Photochemical reactions of [W(CO)$_4$(η^4-nbd)] with hydrosilanes: Generation of new hydrido complexes of tungsten and their reactivity

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ABSTRACT

Photolysis of the norbornadiene (nbd) complex [W(CO)$_4$(η^4-nbd)] (**1**) creates a coordinatively unsaturated d^6 species which interacts with the Si–H bond of tertiary and secondary silanes (Cl$_3$SiH, Et$_3$SiH, Et$_2$SiH$_2$, Ph$_2$SiH$_2$) to yield hydride complexes of varying stability. In reaction of complex **1** with Cl$_3$SiH, oxidative addition of the Si–H bond to the tungsten(0) center gives the seven-coordinate tungsten(II) complex [WH(SiCl$_3$)(CO)$_3$(η^4-nbd)], which has been fully characterized by NMR spectroscopic methods (^{1}H, ^{13}C{^{1}H}, 2D ^{1}H–^{1}H COSY, 2D ^{13}C–^{1}H HMQC and ^{29}Si{^{1}H}). Reaction of **1** with Et$_3$SiH leads to the hydrosilylation of the η^4-nbd ligand to selectively yield *endo*-2-triethylsilylnorbornene (nbeSiEt$_3$). The latter silicon-substituted norbornene gives the unstable pentacarbonyl complex [W(CO)$_5$(η^2-nbeSiEt$_3$)], whose conversion leads to the initiation of ring-opening metathesis polymerization (ROMP). Reaction of secondary silanes (Et$_2$SiH$_2$ and Ph$_2$SiH$_2$) with **1** leads to the hydrosilylation and hydrogenation of nbd and the formation of bis(silyl)norbornane and silylnorbornane as the major products. In reaction of **1** and Et$_2$SiH$_2$, the intermediate dihydride complex [WH(μ-H–SiEt$_2$)(CO)$_x$(η^4-nbd)] was detected by ^{1}H and ^{13}C NMR spectroscopy. As one of the products formed in photochemical reaction of W(CO)$_6$ with Ph$_2$SiH$_2$, the dinuclear complex [{W(μ-η^2-H–SiPh$_2$)(CO)$_4$}$_2$] was identified by NMR spectroscopic methods.

1. Introduction

The oxidative addition of the Si–H bond to a transition metal center has attracted considerable attention in the field of organosilicon chemistry due to its applicability to catalytic processes such as hydrosilylation [1,2]. In the last few years, the focus of our research has involved the activation of Si–H bonds of tertiary and secondary silanes by tungsten(0) and molybdenum(0) carbonyl complexes [3–6]. It is a very well documented observation that in photochemical reactions group 6 metal carbonyls can very easily display carbonyl ligands on silane to yield very unstable σ-complexes of the type [M(η^2-H–SiR$_3$)(CO)$_5$] M = W, Mo, Cr [3,5,7–11], as well as dinuclear complexes more stable in the solid state such as [{M(μ-η^2-H–SiEt$_2$)(CO)$_4$}$_2$], M = W [3,12], Mo [4]. Unfortunately, the latter reaction carried out in the presence of a cyclic olefin such as norbornene or cyclopentene leads to their η^2-coordination and subsequent transformation to polymers, in the ring-opening metathesis polymerization reaction (ROMP), but not to hydrosilylation products [3]. It has been interesting to study and explain why the hydrosilylation does not occur in the case of cyclic olefins, whereas the activation of the Si–H bond of Ph$_2$SiH$_2$ by W(CO)$_6$ has been successfully used in the hydrosilylation of ketones [5]. It must be noted that chromium hexacarbonyl has been shown to be capable of being used as photocatalyst for hydrosilylation of 1,3-dienes [13,14]. This has inspired us to investigate the reason for the lack of catalytic activity of W(CO)$_6$ in hydrosilylation of cyclic olefins by secondary and tertiary silanes.

This article reports studies aimed at elucidating the details of the activation and cleavage of the Si–H bond by the photochemically activated norbornadiene (nbd) complex [W(CO)$_4$(η^4-nbd)] (**1**) and identifying the intermediates that result from these reactions by ^{1}H and ^{13}C NMR spectroscopy. Our principal objective has been to detect and characterize the tungsten complexes formed in the oxidation addition of the Si–H bond to the tungsten(0) center. Two sets of studies have been performed by NMR spectroscopy. In the first set, product formation of a series of silanes with photochemically activated **1** was monitored by ^{1}H NMR. In the second, the products separated from the photochemical reaction of W(CO)$_6$, nbd and silane, carried out in alkane solution, were analyzed by NMR spectroscopy.

2. Results and discussion

2.1. Photochemical reaction of [W(CO)$_4$(η^4-nbd)] (**1**) with Cl$_3$SiH in cyclohexane-d$_{12}$

Photolysis of [W(CO)$_4$(η^4-nbd)] (**1**) creates a coordinatively unsaturated d^6 species which interacts with the Si–H bond of

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Cl₃SiH. When the photochemical reaction of **1** with Cl₃SiH in cyclohexane-d_{12} was monitored by ^{1}H NMR spectroscopy at 293 K, the formation of a W–H bond was observed due to the appearance of a high-field resonance exhibiting [183]W satellites ($^1J_{H-W}$ = 16 Hz) at δ −2.07. This reaction is accompanied by the decay of signals at δ 4.44, 3.84 and 0.98 ppm due to the η^4-nbd ligand of **1** and the appearance of four well-separated groups of signals of the η^4-nbd ligand in the new tungsten hydride complex (**2**) at δ 4.55, 3.82, 3.79 and 1.00 ppm in an intensity ratio of 1:1:1:1, integrated for 8 protons vs. the hydride signal (Fig. 1). The absorption at δ 4.55 is due to two protons attached to one of the two double bonds, while the peak at δ 3.79 is due to two protons attached to the other double bond. The resonance of olefin protons is at a higher and a lower field than that of the η^4-nbd ligand in **1** by 0.11 and 0.65 ppm, respectively, indicating asymmetrical, weaker and stronger interactions of the olefin bonds with the tungsten atom in the new complex **2** than in **1**. Similar conclusions can be drawn from ^{13}C NMR spectra of **2**, which show two olefin carbon signals of the η^4-nbd ligand at δ 70.4 and 46.4 ppm. In 2D [13]C–[1]H HMQC spectra, olefin proton signals at δ 4.55 and 3.79 ppm correlate with carbon signals at δ 70.4 and 46.4 ppm, respectively. The lower-field olefin carbon signal of **2** could be assigned to the carbons of the C≡C unit *trans* to the CO ligand, a better π-acceptor than olefin, and the signal at higher field to the carbons of the double bond *trans* to a ligand with a weaker π-accepting ability than the CO ligand, i.e. a hydride or trichlorosilyl anionic ligand. It must be noted that the formation of the W-Si bond was proved by ^{29}Si{^{1}H} NMR spectroscopy, which showed a signal exhibiting [183]W satellites ($^1J_{Si-W}$ = 214 Hz) at δ 47.8. The ^{13}C NMR spectra of **2** showed two carbonyl resonances, at δ 199.7 and 197.2 ppm, in an intensity ratio of 2:1. The resonance at δ 199.7 can be assigned to the two carbonyls that are mutually *trans*. This resonance is slightly low-field shifted compared with the signal of the CO group that is approximately *trans* to the olefin unit of the η^4-nbd ligand. However, both of the carbon signals of the CO ligands of **2** are high-field shifted compared with the signals of the CO groups of **1** observed here at δ 208.7 and 204.5 in an intensity ratio of 1:1.

The NMR data for **2** are closely related to the corresponding seven-coordinate norbornadiene complexes of tungsten(II) ([WCl(ECl₃)(CO)₃(η^4-nbd)], E = Ge [15], Sn [16]), formed in photo-chemical reaction of complex **1** with GeCl₄ or SnCl₄ (Table 1). The molecular structure of those compounds was revealed earlier by X-ray diffraction studies of single crystals and by NMR and IR spectroscopic methods in solution. In the latter two compounds the η^4-nbd ligand is coordinated asymmetrically with one of the W–C(olefin) bonds *trans* to CO, longer by *ca.* 0.1 Å, and a shorter one *trans* to the chloride ligand. Regarding the origin of this effect, the W–C(olefin) bond distance correlates with the degree of metal ($d\pi$) → olefin(π^*) back-donation, which is reflected in the value of coordination shift of the olefinic proton and olefinic carbon signals in NMR spectra. This is why for all the three analogues, W–Si, W–Ge and W–Sn norbornadiene complexes, the two olefinic carbon and proton signals are detected in a very close region of the NMR spectra (Table 1). This suggests a similar asymmetric coordination of the η^4-nbd ligand in all three members of this family. However, the smallest distortion from symmetrical coordination of the η^4-nbd ligand is seen in the W–Si compound **2**, which contains the smaller anionic (hydride and trichlorosilyl) ligands. NMR data imply that the new compound **2** is best described as a complex with the empirical formula [WH(SiCl₃)(CO)₃(η^4-nbd)] (Scheme 1). A similar oxidative addition of the Si–H bond of Cl₃SiH to the tungsten(0) center of the complex [W(CO)₄(dppe)] and the formation of the seven-coordinate complex [WH(SiCl₃)(CO)₃-(dppe)] has been observed earlier by Piana and Schubert [17].

The formation of the stable enough seven-coordinate tungsten(II) complex **2** may explain the lack of hydrosilylation products of nbd in photochemical reaction of **1** and trichlorosilane. Complex **2** was also detected by NMR spectroscopy in the mixture of products formed in photochemical reaction of W(CO)₆, nbd and Cl₃SiH carried out in alkane solution. However, in the latter reaction the initiation of ROMP of norbornadiene and the appearance of an unsaturated polymer with characteristic olefinic proton signals at δ 5.60, 5.57, 5.37 and 5.20 ppm [18] was observed by ^{1}H NMR spectroscopy. The initiation of the ROMP reaction suggests the formation of a carbene ligand from the η^4-nbd ligand. This rearrangement may be promoted by the formation of a hydride ligand derived from silane. It should be noted that the initiation of terminal alkene metathesis in photochemical reaction of group 6 metal carbonyls and secondary silanes has been recently observed by Bespalova et al. [19].

2.2. Photochemical reaction of a norbornadiene complex **1** with Et₃SiH

Reaction of **1** with Et₃SiH followed a different route than that with trichlorosilane. Monitoring the photochemical reaction of **1** with Et₃SiH in cyclohexane-d_{12} solution by ^{1}H NMR spectroscopy revealed the hydrosilylation of the η^4-nbd ligand and the formation of *endo*-2-triethylsilylnorbornene (nbeSiEt₃) as the major product (*ca.* 99%). Silicon-substituted norbornene, nbeSiEt₃, was detected by ^{1}H NMR due to the characteristic olefinic proton signal at δ 5.93 and the methine protons signals at δ 2.96 and 2.89 ppm in the intensity ratio of 2:1:1 (Fig. 2) [20,21]. However, the hydrogenation of the olefin bond of nbeSiEt₃ gives *endo*-2-triethylsilylnorbornane (nbaSiEt₃). The latter compound was detected by ^{1}H NMR due to the characteristic two methine (HC[1,4]) and one methylene (H₂C[3]) proton signals at δ 2.33, 2.26 and 1.72 (dddd, J_{H-H} = 12.3, 11.6, 4.4, 3.0 Hz), in the intensity ratio of 1:1:1, respectively (Fig. 2). The very low yield of nbaSiEt₃ at the beginning of the reaction (*ca.* 1%) increased with longer time of photolysis, particularly in the presence of an excess of Et₃SiH. The simultaneously formed coordinatively unsaturated "W(CO)₄−ₓ" (x = 0,1) moiety traps the CO and olefin (nbeSiEt₃) molecules to give the complex [W(CO)₅(η^2-nbeSiEt₃)] (**3**). The slow transformation of **3** gives the ring-opening metathesis polymerization (ROMP) product (Scheme 2) [22–24]. The pentacarbonyl moiety can also interact with the H–Si bond of Et₃SiH to provide the complex [W(CO)₅(η^2-H–SiEt₃)],

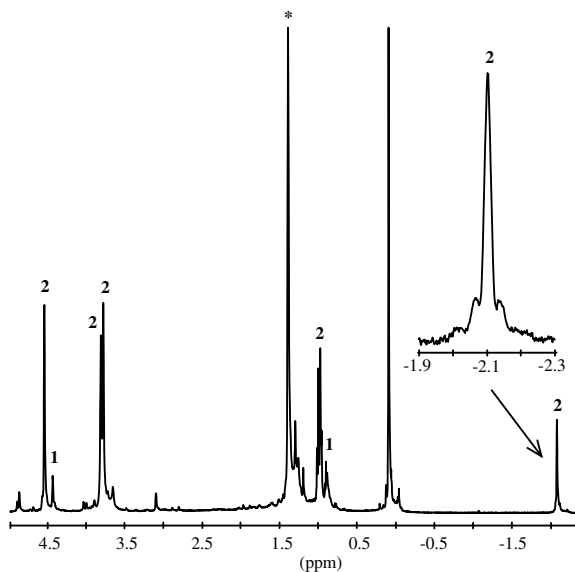**Fig. 1.** The ^{1}H NMR spectrum of **2** in cyclohexane-d_{12} generated in situ from **1** and Cl₃SiH after 15 min photolysis. The proton signals are labeled as complex **1** and **2** and an asterisk denotes the solvent.

Table 1
Selected structural and NMR data for the norbornadiene complexes of tungsten

| Complex	Bond lengths (Å) W–(C=C)	¹H NMR δ_H	¹³C NMR δ_C, nbd	δ_C, CO
$[W(CO)_4(\eta^4\text{-nbd})]$ (**1**)[a]	2.419(5)	4.64 (4H, =CH)	68.8 (4C, =CH)	209.7 (2CO)
	2.412(6)	3.84 (2H, CH)	67.2 (1C, CH₂)	
	2.409(5)	0.97 (2H, CH₂)	48.8 (2C, CH)	204.3 (2CO)
	2.403(6)			
$[WCl(SnCl_3)(CO)_3(\eta^4\text{-nbd})]$[b]	2.407(9)	5.04 (2H, =CH)	81.8 (2C, =CH)	202.3 (1CO)
	2.413(8)	3.87 (2H, CH)	64.0 (1C, CH₂)	
	2.326(8)	3.71 (2H, =CH)	44.2 (2C, CH)	193.5 (2CO)
	2.306(9)	1.51 (2H, CH₂)	43.1 (2C, =CH)	
$[WCl(GeCl_3)(CO)_3(\eta^4\text{-nbd})]$[c]	2.427(10)	5.00 (2H, =CH)	81.1 (2C, =CH)	203.3 (1CO)
	2.412(11)	3.84 (2H, CH)	64.4 (1C, CH₂)	
	2.325(10)	3.57 (2H, =CH)	44.1 (2C, CH)	193.7 (2CO)
	2.325(10)	1.46 (2H, CH₂)	42.7 (2C, =CH)	
$[WH(SiCl_3)(CO)_3(\eta^4\text{-nbd})]$ (**2**)[d]		4.59 (2H, =CH)	70.0 (2C, =CH)	199.0 (2CO)
		4.03 (2H, =CH)	64.5 (1C, CH₂)	
		3.89 (2H, CH)	48.9 (2C, =CH)	196.0 (1CO)
		1.04 (2H, CH₂)	47.0 (2C, CH)	
		−2.36 (1H, W–H)		
$[WH(H\text{-}SiEt_2)(CO)_x(\eta^4\text{-nbd})]$ (**4**)[e]		5.09 (2H, =CH)	75.2 (2C, =CH)	
		3.89 (2H, CH)	65.9 (1C, CH₂)	
		3.31 (2H, =CH)	48.6 (2C, CH)	
		~1.2 (2H, CH₂)	38.5 (2C, =CH)	
		−8.33 (1H, W–H–Si)		
		−11.47 (1H, W–H)		

[a] Ref. [29], NMR data in CDCl₃.
[b] Ref. [16], NMR data in CD₂Cl₂.
[c] Ref. [15], ¹H NMR data in CDCl₃, ¹³C NMR data in CD₂Cl₂.
[d] This work, NMR data in CDCl₃.
[e] This work, NMR data in C₆D₁₂.
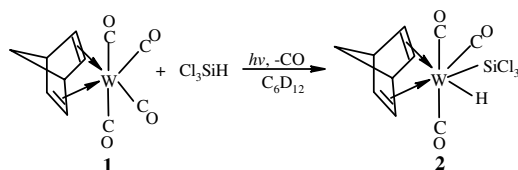
Scheme 1. Formation of complex **2**.

recently detected due to the hydride signal at δ −8.58 [3,7]. The most intriguing aspect of this reaction is the formation of complex **3**, analogous to that observed in photochemical reaction of norbornene (nbe) with $W(CO)_6$ and its transformation to the ROMP polymer [25]. This experiment indicates that under the reaction conditions the η^2-nbeSiEt₃ ligand can easily rearrange in the coordination sphere of the tungsten(0) atom to yield a carbene species initiating the ROMP reaction. The conversion of the η^2-nbeSiEt₃ ligand to a carbene ligand most probably involves a 1,2-hydride shift in the olefinic ligand, promoted by the formation of a hydride ligand derived from the H-Si bond of silane (Scheme 3). The insertion of an olefin ligand into the covalent W–H bond first gives a metal-alkyl bond, and then a carbene species is formed due to α-hydrogen abstraction [18]. The ease of carbene formation from the η^2-nbeSiEt₃ ligand explains the decay of compound **3** and nbeSiEt₃ and the appearance of polynbeSiEt₃ but not the hydrosilylation product bis(silyl)norbornane.

2.3. Photochemical reaction of **1** with Et₂SiH₂

As was revealed by ¹H NMR spectroscopy, photochemical reaction of the norbornadiene complex **1** with Et₂SiH₂ in cyclohexane-d_{12} solution resulted in a very fast decay of **1** and the formation of
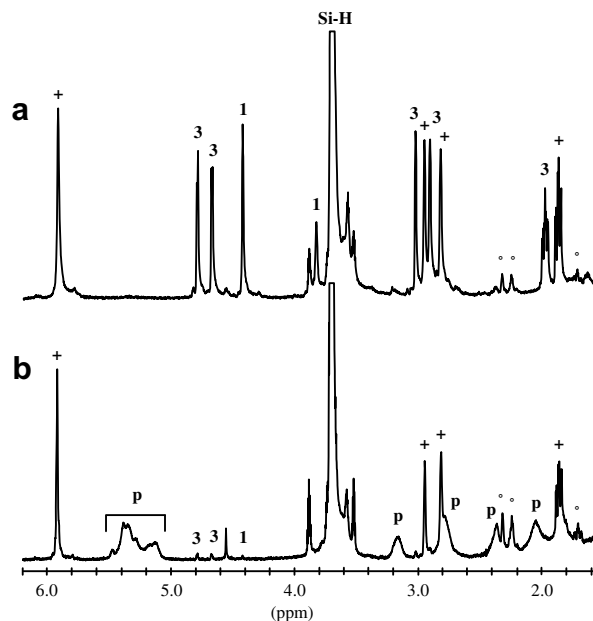

Fig. 2. The ¹H NMR spectra obtained during reaction of **1** with Et₃SiH (Si–H) in cyclohexane-d_{12} solution, showing the formation of endo-2-triethylsilylnorbornene (nbeSiEt₃) (+), endo-2-triethylsilylnorbornane (nbaSiEt₃) (○), the ROMP polymer (p), and the complex $[W(CO)_5(\eta^2\text{-nbeSiEt}_3)]$ (**3**): (a) after 15 min photolysis; (b) after four days without photolysis.

several new compounds (Fig. 3, Scheme 4). The oxidative addition of the H–Si bond of silane to the tungsten(0) center of **1** was indicated by the high-field resonances in the range from δ −8 to −12 ppm. The hydride signal at δ −9.28 was recognized as that
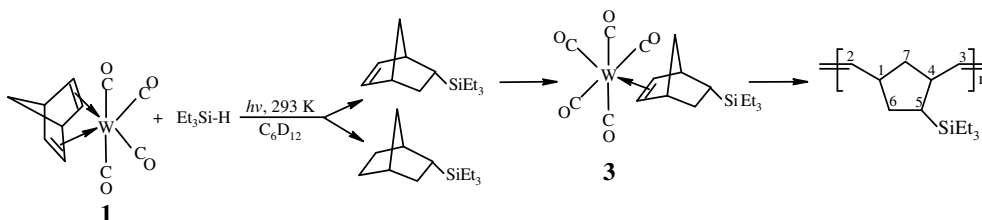
Scheme 2. Compounds detected by NMR spectroscopy in reaction of **1** with Et$_3$SiH in cyclohexane-d_{12} solution.
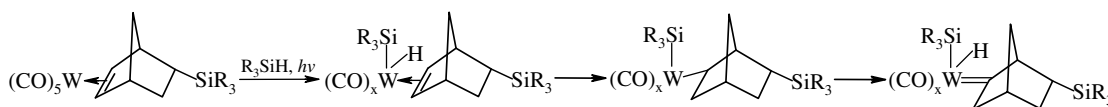

Scheme 3. Possible route for the formation of a carbene ligand from the η^2-nbeSiEt$_3$ ligand.

belonging to the previously characterized dimeric compound [{W(μ-^{2}-H–SiEt$_2$)(CO)$_4$}$_2$] [3,12]. Two equal-intensity doublets at δ −8.33 ($^2J_{H-H}$ = 2.3 Hz, $^1J_{W-H}$ = 52 Hz, $^1J_{Si-H}$ = 29 Hz) and δ −11.47 ($^2J_{H-H}$ = 2.7 Hz, $^1J_{W-H}$ = 38 Hz) together with four equal-intensity signals at δ 5.09, 3.89, 3.31 and 1.2 ppm (integrated for 8 protons vs. the hydride signals) could be assigned to the complex [WH(μ-H–SiEt$_2$)(CO)$_x$(η^4-nbd)] (**4**). This suggestion was proved by 2D ^{1}H–^{1}H COSY and 2D ^{13}C–^{1}H HMQC NMR methods. First of all, in ^{1}H–^{1}H COSY spectrum two hydride resonances correlate, indicating attachment to the same tungsten atom. The olefin proton resonances at δ 5.09 and 3.31 correlate with resonance of the methine protons at δ 3.89 in ^{1}H–^{1}H COSY spectrum and with the olefin carbon resonances at δ 75.2 and 38.5 in the 2D ^{13}C–^{1}H HMQC NMR spectrum. These NMR data for **4** are closely related to the corresponding seven-coordinate norbornadiene complexes of tungsten(II) (Table 1), although the concentration of compound **4** was too low to make it possible to observe the carbonyl carbon signals. The major product of the reaction containing the SiHEt$_2$ silyl moiety was detected due to the proton signal exhibiting ^{29}Si satellites ($^1J_{Si-H}$ = 182 Hz) at δ 3.92 (doublet of quintets, J_{H-H} = 2.8 Hz) and

the methine proton signal of the norbornyl moiety at δ 2.36. The Si–H signal and the methine signals are in an intensity ratio of 1:1. Two other methine proton signals at δ 2.29 and 2.25 are in an intensity ratio of 1:1. The latter two signals and another one at δ 3.72 (doublet of quintets, J_{H-H} = 2.7 Hz, Si–H) are in a stable intensity ratio of 1:1:1. These ^{1}H NMR data suggest the hydrosilylation and hydrogenation of two double bonds of the nbd ligand and the formation of bis(hydrodiethylsilyl)norbornane (nba(Si-HEt$_2$)$_2$) and 2-hydrodiethylsilylnorbornane (nbaSiHEt$_2$) (Scheme 4). Two-dimensional NMR spectroscopy was very helpful in recognizing these two compounds, both forming selectively as endo isomers [20,21].

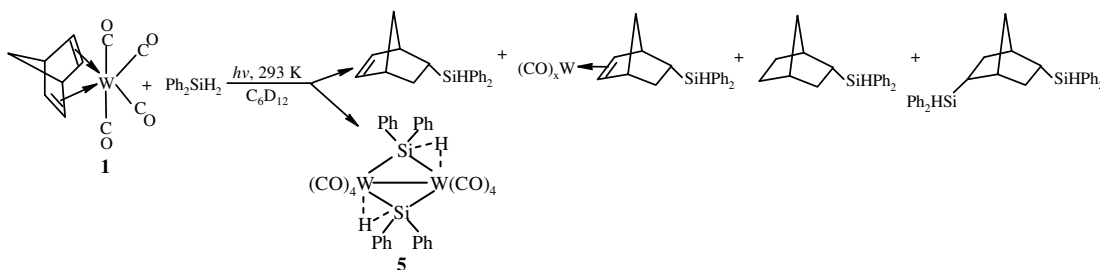### 2.4. Photochemical reaction of **1** with Ph$_2$SiH$_2$

Monitoring of the photochemical reaction of **1** with Ph$_2$SiH$_2$ in cyclohexane-d_{12} solution by ^{1}H NMR spectroscopy revealed a very fast decay of **1** and the formation of products analogous to those detected in reaction with Et$_2$SiH$_2$. Two equal-intensity doublets at δ −4.33 ($^2J_{H-H}$ = 3.4 Hz) and δ −11.15 ($^2J_{H-H}$ = 2.8 Hz) could be assigned to the norbornadiene complex containing the "WH(μ-H–SiPh$_2$)" moiety. The latter complex was detected only by ^{1}H NMR spectroscopy in reactions carried out at a **1**:Ph$_2$SiH$_2$ molar ratio of ca. 1. In the presence of an excess of Ph$_2$SiH$_2$ the hydride signal at δ −7.73 increases in intensity with time of photolysis. This signal was recognized as belonging to the dimeric compound [{W(μ-η^2-H–SiPh$_2$)(CO)$_4$}$_2$] (**5**), fully characterized in a separate experiment (see below). The major organic products of the reaction were detected due to three methine proton signals of the norbornyl moiety at δ 2.46, 2.37 and 2.29. The intensity of the signal at δ 2.46 changes with reaction time vs. the methine proton signals at δ 2.37 and 2.29, which are in a stable intensity ratio of 1:1. These ^{1}H NMR data suggest the hydrosilylation and hydrogenation of two double bonds of the nbd ligand and the formation of bis(hydrodiphenylsilyl)norbornane (nba(SiHPh$_2$)$_2$) and hydrodiphenylsilylnorbornane (nbaSiHPh$_2$) (Scheme 5). The silicon-substituted norbornene (nbeSiHPh$_2$) was detected by ^{1}H NMR due to the olefinic proton signal at δ ca. 6 ppm and the methine proton signals at δ ca. 3 ppm. However, the intensity of the methine proton signals is about twice as great as those of free olefin. This suggests the coordination of olefin compounds to the tungsten atom (the methine proton signals of free and coordinated olefin are within a very close range, δ 3.0–2.9). The olefin proton signals of the η^2-nbeSiHPh$_2$ ligand were located at δ 4.62 and 4.58 ppm (t, J_{H-H} = 4 Hz). Based on this analysis, a yield of the products identified by ^{1}H NMR spectroscopy was calculated. The content of the major product, nbaSiHPh$_2$, was ca. 40%.
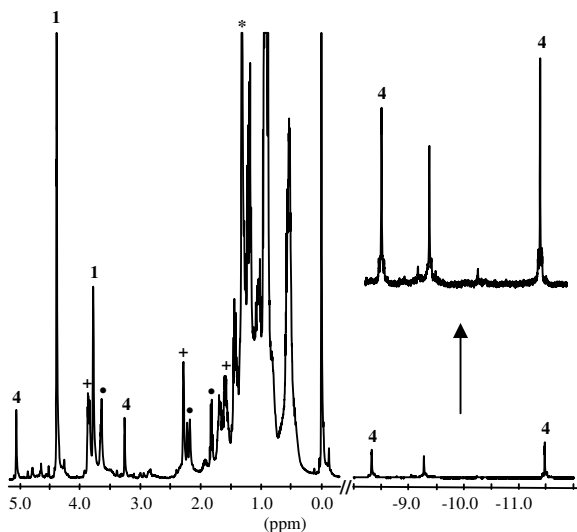
Fig. 3. The ^{1}H NMR spectrum obtained during reaction of **1** with Et$_2$SiH$_2$ in cyclohexane-d_{12} (*) solution showing the formation of [WH(μ-η^2-H–SiEt$_2$)(CO)$_x$(η^4-nbd)] (**4**), bis(hydrodiethylsilyl)norbornane (nba(SiHEt$_2$)$_2$) (+), and 2-hydrodiethylsilyl-norbornane (nbaSiHEt$_2$) (●). The upfield region of the spectrum is shown with the scale expansion.
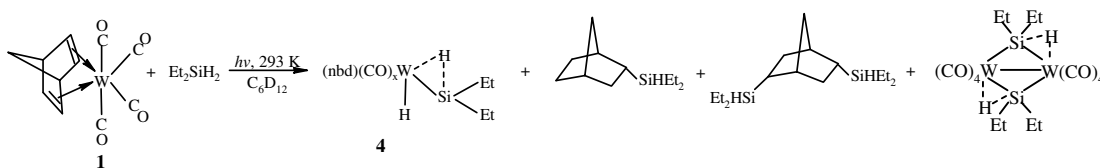
Scheme 4. Compounds detected by NMR spectroscopy in reaction of **1** with Et$_2$SiH$_2$ in cyclohexane-d_{12} solution.



Scheme 5. Compounds detected by NMR spectroscopy in reaction of **1** with Ph$_2$SiH$_2$ in cyclohexane-d_{12} solution.

In photochemical reaction of the norbornadiene complex **1** with Ph$_2$SiH$_2$ monitored by IR spectroscopy in *n*-heptane solution, a very fast decay of the v (C≡O) frequency at 2044 (m), 1957 (vs) 1909 (s) cm^{-1}, characteristic for **1**, and the appearance of bands at 1982 and 1911 cm^{-1}, characteristic for the three carbonyl moieties of the η^6-arene complexes [W(CO)$_3$(η^6-arene)], were observed [26–28]. In the ^{1}H NMR spectrum of this sample in CDCl$_3$ solution, the proton signals characteristic for nbaSiHPh$_2$ and nba(SiHPh$_2$)$_2$ were detected at δ 2.46, 2.37 and 2.29. However, three other signals in a range δ 2.6–2.2 indicate other products containing the norbornyl moiety, most probably stereoisomers of nbaSiHPh$_2$ and nba(SiHPh$_2$)$_2$. The difficulty in interpreting the ^{1}H NMR spectrum results from the fact that the reductive elimination of the hydrosilylation product from the very unstable catalytically active tricarbonyl complex leads to the formation of a coordinatively unsaturated tricarbonyl moiety, W(CO)$_3$, which can coordinate the phenyl ring of the diphenylsilane or its transformation products as an η^6-ligand. [W(CO)$_3$(η^6-arene)] complexes were detected by IR and NMR spectroscopy in all the investigated reactions of **1** and diphenylsilane. The proton signals of the η^6-phenyl ring were observed in the region 5.5–5.0 ppm (doublets and triplets with $^3J_{H-H}$ = 6 Hz) and the carbon signals in the range 98–87 ppm in spectra of CDCl$_3$ solution, while the carbonyl carbon signal of the W(CO)$_3$ moiety was detected at *ca.* 209 ppm. Proton and carbon signals of other tungsten complexes containing η^6-arene and carbonyl ligands have been observed before in a similar range of NMR spectra [26–28].

2.5. Photochemical reaction of W(CO)$_6$ with Ph$_2$SiH$_2$

To detect the intermediate compounds formed in reaction of tungsten(0) carbonyls, we reexamined the previously investigated photochemical reaction of W(CO)$_6$ with Ph$_2$SiH$_2$ [6]. The lower temperature of the reaction allowed us to detect, by NMR spectroscopic methods, not only the recently characterized dinuclear complex [(μ-SiPh$_2$){W(CO)$_5$}$_2$] [6], but also the complex [{W(μ-η^2-H–SiPh$_2$)(CO)$_4$}$_2$] (**5**) containing a bridging silyl ligand, analogous to that previously isolated from reaction of W(CO)$_6$ and Et$_2$SiH$_2$ [3,12]. Complex **5** was identified due to a hydride resonance at δ −7.50 exhibiting ^{183}W and ^{29}Si satellites ($^1J_{W-H}$ = 33 Hz, $^1J_{Si-H}$ = 41 Hz) (Fig. 4). The $^1J_{Si-H}$ value of 41 Hz is a typical J_{Si-H} value for η^2-silane complexes, which usually falls in the range 30–100 Hz [1,3–5,7]. The ^{29}Si{^{1}H} NMR spectra of **5** show a reso-
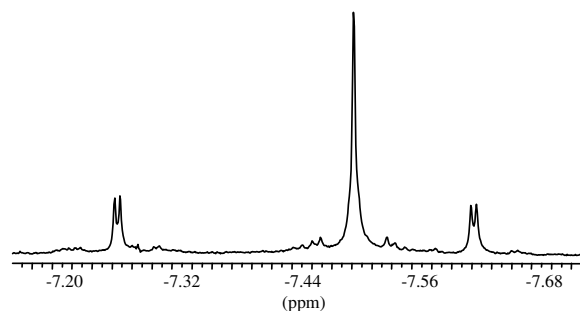

Fig. 4. The upfield region of the ^{1}H NMR spectrum (300 MHz, toluene-d_8, 243 K) showing the hydride resonance of [{W(μ-η^2-H–SiPh$_2$)(CO)$_4$}$_2$] (**5**) at δ −7.50 and at δ −7.26 and −7.62 due to the dihydride complex.

nance at δ 194, which is a little high-field shifted compared with that detected at δ 211 for a tungsten dimer containing a singly bridging silylene SiPh$_2$ ligand [6]. The ^{13}C{^{1}H} NMR spectrum of **5** exhibits three signals in the carbonyl region, at δ 206.5, 198.7 and 192.4 ppm, in the intensity ratio of 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 ligand (Scheme 6). Compound **5** was detected only by NMR spectroscopy of the crude reaction mixture, containing [(μ-SiPh$_2$){W(CO)$_5$}$_2$] as the major product (*ca.* 80% calculated from the intensity of carbonyl groups in the ^{13}C{^{1}H} NMR spectrum). One more hydride complex formed in this reaction was detected due to two high-field resonances observed as doublets (J_{H-H} = 2.7 Hz) of equal intensity at δ −7.26 ($^1J_{W-H}$ = 39 Hz) and −7.62 ($^1J_{W-H}$ = 41 Hz) (Fig. 4). These ^{1}H NMR data imply the formation of a dihydride complex of tungsten. However, the latter species is very unstable and was observed as an intermediate complex at low temperature (243 K). It is highly probable that a similar dihydride species formed in reaction of **1** and Ph$_2$SiH$_2$ is responsible for the observed hydrogenation of silylnorbornene.

2.6. Summary and conclusions

The oxidative addition of the Si–H bond of hydrosilanes to the coordinatively unsaturated tungsten(0) species is a facile route to the formation of the W–H bond. Photochemically activated
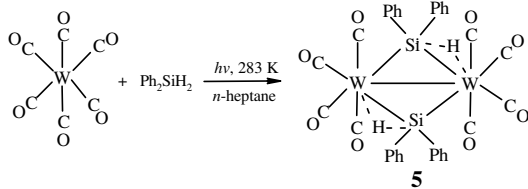
Scheme 6. Schematic view of the ligand arrangement in the complex [{W(μ-η²-H–SiPh₂)(CO)₄}₂] (**5**).

[W(CO)₄(η⁴-nbd)] (**1**) reacts with the Si–H bond of secondary and tertiary silanes. The oxidative addition of Cl₃SiH to complex **1** resulted in the formation of a seven-coordinate complex of tungsten(II), [WH(SiCl₃)(CO)₃(η⁴-nbd)] (**2**), identified by NMR spectroscopy. Complexes analogous to **2** but much more unstable were detected in reaction of **1** with Et₂SiH₂. Reaction of Et₃SiH with **1** clearly gives the hydrosilylation product of norbornadiene *endo*-2-triethylsilylnorbornene (nbeSiEt₃), which converts under photochemical reaction conditions to yield the ring-opening metathesis polymerization product. The most fascinating aspect of these reactions was the unexpected initiation of ring-opening metathesis polymerization and the formation of unsaturated polymers containing silyl substituents.

In reaction of secondary silanes with **1**, the hydrosilylation of both olefin bonds of nbd and the formation of bis(silyl)norbornane was observed. The hydrosilylation of nbd by secondary silanes is accompanied by hydrogenation to give silylnorbornane.

In summary, we have obtained evidence for the activation of the Si–H bond of silanes by a photochemically generated coordinatively unsaturated norbornadiene complex of tungsten(0) and its applicability to hydrosilylation of nbd.

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 dried with CaH_2 and vacuum transferred into small storage flasks prior to use. $W(CO)_6$ (Aldrich) was used as received. The norbornadiene (nbd) complex [W(CO)₄(η⁴-nbd)] (**1**) was prepared in reaction of [W(CO)₄(NCMe)₂] and nbd in *n*-heptane according to the literature procedure [29,30]. IR spectra were measured with a Nicolet 400 FT-IR instrument. ¹H NMR spectra were recorded with a Bruker AMX 300 or 500 MHz instrument. ¹³C, ²⁹Si and two-dimensional (¹H–¹H COSY ¹H–¹³C HMQC) NMR spectra were recorded with a Bruker AMX 500 MHz instrument at 500.13 MHz for ¹H, 125.76 MHz for ¹³C, and 99.36 MHz for ²⁹Si. All proton and carbon chemical shifts were referenced to the residual proton signal for ¹H NMR (δ 7.24 CDCl₃, 2.10 C₇D₈ and 1.40 C₆D₁₂) or the natural abundant carbon signal of the solvent for ¹³C NMR (δ 77.0 CDCl₃, 20.4 C₇D₈ and 26.4 C₆D₁₂). ¹H chemical shifts measured in methylcyclohexane-d_{14} as the solvent were referenced relative to SiMe₄. ²⁹Si NMR chemical shifts were referenced relative to Ph₂SiH₂ (δ 37.08) used as external standard. The photolysis source was an HBO 200 W high-pressure Hg lamp.

3.2. General procedure for NMR experiments

The course of the reaction of complex **1** and silanes (Cl₃SiH, Et₃SiH, Et₂SiH₂ and Ph₂SiH₂) was monitored by ¹H NMR spectroscopy. Following the general procedure for NMR experiments, complex **1** (*ca.* 0.03 g, 0.08 mmol) was weighed into an NMR tube. The tube was then capped with a septum. A portion of silane (*ca.*

0.02 cm³) and C₆D₁₂ (0.6 cm³) was then added to the NMR tube via a syringe. The tube was periodically irradiated and monitored by ¹H NMR spectroscopy at the desired time.

3.3. Identification of [WH(SiCl₃)(CO)₃(ηs⁴-nbd)] (**2**)

3.3.1. Identification of **2** in photochemical reaction of **1** with Cl₃SiH in C₆D₁₂ and C₇D₁₄ solution

The irradiation of **1** and an excess of Cl₃SiH (1:2 to 1:10) in the NMR tube and subsequent analysis by means of ¹H NMR made it possible to observe the decay of **1** (*ca.* 100% conversion in 0.5 h) and the appearance of signals that were assigned to a new compound **2** on the basis of ¹H, ¹³C{¹H}, ¹³C, 2D ¹H-¹H COSY, 2D ¹³C–¹H HMQC and ²⁹Si{¹H} NMR data (see Section 2.1).

¹H NMR (C₆D₁₂, 293 K) δ = 4.55 (s, 2H, =CH), 3.82 (s, 2H, CH), 3.79 (s, 2H, =CH), 1.02 (d, $J_{H–H}$ = 8.8 Hz, 1H, CH₂), 0.98 (d, $J_{H–H}$ = 8.8 Hz, 1H, CH₂), −2.07 (s, $^1J_{H–W}$ = 16 Hz, $^2J_{H–Si}$ = 31 Hz, 1H, W–H). ¹³C{¹H} NMR (C₆D₁₂, 293 K) δ = 199.7 (2C, CO), 197.2 (1C, CO), 70.4 (2C, =CH), 64.6 (1C, CH₂), 47.7 (2C, CH), 46.4 (2C, =CH). ²⁹Si{¹H} NMR (C₇D₁₄, 293 K) δ = 47.8 ($^1J_{Si–W}$ = 214 Hz).

3.3.2. Identification of **2** in photochemical reaction of **1** with Cl₃SiH in n-heptane

A solution of **1** (0.12 g, 0.31 mmol) and Cl₃SiH (0.2 cm³, 1.98 mmol) in freshly distilled *n*-heptane (30 cm³) was irradiated at room temperature. The course of the reaction was monitored by IR measurements in solution, and photolysis was stopped when the IR band of **1** at *ca.* 2044 cm⁻¹ reached its minimum intensity (*ca.* 1 h) and a new ν (C≡O) frequency at 2064 (w) and 1991 (s) cm⁻¹ increased. All volatile materials were then evaporated under reduced pressure at room temperature. The resulting brown solid was analyzed by IR and NMR spectroscopy. The NMR data are identical to those obtained upon *in situ* formation of **2** from **1**. Compound **2** is extremely sensitive to water and attempts to isolate it in pure state have been unsuccessful.

3.3.3. Identification of **2** in photochemical reaction of W(CO)₆ with nbd and Cl₃SiH in C₆H₁₂ solution

A solution of W(CO)₆ (0.10 g, 0.28 mmol), nbd (0.13 g, 0.14 cm³, 1.4 mmol), and Cl₃SiH (0.19 g, 0.14 cm³, 1.4 mmol) in C₆H₁₂ (30 cm³) was stirred and irradiated at 283 K for 2 h. All volatile materials were then evaporated under reduced pressure at room temperature to yield a brown solid. A sample analyzed by NMR methods in C₆D₁₂ and CDCl₃ solution showed the presence of the hydride compound **2** (see above) and an unsaturated polymer of nbd with characteristic olefinic proton signals at δ 5.60, 5.57, 5.37 and 5.20 ppm [17]. However, the chemical shifts of proton and carbon signals of **2** are shifted in the polar solvent CDCl₃ compared with those in C₆D₁₂ and C₇D₁₄ solution. ¹H NMR (CDCl₃, 293 K) δ = 4.59 (s, 2 H, =CH), 4.03 (s, 2H, =CH), 3.89 (s, 2H, CH), 1.06 (d, $J_{H–H}$ = 9 Hz, 1H, CH₂), 1.02 (d, $J_{H–H}$ = 9 Hz, 1H, CH₂), −2.36 ($^1J_{H–W}$ = 16 Hz, $^2J_{H–Si}$ = 31 Hz). ¹³C{¹H} NMR (CDCl₃, 293 K) δ = 199.0 (2C, CO), 196.0 (1C, CO), 70.0 (2C, =CH), 64.5 (1C, CH₂), 48.9 (2C, =CH), 47.0 (2C, CH).

3.4. Photochemical reaction of complex **1** with Et₃SiH in cyclohexane-d_{12} solution

Monitoring of the photochemical reaction of **1** with Et₃SiH (1:8) in cyclohexane-d_{12} solution by ¹H NMR spectroscopy showed the formation of *endo*-2-triethylsilylnorbornene (nbeSiEt₃), [W(CO)₅-(η²-nbeSiEt₃)] (**3**), and [W(CO)₅(η²-H–SiEt₃)]. The last one was detected due to a hydride signal at δ −8.58 [3,7]. The disappearance of complex **3** was accompanied by the appearance of the

ring-opening metathesis polymerization (ROMP) product poly-nbeSiEt$_3$. Prolonged irradiation leads to the formation of *endo*-2-triethylsilylnorbornane (nbaSiEt$_3$).

[W(CO)$_5$(η^2-nbeSiEt$_3$)] (**3**): ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 4.80, 4.67 (1:1, t, J_{H-H} = 4.4 Hz, 2H, HC^{5,6}), 3.03 (s, 1H, HC^1), 2.91 (s, 1H, HC^4), 1.98 (ddd, J_{H-H} = 12.2, 9.1, 3.6 Hz, 1H, H$_2$C^3), 1.33 (ddd, J_{H-H} = 8.7, 5.5, 3.1 Hz, 1H, H$_2$C^7), 0.72 (d, J_{H-H} = 10.7 Hz, 1H, H$_2$C^7), other signals obscured by signals of the solvent and ethyl groups. ^{13}C{^{1}H} NMR (C$_6$D$_{12}$, 293 K) δ = 199.2 (1C, CO), 196.9 (4C, CO), 86.9, 86.7 (1:1, 2C, HC^{5,6}), 46.0 (1C, HC^1), 43.4 (1C, HC^4), 40.7 (1C, HC^7), 28.6 (1C, H$_2$C^3), 23.5 (1C, HC^2), *ca.* 8 (3C, CH$_3$-Et), *ca.* 4 (3C, CH$_2$-Et).

endo-2-Triethylsilylnorbornene (nbeSiEt$_3$): ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 5.93 (t, J_{H-H} = 1.5 Hz, 2H, HC^{5,6}), 2.96 (s, 1H, HC^1), 2.83, (s, 1H, HC^4), 1.88 (ddd, J_{H-H} = 10.9, 9.8, 3.9 Hz, 1H, H$_2$C^3), 1.44 (dd, J_{H-H} = 7.5, 1.6 Hz, 1H, H$_2$C^7), other signals obscured by signals of the solvent and ethyl groups. ^{13}C{^{1}H} NMR (C$_6$D$_{12}$, 293 K) δ = 136.0, 134.9 (1:1, 2C, HC^{5,6}), 52.3 (1C, H$_2$C^7), 45.7 (1C, HC^1), 43.1 (1C, HC^4), 28.2 (1C, H$_2$C^3), 23.2 ($^1J_{Si-C}$ = 56 Hz, 1C, HC^2), 8.1 (3C, CH$_3$-Et), 4.5 ($^1J_{Si-C}$ = 50 Hz, 3C, CH$_2$-Et).

endo-2-Triethylsilylnorbornane (nbaSiEt$_3$). ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 2.33, 2.26, (1:1, s, 2H, HC^{1,4}), 1.72 (dddd, J_{H-H} = 12.3, 11.6, 4.4, 3.0 Hz, 1H, H$_2$C^3), other signals obscured by signals of the solvent and ethyl groups.

Polytriethylsilylnorbornene (polynbeSiEt$_3$): ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 5.47, 5.39, 5.35, 5.29, 5.13 (HC^{2,3}), 3.17, 2.79, 2.38 (HC^{1,4}), 2.06 (H$_2$C^7), other signals obscured.

3.5. Photochemical reaction of **1** with Et$_2$SiH$_2$ in cyclohexane-d$_{12}$ solution

This reaction was carried out in the NMR tube using the above procedure at different molar ratios of **1** and Et$_2$SiH$_2$ (1:1 and 1:16). As was shown by ^{1}H NMR spectroscopy, the photochemical reaction of complex **1** with an excess of Et$_2$SiH$_2$ resulted in a very fast decay of **1** and the formation of several organic products, but none with the olefin bond was observed. As the major products, bis(hydrodiethylsilyl)norbornane (nba(SiHEt$_2$)$_2$) and 2-hydrodiethylsilyl-norbornane (nbaSiHEt$_2$) were identified in a 1:0.8 molar ratio. The dimeric compound [{W(μ-η^2-H–SiEt$_2$)(CO)$_4$}$_2$] was detected due to the hydride signal at δ −9.28 [3,12]. The intensity of the latter signal increases with the time of irradiation. In reaction of **1** and Et$_2$SiH$_2$ (1:1 molar ratio), the intermediate organometallic compound [WH(μ-H–SiEt$_2$)(CO)$_x$(η^4-nbd)] (**4**) was identified by NMR spectroscopy.

[WH(μ-H–SiEt$_2$)(CO)$_x$(η^4-nbd)] (**4**): ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 5.09 (s, 2H, =CH), 3.89 (s, 2H, CH), 3.31 (s, 2H, =CH), *ca.* 1.2 (m, 2H, CH$_2$), −8.33 (d, $^2J_{H-H}$ = 2.3 Hz, $^1J_{W-H}$ = 52 Hz, $^1J_{Si-H}$ = 29 Hz, 1 H, W–H), −11.47 (d, $^2J_{H-H}$ = 2.7 Hz, $^1J_{W-H}$ = 38 Hz, 1H, W–H). ^{13}C{^{1}H} NMR (C$_6$D$_{12}$, 293 K) δ = 75.2 (2C, =CH), 65.9 (1C, CH$_2$), 48.6 (2C, CH), 38.5 (2C, =CH).

endo,*endo*-2,5-Bis(hydrodiethylsilyl)norbornane (nba(SiHEt$_2$)$_2$): ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 3.92 (p, $^3J_{H-H}$ = 3 Hz, $^1J_{Si-H}$ = 182 Hz, 2 H, Si–H), 2.36 (t, J_{H-H} = 4 Hz, 2H, HC^{1,4}), 1.68 (dddd, J_{H-H} = 12.4, 12.4, 4.6, 2.6 Hz, 1H, H$_2$C^3), other signals overlapping with signals of other products, the solvent, and ethyl groups. ^{13}C{^{1}H} NMR (C$_6$D$_{12}$, 293 K) δ = 45.4 (1C, H$_2$C^7), 40.5 (2C, HC^{1,4}), 29.9 (2C, H$_2$C^{3,6}), 27.6 2C, HC^{2,5}, 8.7, 8.6 (1:1, 2C, CH$_3$-Et), 3.8, 3.3 (1:1, 2C, CH$_2$-Et).

endo-2-Hydrodiethylsilylnorbornane (nbaSiHEt$_2$): ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 3.72 (p, $^3J_{H-H}$ = 2.7 Hz, 1H, Si–H), 2.29, 2.25 (1:1, t, J_{H-H} = 4 Hz, 2H, HC^{1,4}), 1.78 (dddd, J_{H-H} = 10.8, 9.8, 4.2, 3.0 Hz, 1H, H$_2$C^3), other signals overlapping with signals of other products, the solvent, and ethyl groups. ^{13}C{^{1}H} NMR (C$_6$D$_{12}$, 293 K) δ = 42.2 (1C, H$_2$C^7), 40.3 (1C, HC^1), 37.9 (1C, HC^4), 34.0 (1C, H$_2$C^3), 30.8 (1C, H$_2$C^5), 27.8 (1C, HC^2), 25.5 (1C, H$_2$C^6), 8.8, 8.7 (1:1, 2C, CH$_3$-Et), 3.8, 3.2 (1:1, 2C, CH$_2$-Et).

3.6. Photochemical reaction of **1** with Ph$_2$SiH$_2$ in cyclohexane-d$_{12}$ solution

This reaction was carried out in the NMR tube using the above procedure. As was shown by ^{1}H NMR spectroscopy, the photochemical reaction of complex **1** with Ph$_2$SiH$_2$ (1:0.4 molar ratio) resulted in a very fast decay of **1** (15 min photolysis) and the formation of several products. Two equal-intensity doublets at δ −4.33 ($^2J_{H-H}$ = 3.4 Hz) and δ −11.15 ($^2J_{H-H}$ = 2.8 Hz) were assigned to a complex containing the "WH(μ-H–SiPh$_2$)" moiety and the hydride signal at δ −7.73 to the dimeric compound [{W(μ-η^2-H–SiPh$_2$)(CO)$_4$}$_2$] (**5**) characterized in a separated experiment. The intensities of the hydride signals were much lower than those of the other proton signals. The yield of the products identified by ^{1}H NMR spectroscopy was calculated based on the integration of the proton signals characteristic for every product.

endo-2-Hydrodiphenylsilylnorbornane (nbaSiHPh$_2$) (40%): ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 4.85 (d, $^3J_{H-H}$ = 6.2 Hz, 1H, Si–H), 2.37, 2.29 (1:1, t, J_{H-H} = 4.5 Hz, HC^{1,4}), 1.86 (dd, J_{H-H} = 11.7, 4.2 Hz, 1H, H$_2$C), 1.63, 1.58 (d, J_{H-H} = 11.8, H$_2$C), 1.31 (s, H$_2$C), 1.26 (dd, J_{H-H} = 12.4, 7.2 Hz, 1H, H$_2$C), 1.10 (dd, J_{H-H} = 8.2, 8.2 Hz, 1H, H$_2$C), other signals overlapping with the signals of other products.

endo,*endo*-2,5-Bis(hydrodiphenylsilyl)norbornane (nba(SiHPh$_2$)$_2$) (27%): ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 4.84 (d, $^3J_{H-H}$ = 6.2 Hz, 2 H, Si–H), 2.46 (t, J_{H-H} = 4.5 Hz, 2H, HC^{1,4}), 1.72 (d, J_{H-H} = 11.8 Hz, 1H, H$_2$C^3), other signals overlapping with the signals of other products.

endo-Hydrodiphenylsilylnorbornene (nbeSiHPh$_2$) (15%): ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 5.94, 5.78 (1:1, s, 2H, HC^{5,6}), 2.96, 2.89 (1:1, s, 2H, HC^{1,4}), other signals overlapping with the signals of other products.

[W(CO)$_x\eta^2$-nbeSiHPh$_2$] (18%): ^{1}H NMR (C$_6$D$_{12}$, 293 K) δ = 4.62, 4.58 (1:1, t, J_{H-H} = 4.0 Hz, 2H, HC^{5,6}), 3.02, 2.93 (1:1, s, 2H, HC^{1,4}), 1.96 (m, 1H, H$_2$C^3), 0.78 (d, J_{H-H} = 10.7 Hz, 1H, H$_2$C^7), other signals overlapping with the signals of other products.

3.7. Photochemical reaction of **1** with Ph$_2$SiH$_2$ in n-heptane solution

A solution of **1** (0.18 g, 0.46 mmol) and Ph$_2$SiH$_2$ (0.11 cm^3, 0.59 mmol) in freshly distilled *n*-heptane (20 cm^3) was irradiated at room temperature. The course of the reaction was monitored by IR measurements in solution, and photolysis was stopped when the IR band of **1** at *ca.* 2044 cm^{-1} reached its minimum intensity (*ca.* 2.5 h). All volatile materials were then evaporated under reduced pressure at room temperature. The resulting brown solid was analyzed by NMR spectroscopy. ^{1}H NMR (CDCl$_3$, 293 K) δ = 7.35–6.90 (Ph), 5.5–5.0 (η^6-Ph), 4.8–4.5 (d, $^3J_{H-H}$ = 6 Hz, H-Si), 2.66, 2.53, 2.46, 2.40, 2.37, 2.29 (s, HC^{1,4}), 1.92 (d, J_{H-H} = 10 Hz), 1.76, 1.67, 1.81, 1.67, 1.60, 1.55, 1.48, 1.44, 1.32, 1.27, 1.17. ^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz) δ = 209.2 (CO), 136-128 (Ph), 97.4, 97.06, 98.8, 96.3, 92.6, 92.2, 91.8, 91.2, 88.6, 88.12, 88.0, 87.8, 87.7 (η^6-Ph), 44.6, 44.2, 41.4, 40.2, 40.0, 39.8, 39.5, 39.2, 37.1, 33.6, 29.9, 29.8, 29.7, 29.6, 27.6, 27.5, 27.4, 27.2, 25.3 (HC^{1,2,4}, H$_2$C^{3,5,6,7}).

3.8. Photochemical reaction of W(CO)$_6$ with Ph$_2$SiH$_2$: identification of [{W(μ-η^2-H–SiPh$_2$)(CO)$_4$}$_2$] (**5**)

A solution of W(CO)$_6$ (0.10 g, 0.28 mmol) and Ph$_2$SiH$_2$ (0.05 cm^3, 0.27 mmol) in *n*-heptane (40 cm^3) was stirred and irradiated at 283 K. 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.* 1983 cm^{-1} reached its minimum intensity (*ca.* 4 h). All volatile materials were then evaporated under reduced pressure at room temperature to yield a brown solid. A sample analyzed by NMR methods in C$_7$D$_8$ solution showed the presence of the compound [(μ-SiPh$_2$){W(CO)$_5$}$_2$] [6] (*ca.* 80%), [{W(μ-η^2-H–

SiPh$_2$)(CO)$_4$}$_2$] (**5**) and a dihydride species, that latter detected only by ^{1}H NMR. The dihydride species was detected by ^{1}H NMR in toluene-d_8 at 243 K due to two equal intensity signals at δ −7.26 (d, $J_{H–H}$ = 2.7 Hz, $^1J_{W–H}$ = 39 Hz) and −7.62 ($J_{H–H}$ = 2.7 Hz, $^1J_{W–H}$ = 41 Hz).

NMR data for [{W(μ-η^2-H–SiPh$_2$)(CO)$_4$}$_2$] (**5**): ^{1}H NMR (toluene-d_8, 243 K) δ = −7.50 ($^1J_{W–H}$ = 33 Hz, $^1J_{Si–H}$ = 41 Hz). ^{13}C{^{1}H} NMR (toluene-d_8, 243 K) δ = 206.5 (1 C, CO), 198.7 (1C, CO), 192.4 (2C, CO). ^{29}Si{^{1}H} NMR (toluene-d_8, 243 K) δ = 194.

Acknowledgements

References

[1] J.Y. Corey, J. Braddock-Wilking, Chem. Rev. 99 (1999) 175.
[2] B. Marciniec, Coord. Chem. Rev. 249 (2005) 2374.
[3] A. Gądek, A. Kochel, T. Szymańska-Buzar, J. Organomet. Chem. 692 (2007) 3765.
[4] M. Stosur, A. Kochel, A. Keller, T. Szymańska-Buzar, Organometallics 25 (2006) 3791.
[5] A. Gądek, T. Szymańska-Buzar, Polyhedron 25 (2006) 1441.
[6] A. Gądek, A. Kochel, T. Szymańska-Buzar, Organometallics 24 (2003) 4869.
[7] S.L. Matthews, V. Pons, D.M. Heinekey, Inorg. Chem. 45 (2006) 6453.
[8] S. Zhang, G.R. Dobson, T.L. Brown, J. Am. Chem. Soc. 113 (1991) 6908.
[9] K.T. Kotz, H. Yang, P.T. Snee, C.K. Payne, C.B. Harris, J. Organomet. Chem. 596 (2000) 183.
[10] T.J. Burkey, J. Am. Chem. Soc. 112 (1990) 8329.
[11] G.J. Kubas, Chem. Rev. 107 (2007) 4152.
[12] M.J. Bennett, K.A. Simpson, J. Am. Chem. Soc. 93 (1971) 7156.
[13] M.A. Schroeder, M.S. Wrighton, J. Am. Chem. Soc. 96 (1974) 6235.
[14] W. Abdelgader, D. Chmielewski, F.-W. Grevels, S. Özkar, N.B. Peynircioglu, Organometallics 15 (1996) 604.
[15] T. Szymańska-Buzar, T. Głowiak, I. Czeluśniak, M. Górski, Inorg. Chem. Commun. 5 (2002) 682.
[16] T. Szymańska-Buzar, T. Głowiak, Polyhedron 16 (1997) 1599.
[17] H. Piana, U. Schubert, J. Organomet. Chem. 411 (1991) 303.
[18] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, San Diego, CA, 1997.
[19] N.B. Bespalova, M.A. Bovina, A.A. Popov, J.C. Mol, J. Mol. Catal. A. Chem. 160 (2000) 157.
[20] H.G. Kuivila, C.R. Warner, J. Org. Chem. 29 (1964) 2845.
[21] K. Karlou-Eyrisch, B.K.M. Müller, C. Herzig, O. Nuyken, Des. Monomers Polym. 7 (2004) 661.
[22] K.L. Makovetsky, E.S. Finkel'shtein, I.Y. Ostrovskaya, E.B. Portnykh, I. Gorbacheva, A.I. Golberg, N.V. Ushakov, Y.P. Yampolsky, J. Mol. Catal. 76 (1992) 107.
[23] E.S. Finkel'shtein, N.V. Ushakov, E.B. Portnykh, J. Mol. Catal. 76 (1992) 133.
[24] K. Karlou-Eyrisch, B.K.M. Müller, C. Herzig, O. Nuyken, J. Organomet. Chem. 606 (2000) 3.
[25] M. Górski, A. Kochel, T. Szymańska-Buzar, Organometallics 23 (2004) 3037.
[26] A. Gądek, A. Kochel, T. Szymańska-Buzar, J. Organomet. Chem. 690 (2005) 685.
[27] C. Lopez, M.A. Muñóz-Hernández, D. Morales-Morales, F. del Rio, S. Hernández- Ortega, R.A. Toscano, J.J. Garcia, J. Organomet. Chem. 672 (2003) 58.
[28] S. Pasynkiewicz, J. Jankowski, Appl. Organomet. Chem. 9 (1995) 335.
[29] F.-W. Grevels, J. Jacke, P. Betz, C. Krüger, Y.-H. Tsay, Organometallics 8 (1989) 293.
[30] R.B. King, A. Fronzaglia, Inorg. Chem. 5 (1966) 1837.