Synthesis, Spectroscopic Characteristics, and Crystal Structure of μ-Diphenylsilylene(decacarbonyl)ditungsten Complex (μ-$SiPh_2$)$W_2(CO)_{10}$

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Photolysis of $W(CO)_6$ in the presence of Ph_2SiH_2 in *n*-heptane leads to the formation of the first μ-silyleneditungsten complex (μ-$SiPh_2$)$W_2(CO)_{10}$. The molecular structure of the new silylene compound was established by single-crystal X-ray diffraction studies and characterized by IR and ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectroscopy. In $CDCl_3$ solution the silylene compound reacts with bicyclo[2.2.1]hept-2-ene to give $W(CO)_5(\eta^2$-$C_7H_{10})$ and 1,3-cyclopentylenevinylene.

Introduction

Over the past few years there have been numerous reports concerning the preparation and structure of transition metal complexes containing silylene ligands SiR_2.[1] These compounds can be regarded as analogues of very well-known carbene complexes.[2] However, in contrast to the well-established chemistry of transition metal carbene complexes,[2] the chemical properties of the analogous silylene complexes remains practically unrevealed.[1] On the other hand, silylene complexes were proposed as key intermediates in many transition metal-catalyzed rearrangements of silicon compounds, including dehydrogenative coupling of dihydrosilanes,[3] redestribution of silanes,[4] and various reactions of silylene transfer to olefins and acetylenes.[5] Therefore, systematic investigations of transition metal silylene complexes and their chemistry appeared to be necessary and may be considered a very important task for silicon and organometallic chemists.

Several methods have been employed to prepare silylene complexes.[1] The first silylene complexes were observed in reaction between disilanes and metal carbonyls: $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$.[6a] Next, the extrusion of $SiMe_2$ from the disilanes $HMe_2Si-SiMe_2R$ (R = H, CH_3) via $Fe_2(CO)_9$ and $Co_2(CO)_8$ was observed.[6b] Furthermore, reactions of dichlorosilanes with metalate anions were used to prepare base-stabilized silylene complexes.[1c] More recently several reactions have been reported to involve the extrusion of silylene from secondary silanes R_2SiH_2.[1a,b,d,i]

Although there have been several ditungsten complexes containing bridged carbene ligands reported in the literature,[7] there have been no accounts of such complexes with μ-silylene ligands. The formation of silylene-bridged complexes was observed in earlier reactions of disilanes and metal carbonyls such as $Fe_2(CO)_9$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Co_2(CO)_8$.[6] However, up to now in the reaction of tungsten carbonyls and R_2SiH_2 (R = Et,[8a] Ph[8b,c]) only bis(μ-silyl)ditungsten complexes were detected. Here, we report an attempt to prepare a silylene complex of tungsten in a photochemical reaction of $W(CO)_6$ and Ph_2SiH_2.

Results and Discussion

Upon photolysis of $W(CO)_6$ (1.4 mmol) and Ph_2SiH_2 (1.4 mmol) in *n*-heptane (80 cm^3), the reaction solution changed from colorless to orange, and IR spectroscopy

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Table 1. Crystal Data and Structure Refinement Parameters for 1

empirical formula	$C_{22}H_{10}O_{10}SiW_2$
fw	830.07
cryst size (mm)	0.15 × 0.10 × 0.06
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a (Å)	17.0613(9)
b (Å)	8.9094(5)
c (Å)	17.7984(12)
β (deg)	106.115(5)
V (Å^3)	2599.2(3)
Z	4
D_{calcd} (g/cm^3)	2.12
diffractometer	Kuma KM4CCD
radiation	Mo Kα (λ = 0.71073 Å), graphite monochromated
temp (K)	100
μ, mm^{-1}	8.94
F(000)	1536
data collected, θ min/max (deg)	3.72/28.45
index ranges	$-22 \le h \le 22$, $-11 \le k \le 11$, $-16 \le l \le 23$
no. of reflns collected	17 374
R_{int}	0.054
abs coeff, min./max.	0.270/0.620
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	6030/0/317
final residuals: R_1, wR_2 ($I > 2\sigma(I)$)	0.0447, 0.0858
R_1, wR_2 (all data)	0.0709, 0.0942
GOF	1.06

indicated the quantitative formation of a new compound. Its IR spectrum in *n*-heptane contained several strong bands in the ν (C≡O) region: 2098, 2058, 2017, 1964, and 1948 cm^{-1}. After evaporation of volatiles under vacuum the residue appeared to be almost analytically pure ($SiPh_2$)$W_2(CO)_{10}$ (**1**). A little higher content of carbon (Anal. Calcd 31.83 vs Found 33.21) may result from contamination with free Ph_2SiH_2, which was removed during the crystallization process. The silylene character of the silicon ligand in **1** was proved by ^{29}Si NMR spectra,[9] which exhibit a characteristic downfield resonance at 211.33 ppm, and by X-ray crystal studies (Tables 1 and 2).

As Figure 1 shows, the silylene ligand in complex **1** is almost symmetrically bonded to both tungsten atoms with W−Si bonds of 2.577(2) and 2.591(2) Å. The bond angles at silicon fall into three distinct groups: one angle, C(11)−Si−C(21) = 104.7(4)°, is close to the sp^3 standard (109.5°), while two angles, C(11)−Si−W(2) and C(21)−Si−W(1), are quite large (114.2(3)° and 115.7(2)°), closer to the sp^2 standard (120°), whereas the W(1)−Si−W(2) = 78.36(7)° angle is noticeably smaller (Table 2).

The two tungsten atoms in complex **1** are separated by 3.265(2) Å, a distance that is consistent with a W−W bond. Only a little shorter W−W bond length was observed in other structurally characterized dinuclear carbonyl complexes of tungsten containing bridging carbene or silyl ligands.[7,8] For example, the W−W bond lengths in (μ-CHPh)$W_2(CO)_{10}$, (μ-CHCH=CMe_2)$W_2(CO)_{10}$, (μ-$SiHEt_2$)$_2W_2(CO)_8$, and (μ-$SiHPh_2$)$_2W_2(CO)_6$($PiPr_3$)$_2$ have been reported to be 3.118(1),[7b] 3.1450(5),[7d] 3.183(1),[8a] and 3.2256(8) Å,[8b] respectively.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for 1

atoms	distance	atoms	angle
W(1)−C(1)	2.015(10)	C(1)−W(1)−C(3)	78.4(3)
W(1)−C(3)	2.018(9)	C(1)−W(1)−C(2)	90.1(3)
W(1)−C(2)	2.059(8)	C(3)−W(1)−C(2)	91.0(3)
W(1)−C(5)	2.067(9)	C(1)−W(1)−C(5)	92.2(3)
W(1)−C(4)	2.096(9)	C(3)−W(1)−C(5)	90.7(3)
W(1)−Si	2.577(2)	C(2)−W(1)−C(5)	177.4(3)
W(2)−C(8)	1.998(9)	C(1)−W(1)−C(4)	160.4(3)
W(2)−C(10)	2.032(9)	C(3)−W(1)−C(4)	82.3(3)
W(2)−C(6)	2.041(9)	C(2)−W(1)−C(4)	86.4(3)
W(2)−C(9)	2.051(9)	C(5)−W(1)−C(4)	91.8(3)
W(2)−C(7)	2.059(9)	C(1)−W(1)−Si	68.0(3)
W(2)−Si	2.591(2)	C(3)−W(1)−Si	146.2(3)
Si−C(21)	1.873(8)	C(2)−W(1)−Si	85.6(2)
Si−C(11)	1.884(9)	C(5)−W(1)−Si	94.2(2)
O(1)−C(1)	1.154(10)	C(4)−W(1)−Si	130.8(2)
O(2)−C(2)	1.130(9)	C(8)−W(2)−C(10)	79.4(3)
O(3)−C(3)	1.135(10)	C(8)−W(2)−C(6)	97.3(3)
O(4)−C(4)	1.129(9)	C(10)−W(2)−C(6)	90.5(3)
O(5)−C(5)	1.125(10)	C(8)−W(2)−C(9)	83.7(3)
O(6)−C(6)	1.148(9)	C(10)−W(2)−C(9)	91.6(3)
O(7)−C(7)	1.161(10)	C(6)−W(2)−C(9)	177.8(3)
O(8)−C(8)	1.147(10)	C(8)−W(2)−C(7)	84.4(3)
O(9)−C(9)	1.130(10)	C(10)−W(2)−C(7)	163.8(3)
		C(6)−W(2)−C(7)	90.8(3)
		C(9)−W(2)−C(7)	87.4(3)
		C(8)−W(2)−Si	146.0(3)
		C(10)−W(2)−Si	70.2(2)
		C(6)−W(2)−Si	97.9(2)
		C(9)−W(2)−Si	82.3(2)
		C(7)−W(2)−Si	125.5(2)

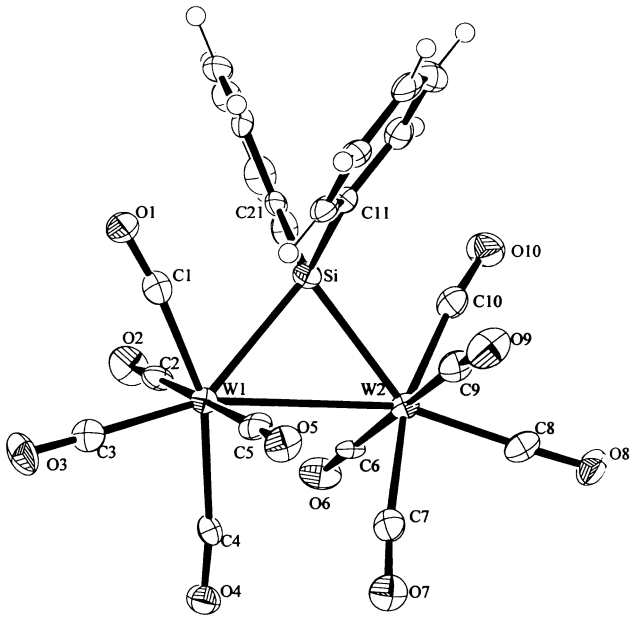

Figure 1. ORTEP diagram of (μ-$SiPh_2$)$W_2(CO)_{10}$ (**1**).

The W−CO bond length falls in the range 1.998(9)−2.096(9) Å. The shortest W−CO bond distance is observed for CO in the *trans* position to the next tungsten atom. In the ^{13}C NMR spectra of compound **1** the carbonyl ligands give two very narrow resonances (δ_C 197.04 and 197.00), differing very much by the tungsten−carbon coupling constant. For comparison, in the spectrum of the diphenylcarbene(pentacarbonyl)tungsten(0) complex the carbonyl carbon signals were observed at 215.3 and 198.4 ppm.[10]

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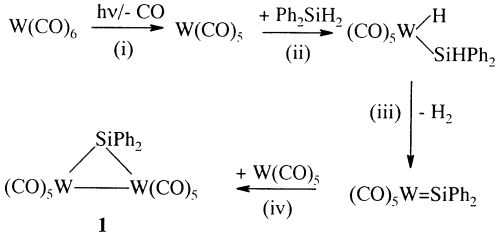
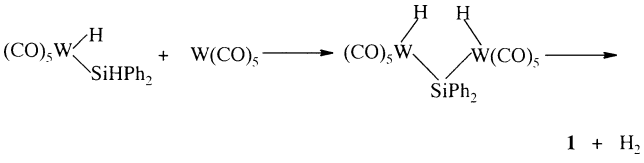
Scheme 1



Scheme 2



A possible mechanism for the formation of complex **1** is shown in Scheme 1: (i) photochemical elimination of a carbonyl group from $W(CO)_6$ to give $W(CO)_5$; (ii) oxidative addition of the Ph_2SiH_2 to the coordinatively unsaturated intermediate $W(CO)_5$ and the formation of a seven-coordinate hydrido-silyl species; (iii) reductive elimination of H_2 and the formation of the silylene intermediate $W(CO)_5(=SiPh_2)$; (iv) coordination of $W(CO)_5$ to the W=Si double bond and the formation of a final *μ*-silyleneditungsten complex **1**.

Most of the intermediate compounds shown in Scheme 1 were uncharacterized by NMR spectroscopy. However, in the hydride region of the ^1H NMR spectrum of a crude product the very low intensity (<0.1%) resonances at δ_H −6.42 (broad), −7.14, and −7.76 were detected. Similar hydride signals were observed during the photochemical reaction of $W(CO)_6$ and Ph_2SiH_2 in cyclohexane-d_{12} solution monitored by ^1H NMR. This suggests that an oxidative addition of Ph_2SiH_2 and the formation of the hydride ligands is a key step in the formation of silylene compound **1**. However, if only $W(H)(SiHPh_2)(CO)_5$ is formed as the intermediate (Scheme 1), one hydride signal must be present. The detection of the three signals suggests the reality of concurrent reaction pathways (Scheme 2).[11]

An intriguing reactivity of the *μ*-silyleneditungsten complex **1** was revealed in the reaction with a large excess of bicyclo[2.2.1]hept-2-ene (norbornene) followed in the NMR tube. In $CDCl_3$ solution the initiation of ring-opening metathesis polymerization (ROMP)[12] of norbornene and the formation of polynorbornene (1,3-cyclopentylenevinylene), as well as $W(CO)_5(\eta^2\text{-}C_7H_{10})$, was identified due to a characteristic olefinic proton signal at δ_H 4.81.[13] The appearance of a low-intensity signal characteristic for *exo*-2-chloronorbornane at δ_H 3.87 suggests the chlorine atom transfer from chloroform to norbornene, during the initiation of ring-opening metathesis polymerization. In an analogous reaction of **1** with norbornene but carried out in cyclohexane-d_{12} solution only $W(CO)_5(\eta^2\text{-}C_7H_{10})$ was detected by NMR spectroscopy.

In acetonitrile solution compound **1** decomposes to give the $W(CO)_5$(NCMe) complex, which was detected by ^{13}C NMR (acetonitrile-d_3) due to characteristic carbonyl carbon signals in a relative intensity ratio 1:4 at δ_C 200.97 ($^1J_{C-W}$ = 157 Hz) and 197.19 ($^1J_{C-W}$ = 131 Hz). Other products were uncharacterized by NMR.

Further efforts to explore properties and catalytic activity of silylene complexes of tungsten are currently in progress.

Experimental Section

General Considerations. The synthesis and manipulation of all chemicals were carried out under nitrogen using standard Schlenk technique. Solvents and liquid reagents were predried with CaH_2 and vacuum transferred into small storage flasks prior to use. Other chemicals, $W(CO)_6$, Ph_2SiH_2, and bicyclo[2.2.1]hept-2-ene (norbornene, NBE), were obtained from commercial suppliers and were used as received. IR spectra were measured with Nicolet-400 FT-IR instrument. ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were recorded with a Bruker AMX 500 MHz instrument. All chemical shifts are referenced to residual solvent protons for ^1H NMR (δ 7.24 $CDCl_3$ and 1.38 cyclohexane-d_{12}) and to the chemical shift of the solvent for ^{13}C NMR (δ 77.00 $CDCl_3$ and 27.8 cyclohexane-d_{12}). The photolysis source was an HBO 200 W high-pressure Hg lamp. Elemental analyses were performed by the Analytical Laboratory in the Faculty of Chemistry at the University of Wrocław with a Perkin-Elmer 2400 CHN instrument. The analysis of the organic products was carried out on a Hewlett-Packard GC-MS system as well as by ^1H and ^{13}C NMR.

Synthesis of 1. A solution of $W(CO)_6$ (0.50 g, 1.4 mmol) and Ph_2SiH_2 (0.26 g, 1.4 mmol) in freshly distilled *n*-heptane (80 cm^3) was irradiated through quartz at room temperature. The course of reaction was monitored by IR measurements in solution, and photolysis was stopped when the IR band of $W(CO)_6$ at 1983 cm^{-1} reached its minimum intensity (about 5 h). The volatile materials were then stripped off the reaction mixture under reduced pressure at room temperature. The residue (0.6 g) was analyzed by elemental analysis (Anal. Calcd for $C_{22}H_{10}O_{10}SiW_2$: C, 31.83; H, 1.21. Found: C, 33.21; H, 1.62), IR in KBr pellets, and NMR spectroscopy. At this stage of the synthesis, all these methods have shown a little contamination with free Ph_2SiH_2 and the hydride intermediates (<0.1% by the integral of resonances at δ_H −6.42 (broad), −7.14, and −7.76). The analytically pure crystalline **1** was obtained during slow crystallization from CH_2Cl_2/pentane (1:20) solution at −70 °C with about 80% yield. Orange single crystals of **1** for X-ray diffraction study were grown from CH_2Cl_2/toluene/pentane (1:1:6) solution at −70 °C.

Spectral Data for 1. IR (KBr pellet, cm^{-1}): 2098 (s), 2056 (vs), 2032 (s), 2020 (w), 2007 (s), 1975 (vs), 1956 (vs), 1948 (vs), 1428 (w), 1090 (w), 741 (w), 698 (w), 587 (s), 565 (s), 490 (vw), 471 (vw), 444 (vw), and 428 (vw). ^1H NMR ($CDCl_3$, 25 °C): δ_H 7.56 (m, 2H), 7.41 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ_C 197.04 ($^1J_{C-W}$ = 137 Hz, 1CO), 197.00 ($^1J_{C-W}$ = 119 Hz, 4CO) 144.31 ($^1J_{Si-C}$ = 57 Hz, C_1−Ph), 134.93 ($^2J_{Si-C}$ = 43 Hz, C_2−Ph), 130.77 (C_4−Ph), 127.98 (C_3−Ph). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ_{Si} 211.33 ($^1J_{Si-W}$ = 54.9 Hz).

NMR Tube Reactions. The solution of compound **1** (0.04 g) and norbornene (0.01 g) in $CDCl_3$ or cyclohexane-d_{12} solution (0.7 cm^3) was periodically analyzed by ^1H NMR over a period of several days at room temperature. The decay of signals due to compound **1** and norbornene and the appearance of the new signals were observed.

X-ray Crystallography. General Considerations. Crystal data for **1** were collected at 100 K on a Kuma KM4CCD diffractometer with graphite-monochromated Mo Kα radiation, generated from a Glass Diffraction X-ray tube operated at 50 kV and 35 mA. An orange crystal with approximate dimensions of 0.15 × 0.10 × 0.06 mm was cut from a larger plate.

(11) The mechanism presented in Scheme 2 has been suggested by a reviewer of this paper, to whom we are very grateful.

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The images were indexed, integrated, and scaled using the KUMA data reduction package.[14] The experimental details together with crystal data are given in Table 1. The structure was solved by the heavy atom method using SHELXS97[15] and refined by the full-matrix least-squares method on all F^2 data.[16] All atoms were included in the refinement, with anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms. The data were corrected for absorption,[14] min./max. absorption coefficients 0.270/0.620. Complex **1** crystallizes with a molecule of solvent, which appears to be a partial molecule of pentane. Attempts to model the solvent proved unsatisfactory; thus, the solvent contribution was subtracted from the reflection data using the program SQUEEZE.[17] Crystallographic data for compound **1** have been deposited at the Cambridge Crystallographic Data Centre with deposition no. CCDC-212597.

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Supporting Information Available: Tables of crystal data and structure refinement parameters, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and bond lengths and angles, and a figure of crystal packing. This material is available free of charge via the Internet at http://pubs.asc.org.

OM030512X

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