



## Facile double-bond migration of allylsilanes in the coordination sphere of tungsten complexes

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### ABSTRACT

Novel tungsten(0) complexes containing  $\eta^2$ -allylsilane ligands ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{SiR}_3$ ,  $\text{R}=\text{Me}$ ,  $\text{OMe}$ ,  $\text{Cl}$ ) have been generated during photolysis of  $\text{W}(\text{CO})_6$  and allylsilanes in alkane solution, and their molecular structure has been elucidated by IR and NMR spectroscopic methods. The catalytic activity of the  $[\text{W}(\text{CO})_5(\eta^2\text{-allylsilane})]$  complexes in double-bond isomerization of allylsilane leading to *Z*- and *E*-1-propenylsilane has been revealed and the mechanism of this reaction is discussed.

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## 1. Introduction

Allylsilanes have been among the most important organosilicon compounds used in organic and organometallic syntheses [1–4]. However, transformation of allylsilanes in such catalytic reactions as metathesis, hydrosilylation, hydrogenation, and isomerization requires a transition metal compound as a catalyst [4–11]. Coordination of allylsilane to the transition metal atom and the formation of an organometallic complex is a very important step in all these catalytic processes [5,10,11]. Tungsten carbonyl complexes are frequently used in organometallic catalysis, and their role in the activation of the olefin bonds has been very well documented, but allylsilane complexes of tungsten have not been described to date and require more study [12]. It was very interesting to observe the effect of coordination of allylsilane to the tungsten(0) atom on their electronic properties and reactivity.

In this paper, we report on the interesting catalytic activity of photochemically generated  $[\text{W}(\text{CO})_5(\eta^2\text{-allylsilane})]$  complexes in isomerization of allylsilanes under smooth conditions. Although the isomerization of allylic compounds is a very well-known process [7,12–15], allylsilanes have not been explored so well [8,9].

## 2. Experimental

### 2.1. General remarks

All reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen, with freshly distilled substrates and solvents.  $\text{W}(\text{CO})_6$  (Aldrich) was used as received. The allylsilanes:  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{SiMe}_3$  ( $\text{ASiMe}_3$ , **a**),  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}(\text{OMe})_3$  ( $\text{ASi}(\text{OMe})_3$ , **b**),  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{SiClMe}_2$  ( $\text{ASiClMe}_2$ , **c**),  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{SiCl}_3$  ( $\text{ASiCl}_3$ , **d**) were stored and used under an atmosphere of nitrogen. Allylsilane complexes of the type  $[\text{W}(\text{CO})_5(\eta^2\text{-allylsilane})]$  (**1a–d**) and *trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-allylsilane})_2]$  (**2a–d**) were generated photochemically in reaction of  $\text{W}(\text{CO})_6$  and the relevant allylsilane (**a–d**) in alkane solution. The photolysis source was an HBO 200W high-pressure Hg lamp.

$^1\text{H}$ ,  $^{13}\text{C}$  NMR, and two-dimensional  $^1\text{H}-^1\text{H}$  COSY and  $^1\text{H}-^{13}\text{C}$  HMQC NMR spectra were recorded with a Bruker AMX 300 or 500 MHz instrument. The  $^{13}\text{C}$  NMR experiments were performed using gated coupled spectra to obtain coupling constants.  $^1\text{H}$  NMR spectra are referenced to the residual protio isotopomer present in a particular solvent ( $\delta$  7.24  $\text{CDCl}_3$  and 1.40  $\text{C}_6\text{D}_{12}$ ), and  $^{13}\text{C}$  NMR spectra are referenced to the natural-abundance carbon signal of the solvent employed ( $\delta$  77.0  $\text{CDCl}_3$  and 26.4  $\text{C}_6\text{D}_{12}$ ).  $^1\text{H}$  chemical shifts measured in methylcyclohexane- $d_{14}$  as the solvent were referenced relative to  $\text{SiMe}_4$  used as an internal standard.  $^{29}\text{Si}$  NMR chemical shifts were referenced relative to  $\text{Ph}_2\text{SiH}_2$  ( $\delta$  37.08) used as an external standard. IR spectra were measured

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with a Nicolet-400 FT-IR instrument in solution and KBr pellets. Analyses of the organosilicon compounds were performed on a Hewlett-Packard GC-MS system.

## 2.2. Photochemical generation of $\eta^2$ -allylsilane complexes of tungsten(0)

### 2.2.1. Reactions in *n*-heptane solution

A solution of  $W(CO)_6$  (0.2 g, 0.57 mmol) and allylsilane (**a-d**) (ca. 0.4 cm<sup>3</sup>, 2.8 mmol) in freshly distilled *n*-heptane (50 cm<sup>3</sup>) was irradiated through quartz at room temperature. The course of the reaction was monitored by IR measurements in solution, and photolysis was stopped when the IR band of  $W(CO)_6$  at ca. 1981 cm<sup>-1</sup> stay unchanged (2–4 h) and new  $\nu(C\equiv O)$  frequencies in the range 2100–1900 cm<sup>-1</sup> increased. All volatile materials were then evaporated under reduced pressure at room temperature. The resulting brown oil was analyzed by IR and NMR spectroscopy, which confirmed the formation of allylsilane complexes of the type  $[W(CO)_5(\eta^2\text{-allylsilane})]$  (**1a-d**) and  $[W(CO)_4(\eta^2\text{-allylsilane})_2]$  (**2a-d**). The molar ratio of the latter two compounds (**1** and **2**) depended on the time of photolysis, the aging time of the sample, and the polarity of the solvent. Generally, a sample freshly analyzed by <sup>1</sup>H NMR in C<sub>6</sub>D<sub>12</sub> solution contained a greater amount of the pentacarbonyl compound than that analyzed in CDCl<sub>3</sub> solution.

### 2.2.2. NMR tube reactions

A solution of  $W(CO)_6$  (0.05 g, 0.14 mmol) and allylsilane in cyclohexane-*d*<sub>12</sub> (0.5 cm<sup>3</sup>) at 293 K was periodically irradiated and analyzed by <sup>1</sup>H NMR spectroscopy over a period of two hours. The decay of photochemically generated compounds and the appearance of new organometallic and organosilicon compounds were followed by <sup>1</sup>H NMR spectroscopy at different temperatures.

## 2.3. Spectral data of $[W(CO)_5(\eta^2\text{-allylsilane})]$ complexes (**1a-d**)

### 2.3.1. $[W(CO)_5(CH_2=CH-CH_2-SiMe_3)]$ (**1a**)

IR ( $\nu$ , cm<sup>-1</sup>): (*n*-heptane)  $\nu(C\equiv O)$  2081 (w), 1960 (s), 1947 (vs). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>, 500 MHz),  $\delta$  = 4.92 (dddd, <sup>3</sup>J<sub>H-H</sub> = 14.7, 12.0, 8.6, 3.0 Hz, 1H, CH<sup>c</sup>), 3.52 (d, <sup>3</sup>J<sub>H-H</sub> = 8.6 Hz, 1H, CH<sup>b</sup>), 3.44 (d, <sup>3</sup>J<sub>H-H</sub> = 14.7 Hz, 1H, CH<sup>a</sup>), 2.24 (dd, <sup>2</sup>J<sub>H-H</sub> = 13.1 Hz, <sup>3</sup>J<sub>H-H</sub> = 3.7 Hz, 1H, CH<sup>d</sup>), 1.19 (dd, <sup>2</sup>J<sub>H-H</sub> = 12.7 Hz, <sup>3</sup>J<sub>H-H</sub> = 12.3 Hz, 1H, CH<sup>d'</sup>), 0.11 (s, <sup>2</sup>J<sub>Si-H</sub> = 35 Hz, 9H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>12</sub>, 126 MHz),  $\delta$  = 200.5 (<sup>1</sup>J<sub>W-C</sub> = 154 Hz, 1C, CO), 197.1 (<sup>1</sup>J<sub>W-C</sub> = 127 Hz, 4C, CO), 91.1 (1C, C<sub>β</sub>), 60.8 (1C, C<sub>γ</sub>), 30.4 (1C, C<sub>α</sub>), -2.0 (3C, Me).

### 2.3.2. $[W(CO)_5(CH_2=CH-CH_2-Si(OMe)_3)]$ (**1b**)

IR ( $\nu$ , cm<sup>-1</sup>): (*n*-heptane)  $\nu(C\equiv O)$  2081 (w), 1961 (s), 1948 (vs). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>, 500 MHz)  $\delta$  = 4.89 (m, 1H, CH<sup>c</sup>), 3.60 (d, <sup>3</sup>J<sub>H-H</sub> = 9.7 Hz, 1H, CH<sup>b</sup>), 3.57 (s, 9H, OMe), 3.55 (d, <sup>3</sup>J<sub>H-H</sub> = 13.2 Hz, 1H, CH<sup>a</sup>), 2.23 (dd, <sup>2</sup>J<sub>H-H</sub> = 13.7 Hz, <sup>3</sup>J<sub>H-H</sub> = 2.5 Hz, 1H, CH<sup>d</sup>), 1.22 (dd, <sup>2</sup>J<sub>H-H</sub> = 13.7 Hz, <sup>3</sup>J<sub>H-H</sub> = 11.7 Hz, 1H, CH<sup>d'</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>12</sub>, 126 MHz),  $\delta$  = 201.4 (1C, CO), 197.0 (4C, CO), 87.7 (1C, C<sub>β</sub>), 62.1 (1C, C<sub>γ</sub>), 50.4 (3C, OMe), 19.5 (1C, C<sub>α</sub>).

### 2.3.3. $[W(CO)_5(CH_2=CH-CH_2-SiClMe_2)]$ (**1c**)

IR ( $\nu$ , cm<sup>-1</sup>): (*n*-heptane)  $\nu(C\equiv O)$  2082 (w), 1965 (s), 1951 (vs). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>, 500 MHz),  $\delta$  = 4.84 (dddd, <sup>3</sup>J<sub>H-H</sub> = 14.5, 12.0, 8.9, 3.0 Hz, 1H, CH<sup>c</sup>), 3.59 (d, <sup>3</sup>J<sub>H-H</sub> = 8.8 Hz, 1H, CH<sup>b</sup>), 3.50 (d, <sup>3</sup>J<sub>H-H</sub> = 14.5 Hz, 1H, CH<sup>a</sup>), 2.46 (dd, <sup>2</sup>J<sub>H-H</sub> = 13.3 Hz, <sup>3</sup>J<sub>H-H</sub> = 3.3 Hz, 1H, CH<sup>d</sup>), 1.37 (dd, <sup>2</sup>J<sub>H-H</sub> = 13.4 Hz, <sup>3</sup>J<sub>H-H</sub> = 11.6 Hz, 1H, CH<sup>d'</sup>), 0.477 (s, 6H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>12</sub>, 126 MHz),  $\delta$  = 200.4 (<sup>1</sup>J<sub>W-C</sub> = 153 Hz, 1C, CO), 196.7 (<sup>1</sup>J<sub>W-C</sub> = 126 Hz, 4C, CO), 85.4 (1C, C<sub>β</sub>), 61.4 (1C, C<sub>γ</sub>), 31.9 (1C, C<sub>α</sub>), 1.4 (2C, Me). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 99 MHz),  $\delta$  = 28.3.

### 2.3.4. $[W(CO)_5(CH_2=CH-CH_2-SiCl_3)]$ (**1d**)

IR ( $\nu$ , cm<sup>-1</sup>): (*n*-heptane)  $\nu(C\equiv O)$  2084 (w), 1963 (s), 1952 (vs). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>, 500 MHz),  $\delta$  = 4.56 (dddd, <sup>3</sup>J<sub>H-H</sub> = 13.9, 11.7, 8.7, 3.0 Hz, 1H, CH<sup>c</sup>), 3.62 (d, <sup>3</sup>J<sub>H-H</sub> = 8.7 Hz, 1H, CH<sup>b</sup>), 3.50 (d, <sup>3</sup>J<sub>H-H</sub> = 13.9 Hz, 1H, CH<sup>a</sup>), 2.88 (d, <sup>2</sup>J<sub>H-H</sub> = 14.3 Hz, 1H, CH<sup>d</sup>), <sup>3</sup>J<sub>H-H</sub> = 1.75 (dd, <sup>2</sup>J<sub>H-H</sub> = 12.8 Hz, <sup>3</sup>J<sub>H-H</sub> = 12.8 Hz, 1H, CH<sup>d'</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>12</sub>, 126 MHz),  $\delta$  = 196.0 (4C, CO), 74.7 (1C, C<sub>β</sub>), 61.3 (1C, C<sub>γ</sub>), 31.6 (1C, C<sub>α</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 99 MHz),  $\delta$  = -7.3.

## 2.4. Spectral data of $trans-[W(CO)_4(\eta^2\text{-allylsilane})_2]$ complexes (**2a-d**)

### 2.4.1. $trans-[W(CO)_4(CH_2=CH-CH_2-SiMe_3)_2]$ (**2a**)

IR ( $\nu$ , cm<sup>-1</sup>): (*n*-heptane)  $\nu(C\equiv O)$  1952 (vs). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>, 500 MHz),  $\delta$  = 3.36 (ddd, <sup>3</sup>J<sub>H-H</sub> = 11.9, 11.5, 9.3, 2.3 Hz, 2H, CH<sup>c</sup>), 2.58, 2.54 (dd, <sup>3</sup>J<sub>H-H</sub> = 9.0 Hz, <sup>2</sup>J<sub>H-H</sub> = 1.2 Hz, 2H, CH<sup>b</sup>), 2.24, 2.20 (d, <sup>3</sup>J<sub>H-H</sub> = 12.3 Hz, 2H, CH<sup>a</sup>), 2.07, 2.03 (dd, <sup>2</sup>J<sub>H-H</sub> = 13.9 Hz, <sup>3</sup>J<sub>H-H</sub> = 2.0 Hz, 2H, CH<sup>d</sup>), 0.83, 0.78 (dd, <sup>2</sup>J<sub>H-H</sub> = 13.5 Hz, <sup>3</sup>J<sub>H-H</sub> = 11.5 Hz, 2H, CH<sup>d'</sup>), 0.12 (s, <sup>2</sup>J<sub>Si-H</sub> = 35 Hz, 18H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>12</sub>, 126 MHz),  $\delta$  = 200.8 (<sup>1</sup>J<sub>W-C</sub> = 124 Hz, 4C, CO), 54.3, 54.1 (2C, C<sub>β</sub>), 37.2 (2C, C<sub>γ</sub>), 30.2, 29.8 (2C, C<sub>α</sub>), -1.8 (6C, Me). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 99 MHz),  $\delta$  = 0.8.

### 2.4.2. $trans-[W(CO)_4(CH_2=CH-CH_2-Si(OMe)_3)_2]$ (**2b**)

IR ( $\nu$ , cm<sup>-1</sup>): (film)  $\nu(C\equiv O)$  1942 (vs). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>, 500 MHz),  $\delta$  = 3.58 (s, 18H, OMe), 3.34 (dddd, <sup>3</sup>J<sub>H-H</sub> = 11.7, 11.1, 9.1, 2.5 Hz, 2H, CH<sup>c</sup>), 2.58, 2.54 (dd, <sup>3</sup>J<sub>H-H</sub> = 9.1 Hz, <sup>2</sup>J<sub>H-H</sub> = 1.5 Hz, 2H, CH<sup>b</sup>), 2.34, 2.29 (dd, <sup>3</sup>J<sub>H-H</sub> = 12.2 Hz, <sup>2</sup>J<sub>H-H</sub> = 1.5 Hz, 2H, CH<sup>a</sup>), 2.09, 2.04 (dd, <sup>2</sup>J<sub>H-H</sub> = 14.7 Hz, <sup>3</sup>J<sub>H-H</sub> = 2.5 Hz, 2H, CH<sup>d</sup>), 0.86, 0.83 (dd, <sup>2</sup>J<sub>H-H</sub> = 14.5 Hz, <sup>3</sup>J<sub>H-H</sub> = 11.7 Hz, 1H, CH<sup>d'</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>12</sub>, 126 MHz),  $\delta$  = 200.6 (4C, CO), 51.5, 51.4 (2C, C<sub>β</sub>), 37.7 (<sup>1</sup>J<sub>W-C</sub> = 13 Hz, 2C, C<sub>γ</sub>), 49.9 (6C, OMe), 22.5, 22.2 (2C, C<sub>α</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 99 MHz),  $\delta$  = -25.6.

### 2.4.3. $trans-[W(CO)_4(CH_2=CH-CH_2-SiClMe_2)_2]$ (**2c**)

IR ( $\nu$ , cm<sup>-1</sup>): (*n*-heptane)  $\nu(C\equiv O)$  1962 (vs). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>, 500 MHz),  $\delta$  = 3.31 (dddd, <sup>3</sup>J<sub>H-H</sub> = 14.3, 11.8, 9.3, 2.4 Hz, 2H, CH<sup>c</sup>), 2.62, 2.58 (dd, <sup>3</sup>J<sub>H-H</sub> = 9.4 Hz, <sup>2</sup>J<sub>H-H</sub> = 1.6 Hz, 2H, CH<sup>b</sup>), 2.30, 2.25 (dd, <sup>2</sup>J<sub>H-H</sub> = 14.2 Hz, <sup>3</sup>J<sub>H-H</sub> = 2.3, 2H, CH<sup>d</sup>), 2.29, 2.24 (dd, <sup>3</sup>J<sub>H-H</sub> = 11.6 Hz, <sup>2</sup>J<sub>H-H</sub> = 1.6, 2H, CH<sup>a</sup>), 1.06, 1.01 (dd, <sup>3</sup>J<sub>H-H</sub> = 14.2 Hz, 11.4 Hz, 2H, CH<sup>d'</sup>), 0.48 (s, 12H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>12</sub>, 126 MHz),  $\delta$  = 200.4 (<sup>1</sup>J<sub>W-C</sub> = 124 Hz, 4C, CO), 50.8, 50.6 (2C, C<sub>β</sub>), 37.0 (2C, C<sub>γ</sub>), 31.6 (2C, C<sub>α</sub>), 1.5 (4C, Me). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 99 MHz),  $\delta$  = 3.9.

### 2.4.4. $trans-[W(CO)_4(CH_2=CH-CH_2-SiCl_3)_2]$ (**2d**)

IR ( $\nu$ , cm<sup>-1</sup>): (*n*-heptane)  $\nu(C\equiv O)$  1972 (vs). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>, 500 MHz),  $\delta$  = 3.27 (ddd, <sup>3</sup>J<sub>H-H</sub> = 14.3, 11.6, 9.5 Hz, 1H, CH<sup>c</sup>), 2.70, 2.66 (d, <sup>3</sup>J<sub>H-H</sub> = 8.9 Hz, 2H, CH<sup>b</sup>), 2.71, 2.65 (d, <sup>3</sup>J<sub>H-H</sub> = 14.3 Hz, 2H, CH<sup>a</sup>), 2.39, 2.33 (d, <sup>3</sup>J<sub>H-H</sub> = 11.3 Hz, 2H, CH<sup>d</sup>), 1.51, 1.48 (dd, <sup>2</sup>J<sub>H-H</sub> = 11.6 Hz, <sup>3</sup>J<sub>H-H</sub> = 11.6 Hz, 2H, CH<sup>d'</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>12</sub>, 126 MHz),  $\delta$  = 198.7 (<sup>1</sup>J<sub>W-C</sub> = 123 Hz, 4C, CO), 45.7, 45.6 (2C, 0.7:1, C<sub>β</sub>), 36.6 (2C, C<sub>γ</sub>), 36.4, 36.1 (2C, 1:0.7, C<sub>α</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 99 MHz),  $\delta$  = -25.7.

## 2.5. NMR data of $[W(CO)_5(\eta^2\text{-1-propenylsilane})]$ complexes

### 2.5.1. $[W(CO)_5(E-CH_3-CH=CH-SiMe_3)]$ (**1-E-e**)

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>, 500 MHz),  $\delta$  = 4.66 (dq, <sup>3</sup>J<sub>H-H</sub> = 15.9, 5.5 Hz, 1H, C<sub>β</sub>H), 3.39 (d, <sup>3</sup>J<sub>H-H</sub> = 15.9 Hz, 1H, C<sub>α</sub>H), 2.32 (dd, <sup>3</sup>J<sub>H-H</sub> = 5.5 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.4 Hz, 3H, Me).

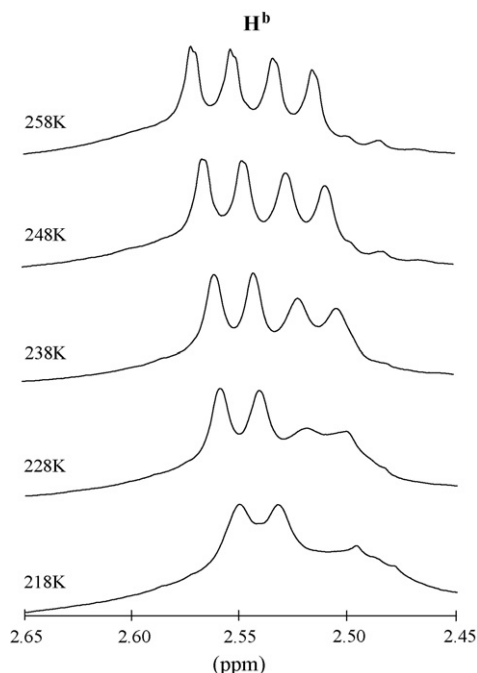
### 2.5.2. $[W(CO)_5(Z-CH_3-CH=CH-SiMe_3)]$ (**1-Z-e**)

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>12</sub>, 500 MHz),  $\delta$  = 5.20 (dq, <sup>3</sup>J<sub>H-H</sub> = 12.4, 6.2 Hz, 1H, C<sub>β</sub>H), 3.25 (d, <sup>3</sup>J<sub>H-H</sub> = 12.4 Hz, 1H, C<sub>α</sub>H), 2.19 (dd, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, 3H, Me).









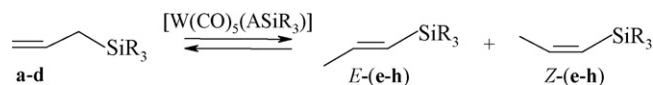
**Fig. 2.** Part of the allyl region ( $H^b$ ) of variable-temperature  $^1H$  NMR spectra (500 MHz,  $CDCl_3$ ) of  $trans-[W(CO)_4(\eta^2-CH_2=CH-CH_2-SiR_3)_2]$  (**2c**).

monoallylsilane complexes **1a–d**. In pentacarbonyl complexes, the C=C unit is *trans* to the CO ligand, which is a better  $\pi$ -acceptor than the olefin bond. The mutually *trans*-orthogonal position of the two allylsilane ligands of the tetracarbonyl complexes **2a–d** permits a stronger  $d\pi-\pi^*$  interaction between the olefin bonds and the tungsten atom. A similar conclusion can be drawn from analyses of the chemical shifts of carbonyl carbon signals observed in the NMR spectra of compounds of type **1** and **2**. The  $^{13}C$  NMR spectrum of **2a** showed one carbonyl resonance of four equatorial CO ligands at  $\delta$  200.8, which is slightly lower-field shifted compared with the signals of the four equatorial CO groups of **1a** observed at  $\delta$  197.1, but very close to that of the CO ligand *trans* to the olefin ligand ( $\delta$  200.5). The slightly greater value of the tungsten-carbon coupling constant for **1a** ( $^1J_{W-C} = 127$  Hz) than for **2a** ( $^1J_{W-C} = 124$  Hz) confirms a stronger interaction of the four equatorial CO ligands in the monoallylsilane complex **1a** compared with the bis(allylsilane) complex **2a**.

Like the coordination shifts  $\Delta\delta_H$  and  $\Delta\delta_C$ , the values of  $\Delta\delta_{Si}$  were calculated on the basis of  $^{29}Si$  chemical shifts of free and coordinated allylsilane ligands of compounds **1a–d** and **2a–d**. The coordination shifts  $\Delta\delta_{Si}$  are greater for the two mutually *trans* allylsilane ligands in the bis(allylsilane) complexes **2a–d** than in the monoallylsilane complexes **1a–d** and depend upon electronic effects of the substituents at the silicon atom. The highest value of  $\Delta\delta_{Si}$  is observed for the two mutually *trans* trichloroallylsilane ligands in complex **2d**, which is in agreement with the strongest interaction between this ligand and the tungsten atom, as is also confirmed by the  $\Delta\delta_H$  and  $\Delta\delta_C$  values.

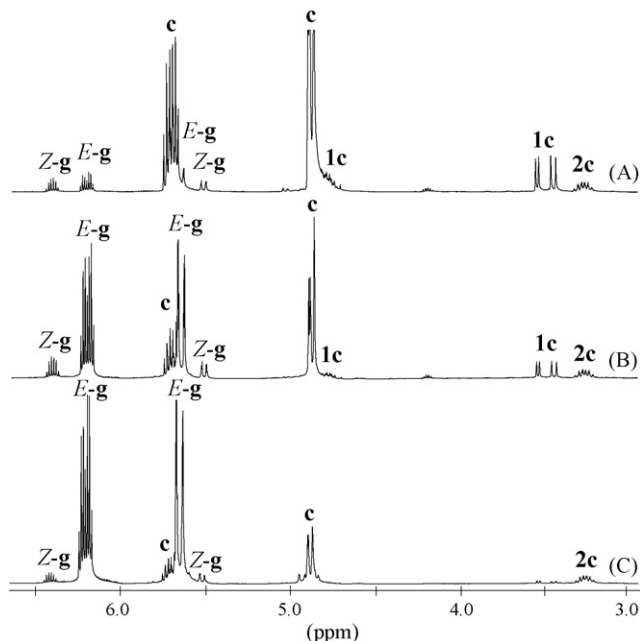
### 3.2. Double-bond migration of allylsilane

The allylsilanes **a–d** have the potential to form both *Z* and *E* isomers of 1-propenylsilanes upon double-bond migration (Scheme 2). This isomerization process has been studied previously with ruthenium-based catalysts [8,9]. In our investigation, double-bond migration was detected by  $^1H$  NMR during the photochemical reactions of all four of the allylsilanes, **a–d**, and  $W(CO)_6$ . How-

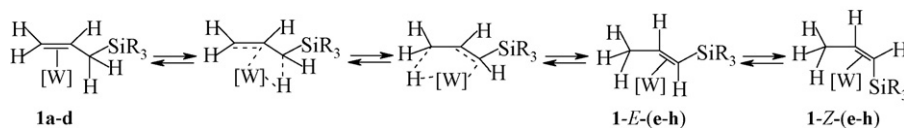


**Scheme 2.** *E* or *Z* products from double-bond migration of allylsilanes in the presence of the allylsilane complex  $[W(CO)_5(\eta^2-CH_2=CH-CH_2-SiR_3)]$ .

ever, during the photolysis of  $W(CO)_6$  and  $ASiR_3$  in cyclohexane- $d_{12}$  solution, the conversion of allylsilanes to 1-propenylsilanes was much lower than to the organometallic compounds **1** and **2**: at the average conversion in the range 15–80% the yield of isomerization was in the range 0.2–20% (Table 1). Next, it was observed by NMR that the decomposition of the pentacarbonyl complexes **1a–d** was accompanied by the appearance of 1-propenylsilanes **e–h** in the dark at room or lower temperature. At the same time the bis(allylsilane) complexes **2a–d** remained unchanged. The isomerization process was investigated further in a series of NMR-tube experiments in cyclohexane- $d_{12}$  solution, during which previously photochemically activated  $W(CO)_6$  was applied in the presence of  $ASiR_3$  (2 h photolysis at 293 K) as an initiator for isomerization followed at 323 K and monitored by  $^1H$  NMR (Fig. 3). Based on the comparison of the extent of isomerization of the allylsilanes **a–d** as a function of time at the above conditions, the rates of double-bond migration were calculated. The calculated values of the rate ( $k_{obs} = 0.019\text{--}0.092\text{ s}^{-1}$ ) change in the order:  $ASiMe_3 < ASiCl_3 < ASiClMe_2 < ASi(OMe)_3$ , which represents a balance between electronic, steric, and probably other factors, such as thermal stability of intermediate complexes (Table 1). On the basis of the latter data, double-bond migration of allylsilane can be described as a result of transformations that occur in the dark due to a previously photogenerated allylsilane–pentacarbonyl complex of type **1**. The catalytic activity of  $W(CO)_5$  species has been observed previously in many reactions of unsaturated hydrocarbons [28–32]. Thus, a plausible mechanism of double-bond migration, presented in Scheme 3, involves the  $\eta^2$ -coordination of



**Fig. 3.** The 500 MHz  $^1H$  NMR spectra of the olefin region of allylsilane **c**, 1-propenylsilane (*E-g* and *Z-g*), and the  $\eta^2$ -allylsilane complexes  $[W(CO)_5(\eta^2-ASiClMe_2)]$  (**1c**) and  $trans-[W(CO)_4(\eta^2-ASiClMe_2)_2]$  (**2c**), showing the decay of **c** and **1c** and the formation of *E-g* and *Z-g* during the reaction in the NMR tube in  $C_6D_{12}$  solution. (A) After 2 h photolysis at 293 K. (B) After 2 h reaction at 323 K. (C) After 3 weeks reaction at 293 K.



**Scheme 3.** A plausible mechanistic pathway for double-bond migration in allylsilanes catalyzed by a pentacarbonyl complex of tungsten(0) denoted by [W].

allylsilanes to the tungsten atom in the pentacarbonyl complexes **1a–d**. The loosely coordinated allylsilane in complex **1** rearranges easily in the coordination sphere of tungsten to give a new pentacarbonyl complex containing  $\eta^2$ -coordinated 1-propenylsilane. The 1,3 hydrogen shift from  $C_\alpha H_2$  to  $C_\gamma H_2$  most probably takes place due to an agostic interaction in the unit  $W \cdots H^d - C_\alpha H^d$ , although the formation of the intermediate  $W-H$  bond has never been detected in this system. However, the formation of the  $\eta^2$ -vinyl complexes **1e–h** was confirmed by  $^1H$  NMR spectroscopy. The vinyl complex **1e** was detected by  $^1H$  NMR spectroscopy due to characteristic chemical shifts, multiplicity, and coupling constants ( $^3J_{H-H}$ ) of the vinyl proton signals. Two sets of vinyl proton signals due to the  $\eta^2$ - $E$ - $CH_3-CH=CH-SiMe_3$  and  $\eta^2$ - $Z$ - $CH_3-CH=CH-SiMe_3$  ligands of the pentacarbonyl complexes **1-E-e** and **1-Z-e** were detected. Two proton resonances of equal intensity at  $\delta$  4.66 (dq,  $^3J_{H-H} = 15.9, 5.5$  Hz) and  $\delta$  3.39 (d,  $^3J_{H-H} = 15.9$  Hz) could be assigned respectively to the olefin protons of the  $C_\beta H$  and  $C_\alpha H$  units of complex **1-E-e**. Two other resonances, at  $\delta$  5.20 (dq,  $^3J_{H-H} = 12.4, 6.2$  Hz) and  $\delta$  3.25 (d,  $^3J_{H-H} = 12.4$  Hz), are assigned respectively to the olefin protons of the  $C_\beta H$  and  $C_\alpha H$  units of complex **1-Z-e**. The coordination shifts  $\Delta\delta_H$  of the vinyl proton resonance assigned to the  $SiC_\alpha H$  unit ( $\Delta\delta$  2.25 for **1-E-e** and  $\Delta\delta$  2.24 for **1-Z-e**) is much greater than  $\Delta\delta$  of the vinyl proton resonance assigned to the  $MeC_\beta H$  unit ( $\Delta\delta$  1.36 for **1-E-e** and  $\Delta\delta$  1.15 for **1-Z-e**). This indicates an asymmetric  $\eta^2$ -coordination of the vinyl unit and a higher degree of  $sp^2 \rightarrow sp^3$  rehybridization at carbon  $C_\alpha$  of the  $SiC_\alpha H$  unit than at carbon  $C_\beta$  of the  $MeC_\beta H$  unit. Comparison of the  $\Delta\delta_C$  values of the corresponding allylsilane complex **1b** ( $\Delta\delta_C = 52.5$  ( $C_\beta$ ) and 45.4 ( $C_\gamma$ )) and the vinylsilane complex **1-Z-f** ( $\Delta\delta_C$  59.9 ( $C_\beta$ ) and 59.8 ( $C_\alpha$ )) may lead to the conclusion that the degree of  $sp^2 \rightarrow sp^3$  rehybridization of the olefin carbons ( $C_\alpha$  and  $C_\beta$ ) of the  $\eta^2$ -vinylsilane ligand of complex **1-Z-f** is higher than the olefin carbons ( $C_\beta$  and  $C_\gamma$ ) of the  $\eta^2$ -allylsilane ligand of complex **1b**. This type of coordination, involving a high degree of  $sp^3$  hybridization of the olefin carbon, is responsible for  $E \rightarrow Z$  isomerization of 1-propenylsilane in the coordination sphere of tungsten, due to rotation around the  $\sigma$  ( $\eta^1$ )  $W-C$  bond [7,33]. Interestingly, a somewhat similar phenomenon, involving  $\eta^2$ -coordination of allylsilane with subsequent isomerization of the olefinic unit and coordination of  $E$ -1-propenylsilane to ruthenium atom, has been reported previously by Sabo-Etienne et al. [34]. In our experiments, the vinylsilanes released the coordination sphere of tungsten as  $E$  or  $Z$  isomers in the presence of an excess of allylsilane (Scheme 3). The  $E/Z$  stereoselectivity of the double-bond migration is a complex effect of the electronic and steric properties of substituents at the silicon atom of allylsilane as well as the thermal stability of the intermediate pentacarbonyl complexes. After 2 h photolysis at 293 K, high  $E$  selectivity was observed for reaction of  $ASiMe_3$  (only the  $E$  isomer was detected at the observed very low yield (0.2%) of isomerization),  $ASiClMe_2$  (72%), and  $ASiCl_3$  (94%), while in reaction of  $ASi(OMe)_3$  mainly the  $Z$  isomer was formed (85%). Next, after 2 h thermal reaction at 323 K,  $E$  stereoselectivity changed, and the  $E/Z$  percentage ratio reached the value of 92/8 for  $ASiMe_3$ , 94/6 for  $ASiClMe_2$ , and 91/9 for  $ASiCl_3$ . However,  $ASi(OMe)_3$  gives a much lower (60/40)  $E/Z$  percentage ratio, although the percentage of the  $E$ -isomer increased during the reaction at a higher temperature (Table 1). During the prolonged reaction in the dark at room temperature, the  $E/Z$  ratio

changed with time to give more than 90% of the  $E$  isomer in reaction of  $ASiMe_3$  (96%),  $ASiClMe_2$  (96%), and  $ASiCl_3$  (91%), while in reaction of  $ASi(OMe)_3$  the geometry of the double-bond observed by  $^1H$  NMR retains a high  $Z$  percentage (53%) even after month. It should be noted that olefin isomerization is a kinetic event, and regardless of the activity of the catalyst, an equilibrium mixture of the olefinic compounds is formed. Thermodynamic data for several  $Z \leftrightarrow E$  isomerizations illustrate the quantitatively greater stability of  $E$ -isomer of non-functionalized olefins [7,33]. However, in reaction of functionalized olefins such as allyl silyl ethers or allyltriethylamine high  $Z$  stereoselectivity was detected [15]. Thus, the formation of much more  $Z$  than  $E$ -1-propenylsilane in isomerization reaction of  $ASi(OMe)_3$  is not surprising. The driving force behind this  $Z$ -selectivity must be the greater stability of the  $Z$ -vinylsilane complex **1-Z-f** compared with the  $E$ -vinylsilane complex **1-E-f**.

In order to determine the activation energy ( $E_a$ ) of the isomerization process, the conversion of  $ASiMe_3$  was observed by  $^1H$  NMR at different temperatures (313, 323, and 333 K) (Fig. 3). The calculated  $k_{obs}$  values (0.011, 0.025 and  $0.087 s^{-1}$ ) were used to obtain the  $E_a$  value. According to these experimental results, a mechanism with a very low energy, ca. 21 kcal mol $^{-1}$ , is involved. This is in agreement with the proposed double-bond migration in the coordination sphere of the tungsten complex.

Solvent polarity seems to be crucial in the transformations of allylsilanes. When  $CDCl_3$  solution of **1c** was kept at room temperature for ca. 24 h, in addition to the mixture of  $Z$  and  $E$  isomers of 1-propenylsilanes observed by  $^1H$  NMR, another set of signals appeared and could be assigned to propene ( $\delta$  5.81, 5.01, 4.92, 1.70) [20], i.e. the product of a Si–C cleavage process. A nonpolar solvent,  $C_6D_{12}$ , slowed down and eliminated the desilylation reaction.

### 3.2.1. Effect of triethylsilane ( $Et_3SiH$ ) addition on reaction of $W(CO)_6$ with $ASiMe_3$ (**a**)

Many transition metal complexes catalyze the isomerization reaction of olefin according to a mechanism that involves the insertion of an olefin into the  $M-H$  bond to form a labile alkyl species [7,33]. In an attempt to establish whether the formation of the  $W-H$  bond and its addition-elimination to the olefin bond may take place during the isomerization of allylsilane, we decided to check the effect of  $Et_3SiH$  as the source of a hydride ligand on the isomerization reaction. For this purpose,  $W(CO)_6$ ,  $ASiMe_3$ , and  $Et_3SiH$  in cyclohexane- $d_{12}$  was periodically irradiated in the NMR tube and then analyzed by  $^1H$  NMR spectroscopy at room temperature. Photolysis of the reaction mixture led to the formation of pentacarbonyl complex **1a** as the major product (95%), while the tetracarbonyl complex **2a** was a minor product (5%). Such a high selectivity of the photochemical formation of complex **1a** has never been observed before and can be described as the effect of  $Et_3SiH$ . It is a very well documented observation that the photochemical substitution of CO in  $W(CO)_6$  by hydrosilane  $R_3SiH$  gives the unstable complex  $[W(CO)_5(\eta^2-H-SiR_3)]$  [16–19]. The very loosely  $\eta^2$ -coordinated  $H-Si$  bond of silane can be exchanged for the olefin ligand, as has recently been observed for the  $[W(CO)_5(\eta^2-H-SiHEt_2)]$  complex [35]. In this way, a larger amount of complex **1a** was obtained relative to the amount of the tetracarbonyl species **2a** compared with direct CO photosubstitution in  $W(CO)_6$  by allylsilane **a**. However, the decay of **1a** accompanied by the appearance

of trimethyl(1-propenyl)silane (**e**) made it impossible to isolate **1a** in a pure state. In this experiment, a clear transformation of complex **1a** to *E* and *Z* vinylsilane, *E-e* and *Z-e*, was observed by  $^1\text{H}$  NMR. The simultaneously detected pentacarbonyl complexes **1-E-e** and **1-Z-e** suggest that the key species (the true catalyst) in the double-bond migration investigated here is the pentacarbonyl complex. This was subsequently confirmed by an experiment in which complex **1a**, synthesized in reaction of substitution of the  $\eta^2\text{-H-SiEt}_3$  ligand with  $\eta^2\text{-ASiMe}_3$  ligand in the pentacarbonyl complex (carried out in the dark), was used as the catalyst for isomerization transforming several portions of allylsilane **a**.

It should be noted that in all photochemical reactions of  $\text{W}(\text{CO})_6$  and allylsilane carried out in the presence of  $\text{Et}_3\text{SiH}$ , the formation of the  $[\text{W}(\text{CO})_5(\eta^2\text{-H-SiEt}_3)]$  complex is manifested by a high-field signal at  $\delta -8.58$  ( $^1J_{\text{W-H}} = 35$  Hz,  $^1J_{\text{Si-H}} = 89$  Hz,  $^3J_{\text{H-H}} = 1.6$  Hz) [16,17]. Another hydride signal detected at  $\delta -5.85$  ( $^1J_{\text{W-H}} = 50$  Hz) could be assigned to a tetracarbonyl species of the type  $[\text{W}(\text{CO})_4(\eta^2\text{-H-SiEt}_3)(\eta^2\text{-ASiMe}_3)]$  formed in photochemical reaction of pentacarbonyl complexes. The intensity of the latter signal was low but remained unchanged during the isomerization reaction. Although such a complex was not fully characterized, the probability of its formation under photochemical conditions is very high. A similar complex containing  $\eta^2\text{-H-Si}$  and  $\eta^2\text{-olefin}$  bonds of coordinated hydrovinylsilane has been described before [34] and recently detected in photochemical reactions of  $\eta^4\text{-norbornadiene}$  complexes  $[\text{M}(\text{CO})_4(\eta^4\text{-nbd})]$  ( $\text{M} = \text{Mo}$  [36],  $\text{W}$  [37]) with hydrosilanes. Based on these observations it can be said that the effect of  $\text{Et}_3\text{SiH}$  has to do with the formation of the catalytically active  $[\text{W}(\text{CO})_5(\eta^2\text{-ASiR}_3)]$  complex rather than with the generation of hydride species. These results provide an additional confirmation that isomerization of allylsilane takes place in the coordination sphere of the pentacarbonyl complex, without an intermediate hydride species being generated. The  $\eta^2\text{-allylsilane}$  complexes are involved in all these transformations and are considered key intermediates in the isomerization process.

#### 4. Conclusions

The photochemical reaction of  $\text{W}(\text{CO})_6$  in *n*-heptane creates a coordinatively unsaturated  $d^6$  species which interacts with the olefin bond of the allylsilane  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{SiR}_3$  in  $\eta^2$  fashion. The initially formed thermally unstable  $\eta^2\text{-allylsilane}$  complexes  $[\text{W}(\text{CO})_5(\eta^2\text{-ASiR}_3)]$  were observed by IR and NMR spectroscopy. Thermally stable tungsten compounds formed in the above photochemical reaction were fully characterized by IR and NMR spectroscopic methods as bis(allylsilane) complexes of the type *trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-ASiR}_3)_2]$ . The thermally unstable pentacarbonyl intermediate complexes rearrange to give vinylsilane complexes of the type  $[\text{W}(\text{CO})_5(\eta^2\text{-CH}_3\text{CH}=\text{CH}-\text{SiR}_3)]$ . The reaction was found to proceed via double-bond migration in the coordination sphere of the tungsten atom. Pentacarbonyl  $\eta^2\text{-allyl}$  and  $\eta^2\text{-vinyl}$  complexes are considered key intermediates in this catalytic reaction.

Photolysis of  $\text{W}(\text{CO})_6$  and triethylsilane,  $\text{Et}_3\text{SiH}$ , in *n*-heptane and subsequent treatment of the resulting thermally unstable  $\eta^2\text{-silane}$  complex  $[\text{W}(\text{CO})_5(\eta^2\text{-CH}_3\text{CH}=\text{CH}-\text{SiR}_3)]$  with allylsilane proved useful for the formation of the  $[\text{W}(\text{CO})_5(\eta^2\text{-ASiR}_3)]$  complex. Once formed, the pentacarbonyl complex  $[\text{W}(\text{CO})_5(\eta^2\text{-ASiR}_3)]$  is capable of catalyzing the reaction in the dark and is the true catalyst for the double-bond migration investigated here.

The yield of double-bond migration and the *E/Z* stereoselectivity of isomerization highly depend on the electronic and steric properties of the substituents at the silicon atom, which influence the

thermal stability of the intermediate compounds. While in reaction of  $\text{ASi}(\text{OMe})_3$  the geometry of the double-bond of 1-propenylsilane observed by  $^1\text{H}$  NMR was high *Z*, more than 90% of the *E* isomer was detected in the equilibrium mixture of  $\text{ASiMe}_3$ ,  $\text{ASiClMe}_2$ , and  $\text{ASiCl}_3$ .

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.09.022.

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