

# Photochemical reactions of $W(CO)_6$ with hydrosilanes: synthesis, spectroscopic characteristic, and crystal structure of $W(CO)_3(\eta^6\text{-PhSiHPh}_2)$

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Received 28 April 2004; accepted 9 August 2004

## Abstract

Photolysis of  $W(CO)_6$  in the presence of  $Ph_3SiH$  in *n*-heptane leads to the formation of the first tricarbonyl( $\eta^6$ -triphenylhydrosilane)tungsten complex  $W(CO)_3(\eta^6\text{-PhSiHPh}_2)$  (**1**) in good yield (ca. 70%). The molecular structure of the new tungsten–silane compound was established by single-crystal X-ray diffraction studies and characterized by IR, UV–Vis,  $^1H$ ,  $^{13}C\{^1H\}$ , and  $^{29}Si\{^1H\}$  NMR spectroscopy.

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**Keywords:** Tungsten; Silicon; X-ray structure; Silane complexes

## 1. Introduction

The chemistry of transition metal–silane complexes has been studied extensively owing to their intermediacy in catalytic hydrosilylation of olefins, acetylenes or ketones [1]. We have recently found that the photochemical reaction of  $W(CO)_6$  with diphenylsilane,  $Ph_2SiH_2$ , gave a dinuclear silylene bridged complex,  $(\mu\text{-SiPh}_2)W_2(CO)_{10}$ , through an intermediate hydrido-silyl species [2]. We have now applied this methodology to a much bulkier silane,  $Ph_3SiH$ , to detect the product of its reaction with  $W(CO)_6$ . Here we report that the reaction of  $W(CO)_6$  with  $Ph_3SiH$  proceeds with retention of the Si–H bond to afford only  $\eta^6$ -arene-type compounds, in

which the  $W(CO)_3$  moiety is bonded to one or two phenyl rings of  $Ph_3SiH$ :  $W(CO)_3(\eta^6\text{-PhSiHPh}_2)$  (**1**) and  $[W(CO)_3(\eta^6\text{-Ph})]_2SiHPh$  (**2**).

Complexes of the  $M(CO)_3(\eta^6\text{-arene})$  type have been intensively studied due to their potential applications in homogeneous catalysis and organic synthesis [3] and in construction of molecules with large second-order optical nonlinearities (NLO materials) [4].

Although there have been several tungsten complexes of the  $W(CO)_3(\eta^6\text{-arene})$  type [5], there have been no accounts of the crystal structure of such a complex with a silyl substituent at the  $\eta^6$ -arene ring. It seemed very interesting to reveal the effect of a hydrosilane substituent at the  $\eta^6$ -aromatic ring on its structure and reactivity.

In an attempt to reveal whether compound **1** could be used, we studied the solution properties of the latter compound by IR, UV–Vis,  $^1H$ ,  $^{13}C\{^1H\}$ , and  $^{29}Si\{^1H\}$  NMR spectroscopy. The solid-state structure of **1** was established by single-crystal X-ray diffraction studies (Fig. 1).

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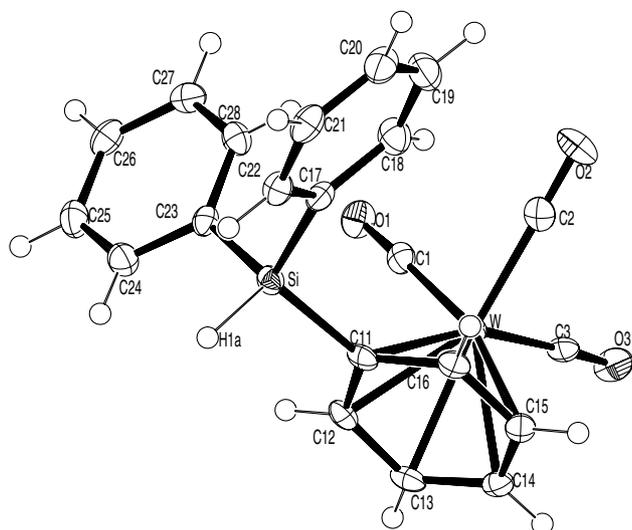


Fig. 1. ORTEP diagram of  $W(CO)_3(\eta^6\text{-PhSiHPh}_2)$  (**1**).

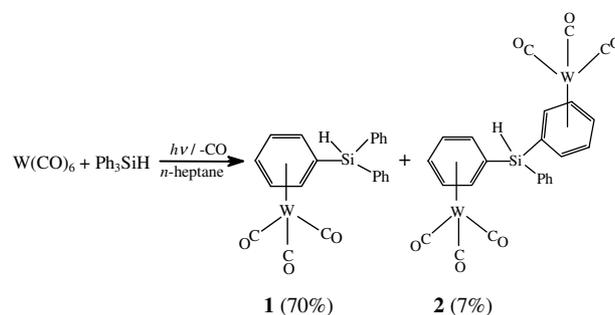
## 2. Results and discussion

### 2.1. Synthesis and spectroscopic characteristic of **1**

Irradiation (6 h) of a solution of  $W(CO)_6$  (1.28 mmol) and  $Ph_3SiH$  (1.28 mmol) in *n*-heptane (80 cm<sup>3</sup>) with a 200 W high-pressure Hg lamp produced quantitatively a new carbonyl compound of tungsten, identified due to two strong bands in the  $\nu(C\equiv O)$  region: 1983 and 1914 cm<sup>-1</sup>. After evaporation of volatiles under vacuum, the residue analyzed for carbon content appeared to be a mixture of compounds containing mainly  $W(CO)_3(Ph_3SiH)$  (**1**), possibly contaminated with a ditungsten complex in which the  $W(CO)_3$  moiety is attached to two phenyl rings of  $Ph_3SiH$ , i.e.  $[W(CO)_3]_2Ph_3SiH$  (**2**) (Anal. Found C, 44.37 vs Calcd 47.75 for **1**, and 36.21 for **2**). Analysis of the crude product by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> solution at room temperature showed the presence of three different compounds containing the Si–H bond. Those compounds were identified as uncoordinated  $Ph_3SiH$  ( $\delta_H = 5.51$ ,  $^1J_{Si-H} = 199$  Hz), compound **1** ( $\delta_H = 5.50$ ,  $^1J_{Si-H} = 210$  Hz), and the ditungsten complex **2** ( $\delta_H = 5.36$ ), approximately in the ratio 0.3/1/0.1, respectively (Scheme 1).

The isolation of compound **1** from the reaction mixture (ca. 0.4 g, 60% yield) was achieved during the purification process (washing off  $Ph_3SiH$  with cold (ca. 0 °C) *n*-heptane and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-heptane at –20 °C). However, the ditungsten complex **2**, was not isolated in a pure state in this case.

The retention of the Si–H bond in compounds **1** and **2** is indicated by proton signals with chemical shifts and the  $^1J_{Si-H}$  coupling constants very close to those of free  $Ph_3SiH$ . The silane character of the  $\eta^6$ -arene ligand in **1** and **2** was also proved by <sup>29</sup>Si NMR spectra, which exhibited characteristic resonances at –16.42 and



Scheme 1. Synthesis of  $W(CO)_3(\eta^6\text{-PhSiHPh}_2)$  (**1**).

–20.71 ppm, respectively. In the IR spectra (KBr) of **1** and **2**, the  $\nu(\text{Si–H})$  band appears at 2158 and 2141 cm<sup>-1</sup>, respectively. The  $\nu(C\equiv O)$  bands for **1** are observed at a similar frequency (1983 and 1914 cm<sup>-1</sup> in *n*-heptane) as for the analogous  $\eta^6$ -arene complexes [5].

In <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of **1**, the proton signals of the  $\eta^6$ -phenyl ring are in their expected positions in the range between 5.5 and 5.1 ppm, while signals of the uncoordinated phenyl protons lie in the region from 7.6 to 7.4 ppm and are shifted downfield by ca. 0.2 ppm in comparison with the free ligand. Comparison with the chemical shift at 5.36 ppm of the unsubstituted benzene ring in  $W(CO)_3(\eta^6\text{-C}_6\text{H}_6)$  [5e] showed that the presence of the  $Ph_2SiH$  group at the  $\eta^6$ -phenyl ring allows  $H_{para}$  protons to resonate at a higher frequency ( $\delta_H = 5.57$ ), while  $H_{ortho}$  and  $H_{meta}$  protons resonate at lower frequencies:  $\delta_H = 5.34$  and 5.19, respectively.

The <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of **1** exhibits four carbon signals, characteristic for the  $\eta^6$ -arene ligand in the region 97–88 ppm. The assignment of those signals was possible due to the characteristic Si–C or C–C coupling constants. The lowest-intensity carbon signal at  $\delta_C = 89.99$  was assigned to carbon *ipso* ( $C_{ipso}\text{-Si}$ ) due to the highest Si–C coupling constants ( $^1J_{Si-C} = 67$  Hz). The latter signal is at much higher field than in spectra of analogous compounds in which the  $\eta^6$ -arene ring is substituted by the alkyl group, e.g. at 109.0 ppm in  $W(CO)_3(\eta^6\text{-C}_6\text{H}_5\text{Me})$  [5e] and at 109.7 in  $W(CO)_3(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)$  [5c,f]. Another interesting feature of the carbon *ipso* signal is the upfield shift upon the lowering of the temperature, while for other carbon signals a downfield shift was observed with the lowering of temperature.

The NMR spectra of compounds **1** and **2** are very close together and, as compound **2** was formed in very low yield, not all signals of that compound were detected and assigned. The better resolved signals are due to carbonyl ligands, which give two narrow resonances:  $\delta_C$  208.74 for **1** and  $\delta$  208.29 for **2**, with the same value of the tungsten–carbon coupling constant  $^1J_{W-C} = 185$  Hz. An unprecedented high value of the tungsten–carbonyl carbon coupling constant evidences strong back-donation from  $d_\pi$  orbitals of the tungsten

atom to  $\pi^*$  orbitals of the CO ligands. This can also correlate with low  $\pi$  acidity of the  $\eta^6$ -phenylsilane ligand in complex **1**.

The  $\eta^6$ -phenyl carbons of **2** resonate in a similar region as for **1** (98–88 ppm), giving seven signals. Only  $C_{ipso}$  carbons of both  $\eta^6$ -phenyl rings resonate at the same frequency with characteristic high-field shift (from 87.17 ppm at 293 K to 86.89 ppm at 248 K), while for others carbon signals the downfield shift with lowering the temperature were observed.

As might be expected, the electronic spectrum of compound **1** is rather similar to those of the  $W(CO)_3(\eta^6\text{-arene})$ -type compounds, which show four absorption bands in the range 220–410 nm [5g,6]. However, all four bands of **1** are at slightly higher energy and more intense than those observed for the  $W(CO)_3(\eta^6\text{-C}_6\text{Me}_6)$  compound [6].

## 2.2. X-ray crystal structure

The solid-state structure of **1** was determined by X-ray crystal structure analysis (Table 1, Fig. 1). Selected bond lengths and angles are listed in Table 2. The structural parameters of **1** are rather similar to those of  $W(CO)_3(\eta^6\text{-C}_6\text{H}_6)$  [5d] and  $W(CO)_3(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)$  [5b]. The average W–CO bond length of 1.975(3) Å in **1** is only slightly longer than the average bond lengths in  $W(CO)_3(\eta^6\text{-C}_6\text{H}_6)$  (1.951(6) Å) [5d]

Table 1  
Crystal data and structure refinement parameters for **1**

Empirical formula	$C_{21}H_{16}O_3SiW$
Formula weight	528.27
Crystal size (mm)	$0.30 \times 0.10 \times 0.10$
Crystal system	Monoclinic
Space group	$P1/c$ (No. 14)
Unit cell dimensions	
$a$ (Å)	6.578(1)
$b$ (Å)	16.625(3)
$c$ (Å)	17.089(3)
$\beta$ (°)	95.02(3)
$V$ (Å <sup>3</sup> )	1861.7(5)
$Z$	4
$D_{\text{calcd}}$ (g/cm <sup>3</sup> )	1.885
Diffractometer	Kuma KM4CCD
Radiation	Mo $K\alpha$ ( $\lambda = 0.71073$ Å)
	Graphite monochromated
Temperature (K)	100
$\mu$ (mm <sup>-1</sup> )	6.287
$F(000)$	1016
No. of data/restraints/params	4474/0/240
Index ranges	$-8 \leq h \leq 8, -21 \leq k \leq 21,$ $-22 \leq l \leq 21$
No. of reflns collected	23,753
Data collected, $\theta$ min./max. (°)	3.11/28.48
$R_{\text{int}}$	0.0474
$S$	1.156
Final residuals: $R_1, wR_2$ ( $I > 2\sigma(I)$ )	0.0262, 0.0518
$R_1, wR_2$ (all data)	0.0347, 0.0539
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.944/–1.000

Table 2  
Selected bond lengths (Å) and angles (°) for **1**

Atoms	Distance	Atoms	Angle
W–C(2)	1.969(3)	C(2)–W–C(1)	89.07(13)
W–C(1)	1.975(3)	C(2)–W–C(3)	89.70(14)
W–C(3)	1.980(4)	C(1)–W–C(3)	85.50(13)
W–C(12)	2.324(3)	C(2)–W–C(11)	106.94(13)
W–C(16)	2.347(3)	C(1)–W–C(11)	102.44(12)
W–C(14)	2.352(3)	C(3)–W–C(11)	161.49(13)
W–C(13)	2.359(3)	C(13)–C(12)–W	73.89(19)
W–C(15)	2.377(3)	C(11)–C(12)–W	74.32(18)
W–C(11)	2.377(3)	C(12)–C(13)–W	71.17(18)
Si–C(17)	1.874(4)	C(14)–C(13)–W	72.12(18)
Si–C(23)	1.874(3)	C(15)–C(14)–W	73.57(18)
Si–C(11)	1.881(4)	C(13)–C(14)–W	72.67(18)
Si–H(1A)	1.44(3)	C(16)–C(15)–W	71.47(18)
C(11)–C(12)	1.432(5)	C(14)–C(15)–W	71.59(19)
C(11)–C(16)	1.433(5)	Si–C(11)–W	130.95(16)
C(12)–C(13)	1.406(5)	C(17)–Si–C(23)	112.60(15)
C(13)–C(14)	1.425(5)	C(17)–Si–C(11)	111.78(15)
C(14)–C(15)	1.416(5)	C(23)–Si–C(11)	109.52(15)
C(15)–C(16)	1.408(5)	C(17)–Si–H(1A)	105.4(13)
		C(23)–Si–H(1A)	109.3(13)
		C(11)–Si–H(1A)	108.0(13)

and in  $W(CO)_3(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)$  (1.95(2) Å) [5b], while the average W–C(Ph) bond length of 2.356(3) Å in **1** is practically the same as the corresponding average bond lengths in  $W(CO)_3(\eta^6\text{-C}_6\text{H}_6)$  (2.365(5) Å) [5d] and in  $W(CO)_3(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)$  (2.35(2) Å) [5b]. As might be expected, the average C–C bond distance of 1.420(5) Å in  $\eta^6$ -phenyl ring of **1** is a slightly longer than the average C–C bond distance of 1.392(5) Å, found for the phenyl rings uncoordinated to the tungsten atom in **1**. A projection of the  $\eta^6$ -phenyl ring plane onto the trigonal plane defined by the three CO ligands in Fig. 2 reveals that the W–CO bonds are close to eclipsing the ring carbon atoms. The least-square plane of the  $\eta^6$ -phenyl ring (rms deviation of fitted atoms = 0.0101 Å) is almost parallel (a deviation angle of  $1.22(5)^\circ$ ) to the plane containing the three carbonyl groups. The distance between the tungsten atom and the center of gravity of the  $\eta^6$ -ring is 1.880(3) Å and relates quite well with the corresponding distance of 1.886(2) Å in  $W(CO)_3(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)$  [5b].

It seemed interesting to compare the solid-state structures of free  $Ph_3SiH$  and  $Ph_3SiH$  coordinated to the  $W(CO)_3$  moiety. Although the structure of  $Ph_3SiH$  had earlier been resolved by X-ray diffraction study at room temperature [7], we decided to repeat this analysis at a lower temperature (100 K), the same as for the measurement of **1** [8]. The average Si–C distance in **1** is 1.876(4) Å, which is not significantly longer than in a molecule of  $Ph_3SiH$  (1.872(2) Å). The sum of the C–Si–C angles is almost the same in free silane molecules ( $333.27(7)^\circ$ ) and those coordinated to  $W(CO)_3$  ( $333.90(15)^\circ$ ). Although it is generally difficult to discuss the Si–H interactions on the basis of X-ray data, the Si–H distance of 1.44(3) Å in **1** is a little longer than the

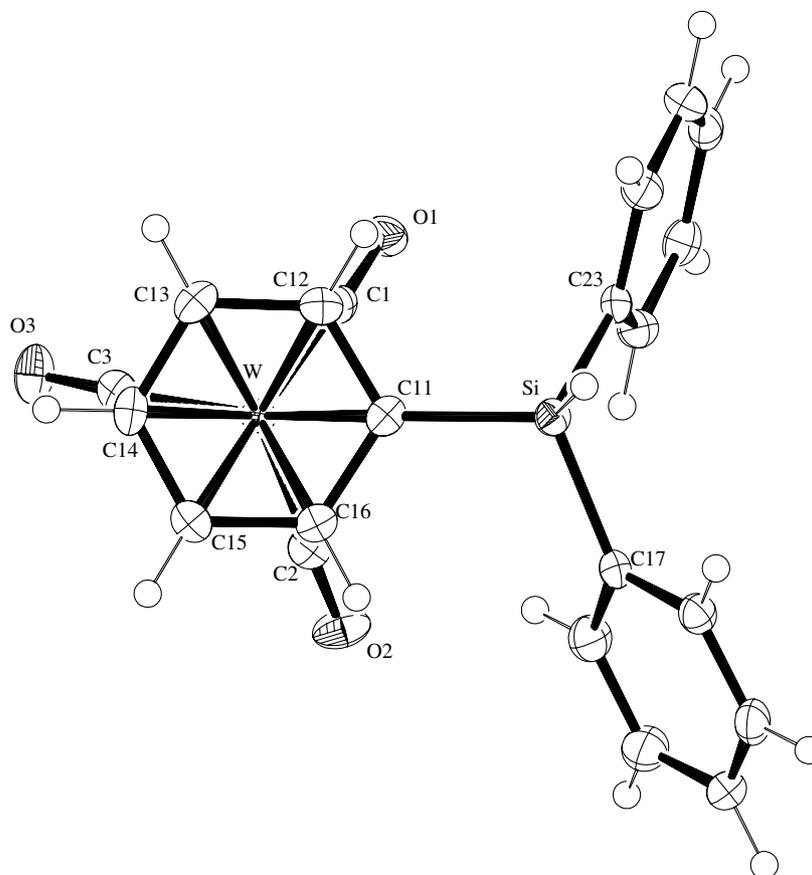


Fig. 2. A projection of the  $\eta^6$ -phenyl ring plane onto the trigonal base defined by the three CO ligands in **1**.

Si–H distance of 1.41(2) Å, detected for  $\text{Ph}_3\text{SiH}$  molecules in our low-temperature X-ray analysis [8].

In conclusion, during the photochemical reaction of  $\text{W}(\text{CO})_6$  and  $\text{Ph}_3\text{SiH}$  the Si–H bond is saved and no oxidative addition reaction is observed.

Further efforts to explore the photochemical reaction of  $\text{W}(\text{CO})_6$  with hydrosilanes in catalytic hydrosilylation of C=O or C=C bonds are currently in progress.

### 3. Experimental

#### 3.1. General information

The synthesis and manipulation of all chemicals was carried out under an atmosphere of nitrogen using the standard Schlenk technique. Solvents and liquid reagents were pre-dried with  $\text{CaH}_2$  and vacuum transferred into small storage flasks prior to use. Other chemicals,  $\text{W}(\text{CO})_6$ ,  $\text{Ph}_3\text{SiH}$ , and  $\text{Ph}_2\text{SiH}_2$ , were obtained from commercial suppliers and were used as received. IR spectra were measured with a Nicolet 400 FT-IR instrument. UV-Vis absorption spectra were recorded on a Hewlett-Packard 8452A rapid scan diode array spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra were recorded with a Bruker AMX 500 MHz instrument. The

chemical shifts for  $^1\text{H}$  NMR spectra were referenced to the residual protons in  $\text{CDCl}_3$  at  $\delta$  7.24.  $^{13}\text{C}$  NMR spectra were calibrated to the natural abundance of  $^{13}\text{C}$  in  $\text{CDCl}_3$  at  $\delta$  77.00.  $^{29}\text{Si}$  NMR shifts were referenced to  $\text{SiMe}_4$ . The photolysis source was an HBO 200W high-pressure Hg lamp. Elemental analyses were performed by the Analytical Laboratory, Faculty of Chemistry, University of Wrocław, with a Perkin-Elmer 2400 CHN instrument.

#### 3.2. Synthesis of **1**

A solution of  $\text{W}(\text{CO})_6$  (0.45 g, 1.28 mmol) and  $\text{Ph}_3\text{SiH}$  (0.33 g, 1.27 mmol) in freshly distilled *n*-heptane (80  $\text{cm}^3$ ) 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 the new compound at  $1914\text{ cm}^{-1}$  reached its maximum intensity (ca. 6 h). The volatile materials were then stripped off the reaction mixture under reduced pressure at room temperature. The residue (0.63 g) analyzed by IR (in KBr pellets), by NMR spectroscopy, and for carbon content appeared to consist mainly of complex **1** contaminated with the ditungsten complex **2** and free  $\text{Ph}_3\text{SiH}$ . The pure compound **1** was separated from this mixture with about 60% yield

(0.4 g) by washing off  $\text{Ph}_3\text{SiH}$  with several portions of cold (ca. 0 °C) *n*-heptane. Isolation of analytically pure compound **1** typically resulted in substantially lower yield due to the ready solubility of this compound. Dark yellow single crystals of **1** for X-ray diffraction study were grown during a slow crystallization process from  $\text{CH}_2\text{Cl}_2/n$ -heptane solution at –20 °C.

### 3.3. Spectral data for **1**

IR (KBr pellet,  $\text{cm}^{-1}$ ): 2158 (s),  $\nu(\text{Si-H})$ ; 1946 (vs), 1879 (s), 1867 (sh,s), 1859 (sh,s),  $\nu(\text{CO})$ ; 1429 (w), 1113 (w), 1092 (w), 811 (w), 797 (w), 742 (w) 700 (w), 653 (vw), 597 (vw), 496 (w), 484 (vw), 469 (vw);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta_{\text{H}}$  7.68 (dd,  $J_{\text{H-H}} = 7.5$  and 1.3 Hz,  $4\text{H}_{\text{ortho}}$ ), 7.51 (t,  $J_{\text{H-H}} = 7.5$  Hz,  $2\text{H}_{\text{para}}$ ), 7.45 (t,  $J_{\text{H-H}} = 7.5$  Hz,  $4\text{H}_{\text{meta}}$ ), 5.57 (t,  $J_{\text{H-H}} = 6.3$  Hz,  $1\text{H}_{\text{para}}$ ), 5.50 (s,  $^1J_{\text{Si-H}} = 210$  Hz,  $1\text{Si-H}$ ), 5.34 (d,  $J_{\text{H-H}} = 6.3$ ,  $2\text{H}_{\text{ortho}}$ ), 5.19 (t,  $J_{\text{H-H}} = 6.3$  Hz,  $2\text{H}_{\text{meta}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta_{\text{C}}$  208.74 ( $^1J_{\text{C-W}} = 185$  Hz,  $3\text{CO}$ ), 135.77 ( $^1J_{\text{C-C}} = 49$  Hz,  $4\text{C}_{\text{ortho}}$ ), 130.91 ( $^1J_{\text{Si-C}} = 72$  Hz,  $^1J_{\text{C-C}} = 49$  Hz,  $2\text{C}_{\text{ipso}}$ ), 130.68 ( $^1J_{\text{C-C}} = 53$  Hz,  $2\text{C}_{\text{para}}$ ), 128.36 ( $^1J_{\text{C-C}} = 53$  and 49 Hz,  $4\text{C}_{\text{meta}}$ ), 96.98 ( $^1J_{\text{C-C}} = 49$  Hz,  $2\text{C}_{\text{ortho}}$ ), 91.73 ( $^1J_{\text{C-C}} = 49$  Hz,  $1\text{C}_{\text{para}}$ ), 89.99 ( $^1J_{\text{Si-C}} = 67$  Hz,  $1\text{C}_{\text{ipso}}$ ), 88.08 ( $^1J_{\text{C-C}} = 49$  Hz,  $2\text{C}_{\text{meta}}$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{Si}}$  –16.42. UV–Vis ( $\lambda_{\text{max}}$ , nm ( $\epsilon \times 10^4$ ,  $1 \text{ mol}^{-1} \text{ cm}^{-1}$ ), *n*-heptane): 226 (4.8), 266 (1.1), 318 (1.2), 370 (0.1).

### 3.4. Spectral data for **2**

IR (KBr pellet,  $\text{cm}^{-1}$ ): 2141  $\nu(\text{Si-H})$ ; (*n*-heptane): 1983 (s), 1914 (s)  $\nu(\text{C}\equiv\text{O})$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta_{\text{H}}$  7.72 (d,  $J_{\text{H-H}} = 7.5$ ,  $2\text{H}_{\text{ortho}}$ ), ca. 7.5 ( $1\text{H}_{\text{para}}$ ), ca. 7.4 ( $2\text{H}_{\text{meta}}$ ), 5.62 (t,  $J_{\text{H-H}} = 6.3$  Hz,  $1\text{H}_{\text{para}}$ ), 5.36 (s,  $1\text{Si-H}$ ), 5.35 (d,  $J_{\text{H-H}} = 6.3$ ,  $2\text{H}_{\text{ortho}}$ ), 5.28 (t,  $J_{\text{H-H}} = 6.3$  Hz,  $2\text{H}_{\text{meta}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta_{\text{C}}$  208.29 ( $^1J_{\text{C-W}} = 185$  Hz,  $6\text{CO}$ ), 134.96, 131.49 ( $1\text{Ph}$ ), 96.83 ( $2\text{C}_{\text{ortho}}$ ), 96.51 ( $2\text{C}_{\text{ortho}}$ ), 92.13 ( $1\text{C}_{\text{para}}$ ), 89.89 ( $1\text{C}_{\text{para}}$ ), 87.80 ( $2\text{C}_{\text{meta}}$ ), 87.72 ( $2\text{C}_{\text{meta}}$ ), 87.19 ( $2\text{C}_{\text{ipso}}$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{Si}}$  –20.71.

### 3.5. X-ray crystallography

A dark yellow crystal of **1** with approximate dimensions of  $0.30 \times 0.10 \times 0.10$  mm was selected for analysis. The data for **1** were collected at 100 K on a Kuma KM4CCD diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation generated from an X-ray tube operated at 50 kV and 35 mA. The images were indexed, integrated, and scaled using the KUMA data reduction package [9]. The crystal data, data collection parameters, and results of the analysis are given in Table 1. The structure was solved by the heavy atom method using SHELXS97 [10] and refined by the full-matrix least-squares method on all  $F^2$  data [11]. Nonhydrogen

atoms were included in the refinement, with anisotropic displacement parameters. Hydrogen atoms were included from geometry of molecules and were not refined. Only the hydrogen atom at the Si atom was included from  $\Delta\rho$  maps and refined isotropically. The data were corrected for absorption [9], min./max. absorption coefficients 0.282/0.728.

## 4. Supplementary material

The X-ray crystallographic data for compound **1** have been deposited at the Cambridge Crystallographic Data Centre with deposition no. CCDC-228072. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1123 336 033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## Acknowledgements

Support of this work was generously provided by the Polish State Committee for Scientific Research (KBN Grant No. 4T09A 19125). We are also grateful to S. Baczyński for the measurement of NMR spectra.

## References

- [1] (a) J.Y. Corey, J. Braddock-Wilking, Chem. Rev. 99 (1999) 175; (b) Z. Lin, Chem. Soc. Rev. 31 (2002) 239; (c) T. Sagawa, Y. Sakamoto, R. Tanaka, H. Katayama, F. Ozawa, Organometallics 22 (2003) 4433; (d) L.D. Field, A. Ward, J. Organomet. Chem. 681 (2003) 91.
- [2] A. Gądek, A. Kochel, T. Szymańska-Buzar, Organometallics 24 (2003) 4869.
- [3] (a) E.L. Muetterties, J.R. Bleeke, E.J. Wucherer, T.A. Albright, Chem. Rev. 82 (1982) 499; (b) U. Englert, R. Haerter, D. Vasen, A. Salzer, B. Eggeling, D. Vogt, Organometallics 18 (1999) 4390; (c) A.R. Pape, P. Kaliappan, E.P. Kündig, Chem. Rev. 100 (2000) 2917; (d) C. Lopez, M.G. Muñoz-Hernández, D. Morales-Morales, F. del Rio, S. Hernández-Ortega, R.A. Toscano, J.J. Garcia, J. Organomet. Chem. 672 (2003) 58; (e) J. Bao, S.-H.K. Park, S.J. Geib, N.J. Cooper, Organometallics 22 (2003) 3309.
- [4] (a) D.R. Kanis, M.A. Ratner, T.J. Marks, Chem. Rev. 94 (1994) 195; (b) J. Heck, S. Dabek, T. Meyer-Friedrichen, H. Wong, Coord. Chem. Rev. 190–192 (1999) 1217; (c) S. Di Bella, Chem. Soc. Rev. 30 (2001) 355; (d) B. Jacques, J.-P. Tranchier, F. Rose-Munch, E. Rose, G.R. Stephenson, C. Guyard-Duhayon, Organometallics 23 (2004) 184.
- [5] (a) R.B. King, A. Fronzaglia, Inorg. Chem. 5 (1964) 1837; (b) F. Calderazzo, R. Poli, A. Barbatì, P.F. Zanazzi, J. Chem. Soc., Dalton Trans. (1984) 1059; (c) S. Pasykiewicz, J. Jankowski, Appl. Organomet. Chem. 9 (1995) 335;

- (d) J.M. Oh, S.J. Geib, N.J. Cooper, *Acta Crystallogr., Sect. C* 54 (1998) 581;
- (e) M.V. Baker, M.R. North, *J. Organomet. Chem.* 565 (1998) 225;
- (f) T. Szymańska-Buzar, K. Kern, *J. Organomet. Chem.* 622 (2001) 74;
- (g) H. Sun, Z. Chen, X. Zhou, *Inorg. Chim. Acta* 355 (2003) 404.
- [6] G.L. Geoffroy, M.S. Wrighton, *Organometallic Chemistry*, Academic Press, New York, CA, 1979, p. 59.
- [7] J. Allemand, R. Gerdil, *Cryst. Struct. Commun.* 8 (1979) 927.
- [8] Crystal data of  $\text{Ph}_3\text{SiH}$ :  $\text{C}_{18}\text{H}_{16}\text{Si}$ ,  $M = 259$ , colorless crystals, crystal size  $0.1 \times 0.1 \times 0.2$  mm,  $a = 10.1284(7)$  Å,  $b = 11.4912(7)$  Å,  $c = 13.3438(9)$  Å,  $\beta = 110.182(6)^\circ$ ,  $V = 1457.7(2)$  Å<sup>3</sup>,  $T = 100$  K,  $d = 1.182$  g cm<sup>-3</sup>,  $\mu = 144$  cm<sup>-1</sup>,  $Z = 4$ , monoclinic, space group  $P2_1/c$ , final residuals:  $R_1 = 0.0492$ ,  $wR_2 (I > 2\sigma(I)) = 0.1309$ , GOF = 1.78, Kuma KM4CCD diffractometer, radiation Mo K $\alpha$  ( $\lambda = 0.71073$  Å).
- [9] Oxford Diffraction Poland Sp., CCD Data Collection and Reduction GUI, Version 1.173.13 beta (Release 14.11.2003) Copyright 1995–2003.
- [10] G.M. Sheldrick, SHELXS97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.
- [11] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.