

# Photochemical synthesis and spectroscopic characteristic of the first vinylsilane carbonyl complexes of tungsten(0)

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## Abstract

A series of new vinylsilane complexes of the type  $[\text{W}(\text{CO})_5(\eta^2\text{-H}_2\text{C}=\text{CHSiR}_3)]$  (**1a–e**) and *trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-H}_2\text{C}=\text{CHSiR}_3)_2]$  (**2a–e**) (R = Me, OMe,  $\text{OCH}_2\text{CH}_2\text{OMe}$ , and Cl) have been synthesized photochemically and characterized by IR and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy. The values of the coordination shifts of the vinylic protons and carbons,  $\Delta\delta = \delta(\text{free vinylsilane}) - \delta(\text{coordinated vinylsilane})$ , strongly suggest that trimethylvinylsilane (**a**) is coordinated more loosely to the tungsten atom in compounds of type **1** and **2** than other vinylsilanes (**b–e**). The strongest  $d\pi-\pi^*$  interaction takes place between the carbonyltungsten moiety and trichlorovinylsilane. Analysis of  $^{13}\text{C}$  NMR data of vinylsilane compounds revealed that the electron-donating methyl substituents and the electron-withdrawing chlorine substituents at the silicon atom cause opposite deviations from the ideal symmetrical  $\eta^2$ -coordination of vinylsilane to the tungsten atom. The bis(vinylsilane) complexes **2a–e** are shown to exist in several isomeric forms, whose solution dynamics were investigated by variable-temperature  $^1\text{H}$  NMR studies.

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**Keywords:** Tungsten; Silicon; Vinylsilane complexes; NMR

## 1. Introduction

Vinylsilanes are convenient reagents in the synthesis of new silicon-containing compounds due to their transformation in transition metal-catalyzed reactions such as metathesis, cross metathesis, and hydrosilylation [1]. Some fundamental steps in their rearrangements with transition metal can be nicely modeled by the use of  $\eta^2$ -vinylsilane complexes. As a consequence, the coordination chemistry of vinylsilane towards transition metals has received increasing attention. A number of vinylsilane complexes have been synthesized and characterized in recent years [2]. To date, isolable transition-

metal vinylsilane complexes have been restricted to Co, Rh, Fe, Ru, Pt, and Ni. The vinylsilane complexes of group 6 metals still remain very scarce [3].

It has long been known that photolysis of group 6 metal carbonyls  $\text{M}(\text{CO})_6$  in the presence of olefin produce  $[\text{M}(\text{CO})_{6-n}(\eta^2\text{-olefin})_n]$  ( $n = 1-3$ ) complexes [4]. We have recently reported the photochemical synthesis and characterization of several tungsten(0) carbonyl complexes that contain one or two olefin ligands [5]. These compounds were prepared by photochemical substitution of carbonyl ligands in  $\text{W}(\text{CO})_6$  by cyclic and acyclic olefins. We now report the extension of this strategy to the preparation of vinylsilane compounds of the type  $[\text{W}(\text{CO})_5(\eta^2\text{-H}_2\text{C}=\text{CHSiR}_3)]$  (**1a–e**) and *trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-H}_2\text{C}=\text{CHSiR}_3)_2]$  (**2a–e**), R = Me, OMe,  $\text{OCH}_2\text{CH}_2\text{OMe}$ , and Cl. It is very interesting to compare the effect of substituents at the silyl groups on the structure and reactivity of the  $\eta^2$ -coordinated vinyl group in compounds of tungsten(0).

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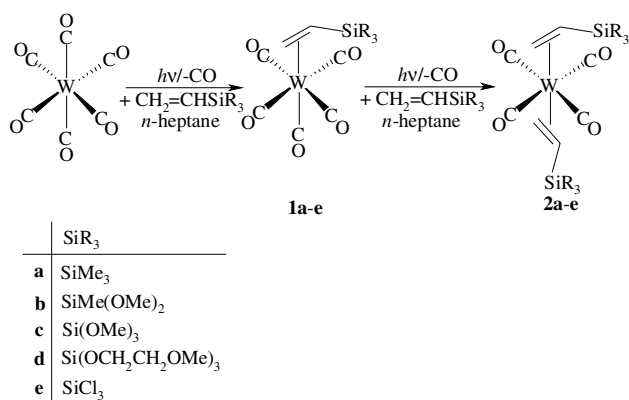
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## 2. Results and discussion

### 2.1. Synthesis of $[W(CO)_5(\eta^2-H_2C=CHSiR_3)]$ (**1a–e**) and $trans-[W(CO)_4(\eta^2-H_2C=CHSiR_3)_2]$ (**2a–e**) complexes

By a method similar to the one we described for the synthesis of  $[W(CO)_5(\eta^2\text{-olefin})]$  and  $trans-[W(CO)_4(\eta^2\text{-olefin})_2]$  complexes [5], involving the photochemical substitution of CO in  $W(CO)_6$  by olefin, we prepared the new  $\eta^2$ -vinylsilane complexes of tungsten(0) (Scheme 1). However, as some photochemical decomposition of vinylsilane compounds always occurs, only a moderate-to-low yield was obtained. The new compounds **1a–e** and **2a–e** are very easily soluble in hydrocarbon solvents but not very stable. Decomposition of the pentacarbonyl compounds (**1a–e**) occurs much faster than the tetracarbonyl ones (**2a–e**). This led to problems in obtaining pure samples suitable for elemental analysis. Characterization of compounds **1a–e** and **2b–e** by NMR spectroscopy was possible only in a mixture containing free vinylsilane and compounds **1** and **2**. Chromatography on silica resulted in substantial decomposition and hydrolysis. In one attempt, chromatographic separation yielded a small portion of **2d** for independent characterization. Pure crystals of **2a** and **2e** were obtained by slow vacuum sublimation.

In all IR spectra of the pentacarbonyl compounds **1a–e**, the CO stretching vibration pattern is almost identical with respect to frequencies as well as relative intensities and is in an agreement with a  $C_{4v}$  symmetry of the  $W(CO)_5$  moiety (Fig. 1A). As expected and in accord with a  $D_{2d}$  symmetry of  $trans$ -bis(olefin)tetracarbonyl compounds of tungsten [4,5], one strong  $\nu(CO)$  band in the region between 1953 (**2a**) and 1971  $cm^{-1}$  (**2e**) and two very weak ones in the region 2080–1990  $cm^{-1}$  were detected in the IR spectra (KBr pellets) of compounds **2a–e** (Fig. 1B). The  $W-C-O$  deformation mode was found between 600 and 560  $cm^{-1}$ . The weak bands



Scheme 1. Photochemical synthesis of vinylsilane complexes of tungsten(0).

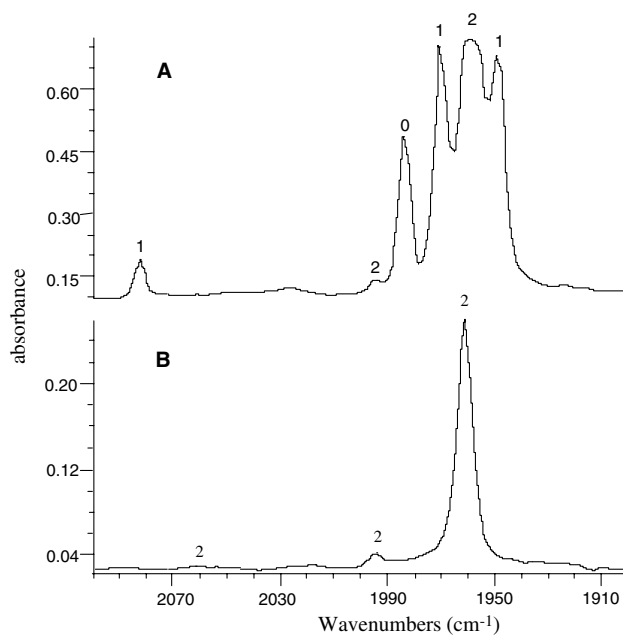


Fig. 1. (A) IR spectrum in the  $\nu(C=O)$  region obtained after 1 h irradiation of  $n$ -heptane solution of  $W(CO)_6$  in the presence of  $H_2C=CHSiMe_3$ . (B) IR spectrum in the  $\nu(C=O)$  region obtained after dissolving the pure compound **2a** in  $n$ -heptane. The bands are labeled as follows: 0,  $W(CO)_6$ ; 1,  $[W(CO)_5(\eta^2-H_2C=CHSiMe_3)]$  (**1a**); 2,  $trans-[W(CO)_4(\eta^2-H_2C=CHSiMe_3)_2]$  (**2a**).

in the region 1300–1250  $cm^{-1}$  can be assigned as the  $\nu(C=C)$  stretching vibration, whose wavenumber is about 300  $cm^{-1}$  lower than that observed for the uncoordinated vinylsilane. This suggests substantial weakening of the olefinic bond due to rehybridization towards  $sp^3$ .

### 2.2. Structure of vinylsilane complexes of tungsten(0) in solution observed by NMR studies

The  $\eta^2$ -coordination of vinylsilane in compounds of type **1** and **2** is confirmed by the observation of coordination shifts of vinyl protons and carbons signals,  $\Delta\delta = \delta(\text{free vinylsilane}) - \delta(\text{coordinated vinylsilane})$ . In the  $^1H$  NMR spectra, three vinyl hydrogens give rise to three multiplets in the region 4–3 ppm for **1a–e** and in the region 3–1.5 ppm for **2a–e**, each integrated as one proton (Fig. 2, Table 1). The multiplets are mutually coupled, which is clearly seen in the  $^1H-^1H$  COSY spectrum. Thus, for **1a** all the three vinyl protons are observed as a doublet of doublets with proton-proton coupling constants of 16.9, 11.9, and 2.7 Hz – considerably smaller than those observed for uncoordinated trimethylvinylsilane, viz. 20.3, 14.6, and 3.8 Hz, respectively. The highest coordination shift is observed for the  $H^c$  protons, that is at the methine carbon, which may indicate more rearrangement around this carbon atom ( $=CH^c$ ), involving partial rehybridization toward  $sp^3$  and an increase in shielding compared with the

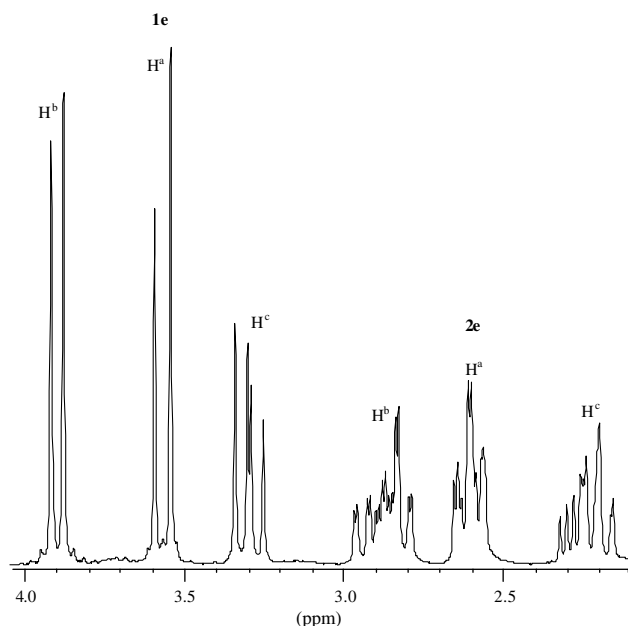


Fig. 2. The vinyl region of the  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of a freshly prepared sample containing **1e** and **2e** in the molar ratio 1.7:1. The vinyl proton signals of **1e** and **2e** are labeled as follows.

methylene carbon. For compounds **1a–e** the value of  $\Delta\delta_{\text{Hc}}$  (ppm) depends upon the substituents at the silicon atom and decreases in the order: 3.0 (Cl) > 2.8 (OMe)  $\geq$  2.8 ( $\text{OCH}_2\text{CH}_2\text{OMe}$ ) > 2.5 (Me). The coordination shift,  $\Delta\delta_{\text{C}}$  (ppm), for the methine carbon ( $=\text{CH}$ ) changes in a similar order: 74.5 (Cl) > 71.1 (OMe) > 70.1 ( $\text{OCH}_2\text{CH}_2\text{OMe}$ ) > 66.3 (Me), as for the methylene carbon ( $=\text{CH}_2$ ): 82.7 (Cl) > 72.4 (OMe) > 71.3 ( $\text{OCH}_2\text{CH}_2\text{OMe}$ ) > 63.9 (Me). The values of the coordination shifts strongly suggest that trimethylvinylsilane (**a**) is coordinated more loosely to the tungsten atom in com-

pounds of type **1** than other vinylsilanes (**b–e**). The strongest interaction occurs between the pentacarbonyl-tungsten moiety and trichlorovinylsilane in **1e**. The same conclusion can be drawn from analysis of the chemical shifts and coupling constants of carbonyl ligands in  $^{13}\text{C}$  NMR spectra of **1a–e**. The highest value of  $^1J_{\text{WC}}$  149 Hz, is observed in the  $^{13}\text{C}$  NMR spectrum of **1a** for the signal at  $\delta_{\text{C}} = 199.82$  of the CO ligand *trans* to the vinylsilane ligand, and the smallest value of  $^1J_{\text{WC}}$  141 Hz, for the signal of CO at  $\delta_{\text{C}} = 199.32$  in the spectrum of **1e**. A similar trend was observed for the signal of the mutually *trans* carbonyl ligands in the  $^{13}\text{C}$  NMR spectra of compounds **1a–e** and **2a–e** (Table 2). The four carbonyl groups of **1a** resonated at 195.24 ppm with a  $^1J_{\text{WC}}$  value of 126 Hz, while for **1e** the corresponding signal was detected at 193.33 ppm with a  $^1J_{\text{WC}}$  value of 124 Hz. The four carbonyl ligands of the bis(vinylsilane) compounds exhibited signals between ca. 198 ppm ( $^1J_{\text{WC}} = 126$  Hz) for **2a** and ca. 194 ppm ( $^1J_{\text{WC}} = 118$  Hz) for **2e**. These data clearly show the better  $\pi$ -acceptor properties of trichlorovinylsilane towards the  $d_{\pi}$  orbitals of tungsten compared with trimethylvinylsilane. Additionally, for compounds **1b–e**, the coordination shift ( $\Delta\delta_{\text{C}}$ ) for the methylene carbon ( $=\text{CH}_2$ ) is larger than for the methine carbon ( $=\text{CH}$ ), and the difference between them increases from **1b** to **1e**, reaching the value of 8.1 ppm for **1e**. However, for compound **1a** a higher value of the coordination shift is observed for the methine carbon ( $\Delta\delta_{\text{C}} = 66.3$  ppm) and a smaller value for the carbon of methylene group ( $\Delta\delta_{\text{C}} = 63.9$  ppm). These data nicely illustrate the opposite effect of the electron-donating methyl and the electron-withdrawing chlorine substituents at the silicon atom, resulting in different deviations from the ideal symmetrical  $\eta^2$ -coordination of vinylsilane (Scheme 2).

Table 1  
 $^1\text{H}$  NMR data (25 °C,  $\text{CDCl}_3$ ) for vinylsilane complexes of the *trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-H}_2\text{C}=\text{CHSiR}_3)_2]$  (**2a–e**) type<sup>A</sup>

–SiR <sub>3</sub>	$\Delta\delta$ (ppm) (multiplicity)				$J$ (Hz)			$\delta\delta$ (ppm)		
	H <sup>b</sup>	H <sup>a</sup>	H <sup>c</sup>	Other protons	$^3J_{\text{HaHc}}$	$^3J_{\text{HbHc}}$	$^2J_{\text{HaHb}}$	H <sup>b</sup>	H <sup>a</sup>	H <sup>c</sup>
–SiMe <sub>3</sub>	<u>2.83</u> (d)	<u>2.36</u> (d)	<u>1.86</u> (dd)	<u>0.16</u> (s); Me	14.3	12.6	0.8	3.1	3.3	4.3
	2.82 (d)	2.35 (d)	1.84 (dd)	0.15 (s); Me	14.3	12.6	0.8	3.1	3.3	4.3
–SiMe(OMe) <sub>2</sub>	<u>2.73</u> (d)	<u>2.42</u> (d)	<u>1.62</u> (dd)	<u>3.56</u> (s); OMe	13.8	12.4	–	3.3	3.4	4.3
	<u>2.70</u> (d)	<u>2.41</u> (d)	<u>1.58</u> (dd)	<u>0.28</u> (s); Me	13.8	12.4	–	3.4	3.5	4.4
–Si(OMe) <sub>3</sub>	<u>2.71</u> (d)	<u>2.37</u> (d)	<u>1.49</u> (dd)	<u>3.63</u> (s); OMe	13.4	13.4	–	3.4	3.6	4.3
	<u>2.67</u> (d)	<u>2.36</u> (d)	<u>1.48</u> (dd)	–	13.4	13.4	–	3.4	3.6	4.3
	<u>2.63</u> (d)	<u>2.34</u> (d)	<u>1.45</u> (dd)	–	13.4	13.4	–	3.4	3.6	4.3
–Si(OCH <sub>2</sub> CH <sub>2</sub> OMe) <sub>3</sub>	<u>2.65</u> (d)	<u>2.38</u> (d)	<u>1.51</u> (dd)	<u>3.92</u> (t), $^3J_{\text{HH}} = 5.1$ ; OCH <sub>2</sub>	14.2	13.3	–	3.4	3.6	4.4
	<u>2.61</u> (d)	<u>2.37</u> (d)	<u>1.48</u> (dd)	<u>3.45</u> (t), $^3J_{\text{HH}} = 5.1$ ; CH <sub>2</sub> O	14.2	13.3	–	3.5	3.7	4.4
	<u>2.58</u> (d)	<u>2.35</u> (d)	<u>1.45</u> (dd)	<u>3.30</u> (s); OMe	14.2	13.3	–	3.5	3.7	4.4
	<u>2.55</u> (d)	<u>2.33</u> (d)	–	–	14.2	13.3	–	3.5	3.7	–
–SiCl <sub>3</sub>	<u>2.92</u> (d)	<u>2.60</u> (d)	<u>2.28</u> (dd)	–	13.2	12.3	2.9	3.3	3.6	4.0
	<u>2.85</u> (d)	<u>2.59</u> (d)	<u>2.25</u> (dd)	–	13.2	12.3	2.9	3.4	3.7	4.0
	<u>2.83</u> (d)	<u>2.57</u> (d)	<u>2.18</u> (dd)	–	13.2	12.3	2.9	3.4	3.7	4.1
	<u>2.79</u> (d)	<u>2.56</u> (d)	<u>2.17</u> (dd)	–	13.2	12.3	2.9	3.4	3.7	4.1

<sup>A</sup> The most intense signal in the group is underlined.

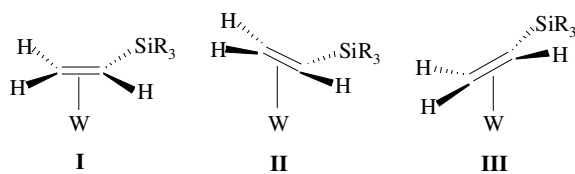
Table 2  
 $^{13}\text{C}$  NMR data (25 °C,  $\text{CDCl}_3$ ) for vinylsilane complexes of the *trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-H}_2\text{C}=\text{CHSiR}_3)_2]$  (**2a–e**) type<sup>a</sup>

-SiR <sub>3</sub>	$\Delta\delta$ (ppm) ( <i>J</i> (Hz))				$\delta\delta$ (ppm)	
	CO ( $^1J_{\text{CW}}$ )	=CH <sub>2</sub> ( $^1J_{\text{CH}}$ , $^2J_{\text{CH}}$ , $^1J_{\text{CW}}$ )	=CH ( $^1J_{\text{CH}}$ , $^2J_{\text{CH}}$ , $^1J_{\text{CW}}$ )	Other carbons	=CH <sub>2</sub>	=CH
-SiMe <sub>3</sub>	198.37 (119) <u>198.29</u> (121)	38.46 (160, 6.3, -)	36.33 (135, 3.4, -) 0.63 ( $^1J_{\text{CSi}} = 52$ Hz) Me	0.77 ( $^1J_{\text{CSi}} = 50$ Hz) Me	92.4	104.0
-SiMe(OMe) <sub>2</sub>	196.91 (119)	<u>36.65</u> (162, -, -) 35.44 (162, -, -)	29.31 (133, -, -) <u>28.97</u> (133, -, -) <u>28.78</u> (133, -, -)	50.36 ( $^1J_{\text{CH}} = 142$ Hz) OMe 0.99 ( $^1J_{\text{CH}} = 119$ Hz) Me	98.7 99.9 103.8	103.2 103.6
-Si(OMe) <sub>3</sub>	196.35 (121) <u>196.29</u> (121) 196.15 (121)	36.53 (160, 3.3, -) <u>36.40</u> (160, 3.3, -) 35.26 (160, 3.3, -) 35.10 (160, 3.3, -)	23.77 (140, 3.3, -) 23.35 (138, 3.3, -) <u>23.30</u> (140, 3.3, -) 23.04 (138, 3.3, -)	50.87 ( $^1J_{\text{CH}} = 143$ Hz) OMe	101.0 101.2 102.3 102.4	103.8 104.2 104.3 104.5
-Si(OCH <sub>2</sub> CH <sub>2</sub> OMe) <sub>3</sub>	196.21 (121) <u>196.10</u> (120) 195.89 (121)	36.34 (160, 4.4, -) <u>36.19</u> (160, 4.4, -) 35.05 (160, 4.4, -) 34.93 (160, 4.4, -)	24.12 (138, 2.2, -) <u>23.71</u> (138, 2.2, -) 23.44 (138, 2.2, -)	73.39 ( $^1J_{\text{CH}} = 140$ Hz) CH <sub>2</sub> O 61.98 ( $^1J_{\text{CH}} = 143$ Hz) OCH <sub>2</sub> 58.67 ( $^1J_{\text{CH}} = 141$ Hz) OMe 102.4	101.0 101.2 102.3	104.4 104.8 105.0
-SiCl <sub>3</sub>	194.14 (118) 194.10 (118) <u>194.01</u> (118)	35.67 (163, 3.6, 9.3) 35.17 (163, 3.6, 9.3) <u>33.73</u> (161, 3.6, 10.6)	32.75 (145, -, 14.6) 32.34 (145, -, 15.9) <u>32.32</u> (144, -, 14.6) 32.21 (145, -, 15.9)		103.6 104.1 105.5	98.4 98.8 98.8 98.9

<sup>a</sup> The most intense signal in the group is underlined.

It should be noted that the asymmetrical  $\eta^2$ -coordination of vinyl ligands was theoretically predicted more than twenty years ago and then experimentally observed for vinyl ether and vinylamine complexes [6].

The coordination shift for the H<sup>c</sup> proton observed in  $^1\text{H}$  NMR spectra of compounds **2a–e** is about one ppm higher than for compounds **1a–e** and varies little with the substituent change: 4.4 (OCH<sub>2</sub>CH<sub>2</sub>OMe) > 4.3 (OMe)  $\geq$  4.3 (Me) > 4.1 (Cl). The coordination shifts,  $\Delta\delta_{\text{C}}$ , detected for compounds of type **2** showed a similar trend to that observed for the pentacarbonyl compounds of type **1**. The largest value of  $\Delta\delta_{\text{C}}$ , 105.5, was obtained for the methylene carbon (=CH<sub>2</sub>) of trichlorovinylsilane in compound **2e**, while for compounds **2a–d** a similar value of  $\Delta\delta_{\text{C}}$  was observed for the methine carbon (=CH). The smallest  $\Delta\delta_{\text{C}}$  value of the methylene carbon (92.4 ppm) and the largest difference (11.6 ppm) between the coordination shifts for the vinyl =CH<sub>2</sub> and =CH carbons was detected for compound **2a** (Table 2). This may suggest a very asymmetrical  $\eta^2$ -coordination of trimethylvinylsilane to the tungsten atom in **2a** but with a deviation opposite to that observed for compound **2e** (Scheme 2). Tungsten satellites due to the coupling between the vinyl carbons and the  $^{183}\text{W}$  nuclei



Scheme 2. Deviations (II) and (III) from ideal symmetrical (I)  $\eta^2$ -coordination of vinylsilanes to the tungsten atom.

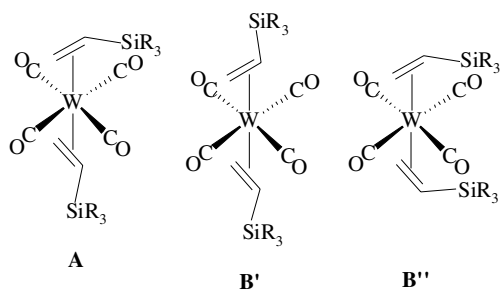
were detected only in the  $^{13}\text{C}$  NMR spectra of compounds **1e** and **2e** (Table 2). That is in agreement with the description of the W- $\eta^2$  bond as metallacyclopropane [7], with a high component of the W-C  $\sigma$ -bond, attributable to the degree of increase in hybridization of the vinyl carbon toward  $\text{sp}^3$ . The slightly larger value of  $^1J_{\text{W-CH}}$  than  $^1J_{\text{W-CH}_2}$  detected for **2e** excellently proves the claim of a higher component of the W-C  $\sigma$ -bond in the W-CH-SiCl<sub>3</sub> moiety. Although for the analogue bis(propene) compound the values of  $^1J_{\text{W-CH}}$  10.2 Hz, and  $^1J_{\text{W-CH}_2}$  12.7 Hz, lie in a similar range as for **2e** [5b], the  $^1J_{\text{W-CH}_2}$  value is slightly greater than  $^1J_{\text{W-CH}}$  indicating that the asymmetry of metallacyclopropane in bis(propene) compound is opposite to that in **2e**.

A comparison of the NMR data for the vinylsilane complexes **1a** and **2a** with those for the previously investigated propene and 1-butene analogues reveals that the  $\Delta\delta_{\text{C}}$  values for the vinylsilane carbons are more than 10 ppm larger, suggesting that the  $d\pi\text{-}\pi^*$  interaction of the tungsten atom with the trimethylvinylsilane ligand is stronger than with propene and 1-butene [5b]. While the  $\Delta\delta_{\text{C}}$  values of vinyl carbon signals observed for compound **2a** are larger than those recently obtained for Co [2a,2b], Rh [2c,2d,2e,2f], and Ni [2o] complexes with this ligand, the difference between the coordination shifts,  $\Delta\delta_{\text{C}}$ , of both vinyl carbons (=CH and =CH<sub>2</sub>) has a similar, over 10 ppm higher value for the methine carbon. This indicates a stronger  $d\pi\text{-}\pi^*$  interaction of the metal atom with the methine carbon in all these trimethylvinylsilane complexes. However, this conclusion does not agree with the observed bond lengths for the structurally characterized vinylsilane complexes [2b,2e].

M-CH bonds have been found to be longer than M-CH<sub>2</sub> ones by ca. 0.05 and 0.03 Å in [(C<sub>5</sub>Me<sub>5</sub>)Co(η<sup>2</sup>-H<sub>2</sub>C=CHSiMe<sub>3</sub>)<sub>2</sub>] [2b] and [(C<sub>5</sub>Me<sub>5</sub>)Rh(η<sup>2</sup>-H<sub>2</sub>C=CHSi(O<sup>i</sup>Pr)<sub>3</sub>)<sub>2</sub>] [2e], respectively. This can be explained by the fact that the X-ray detected bonding asymmetry results from a combination of other factors, such as the component of the M–C σ-bond, steric effects (the presence of a bulky silyl substituent), electronic configuration of the transition metal, and the geometry of the compound.

### 2.3. Dynamic NMR studies of *trans*-[W(CO)<sub>4</sub>(η<sup>2</sup>-H<sub>2</sub>C=CHSiR<sub>3</sub>)<sub>2</sub>] (**2a–e**) complexes

As was theoretically predicted a long time ago [8], for all X-ray analyzed crystals of bis(olefin)tetracarbonyl complexes of tungsten(0), a characteristic *trans*-orthogonal orientation of the two olefin bonds, eclipsed to the respective OC–W–CO axes of the square-planar W(CO)<sub>4</sub> moiety, was observed [4b,4i,4j,5c]. However, in solution, due to possible rotation of the olefin ligands around the W-(η<sup>2</sup>-olefin) bond, such compounds show dynamic behavior, and their NMR spectra are temperature dependent [4b,5a,5b,5c,5d]. Bis(vinylsilane) complexes, like other *trans*-bis(monosubstituted olefin) complexes, can exist in two isomeric forms, **A** and **B**, whose presence results from different orientations of the vinyl group in one molecule of vinylsilane with respect to the other molecule of vinylsilane and the carbonyl ligands (Scheme 3). Isomers **A** and **B** cannot be interconverted by internal rotation about the metal-olefin bond, while **B'** and **B''** are two rotamers of isomer **B**, which interconvert rapidly on the NMR timescale. In isomer **A**, the two H<sup>b</sup> protons are nonequivalent, consequently **A** exists as two enantiomers, which are interconvertible by the rotation of 180°. These isomers give virtually identical IR spectra but are clearly distinguishable by <sup>1</sup>H and <sup>13</sup>C NMR spectra. In the <sup>1</sup>H NMR spectrum of the trimethylsilane complex **2a**, two sets of vinyl proton signals for isomers **A** and **B** are observed at room temperature (Fig. 3). By integration of vinyl resonances it was possible to estimate the molar ratio of isomers **A**



Scheme 3. Different orientations of vinylsilane ligands in molecules of *trans*-bis(vinylsilane)tetracarbonyl complexes of tungsten.

and **B** at about 1:0.8. These two isomers of complex **2a** are detected by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy due to two very narrow resonances of carbonyl ligands (δ = 198.37 and 198.29) and two methyl carbon signals at δ = 0.77 and 0.63 at room temperature. The <sup>1</sup>H NMR spectrum of compound **2a** at –60 °C showed four very well resolved doublets (<sup>3</sup>J<sub>H<sup>b</sup>H<sup>c</sup></sub> = 12.6 Hz) of almost equal intensity due to H<sup>b</sup> protons of rigid isomers (Fig. 3). Other proton signals are not so well resolved.

The variable-temperature <sup>1</sup>H NMR spectra of **2a** in toluene-*d*<sub>8</sub> solution evidenced its dynamic properties too. The signal of the H<sup>b</sup> proton appears as one doublet at 2.68 ppm with a <sup>3</sup>J<sub>H<sup>b</sup>H<sup>c</sup></sub> of 12.6 Hz at 25 °C. Upon warming the toluene-*d*<sub>8</sub> solution of **2a** in the NMR probe to +50 °C, the H<sup>b</sup> signal becomes sharper, and two doublets can be detected at 2.70 and 2.69 ppm in a ratio of 1:0.8, due to isomers **A** and **B**. A further temperature increase leads to the sharpening of the signal, and <sup>2</sup>J<sub>H<sup>a</sup>H<sup>b</sup></sub> of 0.9 Hz can be observed in the signals of the H<sup>a</sup> and H<sup>b</sup> protons. Upon lowering the temperature to –80 °C, broadening and then decoalescence, and sharpening of the vinyl proton signals can be seen. The well resolved signals of the H<sup>b</sup> proton at 2.69, 2.64, 2.60, 2.59 ppm (doublets with <sup>3</sup>J<sub>H<sup>b</sup>H<sup>c</sup></sub> of 12.6 Hz) in an approximate ratio 0.5:1:0.5:0.8 can be detected.

However, the NMR spectra of the other vinylsilane complexes **2b–e**, are more complicated. Both <sup>1</sup>H and <sup>13</sup>C NMR spectra showed the presence of four signals of the CH<sup>b</sup> group in an approximate ratio of 1:0.8:0.5:0.5 at room temperature (Tables 1 and 2). All these spectra change significantly upon lowering the temperature, indicating that the complexes are dynamic, but four signals due to the CH<sup>b</sup> group are observed at –60 °C by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. When comparing the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of compound **2d** at 25 and –40 °C, one can see a very small difference between the chemical shifts and intensities of four =CH<sub>2</sub> and four =CH carbon signals. The latter signals are only better resolved at –60 °C.

It is very difficult to explain what is the origin of such dynamic behavior and what kinds of rotamers are rigid at –60 °C. The expected ratio of two enantiomers **A** and the two rotamers, **B'** and **B''**, should be 1:1:1:1. Another type of dynamic process, such as rotation of the silyl group about the C–Si single bond adjacent to the C=C bond, may lead to a different orientation (eclipsed or staggered) of the silyl group in relation to the C=C bond (Scheme 4) [9]. It is very likely that the hindered rotation of the silyl group in compounds **2b–e** makes it possible to observe eclipsed (*e*) and staggered (*s*) rotamers of both isomers **A** and **B** of these compounds.

While the precise temperature of coalescence (*T*<sub>c</sub>) cannot be calculated from those spectra, it is clear that *trans*-bis(vinylsilane) complexes are very flexible in solution.

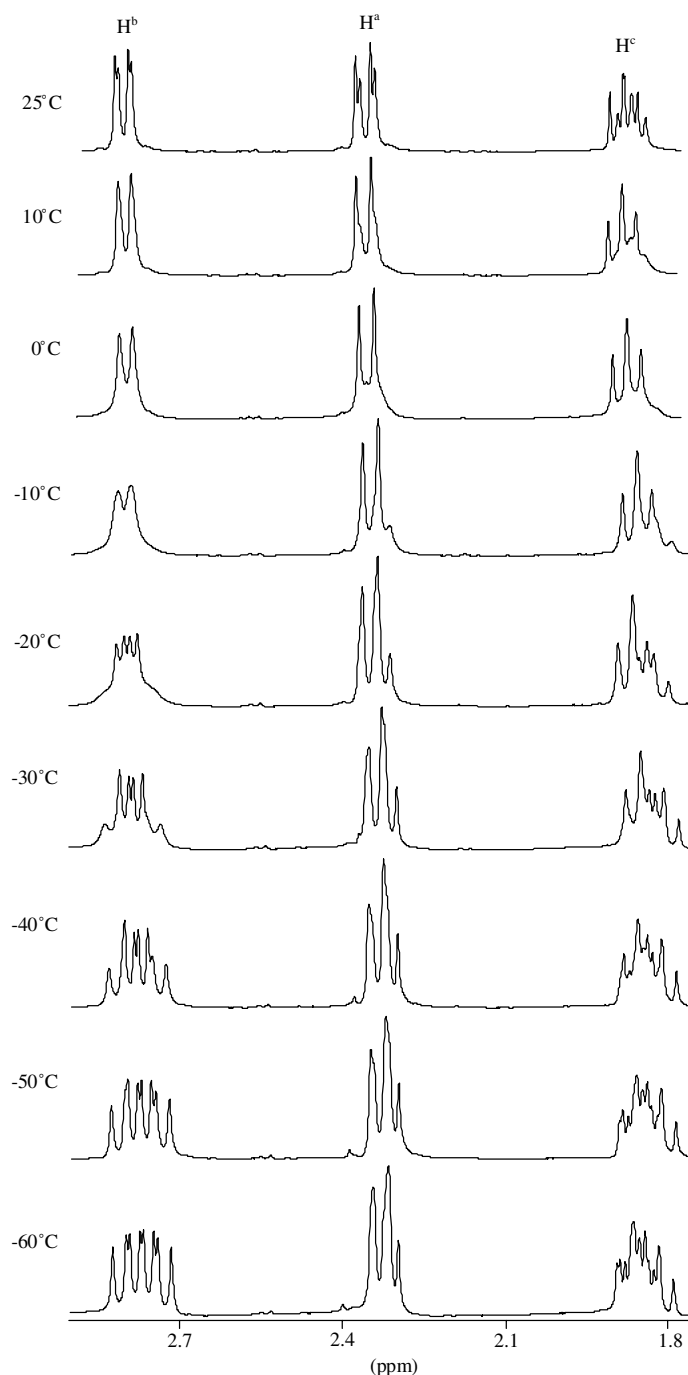
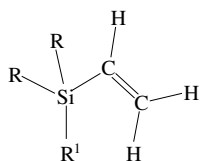


Fig. 3. The vinyl region of variable-temperature  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ ) of  $\text{trans-}[\text{W}(\text{CO})_4(\eta^2\text{-H}_2\text{C}=\text{CHSiMe}_3)_2]$  (**2a**).

#### 2.4. Trends in the $^{29}\text{Si}$ NMR of vinylsilane complexes

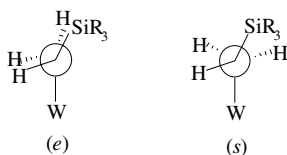
The coordination shift,  $\Delta\delta_{\text{Si}}$  (ppm), of silicon resonance in the  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of vinylsilane complexes of type **1** and **2** vary over a 50 ppm range (Table 3), but several trends are apparent. First of all, the value of  $\Delta\delta_{\text{Si}}$  (ppm) depends on the substituents at the silicon atom. If there are strongly electron-donating groups

such as a methyl group at the silicon atom,  $\eta^2$ -coordination to the tungsten atom leads to a shift of silicon resonance towards lower field ( $\Delta\delta_{\text{Si}} = -10.7$  for **1a** and  $-13.2$  ppm for **2a**). The  $\eta^2$ -coordination of trichlorovinylsilane to the tungsten atom, as in **1e** and **2e**, has the opposite effect on the chemical shift of the silicon resonance, which shifts considerably upfield compared with free vinylsilane ( $\Delta\delta_{\text{Si}} = 18.8$  for **1e** and  $40.8$  ppm for **2e**).



(e) torsion angle  $\tau$  (C=C-Si-R<sup>1</sup>) = ca. 0°

(s) torsion angle  $\tau$  (C=C-Si-R<sup>1</sup>) = ca. 180°



Scheme 4. The eclipsed (e) and staggered (s) conformers of vinylsilane.

## 2.5. Conclusions

A major problem in elucidating the exact mechanism of a catalytic reaction is to characterize the structure and reactivity of thermally unstable intermediates formed along the reaction coordinates. Photolysis of organometallic compounds is one of the best tools for preparing thermally unstable intermediates. The results described here clearly show that a photochemical substitution of CO by vinylsilane in W(CO)<sub>6</sub> can be used in the synthesis of thermally unstable vinylsilane carbonyl complexes of tungsten(0).

The bis(vinylsilane) complexes **2a–e** are very flexible in solution and their dynamic behavior was followed by <sup>1</sup>H NMR spectroscopy.

The NMR studies of vinylsilane complexes in solution revealed a significant asymmetry in η<sup>2</sup>-coordination of vinylsilane. Investigation of the effect of this asymmetry on the reactivity of vinylsilane is in progress.

## 3. Experimental

### 3.1. General information

The synthesis and manipulation of all chemicals were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents and liquid reagents were pre-dried with CaH<sub>2</sub> and vacuum transferred into small storage flasks prior to use. Trimethylvinylsilane (**a**) (Aldrich), dimethoxymethylvinylsilane (**b**) (ABCR), trimethoxyvinylsilane (**c**) (Aldrich), tris(2-methoxyethoxy)vinylsilane (**d**) (Fluka), and trichlorovinylsilane (**e**) (ABCR) were used as supplied. IR spectra were measured with a Nicolet-400 FT-IR instrument. <sup>1</sup>H, <sup>29</sup>Si{<sup>1</sup>H}, <sup>13</sup>C NMR (proton coupled and decoupled), <sup>13</sup>C DEPT, and two-dimensional <sup>1</sup>H–<sup>1</sup>H COSY and <sup>1</sup>H–<sup>13</sup>C HMQC NMR spectra were recorded with a Bruker AMX 300 or 500 MHz instrument. All chemical shifts are referenced to residual solvent protons for <sup>1</sup>H NMR (δ 7.24 CDCl<sub>3</sub>; 7.20 benzene-*d*<sub>6</sub> 2.10 toluene-*d*<sub>8</sub>) and to the chemical shift of the solvent for <sup>13</sup>C NMR (δ 128.00 benzene-*d*<sub>6</sub> 77.00 CDCl<sub>3</sub>; 20.4 toluene-*d*<sub>8</sub>). The photolysis source was an HBO 200W high-pressure Hg lamp.

### 3.2. Photochemical synthesis of vinylsilane complexes of tungsten

Photochemical reaction involving W(CO)<sub>6</sub> and vinylsilane, carried out in alkane solution at room temperature, was monitored by IR spectroscopy. In a typical experiment, a solution of W(CO)<sub>6</sub> (0.1 g, 0.28 mmol) and vinylsilane (ca. 0.2–0.4 g, 1.4 mmol) in freshly distilled *n*-heptane (30 cm<sup>3</sup>) was irradiated through quartz at room temperature. During the irradiation, the color of the reaction mixture changed from yellow to dark brown. After different times of

Table 3  
<sup>29</sup>Si{<sup>1</sup>H} NMR data (25 °C, CDCl<sub>3</sub>) for vinylsilanes and their complexes of tungsten(0)

No.	Compound	δ (ppm)	Δδ (ppm) <sup>a</sup>
<b>a</b>	H <sub>2</sub> C=CHSiMe <sub>3</sub>	−6.91	
<b>b</b>	H <sub>2</sub> C=CHSiMe(OMe) <sub>2</sub>	−14.83	
<b>c</b>	H <sub>2</sub> C=CHSi(OMe) <sub>3</sub>	−55.19	
<b>d</b>	H <sub>2</sub> C=CHSi(OCH <sub>2</sub> CH <sub>2</sub> OMe) <sub>3</sub>	−60.75	
<b>e</b>	H <sub>2</sub> C=CHSiCl <sub>3</sub>	−3.16	
<b>1a</b>	[W(CO) <sub>5</sub> (η <sup>2</sup> -H <sub>2</sub> C=CHSiMe <sub>3</sub> )]	3.75	−10.66
<b>1e</b>	[W(CO) <sub>5</sub> (η <sup>2</sup> -H <sub>2</sub> C=CHSiCl <sub>3</sub> )]	−21.99	+18.83
<b>2a</b>	<i>trans</i> -[W(CO) <sub>4</sub> (η <sup>2</sup> -H <sub>2</sub> C=CHSiMe <sub>3</sub> ) <sub>2</sub> ]	6.29	−13.20
		6.42	−13.33
<b>2b</b>	<i>trans</i> -[W(CO) <sub>4</sub> (η <sup>2</sup> -H <sub>2</sub> C=CHSiMe(OMe) <sub>2</sub> ) <sub>2</sub> ]	−21.93	+7.10
<b>2c</b>	<i>trans</i> -[W(CO) <sub>4</sub> (η <sup>2</sup> -H <sub>2</sub> C=CHSi(OMe) <sub>3</sub> ) <sub>2</sub> ]	−47.45	−7.74
		−47.67	−7.52
<b>2d</b>	<i>trans</i> -[W(CO) <sub>4</sub> (η <sup>2</sup> -H <sub>2</sub> C=CHSi(OCH <sub>2</sub> CH <sub>2</sub> OMe) <sub>3</sub> ) <sub>2</sub> ]	−53.38	−7.37
		−53.20	−7.55
<b>2e</b>	<i>trans</i> -[W(CO) <sub>4</sub> (η <sup>2</sup> -H <sub>2</sub> C=CHSiCl <sub>3</sub> ) <sub>2</sub> ]	−43.98	+40.82

<sup>a</sup> Δδ = δ (free vinylsilane) − δ (η<sup>2</sup>-coordinated vinylsilane).

photolysis (1–3 h) the solvent was removed under vacuum at room temperature, the residual solid dissolved in  $\text{CDCl}_3$  or toluene- $d_8$  ( $0.7 \text{ cm}^3$ ), and the resulting solution transferred to the NMR tube. The solution analyzed immediately by  $^1\text{H}$  NMR showed the presence of vinylsilane pentacarbonyl (**1a–e**) and tetracarbonyl compounds (**2a–e**) whose molar ratio depended on the time of photolysis. In reaction of  $\text{W}(\text{CO})_6$  with trichlorovinylsilane, after 2 h of photolysis, the molar ratio of compounds **1e** and **2e** detected by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  solution was 1.7:1. However, **1e** undergoes decomposition, and after 13 h in the same NMR tube, the molar ratio of compounds **1e** and **2e** was 1.1:1. Separation of **1** and **2** was possible by slow fractional sublimation in vacuum in the temperature range from 20 to 60 °C.

### 3.2.1. $[\text{W}(\text{CO})_5(\eta^2\text{-H}_2\text{C}=\text{CHSiMe}_3)]$ (**1a**)

IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ; *n*-heptane): 2083 (w), 1971 (vs), 1950 (vs).  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 500 MHz, 25 °C): 4.14 (dd,  $^3J_{\text{HbHc}} = 11.9 \text{ Hz}$ ,  $^2J_{\text{HaHb}} = 2.7 \text{ Hz}$ ;  $1\text{H}^{\text{b}}$ ), 3.69 (dd,  $^3J_{\text{HaHc}} = 16.9 \text{ Hz}$ ,  $^2J_{\text{HaHb}} = 2.7 \text{ Hz}$ ;  $1\text{H}^{\text{a}}$ ), 3.60 (dd,  $^3J_{\text{HaHc}} = 16.9 \text{ Hz}$ ,  $^3J_{\text{HbHc}} = 11.9 \text{ Hz}$ ;  $1\text{H}^{\text{c}}$ ), 0.19 (s, 9H; Me).  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 125 MHz, 25 °C): 199.82 (1 CO,  $^1J_{\text{WC}} = 149 \text{ Hz}$ ), 195.24 (4 CO,  $^1J_{\text{WC}} = 126 \text{ Hz}$ ), 73.96 (d,  $^1J_{\text{CH}} = 143 \text{ Hz}$ , 1CH), 66.94 (t,  $^1J_{\text{CH}} = 162 \text{ Hz}$ ,  $^2J_{\text{CH}} = 6.9 \text{ Hz}$ , 1CH<sub>2</sub>), 1.02 (q,  $^1J_{\text{CH}} = 118 \text{ Hz}$ , 3C; Me).  $^{29}\text{Si}^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 99.36 MHz, 25 °C): 3.75.

### 3.2.2. $[\text{W}(\text{CO})_5(\eta^2\text{-H}_2\text{C}=\text{CHSiMe}(\text{OMe})_2)]$ (**1b**)

IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ; *n*-heptane): 2085 (w), 1956 (vs,br).  $^1\text{H}$  NMR ( $\delta$  7.24  $\text{CDCl}_3$ , 500 MHz, 25 °C): 4.04 (dd,  $^3J_{\text{HbHc}} = 12.2 \text{ Hz}$ ,  $^2J_{\text{HaHb}} = 2.5 \text{ Hz}$ ;  $1\text{H}^{\text{b}}$ ), 3.70 (dd,  $^3J_{\text{HaHc}} = 16.7 \text{ Hz}$ ,  $^2J_{\text{HaHb}} = 2.5 \text{ Hz}$ ;  $1\text{H}^{\text{a}}$ ), 3.52 (s, 6H; OMe), 3.13 (dd,  $^3J_{\text{HaHc}} = 16.7 \text{ Hz}$ ,  $^3J_{\text{HbHc}} = 12.2 \text{ Hz}$ ;  $1\text{H}^{\text{c}}$ ), 0.33 (s, 3H; Me).  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 125 MHz, 25 °C): 200.45 (1 CO,  $^1J_{\text{WC}} = 148 \text{ Hz}$ ), 194.78 (4 CO,  $^1J_{\text{WC}} = 125 \text{ Hz}$ ), 65.12 (td,  $^1J_{\text{CH}} = 161 \text{ Hz}$ ,  $^2J_{\text{CH}} = 4.4 \text{ Hz}$ , 1CH<sub>2</sub>), 62.88 (dt,  $^1J_{\text{CH}} = 139 \text{ Hz}$ ,  $^2J_{\text{CH}} = 4.4 \text{ Hz}$ , 1CH), 51.60 (q,  $^1J_{\text{CH}} = 143 \text{ Hz}$ , 2C; OMe), 0.99 (q,  $^1J_{\text{CH}} = 119 \text{ Hz}$ , 1C; Me).

### 3.2.3. $[\text{W}(\text{CO})_5(\eta^2\text{-H}_2\text{C}=\text{CHSi}(\text{OMe})_3)]$ (**1c**)

IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ; *n*-heptane): 2087 (w), 1959 (vs).  $^1\text{H}$  NMR ( $\delta$  7.24  $\text{CDCl}_3$ , 500 MHz, 25 °C): 3.98 (dd,  $^3J_{\text{HbHc}} = 12.2 \text{ Hz}$ ,  $^2J_{\text{HaHb}} = 2.4$ ;  $1\text{H}^{\text{b}}$ ), 3.65 (dd,  $^3J_{\text{HaHc}} = 15.8 \text{ Hz}$ ,  $^2J_{\text{HaHb}} = 2.4$ ;  $1\text{H}^{\text{a}}$ ), 3.59 (s, 9H; OMe), 2.95 (dd, 2H,  $^3J_{\text{HaHc}} = 15.8 \text{ Hz}$ ,  $^3J_{\text{HbHc}} = 12.2 \text{ Hz}$ ;  $1\text{H}^{\text{c}}$ ).  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 125 MHz, 25 °C): 200.73 (1 CO,  $^1J_{\text{WC}} = 147 \text{ Hz}$ ), 194.52 (4 CO,  $^1J_{\text{WC}} = 124 \text{ Hz}$ ), 65.16 (td,  $^1J_{\text{CH}} = 163 \text{ Hz}$ ,  $^2J_{\text{CH}} = 4.1 \text{ Hz}$ ; 1CH<sub>2</sub>), 56.46 (dt,  $^1J_{\text{CH}} = 141 \text{ Hz}$ ,  $^2J_{\text{CH}} = 4.3 \text{ Hz}$ ; 1CH), 50.76 (q,  $^1J_{\text{CH}} = 143 \text{ Hz}$ , 3C; OMe).  $^{29}\text{Si}^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 99.36 MHz, 25 °C): –55.19.

### 3.2.4. $[\text{W}(\text{CO})_5(\eta^2\text{-H}_2\text{C}=\text{CHSi}(\text{OCH}_2\text{CH}_2\text{OMe})_3)]$ (**1d**)

IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ; *n*-heptane): 2085 (w), 1957 (vs,br).  $^1\text{H}$  NMR ( $\delta$  7.24  $\text{CDCl}_3$ , 500 MHz, 25 °C): 3.95 (dd,  $^3J_{\text{HbHc}} = 12.4 \text{ Hz}$ ,  $^2J_{\text{HaHb}} = 2.3$ ;  $1\text{H}^{\text{b}}$ ), 3.84 (t,  $^3J_{\text{HH}} = 5.1$ , 6H; OCH<sub>2</sub>), 3.73 (dd,  $^3J_{\text{HaHc}} = 16.7 \text{ Hz}$ ,  $^2J_{\text{HaHb}} = 2.3$ ;  $1\text{H}^{\text{a}}$ ), 3.42 (t,  $^3J_{\text{HH}} = 5.1$ , 6H; CH<sub>2</sub>O), 3.28 (s, 9H; OMe), 3.03 (dd,  $^3J_{\text{HaHc}} = 16.7 \text{ Hz}$ ,  $^3J_{\text{HbHc}} = 12.4 \text{ Hz}$ ;  $1\text{H}^{\text{c}}$ ).  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 125 MHz, 25 °C): 200.66 (1 CO,  $^1J_{\text{WC}} = 148 \text{ Hz}$ ), 194.55 (4 CO,  $^1J_{\text{WC}} = 125 \text{ Hz}$ ), 73.12 (tt,  $^1J_{\text{CH}} = 139 \text{ Hz}$ ,  $^2J_{\text{CH}} = 2.2 \text{ Hz}$ , 3C; CH<sub>2</sub>O), 66.03 (td,  $^1J_{\text{CH}} = 163 \text{ Hz}$ ,  $^2J_{\text{CH}} = 4.3 \text{ Hz}$ ; 1CH<sub>2</sub>), 61.88 (t,  $^1J_{\text{CH}} = 143 \text{ Hz}$ , 3C; OCH<sub>2</sub>), 58.39 (d,  $^1J_{\text{CH}} = 142 \text{ Hz}$ ,  $^2J_{\text{CH}} = 4.3 \text{ Hz}$ ; 1CH), 58.30 (q,  $^1J_{\text{CH}} = 141 \text{ Hz}$ , 3C; OMe).  $^{29}\text{Si}^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 99.36 MHz, 25 °C): –60.75.

### 3.2.5. $[\text{W}(\text{CO})_5(\eta^2\text{-H}_2\text{C}=\text{CHSiCl}_3)]$ (**1e**)

IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ; *n*-heptane): 2093 (w), 1967 (vs).  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 300 MHz, 25 °C): 3.87 (d,  $^3J_{\text{HbHc}} = 11.6 \text{ Hz}$ ;  $1\text{H}^{\text{b}}$ ), 3.54 (d,  $^3J_{\text{HaHc}} = 14.9 \text{ Hz}$ ;  $1\text{H}^{\text{a}}$ ), 3.27 (dd,  $^3J_{\text{HaHc}} = 14.9 \text{ Hz}$ ,  $^3J_{\text{HbHc}} = 11.6 \text{ Hz}$ ;  $1\text{H}^{\text{c}}$ ).  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 75 MHz, 25 °C): 199.32 (1 CO,  $^1J_{\text{WC}} = 141 \text{ Hz}$ ), 193.33 (4 CO,  $^1J_{\text{WC}} = 124 \text{ Hz}$ ), 56.57 (td,  $^1J_{\text{CH}} = 160 \text{ Hz}$ ,  $^2J_{\text{CH}} = 2.7 \text{ Hz}$ ,  $^1J_{\text{CW}} = 7.3 \text{ Hz}$ , 1CH<sub>2</sub>), 54.51 (dt,  $^1J_{\text{CH}} = 149 \text{ Hz}$ ,  $^2J_{\text{CH}} = 2.7 \text{ Hz}$ ,  $^1J_{\text{CW}} = 11.9 \text{ Hz}$ ,  $^1J_{\text{CSi}} = 113 \text{ Hz}$ ; 1CH).  $^{29}\text{Si}^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 99.36 MHz, 25 °C): 21.99.

### 3.2.6. *Trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-H}_2\text{C}=\text{CHSiMe}_3)_2]$ (**2a**)

IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ; *n*-heptane): 2062 (vww), 2018 (vww), 1995 (w), 1962 (vs). IR ( $\text{cm}^{-1}$ ; KBr): 2959 (w,br), 2063 (vww), 2018 (vww), 1992 (m), 1953 (vs), 1261 (w), 1252 (w), 1187 (vw), 1099 (vw,br), 1042 (vw,br), 840 (m), 803 (vw), 751 (vww), 683 (vww), 669 (vw), 585 (w), 561 (w), 472 (vw), 457 (vw), 420 (w).  $^1\text{H}$  NMR ( $\delta$ , toluene- $d_8$  500 MHz, 80 °C): 2.72, 2.71 (dd,  $^3J_{\text{HbHc}} = 12.6 \text{ Hz}$ ,  $^2J_{\text{HaHb}} = 0.9 \text{ Hz}$ ;  $1\text{H}^{\text{b}}$ ), 2.28, 2.27 (dd,  $^3J_{\text{HaHc}} = 14.6 \text{ Hz}$ ,  $^2J_{\text{HaHb}} = 0.9 \text{ Hz}$ ;  $1\text{H}^{\text{a}}$ ), 1.80, 1.79 (dd,  $^3J_{\text{HaHc}} = 14.6 \text{ Hz}$ ,  $^3J_{\text{HbHc}} = 12.6 \text{ Hz}$ ;  $1\text{H}^{\text{c}}$ ), 0.18 (s, 9H,  $^2J_{\text{SiH}} = 6.3 \text{ Hz}$ ; Me).

### 3.2.7. *Trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-H}_2\text{C}=\text{CHSiMe}(\text{OMe})_2)_2]$ (**2b**)

IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ; *n*-heptane): 1972 (vs).

### 3.2.8. *Trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-H}_2\text{C}=\text{CHSi}(\text{OMe})_3)_2]$ (**2c**)

IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ; *n*-heptane): 1976 (vs). IR ( $\text{cm}^{-1}$ ; KBr): 2946 (w), 2884(w), 2076 (vww), 2013 (w), 1965 (vs), 1303 (vw), 1263 (vw), 1189 (vw), 1093 (m,br), 967 (vww), 808 (w), 772 (w), 579 (w), 562 (w), 422 (vw).  $^1\text{H}$  NMR ( $\delta$ , benzene- $d_6$  300 MHz, 25 °C): 3.53 (s, 9H; OCH<sub>3</sub>), 2.63 (d,  $^3J_{\text{HbHc}} = 12.7 \text{ Hz}$ ;  $1\text{H}^{\text{b}}$ ), 2.52, 2.48, 2.45 (d,  $^3J_{\text{HaHc}} = 14.1 \text{ Hz}$ ;  $1\text{H}^{\text{a}}$ ), 1.56, 1.57, 1.47, (dd,  $^3J_{\text{HaHc}} = 14.1 \text{ Hz}$ ,  $^3J_{\text{HbHc}} = 12.7 \text{ Hz}$ ;  $1\text{H}^{\text{c}}$ ).  $^{13}\text{C}^1\text{H}$



NMR ( $\delta$ , benzene- $d_6$  75 MHz, 25 °C): 197.02, 196.90, 196.71 (4 CO,  $^1J_{WC} = 119$  Hz), 50.56 (3C; OMe), 37.12, 36.97, 35.81 (1C; CH<sub>2</sub>), 24.60, 24.21, 24.14, 23.87 (1C; CH).

### 3.2.9. *Trans*-[W(CO)<sub>4</sub>( $\eta^2$ -H<sub>2</sub>C=CHSi(OCH<sub>2</sub>CH<sub>2</sub>O-Me)<sub>3</sub>)<sub>2</sub>] (**2d**)

IR ( $\nu_{CO}$ , cm<sup>-1</sup>; *n*-heptane): 2047 (v<sub>w</sub>), 2015 (v<sub>w</sub>), 1972 (vs). IR (cm<sup>-1</sup>; KBr): 2930 (w), 2886 (w), 2075 (v<sub>w</sub>), 2013 (w), 1967 (vs) 1919 (w), 1298 (vw), 1262 (vw), 1201 (w), 1143 (m), 1103 (s), 1028 (w), 969 (w), 844 (w), 802 (w), 767 (vw), 580 (w), 561 (w), 472 (vw), 458 (v<sub>w</sub>), 443 (v<sub>w</sub>), 419 (w). <sup>1</sup>H NMR ( $\delta$ , toluene- $d_8$  300 MHz, 25 °C): 4.03 (t,  $^3J_{HH} = 5.1$ , 6H; OCH<sub>2</sub>), 3.41 (t,  $^3J_{HH} = 5.1$ , 6H; CH<sub>2</sub>O), 3.20 (s, 9H; OMe), 2.68 (d,  $^3J_{HbHc} = 12.6$  Hz; 1H<sup>b</sup>), 2.62, 2.56 (d,  $^3J_{HaHc} = 13.9$  Hz; 1H<sup>a</sup>), 1.74, 1.70, 1.69, 1.68 (dd,  $^3J_{HaHc} = 13.5$  Hz,  $^3J_{HbHc} = 12.6$  Hz; 1H<sup>c</sup>). <sup>13</sup>C<sup>1</sup>H NMR ( $\delta$ , toluene- $d_8$  75 MHz, 25 °C): 197.42, 197.25, 197.02 (4 CO,  $^1J_{WC} = 119$  Hz), 73.85, 3C; CH<sub>2</sub>O), 62.70 (3C; OCH<sub>2</sub>), 58.47 (3C; OMe), 37.37, 37.28, 36.06 (1C; CH<sub>2</sub>), 25.56, 25.23, 25.13, 24.89 (1C; CH).

### 3.2.10. *Trans*-[W(CO)<sub>4</sub>( $\eta^2$ -H<sub>2</sub>C=CHSiCl<sub>3</sub>)<sub>2</sub>] (**2e**)

IR ( $\nu_{CO}$ , cm<sup>-1</sup>; *n*-heptane): 2066 (v<sub>w</sub>), 2031 (w), 2000 (vs). IR (cm<sup>-1</sup>; KBr): 2916 (v<sub>w</sub>), 2847 (v<sub>w</sub>), 2083 (v<sub>w</sub>), 2026 (m), 1971 (vs) 1286 (w), 1172 (vw), 1046 (vw), 980 (w), 746 (w), 754 (w), 590 (m), 584 (m), 571 (m), 557 (m), 549 (m), 513 (w), 460 (vw), 446 (m).

### 3.3. Crystal structure determinations

Colorless crystal of **2a** suitable for X-ray analyses, with approximate dimensions of 0.07 × 0.05 × 0.06 mm, was cut from a larger one obtained during slow sublimation in vacuum. Crystal data for **2a** were collected at -173 °C on a KM-4/CCD diffractometer. Crystals of **2a** are monoclinic of space group *C2/m* with *a* = 13.103(3) Å, *b* = 12.119(2) Å, *c* = 6.289(2) Å,  $\beta = 108.52^\circ$ , *V* = 946.9(3) Å<sup>3</sup> and *Z* = 2. In **2a** the vinylsilane and methyl carbon atoms were found to be disordered, and satisfactory results were not be obtained. However, the X-ray structure of a **2a** does confirm the *trans* orientation of two vinylsilane ligands.

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### References

- [1] (a) K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, CA, 1997; (b) Z. Foltynowicz, B. Marciniak, J. Organomet. Chem. 376 (1989) 15; (c) Y. Wakatsuki, H. Yamazaki, M. Nakano, Y. Yamamoto, J. Chem. Soc. Chem. Commun. (1991) 703; (d) B. Marciniak, C. Pietraszuk, Curr. Org. Chem. 7 (2003) 691; (e) C. Pietraszuk, B. Marciniak, H. Fischer, Tetrahedron Lett. 44 (2003) 7121; (f) B. Marciniak, D. Chadyniak, S. Krompiec, J. Mol. Catal. A: Chem. 224 (2004) 111.
- [2] (a) C.P. Lenges, M. Brookhart, B.E. Grant, J. Organomet. Chem. 528 (1997) 199; (b) C.P. Lenges, P.S. White, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 6965; (c) J.W. Fitch, W.T. Osterloh, J. Organomet. Chem. 213 (1981) 493; (d) S.T. Belt, S.B. Duckett, D.M. Haddleton, R.N. Perutz, Organometallics 8 (1989) 748; (e) C.P. Lenges, P.S. White, M. Brookhart, J. Am. Chem. Soc. 121 (1999) 4385; (f) P. Błażejewska-Chadyniak, M. Kubicki, H. Maciejewski, B. Marciniak, Inorg. Chim. Acta 350 (2003) 603; (g) J.W. Fitch, H.E. Herbold, Inorg. Chem. 9 (1970) 1926; (h) H. Sakurai, Y. Kamiyama, Y. Nakadaira, J. Organomet. Chem. 184 (1980) 13; (i) M.I. Rybinskaya, L.V. Rybin, A.A. Pogrebnyak, G.V. Nurtdinova, V.P. Yur'ev, J. Organomet. Chem. 217 (1981) 373; (j) T. Takao, M. Amako, H. Suzuki, Organometallics 20 (2001) 3406; (k) E.M. Haschke, J.W. Fitch, J. Organomet. Chem. 57 (1973) C93; (l) J.W. Fitch, K.C. Chan, J.A. Froelich, J. Organomet. Chem. 160 (1978) 477; (m) L.S. Isaeva, T.A. Peganova, P.V. Petrovskii, F.F. Kayumov, F.G. Yusupova, V.P. Yur'ev, J. Organomet. Chem. 248 (1983) 375; (n) H. Maciejewski, M. Kubicki, B. Marciniak, A. Sydor, Polyhedron 21 (2002) 1261; (o) H. Maciejewski, A. Sydor, M. Kubicki, J. Organomet. Chem. 689 (2004) 3075.
- [3] T.A. Manuel, F.G.A. Stone, Chem. Ind. (London) (1960) 231.
- [4] (a) I.W. Stolz, G.R. Dobson, R.K. Sheline, Inorg. Chem. 2 (1963) 1264; (b) F.-W. Grevels, M. Lindemann, R. Benn, R. Goddard, C. Krüger, Z. Naturforsch., B: Anorg. Chem., Org. Chem. B35 (1980) 1298; (c) F.-W. Grevels, V. Skibbe, J. Chem. Soc., Chem. Comm. (1984) 681; (d) K.R. Pope, M.S. Wrighton, Inorg. Chem. 24 (1985) 2792; (e) M.F. Gregory, S.A. Jackson, M. Poliakov, J.J. Turner, J. Chem. Soc. Chem. Comm. (1986) 1175; (f) S.A. Jackson, R.K. Upmacis, M. Poliakov, J.J. Turner, J.K. Burdett, F.-W. Grevels, J. Chem. Soc., Chem. Comm (1987) 678; (g) F.-W. Grevels, J. Jacke, S. Özkar, J. Am. Chem. Soc. 109 (1987) 7536; (h) F.-W. Grevels, J. Jacke, P. Betz, C. Krüger, Y.-H. Tsay, Organometallics 8 (1989) 293; (i) J.M.D.R. Toma, P.H. Toma, P.E. Fanwick, D.E. Bergstrom, S.R. Byrn, J. Crystallogr. Spectrosc. Res. 23 (1993) 41; (j) F.-W. Grevels, J. Jacke, W.E. Klotzbücher, F. Mark, V. Skibbe, K. Schaffner, K. Angermund, C. Krüger, C.W. Lehmann, S. Özkar, Organometallics 18 (1999) 3278.
- [5] (a) M. Jaroszewski, T. Szymańska-Buzar, M. Wilgocki, J.J. Ziółkowski, J. Organomet. Chem. 509 (1996) 19;

- (b) T. Szymańska-Buzar, K. Kern, *J. Organomet. Chem.* 592 (1999) 212;
- (c) T. Szymańska-Buzar, K. Kern, A.J. Downs, T.M. Greene, L.J. Morris, S. Parsons, *New J. Chem.* 23 (1999) 407;
- (d) M. Górski, A. Kochel, T. Szymańska-Buzar, *Organometallics* 23 (2004) 3037.
- [6] (a) O. Eisenstein, R. Hoffmann, *J. Am. Chem. Soc.* 102 (1980) 6149;
- (b) T.C.T. Chang, B.M. Foxman, M. Rosenblum, C. Stockman, *J. Am. Chem. Soc.* 103 (1981) 7361.
- [7] T.A. Albright, R. Hoffmann, J.C. Thibeault, D.L. Thorn, *J. Am. Chem. Soc.* 101 (1979) 3801.
- [8] C. Bachmann, J. Demuyne, A. Veillard, *J. Am. Chem. Soc.* 100 (1978) 2366.
- [9] K.E. Wiberg, E. Martin, *J. Am. Chem. Soc.* 107 (1985) 5035.