



Synthesis, characterization and catalytic properties of a highly stereoselective olefin metathesis catalyst

Bouchra Rhers^a, Eva Grinerval^a, Mostafa Taoufik^a, Fabienne Fache^b, Eberhardt Herdtweck^c, Jean-Marie Basset^a, Frédéric Lefebvre^{a,*}

^a Université de Lyon, Institut de Chimie de Lyon, Lyon, Université Lyon 1, CPE Lyon, CNRS, UMR C2P2, LCOMS, Bâtiment CPE Curien, 43 Boulevard du 11 Novembre 1918, F-69616, Villeurbanne, France

^b Laboratoire de Chimie Organique, Photochimie et Synthèse, UMR-CNRS 5181, Bâtiment Raulin, 43, bd du 11 Novembre 1918, F-69616, Villeurbanne, France

^c Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenbergstr. 4, D-85747, Garching, Germany

ARTICLE INFO

Article history:

Received 17 December 2008

Accepted 9 January 2009

Available online 16 January 2009

Keywords:

Metathesis

Stereoselectivity

Carbenes

Homogeneous catalysis

Tungsten

ABSTRACT

The X-ray determination of a tungsten based complex allowed to definitively assign its structure and chemical formula to $W(OC_6H_3PhC_6H_4)(OAr)(=CHC(CH_3)_3)Cl$ with $Ar = 2,6-Ph_2C_6H_3$. This complex is a catalytic system which displays high metathesis activity and high stereoselectivity even for bulky functional olefins.

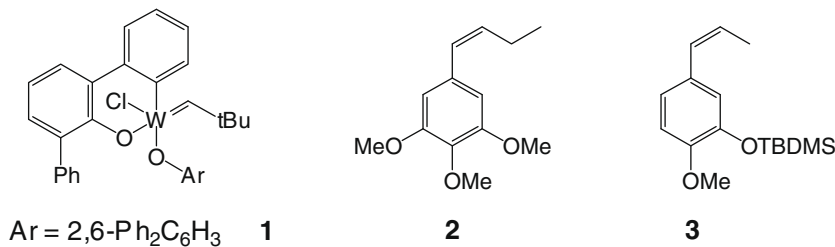
© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Olefin metathesis is a well-known catalytic reaction, which is now widely used for the synthesis of many organic molecules [1–3]. This reaction is catalyzed by alkylidene complexes such as those described by Schrock [4,5] and Grubbs [6–8]. Despite high catalytic activities, the main drawback of these systems is a lack of stereoselectivity as the configuration (*cis* or *trans*) of the resulting olefin is not determined by the configuration of the starting olefin. In the metathesis reaction of *cis*-pent-2-ene for instance, the Schrock system leads to the formation of both *cis* and *trans* olefins with the same probability while the Grubbs system gives, whatever the configuration of the starting olefin, only *trans* olefin which is the most thermodynamically stable isomer [9]. In 1992,

we reported a new catalytic system based on tungsten, which displayed high metathesis activity and high stereoselectivity [10–13]. Unfortunately, the structure of this complex remained unknown even if it was assigned to $W(OC_6H_3PhC_6H_4)(OAr)(=CHC(CH_3)_3)Cl(OEt_2)$, with $Ar = 2,6-Ph_2C_6H_3$ on the basis of NMR data [10–13].

We present in this communication a slightly modified synthesis of the above complex and its characterization by X-ray diffraction, allowing to definitively assign its chemical formula to $W(OC_6H_3PhC_6H_4)(OAr)(=CHC(CH_3)_3)Cl$ (**1**). Stereoselectivity of **1** in olefin metathesis and particularly in the stereoselective self- and cross-metathesis of two bulky functional olefins **2** and **3** will also be described and compared to two commercially available catalysts developed by Schrock and Grubbs.



* Corresponding author. Tel.: +33 472431807; fax: +33 472431795.
E-mail address: lefebvre@cpe.fr (F. Lefebvre).

2. Experimental

All manipulations and reactions were performed in an atmosphere of dry argon by using classical Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use.

Synthesis and X-ray structure of the orthometallated tungsten complex **1** was prepared according to a slightly modified synthesis of the previously published one [10]. Lithium 2,6-diphenylphenoxide (640 mg, 2.22 mmol) was added slowly at 0 °C to a solution of [WCl₃(=CC(CH₃)₃)(dme)] (dme: dimethoxyethane), prepared according to the procedure reported earlier [14], (450 mg, 1.11 mmol) in diethyl ether. The mixture was stirred during 1 h at 0 °C and then 24 h at room temperature. After filtration, the solvent was removed in vacuo and the resulting red solid was recrystallized in diethyl ether at –5 °C (yield 90%).

¹H-NMR (300 MHz, benzene-*d*₆, δ ppm): 10.1 (W=CHC(CH₃)₃); 8.2–6.4 (*H*-aromatics); 0.8 (W=CHC(CH₃)₃). ¹³C(¹H) NMR (300 MHz, benzene-*d*₆, δ ppm): 287.8 (W=CHC(CH₃)₃); 181.8 (*C*-orthometallated); 159.0–123.1 (*C*-aromatics); 50.2 (CHC(CH₃)₃); 31.3 (CHC(CH₃)₃). HRMS-EI M⁺: calcd 776.1808 a.m.u.; found 776.1806 a.m.u. Elemental analysis calculated for C₄₅H₄₅WO₃Cl: W 21.5, C 63.3, H 5.3; found: W 21.8, C 62.9, H 5.3.

For the X-ray crystal structure analysis of **1**, 75659 reflections were measured on a κ-CCD (Area Diffraction System, Nonius) diffractometer equipped with a rotating anode Mo-Kα radiation (λ = 0.71073 Å) and 5803 reflections unique [*R*_{int} = 0.066] were used in all calculations (final *R*1 = 0.0222 [5487 data with *I*_o > 2σ (*I*_o)] and *wR*2 = 0.0623 (all data)). Structure solution and refinement were performed by using SIR92 [15] and SHELTLX [16]. Hydrogen atoms were included in the structure factor calculations but were not refined except the hydrogen atom linked to C1 which was located on the final Fourier difference map and which was refined isotropically.

2.1. Synthesis of the functional olefins

The two functional olefins **2** and **3** were synthesized from commercial products by Wittig reaction in good yield according to the procedure reported earlier [17]:

- Synthesis of 1-(3',4',5'-trimethoxyphenyl)butene (**2**). Potassium bis(trimethyl silyl)amide (Acros, 10 mL of 0.5 M solution in toluene, 5 mmol) was added to propyltriphenylphosphonium bromide (Aldrich 98%, 1.93 g, 5 mmol) in THF (50 mL) under argon at 0 °C. The mixture was stirred at 0 °C for 2 h, cooled to –78 °C and 3,4,5-trimethoxybenzaldehyde (Aldrich 98%, 0.99 g, 5 mmol) was added. The resulting mixture was stirred during 2 h at –78 °C and allowed to warm to room temperature. Water (50 mL) was carefully added and the aqueous layer separated and extracted with ether (3 × 50 mL). The combined organic layers were washed with water (2 × 50 mL), brine (50 mL), dried (MgSO₄) and concentrated in vacuo. Flash column chromatography (petroleum ether/EtOAc 90:10) afforded a mixture of the two isomers of **2** as a colourless oil (*cis*-**2**/*trans*-**2** = 99:1, yield 71%). ¹H-NMR (300 MHz, CDCl₃, δ ppm): 6.47 (s, 2, Ar-*H*); 6.28 (td, 1, ³J_{CIS} 11.5 Hz and ⁴J 1.8 Hz, Ar-CH=CH); 5.58 (td, 1, ³J_{CIS} 11.5 Hz and ³J 7.2 Hz, Ar-CH=CH); 3.82 (s, 9, OCH₃); 2.33 (qd, 2, ³J 7.5 Hz and ⁴J 1.8 Hz, CH₂); 1.04 (t, 3, CH₃).
- Synthesis of 1-(3'-*tert*-butyldimethylsilyloxy-4'-methoxyphenyl)propene (**3**). Three were synthesized from 3-hydroxy-4-methoxybenzaldehyde. As **1** is highly sensitive to hydroxy groups, the alcohol function was first protected with a *tert*-butyldimethylsilyl group according to the following procedure:

a mixture of 3-hydroxy-benzaldehyde (Aldrich 99%, 0.76 g, 5 mmol), imidazole (1.36 g, 20 mmol), *tert*-butyldimethylsilylchloride (1.50 g, 10 mmol) and catalytic quantity of dimethylaminopyridine (20 mg) in dichloromethane was stirred during two days at room temperature. The organic layer was diluted, washed with water (2 × 50 mL), brine (50 mL), dried (MgSO₄) and concentrated in vacuo to afford 3-*tert*-butyldimethylsilyloxy-4-methoxybenzaldehyde. The olefin **3** was then synthesized according to the previous procedure using ethyltriphenylphosphonium bromide (Aldrich 99%, 1.87 g, 5 mmol). Flash column chromatography (petroleum ether/EtOAc 97:3) afforded a mixture of the two isomers of **3** as a colourless oil (*cis*-**3**/*trans*-**3** = 12:1; yield 63%). ¹H-NMR (300 MHz, CDCl₃, δ ppm): 6.81 (m, 3, Ar-*H*); 6.29 (dd, 1, ³J_{CIS} 11.7 Hz and ⁴J 1.8 Hz, Ar-CH=CH); 5.64 (qd, 1, ³J_{CIS} 11.4 Hz and ³J 6.9 Hz, Ar-CH=CH); 3.78 (s, 3, OCH₃); 1.86 (dd, 2, ³J 6.9 Hz and ⁴J 1.8 Hz, CH₂); 0.98 (s, 9, C(CH₃)₃); 0.14 (s, 6, Si(CH₃)₂).

2.2. Catalysis

The metathesis experiments were performed in presence of internal standards (hexane and/or dodecane) according to the following procedures:

- Self-metathesis of *cis*-pent-2-ene: *cis*-pent-2-ene (10 mmol; 500 equiv) and hexane (0.6 mL) were added to **1** (0.02 mmol) in chlorobenzene (3 mL) under argon at 25 °C.
- Self-metathesis of **2**: 1-(3',4',5'-trimethoxyphenyl)butene **2** (0.50 mmol; 25 equiv) and dodecane (0.1 mL) were added to one of the three metathesis catalysts (0.02 mmol) in chlorobenzene (3 mL) under argon at 80 °C.
- Cross-metathesis of **2** and **3**: 1-(3',4',5'-trimethoxyphenyl)butene **2** (0.25 mmol; 12.5 equiv) and 1-(3'-*tert*-butyldimethylsilyloxy-4'-methoxyphenyl)propene **3b** (0.25 mmol; 12.5 equiv) were added to **1** (0.02 mmol) in chlorobenzene (3 mL) under argon at 80 °C. Two internal standards were used: dodecane (0.05 mL) for the liquid phase and hexane (0.03 mL) for the gaseous phase.

Conversions and selectivities were obtained as a function of time by taking periodically aliquots of liquid and/or gaseous phases which were analyzed by GC (on KCl/Al₂O₃ or HP-5).

3. Results and discussion

X-ray crystal structure of **1** and *cis*-pent-2-ene metathesis reaction. The X-ray diffraction analysis of compound **1** (Fig. 1) shows an orthorhombic crystal structure which belongs to a Pca2₁ space group. The lattice is defined by the following values: *a* = 12.3893(1) Å, *b* = 14.0737(1) Å, *c* = 18.9862(1) Å, *V* = 3310.50(4) Å³, *Z* = 4. This structural analysis shows that the tungsten atom of **1** is pentacoordinated with trigonal bipyramid geometry. The two aryloxy ligands are axially located, with quite the same W–O distance, 1.833(2) and 1.837(3) Å, respectively. These values are quite comparable to those usually reported in the literature, typically between 1.83 and 1.85 Å [18]. One of these aryloxy ligands is ortho-metallated to the tungsten atom by one ortho carbon of its phenyl substituents. The corresponding W–C distance (2.16(4) Å) is quite comparable to those reported for W(OC₆H₃PhC₆H₄)₂(PMePh₂)₂ (2.14 and 2.18 Å) [19]. The C–W–O angle is relatively short (82.74(12)°) showing that the structure is relatively strained. The two other ligands are a chlorine atom (W–Cl = 2.431(10) Å) and the neopentylidene group (W=C = 1.887(4) Å). The corresponding distances values are also in agreement with literature data [18–22].

Download English Version:

<https://daneshyari.com/en/article/51544>

Download Persian Version:

<https://daneshyari.com/article/51544>

[Daneshyari.com](https://daneshyari.com)