Activation of the Si–H bond of Et_2SiH_2 in photochemical reaction with $W(CO)_6$: Spectroscopic characterization of intermediate W–Si compounds and the revisited crystal structure of the bis{(μ-$η^2$-hydridodiethylsilyl)tetracarbonyltungsten(I)} complex [{W(μ-$η^2$-H–SiEt$_2$)(CO)$_4$}$_2$]

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Abstract

The photochemical reaction of $W(CO)_6$ with diethylsilane has been used to generate new tungsten–silicon compounds varying in stability. The initially formed $η^2$-silane intermediate complex [$W(CO)_5(η^2$-H–SiHEt$_2$)], characterized by two equal-intensity doublets with $^2J_{H–H} = 10$ Hz at $δ = 5.10$ ($^1J_{Si–H} = 217$ Hz) and $δ = −8.05$ ($^1J_{W–H} = 38$ Hz, $^1J_{Si–H} = 93$ Hz), was detected by the ^{1}H NMR spectroscopy (methylcyclohexane-d_{14}, −10 °C). The $η^2$-silane complex was converted in the dark to give more stable species. One of them was characterized by two equal-intensity proton signals observed as doublets with $^2J_{H–H} = 5.2$ Hz at $δ = −8.25$ and −10.39 ppm. The singlet proton resonance at $δ = −9.31$ flanked by ^{29}Si and ^{183}W satellites ($^1J_{Si–H} = 43$ Hz, $^2J_{Si–H} = 34$ Hz, $^1J_{W–H} = 40$ Hz) was assigned to the agostic proton of the $W(η^2$-H–SiEt$_2$) group in the most stable compound isolated from the photochemical reaction products in crystalline form. The molecular structure of the bis{(μ-$η^2$-hydridodiethylsilyl)tetracarbonyltungsten(I)} complex [{W(μ-$η^2$-H–SiEt$_2$)(CO)$_4$}$_2$] was established by single-crystal X-ray diffraction studies. The tungsten hydride observed in the ^{1}H NMR spectrum at $δ = −9.31$ was located in the structure at a chemically reasonable position between the W and Si atoms of the W–Si bond of the bridging silyl ligand. The reactivity of photochemically generated W–Si compounds towards norbornene, cyclopentene, diphenylacetylene, acetone, and water was studied. As was observed by IR and NMR spectroscopy, the $η^2$-silane ligand in the complex [$W(CO)_5(η^2$-H–SiHEt$_2$)] is very easily replaced by an $η^2$-olefin or $η^2$-alkyne ligand.
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Keywords: Tungsten; Silicon; Si ligands; Agostic interaction; Hydride ligands

1. Introduction

The reactivity of the silicon–hydrogen bond of silanes towards transition metals continues to be an important area of research due to its relevance to the catalytic processes known as hydrosilylation [1–5]. The electron-rich group 6 metal carbonyl complexes are particularly interesting due to their potential to react with a variety of bonds by oxidative addition [6–8]. For example, previous studies have demonstrated that photochemically activated group 6 metal hexacarbonyls react via oxidative addition at the Sn–Cl, Ge–Cl, and Si–H bonds to yield seven-coordinate complexes [8,9].

Recently, in photochemical reaction of group 6 metal hexacarbonyls with secondary and tertiary organosilanes, intermediate $η^2$-silane complexes have been generated and characterized by IR and ^{1}H NMR spectroscopy and by photoacoustic calorimetry [10–14]. The activation of the Si–H bond of diphenylsilane in the photochemical

reaction of $W(CO)_6$ has been applied in the hydrosilylation of ketones, $RR'C=O$ ($R = Me$, $R' = Me$, ^iPr, ^nPr, Ph) and in dehydrogenative silylation of 2-propanol [10]. However, in our earlier studies we have found that the major product in photochemical reaction of $W(CO)_6$ with Ph_2SiH_2 is the complex $[(\mu\text{-}SiPh_2)\{W(CO)_5\}_2]$, which contains two $W(CO)_5$ moieties linked by a bridging diphenylsilylene ligand and a W–W bond [9]. This reaction most likely begins with the oxidative addition of Ph_2SiH_2 to the coordinatively unsaturated intermediate $W(CO)_5$ and the formation of a seven-coordinate hydridosilyl species, although no intermediates were observed and it is not clear at what point dimerization and H_2 loss occurred. In this paper, we report the activation of the Si–H bond of diethylsilane, Et_2SiH_2, using photochemically generated coordinatively unsaturated tungsten(0) carbonyl complexes. Several organometallic products of this reaction have been observed and characterized by IR and NMR spectroscopy. One of them has been shown by X-ray diffraction studies to be a silicon–bridged tungsten dimer which formally contains two tungsten atoms in the first oxidation state bridged by two silyl ligands with an α-agostic Si–H bond. The X-ray crystal structure of an identical tungsten complex was reported by Bennett and Simpson in 1971 [15]. Unfortunately, the hydrogen atoms were not located in the latter compound, and no spectroscopic evidence for W–H or Si–H interaction was offered. An analogous molybdenum complex, $[\{Mo(\mu\text{-}\eta^2\text{-}H\text{-}SiEt_2)(CO)_4\}_2]$, has recently been characterized in solution and in the solid state [16].

2. Results and discussion

2.1. Photochemical reaction of W(CO)_6 with Et_2SiH_2

In an attempt to generate a coordinatively unsaturated tungsten(0) complex capable of activating the Si–H bond, $W(CO)_6$ was irradiated in *n*-heptane containing Et_2SiH_2. In experiments monitored by IR spectroscopy, it was found that the decay of the v (C≡O) frequency at 1981 cm^{-1}, characteristic for $W(CO)_6$, was accompanied by the appearance of new v (C≡O) bands in the region from 2100 to 1900 cm^{-1} (Fig. 1). The relative intensity of the new bands was dependent on the reaction temperature (-10–$25\,^\circ$C), and the time of photolysis (2–6 h) and suggested the formation mixture of penta-, tetra-, and eventually tricarbonyl compounds of tungsten. This possibility was supported by ^{13}C NMR spectroscopy, which revealed several signals in the carbonyl region from $\delta = 213$ ppm to $\delta = 188$ ppm (Fig. 2). These carbonyl compounds varied in stability. The most unstable pentacarbonyl compound (**A**) (Scheme 1), characterized by a v (C≡O) band at 2086 cm^{-1}, was observed only in the course of photolysis but was never detected in the solid state, after evaporation of the solvent (other v (C≡O) bands of the pentacarbonyl moiety are obscured by strong absorption of $W(CO)_6$). That suggests that during the isolation procedure the unstable compound **A** transforms to give a more stable compound (**B**), which
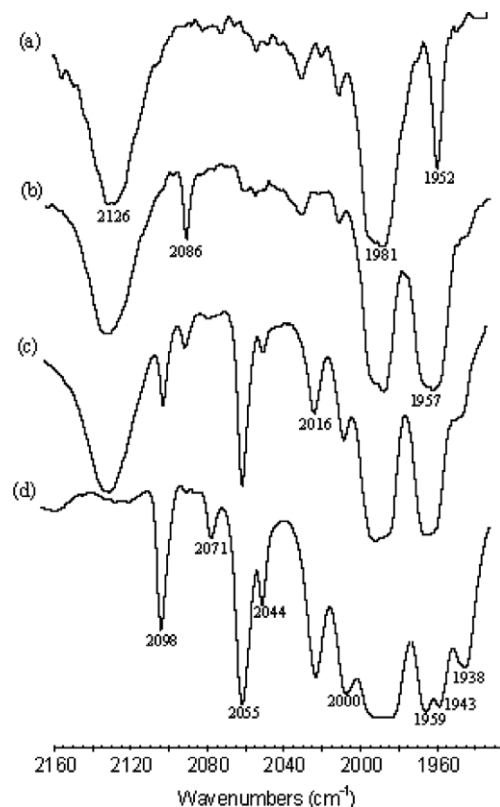

Fig. 1. v (C≡O) stretching region of IR spectra obtained during the monitoring of photochemical reaction of $W(CO)_6$ with Et_2SiH_2 in *n*-heptane solution at 25 °C: (a) before photolysis, (b) after 1 h of photolysis, (c) after 4 h of photolysis, and (d) after removal of volatile materials in vacuum and subsequent dissolution in *n*-heptane.

was identified due to a new v (C≡O) band at 2071 cm^{-1} (Fig. 1). The v (C≡O) band at 2044 cm^{-1}, which appeared after prolonged irradiation at room temperature and whose intensity increased in the IR spectrum of the isolated solid sample, was later assigned to the tetracarbonyl compound (**1**). Two v (C≡O) bands at 2098 (w) and 2055 (s) cm^{-1}, which were observed in IR spectra with similar intensity ratios in solution and in the solid state, could be assigned to the relatively stable μ-diethylsilylene-bis(pentacarbonyltungsten) compound $[(\mu\text{-}SiEt_2)\{W(CO)_5\}_2]$ (**2**) (Scheme 1).

As was shown by ^{1}H NMR spectroscopy, the photochemical reaction of $W(CO)_6$ with diethylsilane yielded a mixture of tungsten hydride complexes varying in stability (Fig. 3). The formation of W–H bonds was evidenced by the detection of several high-field resonances in the range from $\delta = -7$ ppm to $\delta = -12$ ppm. For a sample prepared in *n*-heptane at $-10\,^\circ$C and next dissolved in toluene-d_8, the following signals were observed at $-30\,^\circ$C: $\delta = -7.62$ (d, $^2J_{H-H} = 9$ Hz), -7.66 (s, $^1J_{W-H} = 35$ Hz), -8.25 (d, $^2J_{H-H} = 5.2$ Hz, $^1J_{W-H} = 35$ Hz, $^1J_{Si-H} = 37$ Hz), -9.02 (s, $^1J_{W-H} = 38$ Hz), -9.31 (s, $^1J_{W-H} = 40$ Hz, $^1J_{Si-H} = 43$ Hz, $^2J_{Si-H} = 34$ Hz), -10.28 (s, $^1J_{W-H} = 44$ Hz), -10.39 (d, $^2J_{H-H} = 5.2$ Hz, $^1J_{W-H} = 32$ Hz), and -11.39 (s). Two doublets of equal intensity, at -8.25 and -10.39 ppm, were assigned to the dihydride compound **B**, which was formed
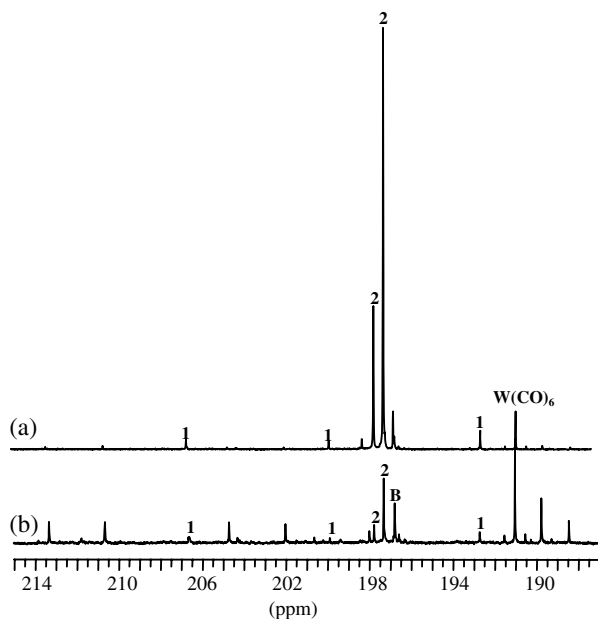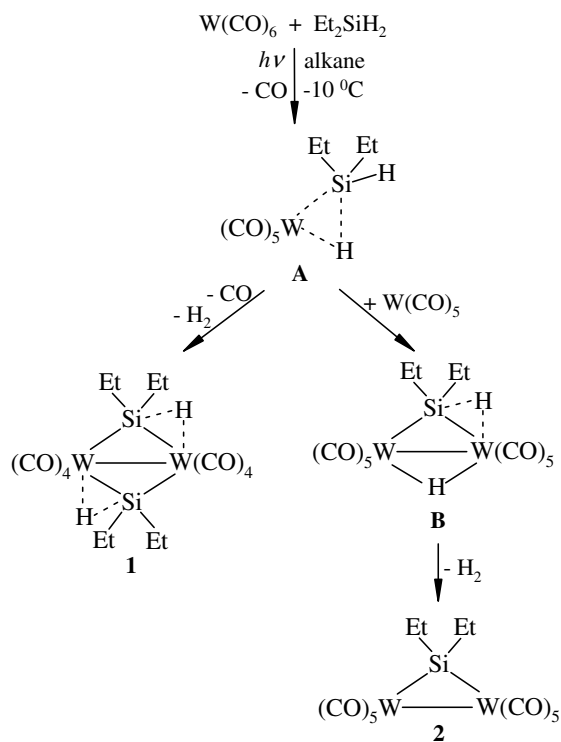
Fig. 2. Carbonyl carbon region of the ^{13}C NMR spectrum (125 MHz, toluene-d_8, -30 °C) showing carbon signals of W–Si compounds formed during the photochemical reaction (4 h): (a) at 25 °C, (b) at -10 °C. Signals denoted by **1** are due to the compound $[\{W(\mu\text{-}\eta^2\text{-H–SiEt}_2)(CO)_4\}_2]$ (**1**), those denoted by **2** are due to $[(\mu\text{-SiEt}_2)\{W(CO)_5\}_2]$ (**2**), that denoted by **B** is due to $[(\mu\text{-H})(\mu\text{-}\eta^2\text{-H–SiEt}_2)\{W(CO)_5\}_2]$ (**B**), and the one at $\delta = 191.04$ is due to $W(CO)_6$.

Fig. 3. Variable-temperature ^1H NMR spectra (300 MHz, toluene-d_8) of the tungsten–hydride complexes showing the high field resonances. Signals are denoted in the same way as the W–Si compounds: **A**, **B**, and **1**.

Scheme 1. Possible mechanistic pathways for the formation of W–Si complexes from $W(CO)_6$ and Et_2SiH_2.

as a result of the addition of a pentacarbonyl moiety to the initially generated η^2-silane complex **A** (Scheme 1). The latter resonances are temperature dependent in a way charac-
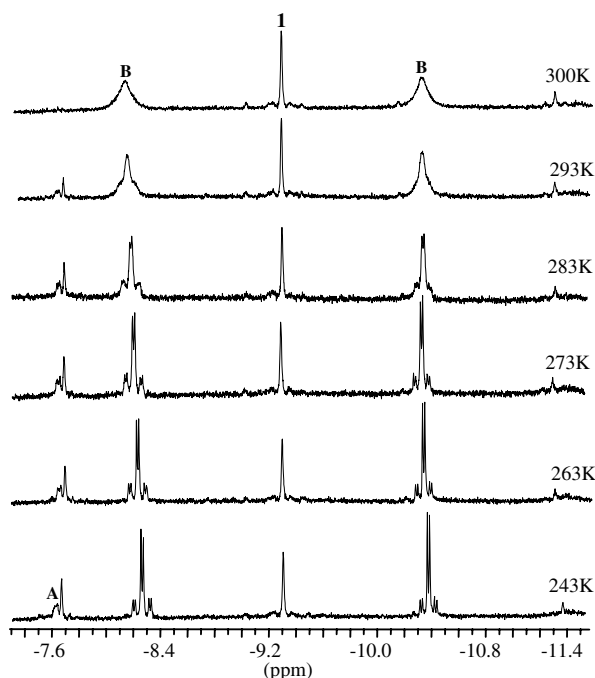
teristic of a dynamic process. At room temperature they are broad, but at -10 °C and lower temperature sharp signals and ^{183}W satellites are nicely observed ($^1J_{W–H} = 35$ Hz and 32 Hz, respectively). Careful analysis of the doublet signal at -8.25 ppm allowed us to detect ^{29}Si satellites that gave rise to the $^1J_{Si–H} = 37$ Hz. This coupling constant suggests a σ (Si–H) interaction with the tungsten center [1,2,10–16,16–23]. Compound **B** decays in toluene-d_8 solution in a few days and can be characterized in a freshly prepared sample obtained in a low temperature reaction (-10 °C). Two other signals, at $\delta = -9.02$ and -10.28, are broad and very low but always of 1:1 equal intensity, and they must be due to another dihydride species.

The yields of the hydride complexes calculated from the intensity ratio of the hydride signals were dependent on the reaction temperature. Photolysis at room temperature afforded a mixture in which the hydride signal at $\delta = -9.31$, subsequently assigned to the $\mu\text{-}\eta^2\text{-H–SiEt}_2$ moiety of compound **1**, dominated (98%). In contrast, when the photochemical reaction was carried out at -10 °C, the yield of compound **B** calculated from the intensity of the two doublets at $\delta = -8.25$ and -10.39 reached 80% in a freshly prepared sample but dropped considerably over a prolonged time (24 h). Two equal-intensity broad signals at $\delta = -9.02$ and -10.28 ppm tentatively assigned to dihydride species were always detected, but the highest intensity of these signals was observed in reaction carried out with longer photolysis times. As was calculated from ^1H NMR spectra, the yield of the latter dihydride compound did not exceed 10%. From this mixture of compounds, only **1** and **2** were stable enough to be isolated in a crystalline

form. Although crystals of **1** and **2** are stable toward air and moisture, in solution they are moisture sensitive. Yellow single crystals were grown through slow crystallization from a saturated *n*-heptane solution at *ca.* −10 °C, and their analysis showed the presence of two W–Si compounds. However, only crystals of one of the compounds (**1**) were of a sufficiently good quality to allow the resolution of its molecular structure by means of X-ray diffraction studies (see below).

2.2. X-ray crystal structure of [{W(μ-η²-H–SiEt₂)(CO)₄}₂] (1)

The crystal data for **1** are given in Table 1, and selected bond lengths and bond angles are listed in Table 2. The structure of **1**, shown in Fig. 4, establishes the unique μ-η² geometry of the bridging H–SiEt₂ ligand. The general structural features of **1** are identical as those found by Bennett and Simpson in 1971 [15], and are similar to those observed for the analogous molybdenum complex, [{Mo(μ-η²-H–SiEt₂)(CO)₄}₂] [16]. A remarkable feature of the current X-ray crystal structure of **1** is that it shows that the hydrogen atom is located between the tungsten

Table 1
Crystal data and structure refinement parameters for [{W(μ-η²-H–SiEt₂)(CO)₄}₂] (**1**)

Empirical formula	$C_{16}H_{22}O_8Si_2W_2$
Formula weight	766.20
Crystal size (mm)	$0.08 \times 0.08 \times 0.07$
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a (Å)	9.122(2)
b (Å)	10.008(2)
c (Å)	12.336(2)
β (°)	98.79(3)
V (Å³)	1113.0(4)
Z	2
D_{calc} (g cm³)	2.286
Diffractometer	Kuma KM4CCD
Radiation	Mo Kα ($\lambda = 0.71073$ Å) graphite monochromated
Temperature (K)	100(2)
μ (mm⁻¹)	10.473
$F(000)$	716
Index ranges	$-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 11$, $-16 \leqslant l \leqslant 16$
Number of reflections collected	13112
Data collected, θ min./max. (°)	3.01/28.52
R_{int}	0.0467
Absorption coefficients, min./max.	0.453/0.657
No. of data/restraints/parameters	2663/0/130
Final residuals: R_1, wR_2 ($I > 2\sigma(I)$)	0.0303, 0.0441
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å⁻³)	1.032/−0.650
GOF	1.090

Table 2
Selected bond lengths (Å) and angles (°) for [{W(μ-η²-H–SiEt₂)(CO)₄}₂] (**1**)[a]

Atoms	Distance	Atoms	Angle
W(1)–C(4)	1.994(5)	C(4)–W(1)–C(2)	79.01(18)
W(1)–C(2)	2.002(5)	C(4)–W(1)–C(3)	90.30(18)
W(1)–C(3)	2.037(5)	C(2)–W(1)–C(3)	90.59(19)
W(1)–C(1)	2.047(5)	C(4)–W(1)–C(1)	91.96(19)
W(1)–Si(1)	2.605(1)	C(2)–W(1)–C(1)	88.76(19)
W(1)–Si(1)^i	2.712(1)	C(3)–W(1)–C(1)	177.49(18)
W(1)–W(1)^i	3.1899(7)	C(4)–W(1)–Si(1)	65.78(14)
Si(1)–C(7)	1.879(5)	C(2)–W(1)–Si(1)	144.08(13)
Si(1)–C(5)	1.883(5)	C(3)–W(1)–Si(1)	96.28(13)
Si(1)–W(1)^i	2.712(1)	C(1)–W(1)–Si(1)	85.66(13)
O(1)–C(1)	1.145(5)	C(4)–W(1)–Si(1)^i	169.44(13)
O(2)–C(2)	1.150(5)	C(2)–W(1)–Si(1)^i	109.49(13)
O(3)–C(3)	1.153(5)	C(3)–W(1)–Si(1)^i	83.51(14)
O(4)–C(4)	1.155(6)	C(1)–W(1)–Si(1)^i	94.42(14)
C(7)–C(8)	1.527(7)	Si(1)–W(1)–Si(1)^i	106.30(3)
C(5)–C(6)	1.524(7)	C(4)–W(1)–W(1)^i	120.05(13)
Si(1)–H(3)	1.54(2)	C(2)–W(1)–W(1)^i	160.93(13)
W(1)^i–H(3)	1.78	C(3)–W(1)–W(1)^i	89.61(13)
		C(1)–W(1)–W(1)^i	90.22(14)
		Si(1)–W(1)–W(1)^i	54.69(3)
		Si(1)^i–W(1)–W(1)^i	51.62(3)
		C(7)–Si(1)–C(5)	105.9(2)
		C(7)–Si(1)–W(1)	115.37(16)
		W(1)–Si(1)–W(1)^i	73.69(3)
		C(7)–Si(1)–H(3)	105.6
		C(5)–Si(1)–H(3)	96.7
		W(1)–Si(1)–H(3)	111.0

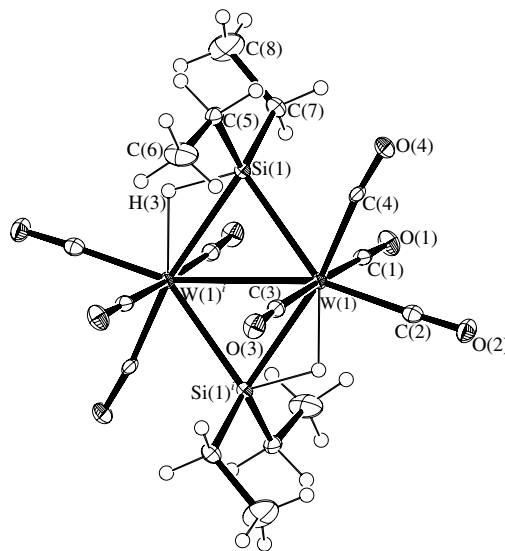[a] Symmetry transformations used to generate equivalent atoms: $i = -x$, $-y + 1$, $-z + 1$.

Fig. 4. ORTEP drawing of [{W(μ-η²-H–SiEt₂)(CO)₄}₂] (**1**). Symmetry code: $i = -x$, $-y + 1$, $-z + 1$.

atom (H–W = 1.78 Å) and the silicon atom (H–Si = 1.54 (2) Å), to bridge one of the W–Si bonds of the bridging silyl ligands. The nonbridged W–Si bond is significantly shorter (W(1)–Si(1) = 2.605(1) Å) than the other one (W(1)–Si(1)^i = 2.712(1) Å) and considerably longer than

observed in other tungsten complexes with nonbridging silyls. The W–Si bond length of 2.560(1) Å has been found in the silyl hydride metallocene complex [Cp$_2$W(H)(SiMe$_3$)] [22]. The bridged W–Si bond in **1** is almost identical as in another dinuclear compound of tungsten containing a bridging diphenylsilyl ligand, [{W(μ-η^2-H– SiPh$_2$)(CO)$_3$- (P^{i}Pr$_3$)}$_2$] (W–Si = 2.708(3) Å) [20]. The 1.78 Å W–H bond in **1** is comparable with those observed for other tungsten hydrides: [Cp(CO)$_2$(μ-H)W=SiH{C(SiMe$_3$)$_3$}] (W–H = 1.82(7) Å) [21], [WH(Cl)(CO)$_2$ (PMe$_3$)$_3$] (W–H = 1.78 Å) [23] and [WH(CO)$_3$(NCMe)(PPh$_3$)$_2$]$^+$ (W–H = 1.71 Å) [24]. The length of the Si–H bond, 1.54(2) Å, is not longer than the typical terminal Si–H distance (1.4–1.5 Å) in free silanes or in nonbridging silyl ligands. A slightly greater Si–H bond lengthening was found for η^2-coordinated silane in cis-[Mo(η^2-H–SiH$_2$Ph)(CO)(depe)$_2$] (η^2-Si–H = 1.77(6) Å, σ-Si–H = 1.42(6) and 1.41(6) Å) [18].

The two tungsten atoms in complex **1** are linked by a long W–W single bond (3.1899(7) Å) [25]. An identical W–W bond length (3.183(1) Å) was observed in **1** by Bennett and Simpson [15], but slightly longer W–W bond distances, 3.2256(8) Å and 3.265(2) Å, have been detected in dinuclear compounds containing another bridging silicon ligand: [{W(μ-η^2-H–SiPh$_2$)(CO)$_3$(P^{i}Pr$_3$)}$_2$] [20], and [(μ-SiPh$_2$){W(CO)$_5$}$_2$] [9], respectively. The (W–Si)$_2$ core is planar, with the angle W(1)–Si(1)–W(1)^i = 73.69(3)°, similar to that in the compound [{W(μ-η^2-H–SiPh$_2$)(CO)$_3$(P^{i}Pr$_3$)}$_2$], where W–Si–W = 76.04(7) [20]. The angle subtended at the silicon atom by the two ethyl groups is close to tetrahedral (C(5)–Si(1)–C(7) = 105.9(2)), while the W(1)–Si(1)–W(1)^i angle is considerably more acute at 73.69(3)°.

The W–CO bond lengths drop in the range 1.994(5)–2.047(5) Å. The two mutually trans carbonyl ligands (C(1)–W(1)–C(3) = 177.49(18)°) are at slightly longer distances from the tungsten atom (W(1)–C(1) = 2.047(5), W(1)–C(3) = 2.037(5) Å), than other two (W(1)–C(4) = 1.994(5), W(1)–C(2) = 2.002(5) Å), which are in the position nearly trans to the silicon (C(4)–W(1)–Si(1)^i = 169.44 (13)°) and tungsten atom (C(2)–W(1)–W(1)^i = 160.93 (13)°). These are in very good agreement with ^{13}C NMR spectra of compound **1**, in which three resonances were observed in the carbonyl carbon region with the intensity ratio 1:1:2 (see below).

2.3. Spectroscopic characterization of compound 1

The IR spectrum of compound **1** in n-heptane solution exhibits four v (C≡O) bands of almost equal intensity at 2044, 1998, 1976, and 1935 cm^{-1}. Similar v (C≡O) frequencies have been observed for the analogous molybdenum(I) complex [{Mo(μ-η^2-H–SiEt$_2$)(CO)$_4$}$_2$] (2046 (s), 1983 (vs), and 1939 (s) cm^{-1}) [16], and for a binuclear complex of tungsten(I), [{W(μ–I)(CO)$_4$}$_2$], (2049, 1991, 1976 cm^{-1}) [26]. The ^{1}H NMR spectrum of **1** (−30 °C, toluene-d_8) revealed a hydride resonance at δ = −9.31 ppm,

which appeared as a singlet (Fig. 3). The high-field chemical shifts of this signal are in agreement with the bridging character of the hydride ligand; δ = − 3.88 with $^1J_{W–H}$ = ∼35 Hz was found for [W(CO)$_5$(η^2-H$_2$)] [27], δ = −4.3 for the terminal hydride in the [WH(CO)$_5$]$^-$ anion [28], while δ = −12.5 was found for the bridging hydride in the [(μ-H){W(CO)$_5$}$_2$]$^-$ anion [29–31]. In addition, ^{183}W satellites and two sets of ^{29}Si satellites were detected on the hydride signal, which provided a tungsten–hydride coupling constant value of 40 Hz and a silicon–hydride coupling constant value of 34 Hz and 43 Hz. Two sets of ^{29}Si satellites of the W–H resonance result from the presence of two silicon ligands at the tungsten centre. The $^1J_{Si–H}$ value of 43 Hz is a typical $J_{Si–H}$ value for η^2-silane complexes, which usually falls in the range 30–100 Hz [1,16–21,32–34], and proves a σ (Si–H) interaction with the tungsten centre. The second $J_{Si–H}$ value of 34 Hz establishes the presence of another silicon atom at the tungsten center, coupled with a proton through two bonds. In addition to the ^{1}H NMR data, the ^{29}Si{^{1}H} NMR spectra (toluene-d_8) show a resonance at δ = 184. In the ^{29}Si NMR spectrum the latter resonance was observed as a broad unresolved multiplet. The large downfield chemical shift of silicon resonance compared to that observed for the parent silane (δ = −22.6 for Et$_2$SiH$_2$) suggests some degree of silylene character of the silicon ligand. The ^{29}Si NMR chemical shift a little more downfield than here has been observed for a tungsten dimer singly bridged by a silylene SiPh$_2$ ligand (δ = 211) [9], and for the molybdenum analogue of **1**, the compound [{Mo(μ-η^2-H–SiEt$_2$)(CO)$_4$}$_2$] (δ = 208 ppm) [16]. For mononuclear tungsten compounds containing nonbridging silylene ligands, [Cp*(CO)$_2$(μ-H)W=Si(H)C(SiMe$_3$)$_3$] [21], [Cp*(dmpe)(H)$_2$W=SiMe$_2$)] [B(C$_6$F$_5$)$_4$] [35], and [Cp*(CO)$_2$(SiMe$_3$)W=SiMes$_2$] [36], ^{29}Si NMR resonances have been detected at δ = 275, 314 and 381 ppm, respectively.

The ^{13}C{^{1}H} NMR spectrum of **1** exhibits three signals in the carbonyl region, at δ = 206.66 ($^1J_{W–C}$ = 117 Hz), 199.88 ($^1J_{W–C}$ = 129 Hz), and 192.71 ($^1J_{W–C}$ = 123 Hz), in the intensity ratio 1:1:2, which is in agreement with the presence of two mutually trans carbonyl ligands and two other carbonyl groups cis to the former but having two different ligands in the trans position with a weaker π-accepting ability than the carbonyl ligands, i.e. the silicon and tungsten atoms (Fig. 2).

In the solid state, compound **1** is stable indefinitely under an inert atmosphere. In toluene-d_8 solution, it is also stable in the absence of air, and no changes in its ^{1}H NMR were observed over a period of days.

2.4. Spectroscopic characterization of compound 2

The IR spectrum of compound **2** in n-heptane solution exhibits three v (C≡O) bands at 2098 (m), 2055 (s), and 1959 (vs) cm^{-1} typical for a pentacarbonyl moiety with a local C_{4v} symmetry observed for octahedral complexes of the type [W(CO)$_5$L] (Fig. 1). The v (C≡O) bands in the

same region as those of **2** have been observed in the IR spectrum of the μ-diphenylsilylene-bis(pentacarbonyltungsten) compound, formed in photochemical reaction of $W(CO)_6$ and Ph_2SiH_2 (KBr disc: 2098 (s), 2056 (vs), 2032 (s), 2020 (w), 2007 (s), 1975 (vs), 1956 (vs), and 1948 (vs) cm^{-1}) [9]. For an analogous pentacarbonyl moiety in the μ-dichlorogermylene compound $[(\mu\text{-}GeCl_2)\{W(CO)_5\}_2]$, the v (C≡O) bands have been observed in KBr disc at 2112 (w), 2071 (s), 2042 (w), 1993 (s,sh), 1969 (vs), and 1943 (s,sh) cm^{-1}[37]. In the ^{13}C NMR spectrum of **2** five carbonyl ligands give two signals at δ 197.8 ($^1J_{W–C} = 137$ Hz) and 197.3 ($^1J_{W–C} = 118$ Hz) in the intensity ratio 1:4, which is in agreement with the presence of four mutually *trans* carbonyl ligands and one carbonyl group *cis* to the former but having a ligand in the *trans* position with a weaker π-accepting ability than the carbonyl ligands, i.e. the silicon ligand. Very similar carbonyl carbon resonances have been detected in the ^{13}C NMR spectrum of $[(\mu\text{-}SiPh_2)\{W(CO)_5\}_2]$ (δ 197.04 ($^1J_{W–C} = 137$ Hz, 1CO) and 197.00 ($^1J_{W–C} = 119$ Hz, 4CO)) [9], but slightly shifted to the high field in the NMR spectrum of $[(\mu\text{-}GeCl_2)\{W(CO)_5\}_2]$ (δ 194.5 ($^1J_{W–C} = 147$ Hz, 1CO) and 192.9 ($^1J_{W–C} = 119$ Hz, 4CO)) [37]. The $^{29}Si\{^1H\}$ NMR spectra (toluene-d_8) show a resonance at $\delta = 239$ ($^1J_{Si–W} = 49$ Hz). The larger downfield chemical shift of silicon resonance compared with that observed for the silyl compound **1** supports the silylene character of the silicon ligand in **2**. This chemical shift is a little more downfield than observed for a tungsten dimer singly bridged by a silylene $SiPh_2$ ligand ($\delta = 211$, $^1J_{Si–W} = 55$ Hz) [9]. In ^{29}Si NMR spectrum the signal at $\delta = 239$ was observed as a quintet of septets with the silicon–hydrogen coupling constant for the $Si–CH_2CH_3$ moiety ($^2J_{Si–H} = 15.3$ Hz and $^3J_{Si–H} = 6.1$ Hz).

2.5. Spectroscopic characterization of intermediate compounds

To characterize the unstable η²-silane compound **A**, a solution of $W(CO)_6$ and diethylsilane in cyclohexane-d_{12} was periodically irradiated in the NMR tube and then analyzed by ^{1}H NMR spectroscopy at 15 °C. After prolonged irradiation under such conditions, three hydride signals, at $\delta = -7.71$, -7.77 ($^1J_{W–H} = 36$ Hz), and -9.28, appeared and increased to reach an intensity ratio of ca. 1:3:6. The intensity of these signals was too low to observe ^{29}Si satellites. The two lower-field signals disappeared at room temperature, but the one at $\delta = -9.28$, attributed to **1**, was stable. Better results were obtained in photochemical reaction carried out in methylcyclohexane-d_{14} solution at -10 °C, subsequently analyzed at temperatures ranging from -10 °C to -50 °C (Fig. 5). The ^{1}H NMR spectrum at -40 °C clearly revealed two signals as doublets with $^2J_{H–H} = ca.$ 10 Hz and the intensity ratio 1:1 at $\delta = 5.10$ and $\delta = -8.05$. The low-field resonance is a partially resolved doublet of quintets with $^2J_{H–H} = 10$ Hz and $^3J_{H–H} = 3$ Hz. The ^{29}Si satellites on this resonance provided the
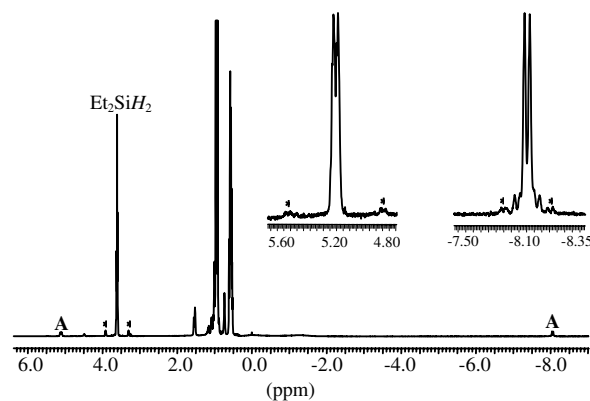

Fig. 5. ^{1}H NMR spectrum (300 MHz, methylcyclohexane-d_{14}, -40 °C) showing proton signals of intermediate η²-silane complex $[W(CO)_5(\eta^2\text{-}H\text{–}SiHEt_2)]$ (**A**) formed during the irradiation of $W(CO)_6$ and Et_2SiH_2 solution in methylcyclohexane-d_{14} at -10 °C. The proton signals at $\delta = 5.10$ and $\delta = -8.05$ denoted by **A** are presented with the scale expansion. Asterisked signals represent ^{29}Si satellites. The signal at $\delta = 3.60$ is due to H–Si bonds of free diethylsilane.

$^1J_{Si–H}$ value of 217 Hz, which allowed the correct assignment of this signal to the silyl $SiHEt_2$ moiety of the η²-silane complex. The higher-field resonance at $\delta = -8.05$ is a very well-resolved doublet with $^2J_{H–H} = 10$ Hz. The ^{29}Si satellites on the latter hydride signal provided the $^1J_{Si–H}$ value of 93 Hz, which is in a similar range as has recently been observed for similar η²-silane compounds ($^1J_{Si–H} = 98$ Hz for $[W(CO)_5(\eta^2\text{-}H\text{–}SiHPh_2)]$) [11], proving the correct assignment of this signal to the η²-H–SiHEt$_2$ moiety of the η²-silane complex. The ^{183}W satellites on the hydride signal allowed us to calculate the $^1J_{W–H} = 38$ Hz, which is very close to those observed for other α-agostic hydrides [10,11,20,21,38]. Based on these data, the signal can be assigned without a doubt to the intermediate compound $[W(CO)_5(\eta^2\text{-}H\text{–}SiHEt_2)]$ (**A**) (Scheme 1). It must be noted that the very low-intensity resonances characteristic of compound **A** were also detected in the ^{1}H NMR spectrum of the post-reaction mixture in toluene-d_8 solution even at room temperature ($\delta = -7.60$ in Fig. 3 and a resonance at $\delta = 5.02$, which is not seen here). This observation confirmed our earlier expectation that the formation of compound **A** could also be observed by IR spectroscopy. The η²-silane compound **A** characterized by a v (C≡O) band at 2086 cm^{-1} transforms to the more stable ditungsten compound **B** containing a μ-η²-H–SiEt$_2$ ligand detected due to a v (C≡O) band at 2071 cm^{-1} (Fig. 1). The binuclear dihydride complex **B**, probably formed as a result of the addition of a pentacarbonyl moiety to the initially generated η²-silane complex **A** (Scheme 1), was identified by ^{1}H NMR spectroscopy as containing a bridging hydride and η²-H–SiEt$_2$ ligands (Fig. 3). The pentacarbonyl moiety of compound **B** was detected by ^{13}C NMR spectroscopy, which revealed two carbonyl carbon resonances in the intensity ratio 4:1 at $\delta = 196.79$ ($^1J_{W–C} = 119$ Hz, 4CO) and 196.58 (1CO), respectively (Fig. 2). In the region of the ^{13}C NMR spectra

very close to the latter, two other carbonyl carbon resonances (δ 197.76 (1CO) and 197.32 (4CO)), assigned to the pentacarbonyl moiety of compound **2**, are always present. The pentacarbonyl compounds **A**, **B**, and **2** show very different reactivity and stability. Based on the IR and ^{13}C NMR spectroscopic data of freshly isolated samples, the approximate yield of compound **2** is in the range 50–80% and that of compound **1** in the range 10–20%. Compound **2** is stable enough even in the presence of such reagents (L) as olefins, water, and acetone, whereas **A** and **B** transform very easily to give new compounds of the type [W(CO)$_5$L] and eventually **1** and/or **2**.

As was shown by ^{29}Si{^{1}H} NMR spectroscopy, the photochemical reaction of W(CO)$_6$ with diethylsilane yielded a mixture of at least four tungsten silicon complexes characterized by ^{29}Si resonances at $\delta = 271$, 239, 214, and 184 ppm. The chemical shift of silicon resonances compared to those observed for the parent silane suggests a different degree of silylene character of the silicon ligand, from very high ($\delta = 271$) to rather small, as in **1** ($\delta = 184$). Only two signals, at $\delta = 184$ and 239 ppm, were assigned without a doubt to compounds **1** and **2**, respectively. The other two signals were too low-intensity and too broad to observe the tungsten satellites or the silicon–hydrogen coupling, making the correct assignment difficult. However, it is very probable that the signal at $\delta = 214$ is due to compound **B**. The observation of the ^{29}Si signal at $\delta = 271$ implies the existence in the reaction mixture of a compound with a terminal silylene ligand, which eventually weakly interacts with the hydride ligand, in a similar way as in [Cp*(CO)$_2$(μ-H)W=Si(H)C(SiMe$_3$)$_3$], for which a ^{29}Si signal has been observed at $\delta = 275.3$ [19].

In the ^{13}C NMR spectra, several carbonyl carbon signals: δ 213.3 ($^1J_{W-C} = 128$ Hz), 210.7 ($^1J_{W-C} = 187$ Hz), 204.7 ($^1J_{W-C} = 128$ Hz), 202.0, 189.8 ($^1J_{W-C} = 125$ Hz), and 188.4 ppm (Fig. 2), were difficult to assign. The relative intensities of the latter signals were different from one sample to another in a way that was hard to control. However, after analysis of numerical ^{13}C NMR spectra measured in toluene-d_8 solution, we noticed that the carbon resonance at $\delta = 210.7$ may originate from the tricarbonyl complex containing η^6-toluene-d_8 in the coordination sphere [39–41]. This supposition was confirmed by the detection of carbon resonances due to η^6-coordinated toluene-d_8 at δ 108.6 (s, 1C-1), 91.9 (t, 2C-3), 89.9 (t, 2C-2), 86.0 (t, 1C-4), and 20.5 (CD$_3$) ppm. The fact that carbonyl carbon signals identical to the latter were detected in all the investigated reactions carried out in toluene-d_8 corroborate the conclusion that the coordinatively unsaturated carbonyl species of tungsten, formed as a result of reductive elimination processes during hydrosilylation, hydrogenation, or dehydrogenative coupling, are stabilized by the η^6 coordination of the solvent (toluene-d_8). For comparison, in the ^{13}C NMR spectrum of CDCl$_3$ solution of the complex [W(CO)$_3$(η^6-toluene)], the carbon resonances had earlier been observed at 209.9 (3CO), 109.0 (C-1), 92.0 (2C-3), 89.8 (2C-2), 86.9 (1C-4), and 20.7 (Me) ppm [41].

2.6. Reactivity of photochemically generated tungsten–silicon compounds

In an attempt to establish whether photochemically generated W–Si compounds could take part in hydrosilylation processes, their reactivity towards norbornene, cyclopentene, diphenylacetylene, acetone, and water was studied. In photochemical experiments monitored by IR spectroscopy, it was found that the presence of olefin, such as norbornene (NBE) or cyclopentene (CP), in n-heptane solution containing W(CO)$_6$ and Et$_2$SiH$_2$ effectively inhibited the formation of compounds **A** and **B** because the photochemically generated pentacarbonyl species was trapped by the olefin to give a more stable complex of the type [W(CO)$_5$(η^2-olefin)] [42]. Simultaneously, the ring-opening metathesis polymerization (ROMP) of NBE and CP was initiated [43]. As was observed by ^{1}H and ^{13}C NMR spectroscopy, all NBE used in such reactions was transformed to poly-1,3-cyclopentylenevinylene (poly-NBE), the trans (60%) and the cis (40%) ROMP polymers. However, complexes **1** and **2** were always detected in the post-reaction mixture. In an experiment in which NBE was added to photochemically generated W–Si compounds in n-heptane solution, a very fast decay of the v (C≡O) band at 2086 cm^{-1}, assigned to **A**, and the appearance of a v (C≡O) band at 2078 cm^{-1}, characteristic for [W(CO)$_5$(η^2-NBE)], were observed [42]. That experiment proved that the η^2-silane ligand in the pentacarbonyl complex **A** was displaced by the η^2-olefin ligand (Scheme 2). In the ^{1}H NMR spectrum, the highest-intensity proton signals were due to the η^2-NBE ligand of [W(CO)$_5$(η^2-NBE)] and the lower-intensity signals were assigned to poly-NBE containing trans (Pt) and cis (Pc) configuration of olefin units; the proton resonance at $\delta = 4.78$ (quintet, $^3J_{H-H} = 2$ Hz, $^1J_{Si-H} = 200$ Hz) may be assigned to the hydrolysis product of silane; no other hydride signals besides that at −9.29 ppm, assigned to **1**, were detected (Fig. 6). In the ^{13}C NMR spectrum of the latter sample, the carbonyl carbon signals of [W(CO)$_5$(η^2-NBE)] were more intense than those of **1** and **2**. Calculating the intensities of the carbonyl carbon signals of the three compounds: [W(CO)$_5$(η^2-NBE)], **2**, and **1**, the respective molar ratio ca. 8:2:1 was obtained. However, within a few
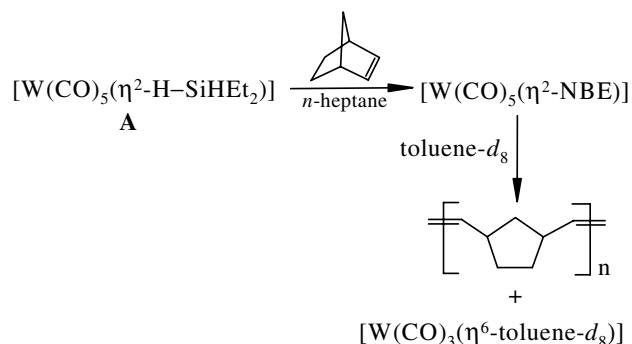
Scheme 2. Conversion of the η^2-silane complex [W(CO)$_5$(η^2-H–SiHEt$_2$)] in the presence of norbornene (NBE).
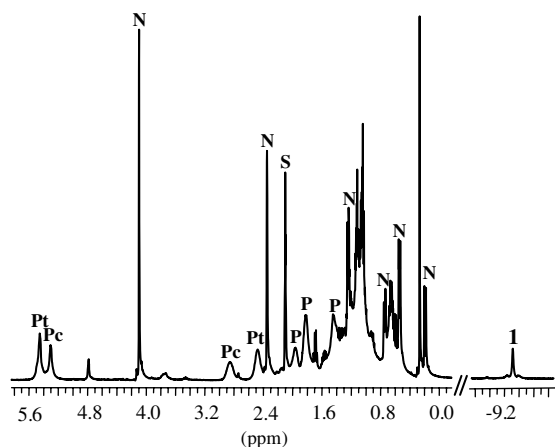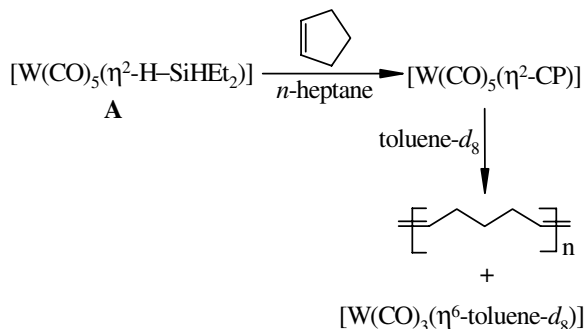
Fig. 6. ^{1}H NMR spectrum (500 MHz, 25 °C, toluene-d_8) showing the formation of [W(CO)$_5$(η^2-NBE)] (N) and poly-1,3-cyclopentylenevinylene (P) containing *trans* (Pt) and *cis* (Pc) olefin units. The signal at $\delta = -9.29$ is due to complex **1**. Signal at $\delta = 2.1$ denoted by **S** is due to the methyl group of solvent.

Fig. 7. ^{13}C{^{1}H} NMR spectrum (125 MHz, toluene-d_8, −30 °C) showing the formation of the [W(CO)$_5$(η^2-CP)] complex (asterisked signals) in reaction of cyclopentene with W–Si compounds formed during the photochemical reaction (4 h) at 25 °C. Signals denoted by **1** are due to the compound [{W(μ-η^2-H–SiEt$_2$)(CO)$_4$}$_2$] (**1**), those denoted by **2** are due to [(μ-SiEt$_2$){W(CO)$_5$}$_2$] (**2**), and the one at $\delta = 191.04$ is due to W(CO)$_6$. Signal at $\delta = 20.4$ denoted by (s) is due to the methyl carbon of solvent.

days the resonances assigned to the compound [W(CO)$_5$(η^2-NBE)] decayed, whereas an increase of signals due to poly-NBE was detected. Simultaneously, a carbonyl carbon resonance at $\delta = 210.7$, assigned to [W(CO)$_3$(η^6-toluene-d_8)], reached an intensity close to that of the one at $\delta = 197.8$ (1CO), assigned to **2**.

A similar effect to that of NBE was observed when cyclopentene (CP) was added to the photochemically generated W–Si compounds in *n*-heptane solution (Scheme 3). In IR spectra, the decay of the *v* (C≡;O) band at 2086 cm^{-1}, assigned to **A**, and the appearance of a *v* (C≡O) band at 2080 cm^{-1}, characteristic for [W(CO)$_5$(η^2-CP)], were observed [42]. The investigation of the latter sample by NMR spectroscopy made it possible for the first time to characterize a very labile pentacarbonyl η^2-CP complex. In the ^{13}C NMR spectrum, the most intense carbonyl carbon signals were due to the pentacarbonyl unit of the [W(CO)$_5$(η^2-CP)] complex at $\delta = 200.5$ (1CO) and 197.1 (4CO), but other, less intense signals in the carbonyl carbon region, assigned to compounds **1**, **2**, and [W(CO)$_3$(η^6-toluene-d_8)], were also detected (Fig. 7).

Scheme 3. Transformation of the η^2-silane complex [W(CO)$_5$(η^2-H–SiHEt$_2$)] in the presence of cyclopentene (CP).

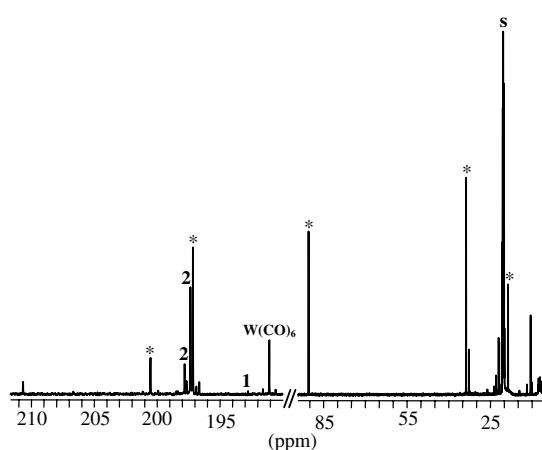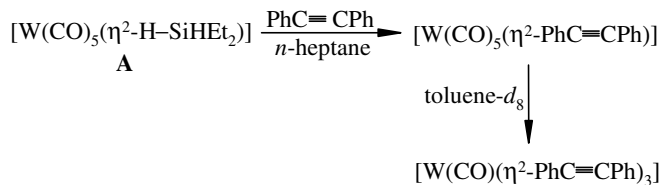Monitoring of the reaction of CP, added to the chloroform-d_1 solution of W–Si complexes isolated from the *n*-heptane solution, by ^{1}H NMR spectroscopy showed the immediate decay of the hydride signals assigned to **B**, and the appearance of proton signals of the η^2-cyclopentene ligand in the pentacarbonylolefin complex of the type [W(CO)$_5$(η^2-CP)]. However, the latter compound is very labile in chloroform-d_1 solution and rearranges to initiate the ROMP reaction [43]. The NMR characterization of the ROMP polymer was almost identical to that described by Dragutan et al. [44].

As was observed by IR spectroscopy, the addition of diphenylacetylene to an *n*-heptane solution of photochemically formed W–Si complexes resulted in the decay of a relatively strong *v* (C≡O) band at 2086 cm^{-1}, assigned to **A**, and the appearance of a weaker *v* (C≡O) band at 2085 cm^{-1}, characteristic for the compound [W(CO)$_5$(η^2-PhC≡CPh)], with a simultaneous slight increase in the intensity of *v* (C≡O) bands assigned to compounds **1** and **2** (other *v* (C≡O) bands of a pentacarbonyl moiety with a C_{4v} local symmetry overlapped due to the absorption of other species). As has been observed before, the pentacarbonylalkyne complexes are very thermally unstable [45]. For that reason the identification of the IR spectrum of [W(CO)$_5$(η^2-PhC≡CPh)] was possible after comparison with a sample prepared in photochemical reaction of W(CO)$_6$ with PhC≡CPh in *n*-heptane solution at −10 °C. However, the latter compound was unidentifiable by NMR spectroscopy. In the NMR spectra of the post-reaction mixture in toluene-d_8 solution, besides resonances assigned to **1** and **2**, new ones were detected (Scheme 4). In the ^{13}C NMR spectrum, carbon signals due to the diphenylacetylene complex [W(CO)(η^2-PhC≡CPh)$_3$] were detected at $\delta = 220.6$ (CO), 192.7 (PhC≡), 174.3 (PhC≡),

$$[W(CO)_5(\eta^2\text{-H–SiHEt}_2)] \xrightarrow[\text{n-heptane}]{\text{PhC} \equiv \text{CPh}} [W(CO)_5(\eta^2\text{-PhC} \equiv \text{CPh})]$$
$$\mathbf{A}$$

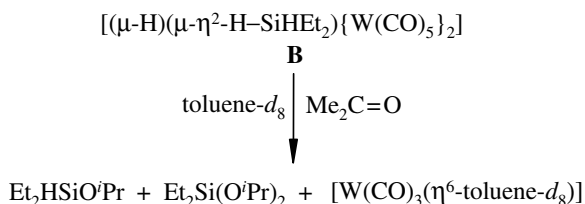$$\downarrow \text{toluene-}d_8$$

$$[W(CO)(\eta^2\text{-PhC} \equiv \text{CPh})_3]$$

Scheme 4. Rearrangement of the η^2-silane complex $[W(CO)_5(\eta^2\text{-H–SiHEt}_2)]$ in the presence of diphenylacetylene $PhC \equiv CPh$.

141.1, and 139.0 (C-1, Ph) [46–48]. As has been observed earlier, the latter compound could be formed as the product of transformation of a thermally very unstable pentacarbonyl compound of the type $[W(CO)_5(\eta^2 - RC \equiv CR')]$ [49].

Photolysis of a cyclohexane-d_{12} solution of $W(CO)_6$, Et_2SiH_2, and acetone in a NMR tube made it possible to observe, by means of ^1H NMR spectroscopy, the decay of acetone and the appearance of its hydrosilylation product, $Et_2HSiOCHMe_2$, detected due to two signals in a 1:1 intensity ratio at $\delta = 4.60$ (quintet, $^1J_{Si–H} = 201$ Hz, $^3J_{H–H} = 2.3$ Hz, H–Si) and $\delta = 4.14$ (septet, $^3J_{H–H} = 5.6$ Hz, H–C) and a six-times-higher-intensity doublet at $\delta = 1.16$ (d, $^3J_{H–H} = 5.6$ Hz, Me, [50]).

Treatment with acetone of toluene-d_8 solution of W–Si complexes freshly prepared in n-heptane solution and subsequent analysis of the reaction products by means of ^1H NMR spectroscopy revealed the instantaneous decay of hydride signals assigned to compound **B** and the appearance of proton signals due to hydrosilylation products of acetone, $Et_2HSiOCHMe_2$, and $Et_2Si(OCHMe_2)_2$. The molar ratio of the latter compounds changed over time, and only the last one was detected after a few days (Scheme 5). In the ^{13}C NMR spectrum of the latter sample, the carbonyl carbon resonances assigned to compounds **1** and **2** and to $[W(CO)_3(\eta^6\text{-toluene-}d_8)]$ were detected. In the higher field of the ^{13}C NMR spectrum, carbon signals of the hydrosilylation product were observed [50].

A very interesting effect of water on the selectivity of products formed in photochemical reaction of $W(CO)_6$ and Et_2SiH_2 was observed. In reaction carried out in the presence of a 1:1 stoichiometric amount of H_2O, only two hydride complexes: the compound **1** and another hydride, characterized by a signal at $ca. -3$ ppm in the respective intensity ratio 58:1, were detected by the ^1H NMR spectroscopy. As was observed by GC–MS analysis and ^1H NMR spectroscopy of the post-reaction mixture, silane was transformed mainly to polysilanes and siloxanes [51].

$$[(\mu\text{-H})(\mu\text{-}\eta^2\text{-H–SiHEt}_2)\{W(CO)_5\}_2]$$
$$\mathbf{B}$$

$$\downarrow \text{toluene-}d_8 \quad Me_2C=O$$

$$Et_2HSiO^iPr + Et_2Si(O^iPr)_2 + [W(CO)_3(\eta^6\text{-toluene-}d_8)]$$

Scheme 5. Conversion of $[(\mu\text{-H})(\mu\text{-}\eta^2\text{-H–SiEt}_2)\{W(CO)_5\}_2]$ (**B**) in the presence of acetone in toluene-d_8 solution.

2.7. Consideration of the formation mechanism of tungsten–silicon complexes

A possible mechanistic pathway for the photochemical conversion of $W(CO)_6$ in the presence of Et_2SiH_2 is shown in Scheme 1. Photochemical dissociation of a CO ligand from $W(CO)_6$ gives a coordinatively unsaturated transient $W(CO)_5$ species, which coordinates the Si–H bond of Et_2SiH_2 in η^2-fashion to give the thermally unstable compound **A**, as was observed by IR and ^1H NMR spectroscopy in an early stage of the reaction at a low temperature. Complex **A** can transform in two ways. One plausible route involves the addition of a pentacarbonyl moiety to the initially generated η^2-silane complex **A** and the formation of the thermally unstable binuclear complex **B**, containing a μ-hydride and a μ-η^2-H–SiEt$_2$ ligand. In the latter compound, each tungsten atom is formally in the first oxidation state stabilized by the formation of a W–W bond. The thermal release of the dihydrogen molecule from compound **B** leads to the formation of the more stable μ-diethylsilylene compound **2**. The highest yield of compound **B** was obtained during photolysis at the temperature of -10 °C, but compound **2** was obtained with higher yields in reaction carried out at room temperature.

The conversion of the η^2-silane complex **A** to **1** involves a release of the CO ligand and the dimerization of the coordinatively unsaturated tungsten compound, followed by the reductive elimination of the dihydrogen molecule. The transformation of **A** to **1** takes place even in the dark and at a low temperature. For that reason, compound **1** has rarely been detected by IR spectroscopy during photolysis at a low temperature (-10 °C), which stabilized complexes **A** and **B**. Higher yields of compound **1** tended to be observed in room temperature reactions and in the solid residue obtained after evaporation of the solvent.

2.8. Summary and conclusions

We have shown that photochemical reaction of $W(CO)_6$ in n-heptane creates a coordinatively unsaturated d^6 species which interacts with the Si–H bonds of Et_2SiH_2 in η^2 fashion. The initially formed thermally unstable η^2-silane complex $[W(CO)_5(\eta^2\text{-H–SiHEt}_2)]$ was observed by IR and ^1H NMR spectroscopy at a low temperature. The latter intermediate complex rearranges to give certain tungsten–silicon complexes. The reaction has been found to proceed via activation of the Si–H bond of Et_2SiH_2 and the formation of a W–H bond. Several hydride complexes were identified by ^1H NMR spectroscopy. The singlet at $\delta = -9.31$ flanked by ^{29}Si and ^{183}W satellites ($^1J_{W–H} = 40$ Hz, $^1J_{Si–H} = 43$ Hz, $^2J_{Si–H} = 34$ Hz) was assigned to the agostic proton of the $W(\eta^2\text{-H–SiEt}_2)$ group in the most stable compound isolated in crystalline form from the mixture of products. The latter compound was examined by X-ray diffraction studies, which established a structure identical to that detected by Bennett and Simpson for $[\{W(\mu - \eta^2\text{-H–SiEt}_2)(CO)_4\}_2]$ in 1971 [15], and analogous

to that recently observed for the molybdenum complex $[\{Mo(\mu\text{-}\eta^2\text{-}H\text{–SiEt}_2)(CO)_4\}_2]$ [16]. The tungsten hydride observed in the ^{1}H NMR spectrum at $\delta = -9.31$ was located in the structure at a position between the W and Si atoms of the W–Si bond of the bridging silyl ligand with a Si–H bond length of 1.54(2) Å and that of the W–H bond amounting to 1.78 Å.

Another thermally stable dinuclear compound of tungsten formed in the above photochemical reaction was fully characterized by IR and NMR spectroscopic methods as the μ-silylene complex $[(\mu\text{-SiEt}_2)\{W(CO)_5\}_2]$. Although some W–Si compounds have been characterized, some others remain mysterious and unidentifiable because of their thermal interconversion.

It has been shown that the η^2-silane ligand in $[W(CO)_5(\eta^2\text{-}H\text{–SiHEt}_2)]$ is very easily replaced by η^2-olefin and η^2-alkyne ligands. The photochemically generated W–Si compounds take part in hydrosilylation of acetone.

3. Experimental

3.1. General considerations

The synthesis and all operations were conducted under an atmosphere of nitrogen using standard Schlenk techniques. Solvents and liquid reagents were predried with CaH_2 and vacuum transferred into small storage flasks prior to use. IR spectra were measured with a Nicolet 400 FT-IR instrument. ^{1}H NMR spectra were recorded with a Bruker AMX 300 or 500 MHz instrument. ^{13}C, ^{29}Si, and two-dimensional ^{1}H–^{1}H COSY NMR spectra were recorded with a Bruker AMX 500 MHz instrument at 500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C, and 99.36 MHz for ^{29}Si. ^{13}C and ^{29}Si NMR experiments were performed using gated coupled spectra to obtain coupling constants. All proton and carbon chemical shifts were referenced to the residual proton signal for ^{1}H NMR (δ 7.24 CDCl$_3$, 1.40 C$_6$D$_{12}$, and 2.1 toluene-d_8) or the natural abundant carbon signal of the solvent for ^{13}C NMR (δ 77.0 CDCl$_3$ and 20.4 toluene-d_8). ^{1}H chemical shifts measured in methylcyclohexane-d_{14} as the solvent were referenced relative to SiMe$_4$. The photolysis source was an HBO 200 W high-pressure Hg lamp.

3.2. Photochemical generation of tungsten–silicon compounds

A solution of W(CO)$_6$ (0.10 g, 0.28 mmol) and Et$_2$SiH$_2$ (0.05 cm^3, 0.39 mmol) in freshly distilled *n*-heptane (40 cm^3) was irradiated through quartz at $-10\,°$C or 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^{-1} reached its minimum intensity (2–4 h) and a new v (C≡O) frequency at 2098, 2086, 2055, 2044, and 2016 cm^{-1} increased. All volatile materials were then evaporated under reduced pressure at room temperature, which resulted in a

color change from yellow to orange. The resulting orange solid was analyzed by IR and NMR spectroscopy. A sample prepared at $-10\,°$C and freshly analyzed by the ^{1}H NMR method at $-30\,°$C in toluene-d_8 solution showed the presence of hydride compounds characterized by signals at $\delta = -7.62$ (d, $^2J_{H-H} = 9$ Hz), -7.66 (s, $^1J_{W-H} = 35$ Hz), -8.25 (d, $^2J_{H-H} = 5.2$ Hz, $^1J_{W-H} = 35$ Hz, $^1J_{Si-H} = 37$ Hz), -9.02 (s, $^1J_{W-H} = 38$ Hz), -9.31 (s, $^1J_{W-H} = 40$ Hz, $^1J_{Si-H} = 43$ Hz, $^2J_{Si-H} = 34$ Hz), -10.28 (s, $^1J_{W-H} = 44$ Hz), -10.39 (d, $^2J_{H-H} = 5.2$ Hz, $^1J_{W-H} = 32$ Hz) and -11.39 (s). A signal at $\delta = 5.02$ (d, $^2J_{H-H} = 10$ Hz) was of comparable intensity as that at $\delta = -7.62$. The lower-field proton signals which appeared in the range 4.89–4.74 ppm as quintets with $^3J_{H-H} = ca.$ 2 Hz, $^1J_{Si-H} = ca.$ 200 Hz were assigned to products of dehydrogenative coupling and hydrolysis of silane [51]. A mixture of yellow crystalline compounds, $[\{W(\mu\text{-}\eta^2\text{-}H\text{–SiEt}_2)(CO)_4\}_2]$ (**1**) and $[(\mu\text{-SiEt}_2)\{W(CO)_5\}_2]$ (**2**), was obtained by cooling a saturated *n*-heptane solution to *ca.* $-10\,°$C.

Spectral data for **1**: IR (v, cm^{-1}): (*n*-heptane): v (C≡O) 2044 (s), 1998 (s), 1976 (s), 1936 (s). ^{1}H NMR (toluene-d_8, $-30\,°$C): $\delta = 1.16$ (t, $^3J_{H-H} = 7.8$ Hz; 6 H, CH$_2$Me), 0.63 (q, $^3J_{H-H} = 7.8$ Hz; 4H, CH$_2$Me), -9.31 (s, 1 H; $^1J_{W-H} = 40$ Hz, $^1J_{Si-H} = 43$ Hz, $^2J_{Si-H} = 34$ Hz). ^{13}C NMR (toluene-d_8, $-30\,°$C): $\delta = 206.7$ ($^1J_{W-C} = 117$ Hz, 1CO), 199.9 ($^1J_{W-C} = 129$ Hz, 1CO), 192.7 ($^1J_{W-C} = 123$ Hz, 2CO), 7.2 (t, $^1J_{C-H} = 117$ Hz, $^1J_{Si-C} = 61$ Hz, CH$_2$Me), 6.9 (q, $^1J_{C-H} = 125$ Hz, CH$_2$Me). ^{29}Si{^{1}H} NMR (toluene-d_8): $\delta = 184$.

Spectral data for **2**: IR (v, cm^{-1}): (*n*-heptane) v (C≡O) 2098 (m), 2055 (s), 1959 (vs); (KBr) v (C≡O) 2098 (s), 2055 (s), 1963 (vs), 1943 (vs), δ (WCO) 591 (w), 566 (w). ^{13}C NMR (toluene-d_8, $-30\,°$C: $\delta = 197.8$ ($^1J_{W-C} = 137$ Hz, 1CO), 197.3 ($^1J_{W-C} = 118$ Hz, 4CO). ^{29}Si NMR (toluene-d_8): $\delta = 239$ ($^1J_{W-Si} = 49$ Hz, $^2J_{Si-H} = 15.3$ Hz, $^3J_{Si-H} = 6.1$ Hz).

3.3. NMR tube reactions: identification of $[W(\eta^2\text{-}H\text{–SiHEt}_2)(CO)_5]$ (A)

A solution of W(CO)$_6$ (0.01 g, 0.028 mmol) and Et$_2$SiH$_2$ in cyclohexane-d_{12} (0.5 cm^3) at 15 °C or in methycyclohexane-d_{14} at $-10\,°$C was periodically irradiated and analyzed by ^{1}H NMR spectroscopy over a period of several hours. In cyclohexane-d_{12} at 15 °C, two broad, very low-intensity signals at $\delta = -7.71$ and -7.77 ppm were observed, which decayed in the dark with the appearance of a new proton signal at $\delta = -9.28$, characteristic for compound **1**. In photochemical reaction carried out in methylcyclohexane-d_{14} solution at $-10\,°$C and then analyzed at temperatures ranging from -10 to $-50\,°$C, ^{1}H NMR spectra (300 MHz, methylcyclohexane-d_{14}, $-50\,°$C) revealed two signals as doublets in the intensity ratio 1:1 at $\delta = 5.10$ (doublet of quintets, $^2J_{H-H} = 10$ Hz, $^3J_{H-H} = 3$ Hz, $^1J_{Si-H} = 217$ Hz) and $\delta = -8.05$ (d, $^2J_{H-H} = 10$ Hz, $^1J_{W-H} = 38$ Hz $^1J_{Si-H} = 93$ Hz). In the ^{1}H–^{1}H COSY NMR spectra the set of Si–H bond resonance at $\delta = 5.10$ correlated to the

proton resonance at $\delta = -8.05$ and ca. 1 ppm (Si–CH$_2$). These signals decayed in the dark with the appearance of proton signals at $\delta = -8.46$ (d, $^2J_{H-H} = 5.4$ Hz), -9.18 (s), -9.41 (s), -10.47 (s), -10.51 (d, $^2J_{H-H} = 5.4$ Hz). The intensity ratio of these signals depended upon the aging time of the sample with the preference increase of the signal at $\delta = -9.41$ assigned to **1**.

3.4. Reaction of photochemically generated W–Si compounds with NBE monitored by IR spectroscopy in n-heptane solution

A solution of W(CO)$_6$ (0.10 g, 0.28 mmol) and Et$_2$SiH$_2$ (0.05 cm^3, 0.39 mmol) in *n*-heptane (40 cm^3) was irradiated at room temperature. After 4.5 h of photolysis, when the IR spectrum showed the almost complete decay of W(CO)$_6$ and the appearance of ν (C≡O) bands characteristic for the W–Si compounds **A** and **2**, NBE (0.05 g, 0.53 mmol) was added and the solution was stirred for 30 min at room temperature. The course of the reaction was monitored by IR measurements in solution, showing the decay of the ν (C≡O) band at 2086 cm^{-1}, characteristic for the W–Si compound **A**, and the appearance within 15 min of a high intensity band at 2078 cm^{-1}, due to [W(CO)$_5$(η^2-NBE)] [42], and low intensity bands at 2071 and 2044 cm^{-1}, due to compounds **B** and **1**, respectively. After 30 min, volatiles were removed in vacuum without warming and the remaining residue was extracted with toluene-d_8 (0.5 cm^3) and analyzed by NMR spectroscopy. ^{1}H NMR (toluene-d_8, 25 °C): $\delta = 5.45$ (*trans*-HC=CH, 60%), 5.30 (*cis*-HC=CH, 40%), 2.86 (*cis*, CH), 2.47 (*trans*, CH), 1.96 (CH$_2$), 1.81 (CH$_2$), 1.45 (CH$_2$), poly-NBE; 4.09 (s, 2H, HC=CH), 2.35 (s, 2H, CH), 1.24 (d, 2H, CH$_2$), 0.75 (d, 1H, CH$_2$), 0.55 (d, 2H, CH$_2$), 0.20 (d, 1H, CH$_2$) [W(CO)$_5$(η^2-NBE)]) [42], $\delta = -9.29$ (**1**).

3.5. Photochemical reaction of W(CO)$_6$, Et$_2$SiH$_2$, and NBE in n-heptane

A solution of W(CO)$_6$ (0.10 g, 0.28 mmol), Et$_2$SiH$_2$ (0.05 cm^3, 0.39 mmol), and NBE (0.03 g, 0.32 mmol) in *n*-heptane (50 cm^3) was irradiated at -10 °C. After 4 h of photolysis, the IR spectrum showed the almost complete decay of W(CO)$_6$ and the appearance of ν (C≡O) bands characteristic for W–Si compounds observed earlier in the reaction without NBE (see above) and an additional ν (C≡O) band at 2078 cm^{-1}, characteristic of [W(CO)$_5$-(η^2-NBE)] [42]. ^{1}H NMR (δ, toluene-d_8, 25 °C): resonances of poly-NBE (see above); very low intensity signals of [W(CO)$_5$(η^2-NBE)]) and of **1**.

3.6. Reaction of photochemically generated W–Si compounds with cyclopentene (CP) monitored by IR spectroscopy in n-heptane solution

A solution of W(CO)$_6$ (0.10 g, 0.28 mmol) and Et$_2$SiH$_2$ (0.05 cm^3, 0.39 mmol) in *n*-heptane (40 cm^3)

was irradiated at -10 °C. After 3.5 h of photolysis, when the IR spectrum showed the almost complete decay of W(CO)$_6$ and the appearance of ν (C≡O) bands characteristic for the W–Si compounds **A** and **2**, CP (0.02 cm^3, 0.28 mmol) was added, and the solution was stirred for 30 min at room temperature. The course of the reaction was monitored by IR measurements in solution, showing the decay of the ν (C≡O) band at 2086 cm^{-1}, characteristic for the W–Si compound **A** and the appearance within 15 min of a high intensity band at 2080 cm^{-1}, due to [W(CO)$_5$(η^2-CP)] (two lower ν (C≡O) frequencies at ca. 1950 cm^{-1} overlap with the ν (C≡O) bands of other pentacarbonyl compounds), and low intensity bands at 2071 and 2044 cm^{-1}, due to compounds **B** and **1**, respectively. The ^{1}H NMR spectrum (toluene-d_8, -30 °C) showed the highest-intensity resonances due to protons of the η^2-CP ligand of the [W(CO)$_5$(η^2-CP)] complex, and low-intensity hydride signals of **B** and **1**, in the respective intensity ratio 64:1:17, were detected. In the ^{13}C NMR spectrum, besides the resonances of the [W(CO)$_5$(η^2-CP)] complex, signals of compounds **1** and **2**, and a signal at 210.63 ppm, due to [W(CO)$_3$(η^6-toluene-d_8)], were also detected.

Spectral data for [W(CO)$_5$(η^2-CP)]: IR (ν, cm^{-1}): (*n*-heptane) ν (C≡O) 2080 (w) (other obscured); (KBr) ν (C≡O) 2078 (m), 1928 (vs), δ (WCO) 600 (w), 581 (w); ^{1}H NMR (toluene-d_8, 500 MHz, -30 °C): $\delta = 4.15$ (s, 2H; HC-1,5), 2.05 (m, 2H), 1.99 (m, 2H), 1.60 (dt, 2H, $J_{H-H} = 8$ Hz); ^{13}C{^{1}H} NMR (toluene-d_8, 125 MHz, -30 °C): $\delta = 200.49$ (1CO, $^1J_{W-C} = 155$ Hz), 197.12 (4CO, $^1J_{W-C} = 127$ Hz), 90.40 (2C; C-1,5), 33.74 (2C; C-2,4), 18.65 (1C; C-3).

3.7. Reaction of W–Si compounds with CP monitored by ^{1}H NMR spectroscopy in CDCl$_3$ solution

One drop of cyclopentene was added via a microliter syringe to an NMR tube containing a mixture of W–Si compounds in chloroform-d_1 solution prepared, in a manner analogous to that described above. The result of the reaction, monitored by ^{1}H NMR spectroscopy at -30 °C, showed the instantaneous decay of two doublets, at δ -8.25 and -10.48 ppm, assigned to **B**, and the appearance of signals at δ 5.36 (s, 2H), 1.95 (m, 4H), 1.37 (m, 1H) and 1.28 (m, 1H), due to protons of η^2-cyclopentene in [W(CO)$_5$(η^2-CP)]. The hydride signals at δ -9.32 and two 1:1 intensity signals at δ -9.10 and -10.39 ppm did not change. In the ^{13}C NMR spectrum at -30 °C, the carbonyl carbon signals due to the [W(CO)$_5$(η^2-CP)] complex and signals of compounds **1** and **2** were detected. The initially observed [W(CO)$_5$(η^2-CP)] compound as well as free cyclopentene disappeared to give the ROMP polymer with characteristic signals at $\delta = 5.4$ and 2.0 ppm. ^{13}C{^{1}H} NMR of a polypentenamer (toluene-d_8, -30 °C): $\delta = 130.2$ (73%, *trans*-HC=CH), 129.7, 129.6 (27%, *cis*-HC=CH), 32.1, 29.7, 29.5, 29.3, 26.6, 29.7, 29.3 (CH$_2$).

3.8. Reaction of photochemically generated W–Si compounds with diphenylacetylene monitored by IR Spectroscopy in n-heptane solution

A solution of $W(CO)_6$ (0.10 g, 0.28 mmol) and Et_2SiH_2 (0.05 cm^3, 0.39 mmol) in *n*-heptane (40 cm^3) was irradiated at −10 °C. After 4 h of photolysis, when the IR spectrum showed the almost complete decay of $W(CO)_6$ and the appearance of v (C≡O) bands characteristic for the W–Si compounds **A** and **2**, diphenylacetylene (0.05 g, 0.28 mmol) was added as heptane solution. Periodic monitoring by IR spectroscopy at room temperature showed the decay of compound **A** and the initial increase in the intensity of bands assigned to compounds **B**, **1**, and **2**. $^{13}C\{^1H\}$ NMR (toluene-d_8, −30 °C): $\delta = 220.6$ (1CO), 192.7 (PhC≡), 174.3 (PhC≡), 141.1, 139.0 (C-1, Ph), other signals of $[W(CO)(\eta^2\text{-PhC}\equiv\text{CPh})_3]$ were obscured by carbon resonances of the solvent; carbon signals of **1** and **2** as above.

3.9. Hydrosilylation of acetone

A solution of $W(CO)_6$, acetone, and Et_2SiH_2 in cyclohexane-d_{12} at 15 °C was periodically irradiated and analyzed by ^1H NMR spectroscopy. The slow decay of acetone ($\delta = 1.99$) and the appearance of its hydrosilylation product Et_2H-SiOCHMe$_2$ was observed. ^1H NMR (cyclohexane-d_{12}, 25 °C): $\delta = 4.60$ (quintet, 1H, $^1J_{Si-H} = 201$ Hz, $^3J_{H-H} = 2.3$ Hz, H–Si), 4.14 (septet, 1H, $^3J_{H-H} = 5.6$ Hz; H–C), 1.16 (d, 6H, $^3J_{H-H} = 5.6$ Hz, Me), 0.98 (t, 6H, $^3J_{H-H} = 8$ Hz, Me), 0.54 (quintet, 4H, $^3J_{H-H} = 8$ Hz, CH$_2$).

4. Reaction of photochemically generated W–Si compounds with acetone

A solution of $W(CO)_6$ (0.10 g, 0.28 mmol) and Et_2SiH_2 (0.05 cm^3, 0.39 mmol) in *n*-heptane (40 cm^3) was irradiated at −10 °C. After 4 h of photolysis, when the IR spectrum showed the almost complete decay of $W(CO)_6$ and the appearance of v (C≡O) bands characteristic for the W–Si compounds **A** and **2**, the volatile materials were stripped off the reaction mixture under reduced pressure at room temperature and the residue was dissolved in toluene-d_8. The sample, analyzed by the ^1H NMR method at room temperature, showed the presence of hydride compounds characterized earlier as **B** and **1**. One drop of acetone was added to a solution of the W–Si compounds in an NMR tube via a microliter syringe. The result of the reaction, monitored by ^1H NMR spectroscopy at −30 °C, showed the instantaneous decay of proton signals assigned to **B** and the appearance of signals due to $Et_2HSiOCHMe_2$, and $Et_2Si(OCHMe_2)_2$.

NMR data of Et$_2$Si(OCHMe$_2$)$_2$ [50]: ^1H NMR (toluene-d_8, 25 °C): $\delta = 4.16$ (septet, 2H, $^3J_{H-H} = 6$ Hz; H–C), 1.22 (d, 12H, $^3J_{H-H} = 6$ Hz, Me), 1.01 (t, 6H, $^3J_{H-H} = 8$ Hz, Me), 0.63 (quintet, 4H, $^3J_{H-H} = 8$ Hz, CH$_2$). $^{13}C\{^1H\}$ NMR (toluene-d_8, 25 °C): $\delta = 64.7$ (2C, CH), 26.1 (4C, Me), 7.8 (2C, Me), 6.8 (2C, CH$_2$).

4.1. Photochemical reaction of W(CO)₆ and Et₂SiH₂ in n-heptane in the presence of H₂O

A solution of $W(CO)_6$ (0.10 g, 0.28 mmol), Et_2SiH_2 (0.05 cm^3, 0.39 mmol), and H_2O (0.01 cm^3, 0.56 mmol) in *n*-heptane (40 cm^3) was irradiated at room temperature. After 2.5 h of photolysis, the IR spectrum showed the almost complete decay of $W(CO)_6$ and the appearance of v (C≡O) bands characteristic for compound **1**. The volatile materials (solvent and unreacted $W(CO)_6$) were then removed under reduced pressure at room temperature and the residue dissolved in toluene-d_8. Analysis of the sample by ^1H NMR spectroscopy showed the presence of compound **1** ($\delta = -9.28$) and another hydride compound ($\delta = -2.98$, $^1J_{W-H} = 16$ Hz) in a ratio of *ca.* 1:1. The lower-field resonances were assigned to hydrolysis products of silane. ^1H NMR (toluene-d_8, −30 °C): $\delta = 4.81$ (quintet, $^3J_{H-H} = 2.5$ Hz, $^1J_{Si-H} = 199$ Hz, Si–H), 4.80 (quintet, $^3J_{H-H} = 2.5$ Hz, $^1J_{Si-H} = 199$ Hz, Si–H), 4.76 (quintet, $^3J_{H-H} = 2.5$ Hz, $^1J_{Si-H} = 203$ Hz, Si–H), 4.52 (s, O–H). GC–MS vapor analysis: ($C_8H_{22}Si_2O$, $M_r = 190.43$, m/z (relative intensity): 190 (M^+, 3), 161 (100), 133 (98), 105 (57).

4.2. Reaction of photochemically generated W–Si compounds with H₂O

A solution of $W(CO)_6$ (0.10 g, 0.28 mmol) and Et_2SiH_2 (0.05 cm^3, 0.39 mmol) in *n*-heptane (40 cm^3) was irradiated at −10 °C. After 3.5 h of photolysis, when the IR spectrum showed the almost complete decay of $W(CO)_6$ and the appearance of v (C≡O) bands characteristic for the W–Si compounds **A** and **2**, one drop of water was added to the reaction mixture. The IR spectra showed the immediate decay of the v (C≡O) band at 2086 cm^{-1}, due to compound **A**, and slightly increase in the intensity of the v (C≡O) bands characteristic for compound **1**. A sample freshly analyzed by the ^1H NMR method at 25 °C in toluene-d_8 solution showed the presence of compounds **B** and **1**, and the hydrolysis product of silane (see above).

4.3. X-ray crystallography

Crystal data were collected at 100 K on a Kuma KM4-CCD diffractometer with graphite-monochromated Mo Kα radiation, generated from an X-ray tube operated at 50 kV and 35 mA. The images were indexed, integrated, and scaled using the Oxford Diffraction data reduction package [52]. A yellow crystal with the approximate dimensions of $0.08 \times 0.08 \times 0.07$ mm was used for data collection. The experimental details together with crystal data are given in Table 1. The structure was solved by the heavy atom method using SHELXS-97 [53] and refined by the full-matrix least-squares method on all F^2 data using SHELXL-97 [54]. The non-hydrogen atoms were included in the refinement with anisotropic displacement parameters, and the hydrogen atoms bounded to carbon atoms were included from ideal geometry of molecules and were not refined. The positions

of the hydrogen atom bounded to Si and W atoms were located in the difference Fourier electron-density map and refined isotropically. The data were corrected for absorption (min./max. absorption coefficients of 0.453/0.657) [52].

5. Supplementary material

CCDC 293006 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via 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) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

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