

# A comparative study of hydrosilane compounds as cocatalysts in the metathesis of 1-hexene

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## Abstract

The selectivity of 1-hexene metathesis using  $WCl_6$  as catalyst was evaluated with a series of hydrosilane-compounds as cocatalysts:  $Ph_3SiH$ ,  $Ph_2SiH_2$ ,  $PhSiH_3$  and polymethylhydrosiloxane (PMHS). The metathesis reaction is favored by the addition of promoters. When in the presence of  $WCl_4(OAr)_2$ ,  $OAr = 2,6$ -dichlorophenoxide, 2,6-difluorophenoxide, olefin metathesis occurs with good selectivity without the use of promoters. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Tungsten catalyst; Hydrosilane cocatalysts; 1-Hexene metathesis

## 1. Introduction

In recent years, the use of derivatives of  $WCl_6$  with oxygen-containing ligands has shown growing interest [1–8]. Several tungsten(VI) phenoxide complexes have been employed in different types of metathesis reactions, such as insect pheromone synthesis [9], ring-opening polymerizations [6] and ring-closing metathesis [10]. Aryloxy alkyldene complexes of tungsten obtained from  $WCl_x(OAr)_{6-x}$  [11,12] were shown to be very efficient in several types of metathesis reactions. Moreover, supported aryloxy tungsten complexes have been used in the metathesis of 1-pentene showing high activity [13,14]. It is well established that metallocyclobutane complexes are important intermediates in olefin metathesis reactions when alkyl-

dene complexes of some metals such as tungsten, molybdenum, rhenium and ruthenium are present [8]. Rappé and Goddard [15] suggested that a precursor with a W–O bond leads to a smaller activation energy for metal carbene formation when compared to one with only W–Cl bonds. Furthermore, catalytic systems containing  $WCl_6$  have been modified by addition of phenols or other oxygen-containing compounds to enhance activity [16,17].

Among the cocatalysts largely employed in W-based olefin metathesis, tetraalkyltin compounds are the most requested. However, in the  $WCl_6-SnR_4$  systems, tetraalkyltin compounds react with tungsten hexachloride to yield trialkyltin derivatives, which are insidious poisons to the central nervous system, causing cerebral edema on inhalation and skin and mucous membranes necrosis on contact [18]. In order to find alternatives to the use of the tetraalkyltin, some

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silicon compounds have been tested with good results [19–24].

In a previous study [19], we have reported the use of polymethylhydrosiloxane (PMHS) as cocatalyst in the metathesis reaction of functionalized olefins with  $\text{WCl}_6$  as the catalytic precursor. This cocatalyst behaves similarly to  $\text{SnMe}_4$  in the above mentioned reactions. In the present work, a comparative study of  $\text{WCl}_6$  plus several hydrosilane cocatalysts has been undertaken using as a model reaction the metathesis of 1-hexene. The use of ethyl acetate, acetonitrile and phenols as promoters was also investigated in an attempt to generate in situ precursors as phenoxide compounds or other complexes that might be formed. Moreover, the compounds  $\text{WCl}_4(\text{OAr})_2$ , where  $\text{OAr} = 2,6\text{-dichlorophenoxide}$ ,  $2,6\text{-difluorophenoxide}$ , were also tested as precursors under the same reaction conditions.

## 2. Experimental

$\text{WCl}_6$ ,  $\text{WOCl}_4$ ,  $\text{Ph}_3\text{SiH}$ ,  $\text{Ph}_2\text{SiH}_2$ ,  $\text{PhSiH}_3$ , PMHS,  $2,6\text{-Cl}_2\text{-PhOH}$ ,  $2,6\text{-F}_2\text{-PhOH}$ , 1-hexene and the standard olefins ( $\text{C}_{10}$  and  $\text{C}_{12}$ ) were purchased from Aldrich Chemical and used without further purification. Toluene, 1-hexene and the promoters ethyl acetate and acetonitrile (analytical grade) were deoxygenated and dried using standard techniques. All experiments were performed under inert atmosphere using the Schlenk technique.

The compounds  $\text{Cl}_4\text{W}(2,6\text{-dichlorophenoxide})_2$  and  $\text{Cl}_4\text{W}(2,6\text{-difluorophenoxide})_2$  were synthesized according to the literature [25].

The reactions were performed in a  $50\text{ cm}^3$  flask, connected to a condenser. The reactants were introduced into the flask with degassed toluene in the following order 1-hexene,  $\text{WCl}_6$  ( $10^{-4}$  mol) and cocatalyst according to the molar ratio 100:1:4, respectively. Promoters, when used, were added later in lower absolute amounts ( $10^{-5}$  mol). The reactions were carried out at 323 K for 4 h and were interrupted by

permitting air contact, followed by filtration through a silica/celite preparative column. Cyclohexane was added to the reaction mixture as an internal standard for GC analysis.

The products were analysed on a HP-5890 GC instrument, equipped with a methyl-silicone megabore column (HP-1) and FID detector. The internal standard method (with cyclohexane) was used to calculate the mass percentage of 1-hexene and products. Peak identification was performed using GC/MS and spiking with authentic samples.

Mass spectra were measured on a HP 5988A mass spectrometer coupled to a HP 5890 GC. The mass spectra signals were (EI, 70 eV)  $m/z$  140 (M), 70 (M -  $\text{C}_5\text{H}_{10}$ ), 69 (M -  $\text{C}_5\text{H}_{11}$ ), 55 (M -  $\text{C}_6\text{H}_{13}$ ), for decene and 97 (M -  $\text{C}_6\text{H}_{11}$ ), 70 (M -  $\text{C}_7\text{H}_{14}$ ), 69 (M -  $\text{C}_7\text{H}_{15}$ ), 55 (M -  $\text{C}_8\text{H}_{17}$ ), for dodecene.

Results are presented as yields in 5-decene and dodecenes (sum of the different isomers formed), that are defined as:

$$\text{Yield in } \text{C}_{10} = \frac{m_{(5\text{-decene})}}{m_{\text{unreacted 1-hexene}} + \sum m_{\text{products}}} \quad (1)$$

$$\text{Yield in } \text{C}_{12} = \frac{m_{(\text{dodecenes})}}{m_{\text{unreacted 1-hexene}} + \sum m_{\text{products}}} \quad (2)$$

The ' $\sum m_{\text{products}}$ ' term includes the ethylene mass, taking into account that 1 mol of ethylene is liberated by each formed 5-decene mole.

The total conversion and selectivities can be calculated as:

$$\text{Total Conversion} = \text{Yield in } \text{C}_{10} + \text{Yield in } \text{C}_{12} \quad (3)$$

$$\text{Selectivity in } \text{C}_{10} = \frac{\text{Yield in } \text{C}_{10}}{\text{Total Conversion}} \quad (4)$$

## 3. Results and discussion

The reaction of 1-hexene in the presence of  $\text{WCl}_6$ -hydrosilane leads to metathesis

Table 1  
Metathesis yields of 1-hexene in the presence of  $WCl_6$ -hydro-silane cocatalysts<sup>a</sup>

Cocatalyst	Reaction products (%)	
	5-Decene	Dodecenes
PhSiH <sub>3</sub>	3	85
Ph <sub>2</sub> SiH <sub>2</sub>	5	79
Ph <sub>3</sub> SiH	0	78
PMHS	5	86

<sup>a</sup>All the data are an average of at least three experiments. Olefin/W/Si molar ratio = 100:1:4. Solvent: toluene. Temperature 323 K. Addition order: solvent, olefin, catalyst and cocatalyst.

(5-decene) and dimerization (dodecenes) products. Table 1 shows the yields obtained with catalytic systems. Higher alkenes were detected as traces and were rejected during internal normalization.

The results show that the dominant reaction is dimerization, in contrast to the classical  $WCl_6$ -SnMe<sub>4</sub> system. Regarding the catalytic systems, Nametkin et al. [21,22], observed that combining  $WCl_6$  and Et<sub>3</sub>SiH or Ph<sub>2</sub>SiH<sub>2</sub>,  $\alpha$ - and  $\beta$ -olefins metathesis resulted in conversions of 15–50%, with very good selectivities for  $\beta$ -olefins (~ 100%), and lower selectivities for  $\alpha$ -olefins (~ 80%). For 1-hexene specifically, the authors used either Et<sub>3</sub>SiH or silacyclobutane as cocatalysts, compounds not used in this work. Levisalles et al. [23,24] also studied 3-hexene [23] and 2-pentene [24] metathesis employing  $WCl_6$ -Ph<sub>2</sub>SiH<sub>2</sub> as catalytic system at

lower temperature (273 K), but in the latter case, isomerization or dimerization side reactions cannot occur [26]. Very recently, it was observed that tungsten(VI) phenoxides cocatalyzed by Bu<sub>4</sub>Sn yield dimerization of 1-octene in addition to the primary metathesis product [1]. The metathesis reaction of 1-alkenes might give lower selectivities in the metathesis product since, in this case, side reactions such as dimerization, isomerization, and cross metathesis between the different olefins formed might take place.

Under the same experimental conditions, our previous results show selectivities close to 100%, employing functionalized olefins [19], in which the Si-H bond number seems to influence the activity [20]. Based on the results reported in Ref. [19], we decided to introduce functional groups as promoters in the reactional milieu in a 10:1 catalyst:promoter ratio. According to Table 2, all the cocatalysts, with the exception of PMHS, produced an increase in metathesis yield when acetonitrile was added as promoter. A similar behavior took place when ethyl acetate was employed. In this case, Ph<sub>2</sub>SiH<sub>2</sub> exhibited a higher selectivity in metathesis than in the preceding case.

In order to investigate the effect of the ratio promoter:catalyst in such systems, PhSiH<sub>3</sub> was used as cocatalyst and ethyl acetate as promoter. The choice of this cocatalyst resides in the fact that in the presence of ethyl acetate it shows

Table 2  
Metathesis yields of 1-hexene in the presence of  $WCl_6$ -hydrosilane systems with promoters<sup>a</sup>

Cocatalyst	Promoter							
	Acetonitrile		Ethyl acetate		Dichlorophenol		Difluorophenol	
	5-C <sub>10</sub> (%)	C <sub>12</sub> 's (%)	5-C <sub>10</sub> (%)	C <sub>12</sub> 's (%)	5-C <sub>10</sub> (%)	C <sub>12</sub> 's (%)	5-C <sub>10</sub> (%)	C <sub>12</sub> 's (%)
PhSiH <sub>3</sub>	55	27	38	44				
Ph <sub>2</sub> SiH <sub>2</sub>	16	70	74	12	76	4	40	58
Ph <sub>3</sub> SiH	54	26	69	11				
PMHS	0	82	2	80	88	2	90	0

<sup>a</sup>All the data are an average of at least three experiments. Olefin/W/Si/promoter molar ratio = 100:1:4:10. Solvent: toluene. Temperature 323 K. Addition order: solvent, olefin, catalyst, cocatalyst and promoter.

Table 3

Metathesis yields of 1-hexene using  $WCl_6$ - $PhSiH_3$  in the presence of ethyl acetate<sup>a</sup>

Promoter:catalyst molar ratio	5-Decene (%)	Dodecenes (%)
—	3	78
0.1:1	38	44
2:1	80	2
10:1	54	28

<sup>a</sup>All the data are an average of at least three experiments.

Ratio X:1 (promoter:catalyst), X = 0–10. Solvent: toluene. Temperature 323 K. Addition order: solvent, olefin,  $WCl_6$ ,  $PhSiH_3$ , ethyl acetate

approximately 50% selectivity (Table 2), being more sensitive on selectivity variations. The promoter was added in ratios X:1 (promoter:catalyst), with X varying from 0 to 10. Table 3 shows that the selectivity reaches a maximum at the ratio 2:1, decreasing at higher promoter concentrations.

These results suggest a competition for the catalytic sites between the promoters (polar compounds) and the olefin. Higher promoter concentrations may block one of the sites necessary for the metathesis reaction. The possibility of destruction of the active sites by the added promoters cannot be neglected.

Monitoring the reaction by GC it can be seen that such systems possess a long induction time, ~ 30 min (Fig. 1), and in approximately 2 h the reaction is almost completed. After 60 min reac-

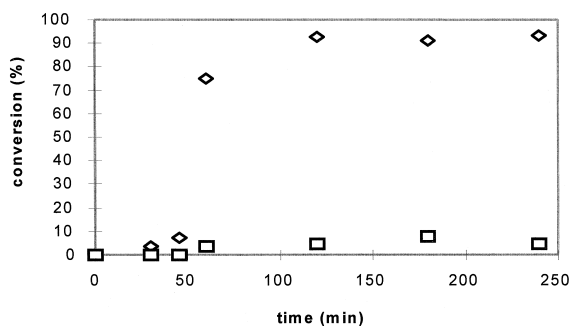


Fig. 1. Conversion of 1-hexene into decene and dodecene as a function of the reaction time. Catalytic system:  $WCl_6$ / $PhSiH_3$ /ethyl acetate in 1:2:2 molar ratio. Temperature, 50°C. -◇-, 5-decene; -□-, dodecenes.

tion, dimerization products are detected, probably due to a W–H complex generation, which is known to be an active species for oligomerization.

Balcar et al. [27] demonstrated the formation of  $WOCl_4$ :ester species when  $WCl_6$  is in the presence of an ester. Moreover, as mentioned before, it is known that  $WOCl_4$  leads to a smaller activation energy for metathesis than  $WCl_6$ . Thus, the increase in metathesis selectivity upon the addition of promoters could be considered as a result of  $WOCl_4$  formation, which would also explain the good performance of such systems with functionalized olefins, where the substrate would have the role of producing the oxygen-containing catalytic species. For comparative reasons, we performed the 1-hexene reaction using  $WOCl_4$ - $PhSiH$  under the same experimental conditions. The decene yield was about 17% and dodecene yield was 10%. It is worth mentioning that in contrast to the products of the  $WCl_6$ -based system, the formation of higher oligomers ( $C_{18}$  and  $C_{20}$ ) in 8% of yield was observed. Thus, the results found previously for  $WCl_6$ /hydrosilanes/promoters cannot be attributed exclusively to an in situ  $WOCl_4$  formation, but to other active derivatives, generated in the presence of hydrosilanes.

In the case of the acetonitrile promoter, it is believed that a tungsten alkylidene compound

Table 4

Metathesis yields of 1-hexene in the presence of hydrosilane cocatalysts using tungsten phenoxides as catalysts<sup>a</sup>

Cocatalyst	Catalyst			
	$Cl_4W$ - (dichlorophenoxide) <sub>2</sub>		$Cl_4W$ - (difluorophenoxide) <sub>2</sub>	
	5-Decene (%)	Dodecenes (%)	5-Decene (%)	Dodecenes (%)
$Ph_2SiH_2$	81	9	85	5
PMHS	56	24	77	3

<sup>a</sup>All the data are an average of at least three experiments.

Olefin/W/Si molar ratio = 100:1:4. Temperature 323 K. Solvent: toluene. Addition order: solvent, olefin, catalyst and cocatalyst.

with a W–N bond is formed. Schrock et al. [28] showed that such compounds are very efficient catalysts in olefin metathesis.

The best results for metathesis were obtained with the addition of phenols as promoters, even using PMHS as cocatalyst, as shown in Table 2. In order to investigate this effect, we synthesized the  $WCl_4(2,6\text{-dichlorophenoxide})_2$  and  $WCl_4(2,6\text{-difluorophenoxide})_2$  compounds and tested these in the same reaction. The results (Table 4) show that these compounds, as opposed to  $WCl_6$ , catalyse the metathesis reaction with no need of promoters, confirming the results discussed above. On the other hand, the behavior of PMHS is not yet well understood: it may be due to a side reaction between the promoter and the cocatalyst, when the promoters are acetonitrile and ethylacetate.

#### 4. Conclusion

$WCl_6$  in the presence of the employed hydrosilane compounds tested leads mainly to dimerization reactions of 1-hexene. Thus, these cocatalysts do not promote the formation of a metal carbene, but of a W–H species. Addition of promoters increases the yield of metathesis reaction products showing the importance of an oxygen-containing compound for metal carbene formation. On the other hand, phenoxides derivatives do not need the addition of promoters to promote the metathesis reaction of 1-hexene.

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