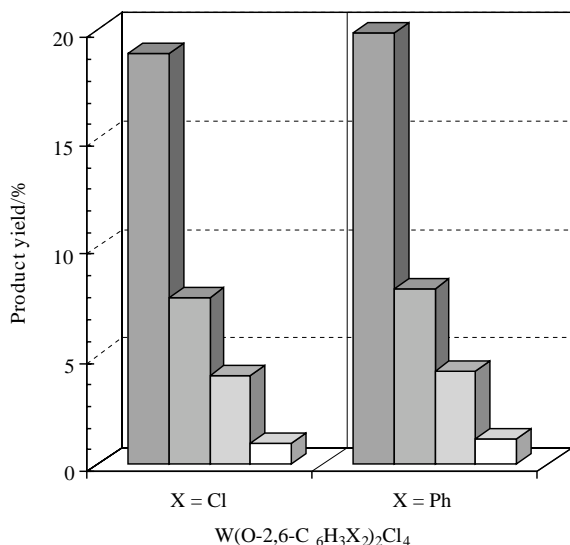


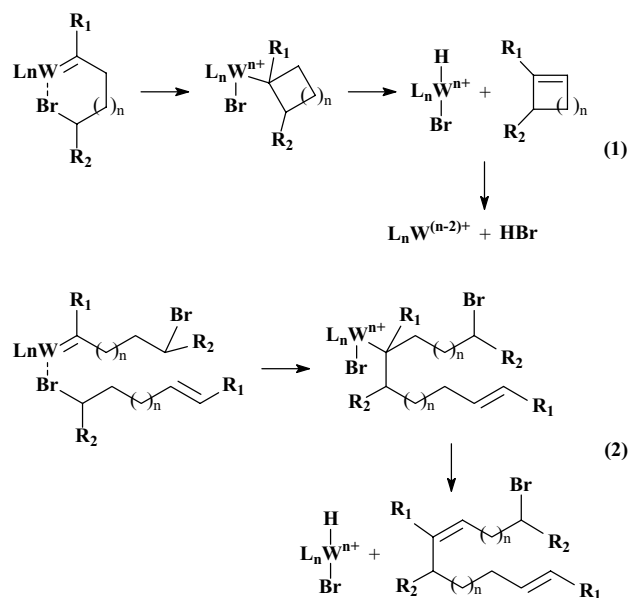
Fig. 7. The yields of alkenes resulting from the metathesis of brominated methyl linoleate in the presence of the $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ catalytic systems. Reaction temp. = 85 °C. Ester:Sn:W = 30:1:3. Reaction time = 6 h. (■) Monoenes; (▒) dienes; (▓) trienes; (□) tetraenes.

compounds and the carbon–carbon double bond for the metal centre. As a result, less deactivation is obtained with the phenyl substituent than with the chloride substituent.

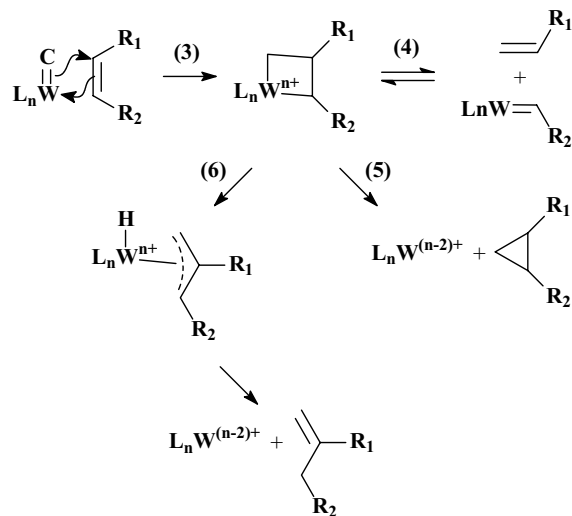
Since unsaturated fatty esters have both the olefinic bond and the ester group in the same molecule, deactivation by the ester group is inevitable. Indeed deactivation of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic system was greater compared to that of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system. The observed difference in the catalytic activity of tungsten-based catalysts could be attributed to the difference in the electron-withdrawing properties of the substituents in the *o,o'*-position of the oxoaryl ligands. The highly electron-withdrawing Cl substituent strongly activates the metal center for attack by the ester group. This kind of metal activation is less pronounced when X = Ph.

In the case of brominated alkenes, rapid deactivation could be attributed to the increased interaction between the tungsten atom and the electron-rich bromides, in addition to a side reaction with the ester group. In this regard, two deactivation pathways seem possible, namely, intramolecular and intermolecular coordination of Br and W atom (Scheme 3). Kawai et al. [16] previously proposed similar deactivation pathways for the reaction of bromine-containing alkenes with the Re_2O_7/Al_2O_3 catalytic system.

In the first mechanistic pathway: (1) the bromine atom interacts with the metal center intramolecularly and blocks the coordination site needed for metathesis. Such an interaction leads to the formation of an intermediate that undergoes β -elimination of a hydrogen atom to form a cycloalkene and $H-W^{n+}-Br$ complex. The $H-W^{n+}-Br$ complex loses HBr by reductive elimination to form $W^{(n-2)+}$. In the second mechanism: (2) deactivation occurs as a result of an intermolecular interaction between the bromine atom of a differ-



Scheme 3.



Scheme 4.

ent molecule and the metal to form an intermediate followed by β -elimination of a hydrogen atom.

Deactivation could also occur by reductive elimination of the metal carbene as shown in Scheme 4 [12,17]. Once the metal carbene has formed (3), it could either split productively to form a new alkene (4) or could undergo reductive elimination to form a cycloalkane (5) or an alkene (6).

4. Conclusions

Promoted with a small amount of Me_4Sn , the $W(O-2,6-C_6H_3X_2)_2Cl_4$ (X = Ph, Cl) complexes are active metathe-

sis catalysts for polyunsaturated fatty esters. These catalytic systems are highly selective towards primary metathesis products (>95%). In the presence of the ester group, the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system shows more resistance against deactivation compared to the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Me_4Sn$ catalytic system. The relatively lower activity of the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic system, in the presence of the ester group, result from the highly deactivating nature of the Cl substituents on the *o,o'*-position of the aryloxy ligand. Highly electron-withdrawing Cl substituents cause the tungsten atom to be electron-deficient and thus more susceptible to attack by the electron-rich ester groups. However, the $W(O-2,6-C_6H_3Cl_2)_2Cl_4/Me_4Sn$ catalytic system is relatively more selective towards dicarboxylic esters which are interesting starting materials for the synthesis of polyesters and polyamides. Generally, the $W(O-2,6-C_6H_3X_2)_2Cl_4/Me_4Sn$ ($X = Ph, Cl$) catalytic systems are rapidly deactivated by the bromine-containing olefinic esters. Deactivation is the result of a side reaction between the bromine group and the electron-deficient tungsten-centre.

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