

Homogeneous catalyst systems with organosilicon components for olefin metathesis

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Abstract

Two silicon-containing catalyst systems for the olefin metathesis reaction are described. The first system, WCl_6/Ph_2SiH_2 , is active for all kinds of olefinic substrates: acyclic, cyclic and functionalized olefins, and alkadienes. The second system, $W(CO)_6/Ph_2SiH_2$, is active for the metathesis of terminal olefins, but only under UV irradiation.

Upon reaction between the catalyst components, a tungsten–silylene intermediate is formed as the precursor of the active species for metathesis. The product of a [2 + 2] cycloaddition of the tungsten–silylene complex was isolated. It showed catalytic activity for the metathesis of 1-hexene under UV irradiation, or at elevated temperature, when tungsten–silylene species could be generated from $[W(CO)_4]_2[\mu^2-Si(C_6H_5)_2]_2$. This is the first example of olefin metathesis with metal–silylene activation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Olefins; Metathesis; Organosilicon cocatalyst; Tungsten–silylene intermediate

1. Introduction

Nowadays, olefin metathesis attracts the attention of many chemists as a convenient reaction for the synthesis of fine chemicals and natural products. A wide range of homogeneous and heterogeneous catalysts for this reaction is known [1]. Application of most of these catalysts is limited because of their low activity for the metathesis of functionalized olefins. Two popular types of homogeneous catalysts are the well-defined, stable molybdenum alkylidene complexes developed by Bazan et al. [2], and the ruthenium carbene complexes of Schwab et

al. [3,4], which have high activity, stability and tolerance to many functional groups.

Before the advent of well-defined metal carbene catalysts, several “classical” catalyst systems were developed that are active in the metathesis of functionalized olefins, such as WCl_6 in combination with a silicon-containing cocatalyst [1]. From organosilicon chemistry, it is known that a number of stoichiometric and catalytic reactions based on silicon-containing transition metal systems involve silylene complexes as intermediates [5]. Numerous base-stabilized silylene complexes of the type $L_nM = SiR_2(\text{donor})$ [6] have been reported, as well as base-free silylene complexes of Pt and Ru [7]. The synthesis and structural characterization of transition-metal-substituted silylene com-

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plexes of Os, Pt, and Ru have also been described in the literature [8–10]. Possible applications in catalysis have driven progress towards defined properties and reactivities of silylene complexes of ruthenium [11] and rhodium [12]. Thus, a number of metal–silylene complexes that can be considered as analogues of metal–carbene complexes are well defined, although all of them are less stable.

Our present study is devoted to catalyst systems for olefin metathesis based on tungsten compounds and organosilicon cocatalysts. These catalysts are of interest, not only because of their high activity in the metathesis of functionalized olefins, but also because of a rather unusual route for the formation of the active species. As a result of the reaction between the catalyst components, the formation of a tungsten–silylene complex is possible. For this reason, the study of the photo-activated reaction of the tungsten compound with Ph_2SiH_2 can elucidate the appearance of the catalytic activity. A mechanism with tungsten–silylene intermediates as the precursors of active species for olefin metathesis will be discussed.

2. Experimental

2.1. General procedures

All manipulations were carried out using either high-vacuum techniques, or under an inert atmosphere with standard Schlenk techniques. Benzene and toluene were distilled from Na/K alloy.

Ph_2SiH_2 , $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{SiH}_2$, MePhSiH_2 , Et_3SiH and $(n\text{-C}_3\text{H}_7)_2\text{SiH}_2$ were prepared as described in the literature [13–16]. These compounds were distilled from CaH_2 and degassed with two freeze–pump–thaw cycles prior to use. WCl_6 , WOCl_4 , $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ were purified by vacuum sublimation and kept under argon. All of the esters — methyl, ethyl, and butyl 4-pentenoate and the corresponding alkyl-(2-allyl) 4-pentenoates — were prepared

from the alkyl bromide and alkyl acetoacetate according to known procedures [17] and distilled before use. Bicyclo[2.2.1]-2-heptene (Fluka) was distilled from sodium wire. N-trifluoroacetyl-6,6-bis(trifluoromethyl)-5-azabicyclo[2.2.1]-2-heptene (**6**) was prepared by a Diels–Alder reaction of 1,1,1,5,5,5-hexafluoro-2-trifluoromethyl-3-aza-4-oxo-2-pentene and cyclopentene in Et_2O and hydroquinone as catalyst: yield 50%. Anal. calcd. for $\text{C}_{10}\text{H}_6\text{F}_9\text{NO}$ (**6**): C, 36.71; H, 1.85; N, 4.28. Found: C, 36.82; H, 1.90; N, 4.16. b.p. $110^\circ\text{C}/19$ mm Hg. Mass spectrum (m/z , I, %): 327 (M^+ , 10), 288 (5), 280 (6), 268 (23), 69 (17), 66 (100), 39 (8). ^1H nuclear magnetic resonance (NMR) (CDCl_3 , 300 MHz) δ (ppm) 6.70 (m), 6.51 (m) (2H, $-\text{HC}=\text{CH}-$), 5.20 (s, 1H, HC), 3.82 (s, 1H, HC), 2.10 (s, 1H, H_2C), 1.82 (s, 1H, H_2C).

2.2. Metathesis experiments

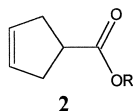
The reactions were carried out in the liquid phase in sealed tubes under vacuum (1×10^{-3} mm Hg) as described before [18]. A calculated amount of the unsaturated substrate(s) was introduced into the tube, followed by the solution of WCl_6 or WOCl_4 in benzene. Next, a benzene solution of Ph_2SiH_2 was added. Then, the reaction mixture was frozen with liquid nitrogen. The argon was pumped off and the tube sealed. The reaction mixture was kept at $50\text{--}60^\circ\text{C}$ for 6–10 h with stirring. After cooling and quenching with water, the mixture was extracted with Et_2O , filtered and dried over CaSO_4 , and the ether was distilled off. Products were fractionated by vacuum distillation. Analysis was performed by GC (a glass column containing 8% SE-30 with DMCS on Carbowax W 80/100 mesh) and by gas chromatography mass spectrometry (GC-MS) (Kratos MS-80 spectrometer at ionization voltage of 70 eV).

Photo-activated reactions were carried out in quartz tubes without solvent in a manner analogous to the previous experiments. A calculated amount of solid $\text{W}(\text{CO})_6$ or $\text{Mo}(\text{CO})_6$ was placed in the tube and 1-hexene and the

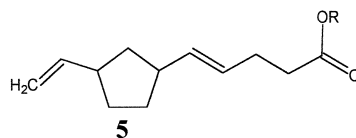
organosilicon cocatalyst were added under an argon atmosphere. The tube was attached to a vacuum line. The mixture was frozen with liquid nitrogen and the argon was removed. The tube was then flame-sealed under vacuum. Irradiation was carried out with a medium-pressure Hg lamp (500 W) at 45°C. During irradiation, $M(CO)_6$ dissolved in 1-hexene. The liquid phase was analysed after the reaction by GC and GC-MS.

$[M^+]$, 27). Ethyl 3-cyclopentene-1-carboxylate: b.p. 60–61°C (10 mm Hg). MS (m/z): (140 $[M^+]$, 35). Butyl 3-cyclopentene-1-carboxylate: b.p. 84–86°C (10 mm Hg). MS (m/z): (168 $[M^+]$, 32).

2.3. Characterization of the main products

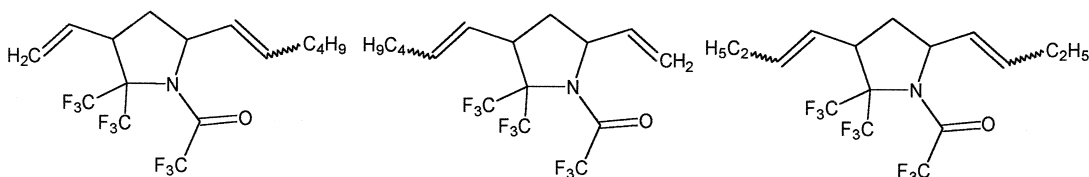


Methyl 3-cyclopentene-1-carboxylate: b.p. 52–53°C (9 mm Hg). MS (m/z) (I, %): (126

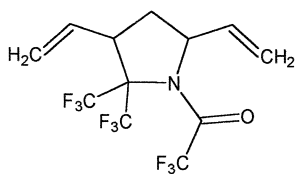


Ethyl 5-(3-vinylcyclopentyl)-4-pentenoate: b.p. 109–111°C (3 mm Hg). MS (m/z): (222 $[M^+]$, 5). Butyl 5-(3-vinylcyclopentyl)-4-pentenoate: b.p. 108–109°C (0.6 mm Hg). MS (m/z): (250 $[M^+]$, 7).

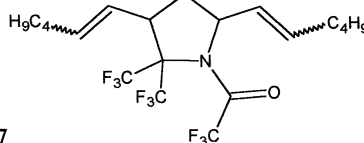
GC-MS analysis of the product mixtures of reaction 3 showed the presence of the following cross-metathesis products:



with 411 $[M^+]$, 5, 411 $[M^+]$, 4, 411 $[M^+]$, 7. The other products were detected as:



with 355 $[M^+]$, 7



with 467 $[M^+]$, 4.

2.4. Preparation of $[W(CO)_4]_2[\mu-Si(C_6H_5)_2]_2$ (**9**)

The reaction was carried out in a quartz reactor with sealed glass tubes and breakable membranes for evacuation of gaseous products during the reaction. The tubes could be attached to a vacuum line for use in a trap-to-trap technique. $W(CO)_6$ (54 mmol) was placed in the reactor under argon. Then, degassed Ph_2SiH_2 (54 mmol) and hexane (8 ml) were added. The mixture was frozen with liquid nitrogen and the argon was pumped off before the reactor was flame-sealed under a vacuum of 1×10^{-3} mm Hg. The reaction mixture was irradiated with a medium-pressure Hg lamp (500 W) at 45°C for 50 h with stirring. The reaction mixture changed from colourless to orange, accompanied by evolution of gases, which were detected by GC and MS as H_2 and CO. The reactor was attached to the vacuum line using the sealed tubes every 2–3 h and the reaction mixture was frozen. The glass membrane was broken and CO and H_2 were evacuated under reduced pressure. After 50 h, the reactor was attached to the vacuum line again and hexane, unreacted Ph_2SiH_2 and $W(CO)_6$ were removed by distillation at 95°C using a liquid nitrogen trap. The resulting orange-brown residue was crystallized from 2 ml of hexane at $-40^\circ C$. Compound **9** was obtained in 40% yield as orange needles, which are stable under argon. Anal. calcd. for $C_{32}H_{20}O_8Si_2W_2$ (**9**): C, 40.19; H, 2.11. Found: C, 40.12; H, 2.18. m.p. 147–147.5°C. 1H NMR (C_6D_6 , 300 MHz) δ (ppm) 6.6 (m, 3H Ph), 7.1

(m, 2H Ph). ^{13}C NMR (C_6D_6 , 75 MHz) δ (ppm) 128.3 (m, Ph), 131.1 (m, Ph), 131.9 (m, Ph), 134.2 (m, Ph), 196.2–197.6 (m, CO). IR (cm^{-1}): 169, 211, 319 (unsymmetrical vibrations for four-membered ring), 376, 427, 442, 470, 489, 534, 564, 686, 740, 935, 998, 1067, 1097, 1123, 1376, 1427; 1948, 1975, 2030, 2055, 2097 (valence vibrations for CO), 3020, 3080. MS (70 eV) m/z (I, %): 296 ($W(CO)_4$, 54), 268 ($W(CO)_3$, 17), 240 ($W(CO)_2$, 9), 182 (Ph_2Si , 52), 105 ($PhSi$, 28), 77 (Ph, 100).

3. Results and discussion

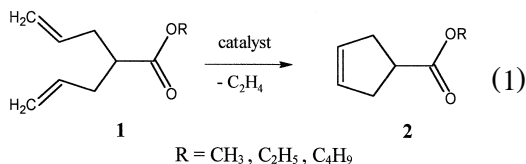
Previously, we have shown that the systems $WCl_6/1,1,3,3$ -tetramethyl-1,3-disilacyclobutane [18] and WCl_6/Ph_2SiH_2 [19] are active catalysts for olefin metathesis. The latter catalyst system was used earlier for the metathesis of functionalized olefins by Levisalles et al. [20]. We showed that a catalyst based on WCl_6 and Ph_2SiH_2 can also be applied to the synthesis of five-membered carbocyclic and heterocyclic compounds either via ring-closing metathesis (RCM) of unconjugated functionalized dienes, or via cross-metathesis of norbornene derivatives with linear olefins, giving high yields and selectivity [19]. Table 1 shows new results with these catalyst systems. In the table, the yields are given of the derivatives of 3-cyclopentene-1-carboxylic acids (**2**) obtained by RCM of the corresponding dienes (alkyl 2-allyl-4-pentenoate (**1**)) at 60°C in a benzene solution of

Table 1
RCM of **1** in the presence of the catalyst system, WCl_6/Ph_2SiH_2 or $WOCl_4/Ph_2SiH_2$ ^a

R	Molar ratio of 1:W	WCl_6/Ph_2SiH_2		$WOCl_4/Ph_2SiH_2$	
		Conversion of 1 (%)	Selectivity (%)	Conversion of 1 (%)	Selectivity (%)
C_2H_5	25:1	35	90	38	91
C_2H_5	50:1	41	96	44	97
C_2H_5	100:1	30	97	35	97
CH_3	50:1	42	95	47	96
C_4H_9	50:1	37	91	41	95

^aReaction conditions: temperature 60°C, molar ratio W/Si = 1, reaction time 10 h, solvent benzene.

WCl_6/Ph_2SiH_2 or $WOCl_4/Ph_2SiH_2$ (reaction 1).



The best results were obtained with a molar substrate/catalyst ratio of 50/1; in all cases,

the selectivity was high. This might be of interest for, e.g., medicinal chemistry, because compounds of type **2** are components of a remedy against leprosy [21].

Another way of synthesizing five-membered cyclic compounds is the cross-metathesis between norbornene, or its derivatives, and linear substrates. We used the catalyst system WCl_6/Ph_2SiH_2 for cross-metathesis of norbornene and azanorbornene derivatives with linear olefins or unsaturated esters (reaction 2).

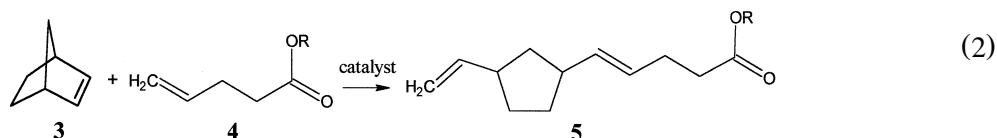
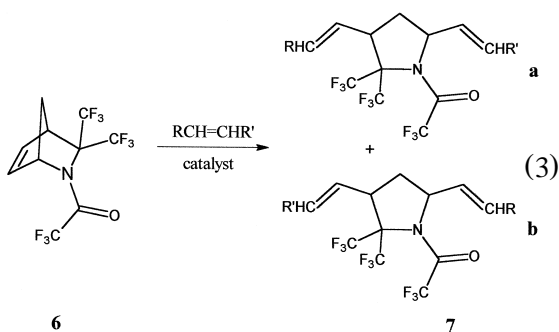


Table 2 shows the results for the cross-metathesis of norbornene with ethyl 4-pentenoate. A rather high selectivity was obtained: the formation of the unsymmetrical substituted products is favoured. The side reactions were self-metathesis of both substrates and secondary metathesis reactions, leading to symmetrical products.

Cross-metathesis of an azanorbornene derivative with a simple olefin produces pyrrolidine derivatives (reaction 3). The yields of pyrrolidine derivatives (**7a,b**) were not high (Table 3). High-molecular weight products of the self-metathesis of the azanorbornene derivative were also obtained:

kinds of substrate, but also because of the unusual route for active species formation. Levisalles et al. [20] supposed that in this case, the reactions occur via tungsten–silylene intermediates, although evidence was not provided. It is indeed impossible to characterize tungsten–silylene complexes that could be produced during that reaction. Therefore, we studied the model catalyst system $W(CO)_6/Ph_2SiH_2$, and some related systems, in the olefin metathesis reaction. These systems showed catalytic properties for the metathesis of terminal olefins under UV irradiation. Table 4 gives the results of the metathesis of 1-hexene in the presence of the catalyst system $M(CO)_6/R_2SiH_2$, $M = W$ or Mo . All of the reactions were carried out



The catalyst system WCl_6/Ph_2SiH_2 is of interest, not only because of its activity for all

Table 2

Cross-metathesis of norbornene (**3**) with ethyl (or butyl) 4-pentenoate (**4**) in the presence of the catalyst system, WCl_6/Ph_2SiH_2

R	Molar ratio of 3:4:(WCl_6)	Conversion of 3 (%)	Selectivity (%)
C ₂ H ₅	25:25:1	37	60
C ₂ H ₅	50:50:1	34	63
C ₄ H ₉	25:25:1	41	57

^aReaction conditions: temperature 50°C, molar ratio W/Si = 1, reaction time 6 h, solvent benzene.

Table 3

Cross-metathesis of azanorbornene derivative **6** with olefins in the presence of the catalyst system $WCl_6/Ph_2SiH_2^a$

R	R'	Yield of 7 (%)	Selectivity (%)
H	C ₄ H ₉	22	51
C ₂ H ₅	C ₂ H ₅	17	63

^aReaction conditions: temperature 50°C, molar ratio **6**:RCH = CHR':W:Si = 30:30:1:1, reaction time 6 h, solvent benzene.

without a solvent under UV irradiation using a 500 W Hg lamp. By-products formed were 2-hexene and cross-metathesis products. The best catalyst system was $W(CO)_6$ in combination with the cocatalysts containing two aromatic groups, viz. Ph_2SiH_2 or $(p-Tol)_2SiH_2$. The catalyst systems with $Mo(CO)_6$ showed lower activity compared with the tungsten-containing catalyst. R_3SiH did not form an active catalyst with $W(CO)_6$ or $Mo(CO)_6$.

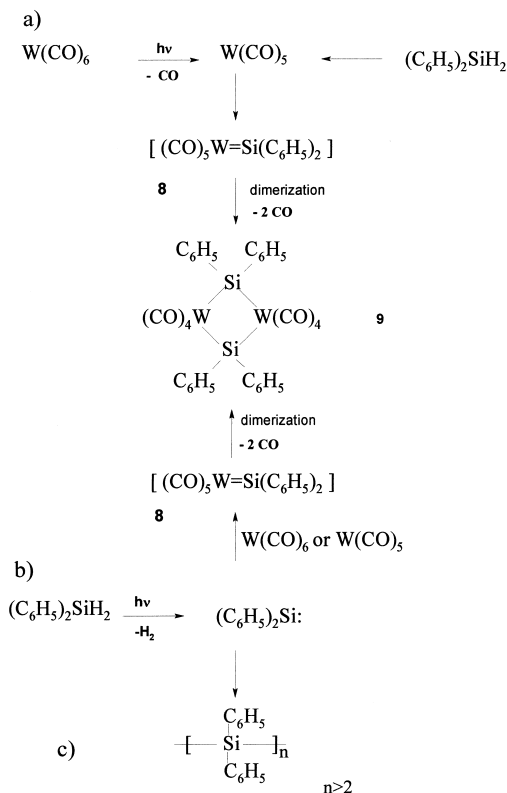
Formation of active species for these catalyst systems might be possible via metal–silylene intermediates, $L_nW=SiR_2$. We studied a model reaction between equimolar amounts of $W(CO)_6$ and Ph_2SiH_2 under UV irradiation. Scheme 1 shows two routes (a and b) that can be envisaged for tungsten–silylene formation. The tungsten–silylene intermediate **8** is suggested as being formed during the photo-activated reaction. This complex, with a double bond between tungsten and silicon atoms, is very unstable, similar to other compounds with a double bond to the silicon atom [22,23]. As a result, metallacycle **9** is formed via a [2 + 2] cycloaddition

Table 4

Activity of photo-activated catalyst systems, $M(CO)_6-R_2SiH_2-h\nu$ in the metathesis of 1-hexene^a

$M(CO)_6$	Organosilicon cocatalyst	Conversion of 1-hexene (%)	Selectivity (%)
$W(CO)_6$	$(p-CH_3C_6H_4)_2SiH_2$	44	84
$W(CO)_6$	$(C_6H_5)_2SiH_2$	47	93
$W(CO)_6$	$(CH_3)(C_6H_5)SiH_2$	12	60
$W(CO)_6$	$(n-C_3H_7)_2SiH_2$	5	–
$Mo(CO)_6$	$(p-CH_3C_6H_4)_2SiH_2$	13	65
$Mo(CO)_6$	$(C_6H_5)_2SiH_2$	10	67

^aReaction conditions: temperature 45°C, molar ratio 1-hexene: $M(CO)_6$:cocatalyst = 100:1:1, reaction time 10 h, solvent benzene.



Scheme 1.

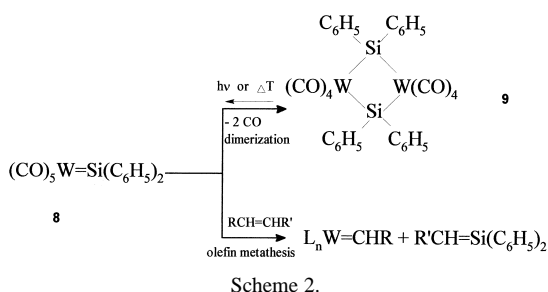
reaction. The same reaction was observed for a ruthenium–silylene complex [10]. Product **9** was the only compound that could be isolated, as stable (under argon) orange needles with m.p. 147–147.5°C. The reaction took place in hexane for 50 h at 45°C under irradiation with a 500 W Hg lamp. When CO and H₂ were removed every 2 h, the yield of **9** was 40%. In a separate experiment, it was demonstrated that photolysis of Ph_2SiH_2 results in the formation of polysilanes and elimination of H₂ (route c).

Table 5

Metathesis of 1-hexene in the presence of **9**^a

Temperature (°)	UV irradiation	Time (h)	Conversion of 1-hexene (%)	Selectivity (%)
45	no	20	0	–
60	no	20	< 1	–
105	no	2	40	89
45	yes	10	37	83

^aMolar ratio 1-hexene:W = 100:1.



The cyclodimer **9** was tested for 1-hexene metathesis under UV irradiation or elevated temperature (Table 5). The results demonstrate that the cyclodimer **9** can act as a catalyst precursor for the metathesis of terminal olefins when the reverse reaction of the [2 + 2] cycloaddition with formation of tungsten silylene species takes place.

The results also show that the tungsten–silylene complex **8**, which was produced during the reaction of $W(CO)_6$ and Ph_2SiH_2 , can act as an active species and interact with the double bond of the olefinic substrate as well as metal–carbene complexes do. On the other hand, a [2 + 2] cycloaddition can take place with the formation of a four-membered cyclic compound (**9**), resulting in the disappearance of catalytic properties. At elevated temperature, or under UV irradiation, when compound **9** was destroyed with generation of tungsten–silylene species, it again showed catalytic properties (Scheme 2).

Complex **8** may be considered as an analogue of the carbene complex $(CO)_5W=CPh_2$ that shows some catalytic activity for the metathesis of 2-pentene [24]. It can be concluded that formation of active species for olefin metathesis seems to be possible via tungsten–silylene or tungsten–silacyclobutane intermediates.

4. Conclusions

The two catalyst systems, WCl_6/Ph_2SiH_2 and $W(CO)_6/Ph_2SiH_2-h\nu$, are active in the

metathesis of olefins. Upon reaction between the catalyst components, a tungsten–silylene intermediate is formed as the precursor of the active species for metathesis. This is the first example of olefin metathesis with metal–silylene activation, and opens new possibilities for creating novel types of olefin metathesis catalysts.

Acknowledgements

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