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# The UV-Light Initiated Reaction of Organosilanes with Tungsten Hexacarbonyl: Formation of an Organosilylene Complex and Organosilylium Salts

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Klaus Jurkschat\*<sup>[a]</sup>

Dedicated to Professor Michael Veith on the occasion of his 65th birthday.

**Keywords:** Silicon, Carbene homologues, Tungsten, Silylene Complex, Organosilylium cation,

UV-irradiation of the diorganosilane [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]SiH<sub>2</sub>Ph in the presence of W(CO)<sub>6</sub> provided a mixture consisting of the diorganosilylene tungsten pentacarbonyl complex [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>](Ph)SiW(CO)<sub>5</sub>, **2**, the organosilylium salt [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Si(H)Ph]<sup>+</sup>[(CO)<sub>5</sub>W]<sub>2</sub>H<sup>-</sup>, **3**, and an unidentified species. UV-irradiation of the triorganosilane [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]SiHPh<sub>2</sub> in presence of W(CO)<sub>6</sub> provided the organosilylium salt [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>SiPh<sub>2</sub>]<sup>+</sup>[(CO)<sub>5</sub>W]<sub>2</sub>H<sup>-</sup>, **6**, whereas, under the same conditions, no reaction was observed between the tetraorganosilane [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]SiPh<sub>3</sub> and W(CO)<sub>6</sub>. The reaction of compound **2** with Ph<sub>3</sub>C<sup>+</sup>PF<sub>6</sub><sup>-</sup> gave the fluorine-substituted silylene complex [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>](F)SiW(CO)<sub>5</sub>, **4**, whereas the reactions of **3** with Ph<sub>4</sub>PBr and **5** with water gave the benzoxasilaphospholes **3a**, **3b**, and **7**, respectively. The compounds **2** and **6** were isolated and characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, <sup>31</sup>P NMR, and IR-spectroscopy, electrospray ionization mass spectrometry, and in case of **2** also by single-crystal X-ray diffraction analysis. The compounds **3**, **3a**, **3b**, **4**, and **7** were not isolated but identified unambiguously by NMR spectroscopy and electrospray ionization mass spectrometry.

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## Introduction

In context with the ongoing interest in carbenes [1] and their heavy element analogues [2], divalent silicon compounds have attracted considerable interest over the last three decades [3]. The concepts that allow stabilization of these reactive species include the use of bulky substituents, bonding of the silicon atom to  $\Pi$ -electron donor atoms such as nitrogen, increase of the coordination number at the silicon atom by intramolecular donor-acceptor interaction, and complexation of silylenes by transition metal moieties. The idea behind the latter is related to the isolation of carbene transition metal complexes in the late sixties [4].

The first organosilylene transition metal complex, namely  $\text{Me}_2\text{Si}(\text{Et}_2\text{NH})\text{Fe}(\text{CO})_4$ , was prepared by UV-irradiation of an equimolar mixture containing  $\text{Fe}(\text{CO})_5$  and  $\text{HSiMe}_2(\text{NEt}_2)$  [5]. Over the years, alternative synthetic routes to organosilylene transition metal complexes such as dehalogenation of silicon(IV) compounds by transition metal dianions [6] and the reaction of stable silylenes with transition metal compounds [3b, 7] were developed, and the reactivity of transition-metal silylene complexes was systematically investigated [8]. Nevertheless, UV-irradiation of Si-H containing organosilanes with transition metal compounds still is a rather fruitful methodology for the synthesis of both base-free [9-16] and base-stabilized [17-19] silylene complexes. Associated with this is the desire to get more insight into the mechanism of Si-H bond activation by transition metal compounds [20-29] which in turn is relevant even for the topic of C-H bond activation [30] as well as for the understanding of transition metal-catalyzed oligo- and polysilane formation [31].

The synthesis and characterization of silylium salts,  $\text{R}_3\text{Si}^+\text{X}^-$ , is another intensively studied topic in contemporary silicon chemistry and major achievements have recently been reviewed [32]. Notably, in context with the investigations on Si-H bond-activation by transition metal complexes we are not aware of any silylium salts that contain transition metal-based anions.

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3 For some years we have been interested in the application of phosphorus-containing  
4 O,C,O-coordinating pincer-type ligands to the synthesis of, among others [33-36],  
5 intramolecularly coordinated organoelement compounds of types (A) - (E) (Figure 1) [37, 38].  
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10 {Insert Figure 1 here}  
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15 With the intention to extend this series by the related silicon-containing representative [4-  
16 *t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>2</sub>](Ph)SiW(CO)<sub>5</sub> we performed the reaction of [4-*t*-Bu-2,6-  
17 {P(O)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]SiH<sub>2</sub>Ph with W(CO)<sub>6</sub> and learned that what had been thought to be a  
18 routine-type investigation turned out to be rather complex and to give not only a novel  
19 organosilylene complex but also evidence for formation of an organosilylium salt.  
20 Furthermore, in the course of our studies we obtained some insight into the role of  
21 intramolecularly coordinating phosphonyl groups on the product distribution.  
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## 34 Results and discussion

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36 *Reaction of {4-*t*-Bu-2,6-[P(O)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>2</sub>}SiH<sub>2</sub>Ph with W(CO)<sub>6</sub>.*  
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38 The <sup>31</sup>P-NMR spectrum (THF, D<sub>2</sub>O-capillary, 121.49 MHz, Figure 2) of a sample (hereafter  
39 referred to as sample 1, Experiment 1) taken from a reaction mixture in THF containing the  
40 diorganosilane {4-*t*-Bu-2,6-[P(O)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>2</sub>}Si(H)<sub>2</sub>Ph, **1**, and tungsten hexacarbonyl,  
41 W(CO)<sub>6</sub>, in a molar ratio of 1:1.5 which had been irradiated with UV-light for 40 min  
42 displayed resonances at δ 16.5 (integral 4.6, 3-*t*-Bu-1,5-[P(O)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), δ 18.2 (integral  
43 7.6, **1**), δ 19.2 (integral 13.5, signal A), δ 21.6 (integral 9.6, signal B), δ 25.9 (integral 92.8,  
44 signal C), δ 27.3 (integral 25.3, signal D), and δ 28.5 (integral 11.0, signal E). The <sup>31</sup>P NMR  
45 spectrum (Figure 2) of the same reaction mixture which had been irradiated for further 45 min  
46 and stirred for another 50 min (sample 2) showed almost complete disappearance of the  
47 signals between 16.5 and 21.6 ppm and change of the integral ratio of the signals C:D:E to  
48 9.9:47.6:34.2.  
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{Insert Figure 2 here}

The  $^{29}\text{Si}$  NMR spectrum of this reaction mixture from which the THF had been removed in vacuo and which had been re-dissolved in  $\text{C}_6\text{D}_6$  (sample 3) displayed a triplet resonance at  $\delta$  58.1 ( $J(^{29}\text{Si}-^{31}\text{P}) = 9.4$  Hz,  $^1J(^{29}\text{Si}-^{183}\text{W}) = 131$  Hz, signal F) and a singlet at  $\delta$  -76.7 (signal G). Signals D ( $^{31}\text{P}$ ) and F ( $^{29}\text{Si}$ ) are assigned to the heteroleptic diorganosilylene tungsten pentacarbonyl complex  $[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{O}i\text{-Pr})_2\}_2\text{C}_6\text{H}_2](\text{Ph})\text{SiW}(\text{CO})_5$ , **2**, (see below) whereas signals E ( $^{31}\text{P}$ ) and G ( $^{29}\text{Si}$ ) belong to the diorganosilylium salt  $[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{O}i\text{-Pr})_2\}_2\text{C}_6\text{H}_2]\text{Si}(\text{H})\text{Ph}^+ [\{(\text{CO})_5\text{W}\}_2\text{H}]^-$ , **3**. The assignment of the latter gets support from (i) the  $^1\text{H}$ -coupled  $^{29}\text{Si}$  NMR spectrum showing a doublet resonance at  $\delta$ -76.9 ( $^1J(^{29}\text{Si}-^1\text{H}) = 307$  Hz) with both the chemical shift and the coupling constants being almost identical to those reported for  $[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{O}i\text{-Pr})_2\}_2\text{C}_6\text{H}_2]\text{Si}(\text{H})\text{Ph}^+ \text{PF}_6^-$  ( $\delta$  -77.9, 305 Hz) [34] and (ii) the  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 300.13 MHz) showing a triplet resonance for the Si-*H* proton at  $\delta$  5.76 ( $J(^1\text{H}-^{31}\text{P}) = 14$  Hz) and a singlet resonance for the bridging  $\text{W}_2\text{H}$  proton at  $\delta$  -11.90 ( $^1J(^1\text{H}-^{183}\text{W}) = 42$  Hz). The chemical shift [39], the coupling pattern as well as the signal-to-satellite integral ratio (2.98:14.39:65.29:14.39:2.95) of the latter signal unambiguously indicate the presence of the  $[\{(\text{CO})_5\text{W}\}_2\text{H}]^-$  anion [39]. Notably, this anion was characterized in the solid state, as its tetraethyl ammonium respectively tetraphenylphosphonium salt, by neutron diffraction analysis [40]. Furthermore, a HMBC-spectrum shows a correlation of this  $^1\text{H}$ -resonance with the  $^{13}\text{C}$  carbonyl resonances at  $\delta$  199.7 and  $\delta$  201.8. Finally, the electrospray ionization mass spectrum (positive mode) showed a major mass cluster centred at  $m/z = 567.3$  which corresponds to the empirical formula  $\text{C}_{28}\text{H}_{45}\text{O}_6\text{P}_2\text{Si}$ , that is the cation of compound **3**. In the negative mode there are mass clusters centred at 592.7 (minor), 480.7, and 452.7 that correspond to  $[\text{W}_2(\text{CO})_8\text{H}]^-$ ,  $[\text{W}_2(\text{CO})_4\text{H}]^-$ , and  $[\text{W}_2(\text{CO})_3\text{H}]^-$ , respectively. Despite many attempts we failed to isolate analytically pure

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3 compound **3**. However, its existence is supported further by a subsequent reaction. Thus, the  
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5  $^{31}\text{P}$  NMR spectrum (121.49 MHz, toluene/ $\text{C}_6\text{D}_6$ ) of a reaction mixture containing compound **3**  
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7 (generated *in situ* as described above) to which had been added one molar equiv  $\text{Ph}_4\text{PBr}$  and  
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9 which had been kept for two hours at  $40^\circ\text{C}$  showed complete disappearance of **3** and, in  
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11 addition to a singlet at  $\delta$  24.1 ( $\text{Ph}_4\text{P}^+$ ) two pairs of doublets at  $\delta$  16.6 (d,  $^4J(^{31}\text{P}-^{31}\text{P}) = 7.2$   
12  
13 Hz)/19.4 (d,  $^4J(^{31}\text{P}-^{31}\text{P}) = 7.2$  Hz) (integral 60) and  $\delta$  17.1 (d,  $^4J(^{31}\text{P}-^{31}\text{P}) = 7.2$  Hz)/19.6 (d,  
14  
15  $^4J(^{31}\text{P}-^{31}\text{P}) = 7.2$  Hz) (integral 40). The pairs of doublets are assigned to the two diastereomers  
16  
17 of the benzoxasilaphosphole **3a**, **3b** (Figure 3). The synthesis and molecular structure of a  
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19 related methyl/phenyl substituted benzoxasilaphosphole was already reported by us [41].  
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27 {Insert Figure 3 here}

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32 Most interestingly, the  $^1\text{H}$  NMR spectrum (599.83 MHz, THF, suppression of solvent  
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34 signals, Figure 4) of sample 1 (see above) displayed in addition to the signals for the bridging  
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36  $\text{W}_2\text{H}$  proton ( $\delta$  -12.63,  $^1J(^1\text{H}-^{183}\text{W}) = 42$  Hz), the methyl and *t*-butyl protons ( $\delta$  0.75-1.5), the  
37  
38 *OCH* protons ( $\delta$  4.70-4.90), the aromatic protons ( $\delta$  7.00-8.40), the Si-H protons ( $\delta$  5.28,  
39  
40  $^1J(^1\text{H}-^{29}\text{Si}) = 206$  Hz, integral 2.00, **1**;  $\delta$  5.38,  $^1J(^1\text{H}-^{29}\text{Si}) = 307$  Hz,  $J(^1\text{H}-^{31}\text{P}) = 14$  Hz,  
41  
42 integral 0.72, **3**) two equally intense AB-type resonances located at  $\delta$  5.84 (integral 0.79,  
43  
44  $J(^1\text{H}-^1\text{H}) = 9$  Hz, signal H) and  $\delta$  5.98 (integral 0.79,  $J(^1\text{H}-^1\text{H}) = 9$  Hz,  
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46 signal I).  
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51 {Insert Figure 4 here}

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56 Also present were two singlet resonances at  $\delta$  6.31 (integral 0.90, signal J) and  $\delta$  6.76  
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58 (integral 0.56, signal K). After the sample had been left at room temperature for 12 h the  
59  
60 signal assigned to the diorganosilane **1** and the signals H – K almost completely disappeared

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3 leaving the triplet resonance at  $\delta$  5.38 assigned to the diorganosilylium salt **3** as the only Si-H-  
4  
5 containing species.  
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8 The same picture was seen in the  $^1\text{H}$  NMR spectrum of a sample obtained by addition of the  
9  
10 diorganosilane **1** to  $\text{W}(\text{CO})_5(\text{THF})$  which had been generated in situ by UV-irradiation of  
11  
12  $\text{W}(\text{CO})_6$  in THF (sample 4). In a control experiment a solution in THF of the diorganosilane **1**  
13  
14 was UV-irradiated for 80 min in absence of  $\text{W}(\text{CO})_6$ . The  $^1\text{H}$  NMR spectrum (599.83 MHz,  
15  
16 suppression of solvent signals) showed in addition to the singlet at  $\delta$  5.28 (diorganosilane **1**)  
17  
18 at least six singlet resonances with different integrals between 5.05 and 5.20 ppm and a singlet  
19  
20 resonance at  $\delta$  6.10. These resonances were not assigned. Most importantly, no AB-type  
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22 resonances as described above (signals H, I) were observed.  
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27 In order to see the influence of the phosphonyl moieties in the diorganosilane **1** on the  
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29 outcome of the UV-irradiation experiments, we performed the reaction under the same  
30  
31 conditions with diphenylsilane,  $\text{Ph}_2\text{SiH}_2$ . The  $^1\text{H}$  NMR spectrum (THF,  $\text{D}_2\text{O}$ -capillary, 599.83  
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33 MHz, suppression of solvent signals) of a sample taken from a reaction mixture in THF  
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35 containing  $\text{Ph}_2\text{SiH}_2$  and  $\text{W}(\text{CO})_6$  in a molar ratio of 1:1.5 which had been irradiated with UV-  
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37 light for 20 min and which had been stored at room temperature for 3 h (sample 5) displayed  
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39 in addition to the signals for the phenyl protons ( $\delta$  7.20-7.60) and the singlet resonance for  
40  
41 the Si-H protons of  $\text{Ph}_2\text{SiH}_2$  ( $\delta$  4.88,  $^1J(^1\text{H}-^{29}\text{Si}) = 198$  Hz) a resonance at  $\delta$  -3.85 ( $^1J(^1\text{H}-$   
42  
43  $^{183}\text{W}) = 18$  Hz). The integral of the latter signal increased with time (without further  
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45 irradiation) whereas that of the Si-H resonance decreased. Moreover, new signals appeared in  
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47 the phenyl region together with a singlet at  $\delta$  7.27 ppm that is assigned to benzene.  
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54 *One* possibility/proposal to rationalize the experiments described above is shown in Scheme  
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58 {Insert Scheme 1 here}  
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3 In the first step the diorganosilane tungstenpentacarbonyl complex  $(\text{CO})_5\text{W}(\eta^2\text{-RPhSiH}_2)$ , (**I**),  
4 is formed. It has a limited life-time and was identified only for  $\text{R} = 4\text{-}t\text{-Bu-2,6-[P(O)(O}i\text{-}$   
5  $\text{Pr})_2]_2\text{C}_6\text{H}_2$  by the AB-type  $^1\text{H}$ -resonance. Complex of type (**I**) reacts further to give the  
6 insertion product of type (**II**) which can be represented by canonical formulas (**IIa**) and (**IIb**).  
7 This intermediate is highly reactive and was not detected by NMR spectroscopy. Its reactivity  
8 towards  $\text{W}(\text{CO})_5(\text{THF})$  that is still present in the reaction mixture depends on the identity of  
9 the substituent R. For  $\text{R} = \text{Ph}$ , the bis(pentacarbonylhydridotungsten)diphenylsilane  
10  $\text{Ph}_2\text{Si}[\text{W}(\text{CO})_5\text{H}]_2$  (**III**) is formed which was identified by its  $^1\text{H}$  resonance at  $\delta\text{-}3.85$  ( $^1J(^1\text{H-}$   
11  $^{183}\text{W}) = 18$  Hz). On the other hand, the complex of type (**II**) with  $\text{R} = 4\text{-}t\text{-Bu-2,6-[P(O)(O}i\text{-}$   
12  $\text{Pr})_2]_2\text{C}_6\text{H}_2$  yields the diorganosiliconium salt **3**. Apparently, the intramolecularly coordinating  
13 phosphonyl groups in the latter stabilize the siliconium cation and make this reaction path  
14 possible. Formation under different reaction conditions of the diphenylsilylene-bridged  
15 ditungstendecacarbonyl complex  $\text{Ph}_2\text{SiW}_2(\text{CO})_{10}$ , (**IV**), as reported by *Szymanska-Buzar* et al  
16 [15a-c], appears feasible by loss of hydrogen,  $\text{H}_2$ , from complex (**III**). However, it is not clear  
17 to us how the diorganosilylene complex **2** is formed. *One* hypothesis is that for  $\text{R} = 4\text{-}t\text{-Bu-}$   
18  $2,6\text{-[P(O)(O}i\text{-Pr})_2]_2\text{C}_6\text{H}_2$  loss of hydrogen,  $\text{H}_2$ , from complex (**II**) (path 2) is competitive with  
19 the reaction of path 3 and that for this particular R the rate constants for the reactions of paths  
20 2 and 3 are bigger than the rate constant for the reaction according to path 1. This would also  
21 explain why the intramolecularly coordinated diorganosilane **1** reacts with  $\text{W}(\text{CO})_6$  to give the  
22 mononuclear tungstenpentacarbonyl complex **2** and not  $\text{PhRSiW}_2(\text{CO})_{10}$ , the dinuclear  
23 silylene-bridged analogue of  $\text{Ph}_2\text{SiW}_2(\text{CO})_{10}$ . Notably, diphenylsilane,  $\text{Ph}_2\text{SiH}_2$ , was reported  
24 to react, under different reaction conditions, with tungsten hexacarbonyl,  $\text{W}(\text{CO})_6$ , to give  
25  $[(\text{CO})_4\text{WSiPh}_2]_2$  [15d].

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58 Our findings concerning the AB-type resonances in the  $^1\text{H}$  NMR spectra of samples 1  
59 and 4 deserve some further comments as they are complementary/contradictory to results  
60 previously reported for diphenylsilane transition metal complexes of type  $\text{L}_n\text{M}(\text{Ph}_2\text{SiH}_2)$

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3 (L<sub>n</sub>M = C<sub>6</sub>Me<sub>6</sub>(CO)<sub>2</sub>Cr [42], Cp<sub>2</sub>(PMe<sub>3</sub>)Ti [24], (CO)<sub>5</sub>W [28]). The <sup>1</sup>H NMR spectra of all  
4 these complexes are characterized by two equally intense Si-H resonances which are (i)  
5 separated by at least 10 ppm and (ii) exhibit  $J(^1\text{H}-^{29}\text{Si})$  satellites being bigger respectively  
6 smaller than the  $^1J(^1\text{H}-^{29}\text{Si})$  coupling in uncoordinated diphenylsilane. These results were  
7 interpreted in terms of Ph<sub>2</sub>SiH<sub>2</sub> being η<sup>2</sup>-coordinated with one proton strongly interacting with  
8 the transition metal. In fact, the rather high-field shifts of one of the proton resonances even  
9 suggest complete oxidative addition of the Ph<sub>2</sub>SiH<sub>2</sub> to give L<sub>n</sub>M(H)-Si(H)Ph<sub>2</sub>. In our case  
10 (Figure 2, complex **I** in Scheme 1), however, the <sup>1</sup>H resonances of the two protons are  
11 separated by only 0.14 ppm, both resonances fall in the chemical shift region for Ph<sub>2</sub>SiH<sub>2</sub>, and  
12 only one resonance displayed  $J(^1\text{H}-^{29}\text{Si})$  satellites. So far, we have no straightforward  
13 explanation to account for this phenomenon. One possibility is that in complex (**I**)  
14 intramolecular P=O...H-Si(W) hydrogen bridges play a role and counterbalance the high-field  
15 shift induced by the influence of tungsten. An alternative is that compound **1** is indeed side-on  
16 coordinated to the tungsten atom with the hydrogen atom keeping its Si-bound character.  
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39 Compound **2** was isolated as its toluene solvate [**2** · 0.25 C<sub>7</sub>H<sub>8</sub>] from the reaction  
40 mixture obtained by Experiment 1. It is a yellow, crystalline, sharp melting compound which  
41 is well soluble in organic solvents such as benzene, CH<sub>2</sub>Cl<sub>2</sub>, and THF.  
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45 The molecular structure of compound **2** is shown in Figure 5 and selected bond  
46 distances and bond angles are given in Table 1.  
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{Insert Figure 5 here}

{Insert Table 1 here}

The silicon atom in **2** adopts a distorted trigonal-bipyramidal configuration (geometrical goodness [43-45]  $\Delta\Sigma(\theta) = 56.5^\circ$ ) with C(1), C(21) and W(1) occupying the equatorial and O(1) and O(2) occupying the axial positions. The Si(1) atom is displaced from the plane defined by C(1), C(21), W(1) by 0.339 (7) Å in direction of the O(1) atom. As result of ligand constraint, the O(1)-Si(1)-O(2) bond angle amounts to 162.2(3)°. The equatorial C(1)-Si(1)-C(21), C(1)-Si(1)-W(1), and C(21)-Si(1)-W(1) angles amount to 105.4(4), 122.5(4), and 124.5(4)°, respectively. The small C(21)-Si(1)-C(1) angle is the result of the steric interaction between the tungsten pentacarbonyl fragment and the silicon-bound phenyl group. The Si(1)-O(1) [1.986(7) Å] and Si(1)-O(2) [2.670(7) Å] distances are rather different. The short distance is close to the corresponding distances in the triorganosilylium salt [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]SiPh<sub>2</sub><sup>+</sup> PF<sub>6</sub><sup>-</sup> (1.922(1), 1.931(1) Å) [33] whereas the long distance is similar to the P=O→Si distance determined for the benzoxasilaphosphole [1(*P*),3(*Si*)-P(O)(OEt)OSi(Ph)(Me)-6-*t*-Bu-4-P(O)(OEt)<sub>2</sub>]C<sub>6</sub>H<sub>2</sub> (2.614(2) Å) [41]. The Si(1)-W(1) distance of 2.636(7) Å is even longer than the Si-W distances reported for ( $\mu$ -SiPh<sub>2</sub>)W<sub>2</sub>(CO)<sub>10</sub> (2.577(2)/2.591(2) Å) [15] which in turn are the longest of such distances out of nine examples listed in the *Cambridge Crystallographic Data Base* [46, 47]. The shortest Si-W distances were found for [Cp<sup>\*</sup>(dmpe)(H)<sub>2</sub>WSiMe<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (2.358(2) Å) [48] and ( $\eta$ -C<sub>5</sub>Me<sub>4</sub>Et)W(CO)<sub>2</sub>(SiMes<sub>2</sub>SiMe<sub>3</sub>) (2.3850(12) Å) [49] containing three-coordinate silicon whereas an intermediate Si-W distance of 2.487(3) Å was determined for Cp<sup>\*</sup>(CO)<sub>2</sub>W{ $\kappa^2$ (Si,C)-SiMe<sub>2</sub>-NMe<sub>2</sub>(*o*-C<sub>6</sub>H<sub>4</sub>)}[19]. Apparently, the intramolecular O(1)→Si(1) and O(2)→Si(1) interactions in complex **2** decrease the  $\Pi$ -acceptor strength of the silicon atom and cause the lengthening of the Si(1)-W(1) distance.

1  
2  
3 In previous work we have shown that triphenylmethyl hexafluorophosphate,  
4  $\text{Ph}_3\text{C}^+\text{PF}_6^-$ , reacts with  $[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{OEt})_2\}_2\text{C}_6\text{H}_2]\text{SiPh}_3$  under Si-C bond cleavage to  
5  
6 give the corresponding triorganosilylium salt  $[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{OEt})_2\}_2\text{C}_6\text{H}_2]\text{SiPh}_2^+\text{PF}_6^-$   
7  
8 [41]. In this context and in view of the general interest in silylium cations [32] we looked at  
9  
10 the reactivity of the silylene complex **2** towards  $\text{Ph}_3\text{C}^+\text{PF}_6^-$ . Indeed, the  $^{31}\text{P}$ ,  $^{19}\text{F}$  and  $^{29}\text{Si}$  NMR  
11  
12 spectra of a sample taken from a solution in toluene/ $\text{C}_6\text{D}_6$  containing equimolar amounts of  
13  
14 compound **2** and  $\text{Ph}_3\text{C}^+\text{PF}_6^-$  which had been stirred at room temperature for 4.5 h showed a  
15  
16 doublet resonance at  $\delta 26.4$  ( $J(^{31}\text{P}-^{19}\text{F})$  9.4 Hz), a triplet resonance at  $\delta -154.7$  ( $J(^{19}\text{F}-^{31}\text{P})$  9.5  
17  
18 Hz,  $^1J(^{19}\text{F}-^{29}\text{Si})$  255.5 Hz), and a doublet of triplet resonance at  $\delta -87.3$  ( $^1J(^{29}\text{Si}-^{19}\text{F})$  255.5 Hz,  
19  
20  $J(^{29}\text{Si}-^{31}\text{P})$  12.5 Hz), respectively. The data unambiguously indicate formation of the fluorine-  
21  
22 substituted silylene complex  $[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{O}i\text{-Pr})_2\}_2\text{C}_6\text{H}_2](\text{F})\text{SiW}(\text{CO})_5$ , **4** (eq 1).  
23  
24 Moreover, the  $^{13}\text{C}$  NMR spectrum of this sample showed, in addition to other signals, a  
25  
26 resonance at  $\delta 65.0$  that is assigned to the quaternary carbon of tetraphenyl methane,  $\text{Ph}_4\text{C}$   
27  
28 [50]. It supports the reaction shown in eq 1.  
29  
30  
31  
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38

39 **{Insert Equation 1 here}**  
40  
41  
42

43  
44 Apparently, the cation  $\{[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{O}i\text{-Pr})_2\}_2\text{C}_6\text{H}_2]\text{SiW}(\text{CO})_5\}^+$  that is formed in the  
45  
46 first reaction step is a rather strong Lewis acid and reacts with the  $\text{PF}_6^-$  anion to give  
47  
48 compound **4** and  $\text{PF}_5$ . Notably, the organosilylene complex  $2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4(\text{H})\text{SiCr}(\text{CO})_5$   
49  
50 was reported to react with  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  to give  $2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4(\text{F})\text{SiCr}(\text{CO})_5$ ,  $\text{Ph}_3\text{CH}$ , and  
51  
52  $\text{BF}_3$  [17].  
53  
54  
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57

58 *Reaction of tri- and tetraorganosilanes, respectively,  $[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{O}i\text{-Pr})_2\}_2\text{C}_6\text{H}_2]\text{SiRPh}_2$  ( $R = \text{H}, \text{Ph}$ ) with  $\text{W}(\text{CO})_6$ .*  
59  
60

1  
2  
3 In previous work it was demonstrated that Si-H bond activation is not the only reaction that  
4 takes place upon UV-irradiation of a triorganosilane in presence of a transition metal  
5 carbonyl. Thus, formation of  $W(CO)_3(\eta^6\text{-PhSiHPh}_2)$  was observed in the reaction of  $\text{Ph}_3\text{SiH}$   
6 with  $W(CO)_6$  [51]. In contrast to this finding, reaction in THF under UV-irradiation of the  
7 intramolecularly coordinated triorganosilane  $[4\text{-}t\text{-Bu-2,6-}\{\text{P(O)(}i\text{-Pr)}_2\}_2\text{C}_6\text{H}_2\}\text{SiPh}_2\text{H}$  with  
8 tungsten hexacarbonyl,  $W(CO)_6$ , exclusively and independent of the ratio of the reactants  
9 provided the triorganosilylium salt  $[4\text{-}t\text{-Bu-2,6-}\{\text{P(O)(}i\text{-Pr)}_2\}_2\text{C}_6\text{H}_2\}\text{SiPh}_2^+ [(\text{CO})_5\text{W}]_2\text{H}^-$ ,  
10  
11  
12  
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14  
15  
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19  
20 **6** (eq 2).

21  
22 **{Insert Equation 2 here}**  
23  
24  
25  
26

27 Compound **6** was isolated as an amorphous sharp melting solid that is soluble in  
28 dichloromethane, diethyl ether, and thf. In addition to elemental analysis, its identity was  
29 confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^{31}\text{P}$  NMR spectra showing, among others, resonances at  $\delta$   
30  $-11.9$  ( $W_2(CO)_{10}H$ ),  $\delta$   $199.4$  ( $^1J(^{13}\text{C}-^{183}\text{W})$  124 Hz,  $W_2(CO)_{10}H$ )/ $201.4$  ( $^1J(^{13}\text{C}-^{183}\text{W})$  162 Hz,  
31  $W_2(CO)_{10}H$ ),  $\delta$   $159.8$  (t,  $^2J(^{13}\text{C}-^{31}\text{P})$  12.6 Hz, SiC),  $\delta$   $-67.2$  ( $^{29}\text{Si}$ ), and  $\delta$   $26.9$  ( $^{31}\text{P}$ ),  
32  
33 respectively, with the two latter ones being almost identical with the corresponding  
34 resonances reported for  $[4\text{-}t\text{-Bu-2,6-}\{\text{P(O)(}i\text{-Pr)}_2\}_2\text{C}_6\text{H}_2\}\text{SiPh}_2^+[\text{PF}_6]^-$  [33]. The electrospray  
35 mass spectrum (positive mode) displayed a mass cluster centred at  $m/z$  643.4 that corresponds  
36 to the triorganosilylium cation  $[4\text{-}t\text{-Bu-2,6-}\{\text{P(O)(}i\text{-Pr)}_2\}_2\text{C}_6\text{H}_2\}\text{SiPh}_2^+$ . In the negative mode  
37 a mass cluster centred at  $m/z$  480.9 was observed that corresponds to  $[W_2(CO)_4H]^-$ .  
38  
39 Moreover, the  $^{31}\text{P}$  NMR spectrum of a sample of **6** in thf/ $\text{C}_6\text{D}_6$  to which had been added a  
40 droplet of water and which had been kept for 24 h at room temperature displayed equally  
41 intense doublet resonances at  $\delta$   $18.6$  ( $J(^{31}\text{P}-^{31}\text{P})$  5.5 Hz) and  $\delta$   $21.3$  ( $J(^{31}\text{P}-^{31}\text{P})$  5.5 Hz). These  
42 resonances are assigned to the benzoxasilaphosphole **7** [52] (Figure 3). The assignment is  
43 unambiguous as addition of a small amount of compound **7** caused the integral of the two  $^{31}\text{P}$   
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45  
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60 NMR resonances to increase.

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3 It is rather likely that formation of the triorganosiliconium salt **6** proceeds, in the rate-  
4 determining step, via the intermediate  $[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{O}i\text{-Pr})_2\}_2\text{C}_6\text{H}_2\text{SiPh}_2]^+[(\text{CO})_5\text{WH}]^-$ ,  
5  
6  
7  
8 (V), and that this intermediate reacts fast with  $\text{W}(\text{CO})_5(\text{THF})$ . This is in line with the  
9  
10 discussion concerning Scheme 1.  
11

12  
13 No reaction, however, was observed upon UV-irradiation in THF of the  
14  
15 tetraorganosilane  $[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{O}i\text{-Pr})_2\}_2\text{C}_6\text{H}_2\text{SiPh}_3$  with  $\text{W}(\text{CO})_6$ .  
16  
17

## 18 19 20 **Conclusion**

21  
22 In analogy to previous work [17, 18] we have shown that UV-irradiation of diorganosilanes  
23  
24 with transition metal carbonyls gives access to organosilylene complexes, and here especially  
25  
26 to the novel heteroleptic diorganosilylene tungsten pentacarbonyl complex  $[4-t\text{-Bu-2,6-}$   
27  
28  $\{\text{P}(\text{O})(\text{O}i\text{-Pr})_2\}_2\text{C}_6\text{H}_2](\text{Ph})\text{SiW}(\text{CO})_5$ , **2**. In addition to this previous work, however, we  
29  
30 learned that potentially intramolecularly coordinating substituents in the organosilane  
31  
32 precursor control the product distribution and support the formation of organosilylium salts  
33  
34 such as  $[4-t\text{-Bu-2,6-}\{\text{P}(\text{O})(\text{O}i\text{-Pr})_2\}_2\text{C}_6\text{H}_2\text{Si}(\text{R})\text{Ph}]^+[(\text{CO})_5\text{W}]_2\text{H}]^-$ , (**3**, R = H; **6**, R = Ph)  
35  
36  
37  
38 Noteworthy, no formation of related organosilylium salts were reported in course of the  
39  
40 synthesis of aminoaryl silanediyl-transition metal complexes [18]. The question remains to be  
41  
42 answered whether these organosilylium salts were overlooked (difficult in situ monitoring of  
43  
44 the reaction mixture because no NMR-friendly phosphorus nucleus present) or whether the  
45  
46 identity and number of the donor functions (here two P=O versus one or two  $\text{Me}_2\text{N}$ ), and/or  
47  
48 the identity of the transition metal (here W versus Fe, Mo, Cr, Mn) control the formation of  
49  
50 such organosilylium salts.  
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52  
53  
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## 57 58 **Experimental**

59  
60 **General.** All solvents were dried and purified by standard procedures. All reactions were  
carried out under argon atmosphere using Schlenk techniques. The diorganosilane **1** was

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2  
3 prepared as previously reported [34]. The UV-irradiation was performed with a Normag TQ  
4  
5 150 (150 W, 85 V) mercury lamp. Bruker DPX-300, DRX-400, and Varian INOVA 600  
6  
7 spectrometers were used to obtain  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$  NMR spectra at room temperature.  $^1\text{H}$ ,  
8  
9  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$  NMR chemical shifts  $\delta$  are given in ppm and were referenced to  $\text{Me}_4\text{Si}$  and  
10  
11  $\text{H}_3\text{PO}_4$  (85%,  $^{31}\text{P}$ ). For the  $^1\text{H}$  NMR spectra in THF/ $\text{D}_2\text{O}$ -capillary the suppression of the  
12  
13 proton resonances of THF including their  $^{13}\text{C}$ -satellites, and of the signal of residual  $\text{H}_2\text{O}$   
14  
15 from the  $\text{D}_2\text{O}$ -capillary was performed with Scont-scan NMR and WET solvent suppression.  
16  
17 The IR spectra ( $\text{cm}^{-1}$ ) were recorded on a Bruker IFS 28 spectrometer and electrospray mass  
18  
19 spectra were obtained using a Thermoquest-Finnigan instrument with  $\text{CH}_3\text{CN}$  as the mobile  
20  
21 phase. Elemental analyses were performed on a LECO-CHNS-932 analyzer.  
22  
23  
24  
25  
26  
27  
28

## 29 Crystallography

30  
31  
32 A single crystal suitable for X-ray analysis was directly taken from the reaction  
33  
34 mixture and sealed with some dry paraffin oil. Crystal data and structure solution of **2**:  
35  
36  $\text{C}_{34}\text{H}_{44}\text{O}_{11}\text{P}_2\text{SiW} \cdot 0.25 \text{C}_7\text{H}_8$ ,  $M_r = 913.60$ , triclinic, P-1,  $a = 10.683(2)$ ,  $b = 10.931(2)$ ,  $c =$   
37  
38  $19.081(4)$  Å,  $\alpha = 74.095(12)^\circ$ ,  $\beta = 85.738(10)^\circ$ ,  $\gamma = 82.223(9)^\circ$ ,  $V = 2121.6(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x =$   
39  
40  $1.430 \text{ Mg}\cdot\text{m}^{-3}$ ,  $F(000) = 921$ ,  $\lambda(\text{MoK}\alpha) = 0.71073$  Å,  $\mu = 2.877 \text{ mm}^{-1}$ ,  $T = 173(1)$  K. The data  
41  
42 collection covered almost the whole sphere of reciprocal space with 3 sets at different k-  
43  
44 angles with 153 frames via  $\omega$ -rotation ( $\Delta/\omega = 2^\circ$ ) at two times 60s per frame. The crystal-to-  
45  
46 detector distances were 3.4 cm. Crystal decay was monitored by repeating the initial frame at  
47  
48 the end of data collection. The data was not corrected for absorption effects. Analyzing the  
49  
50 duplicate reflections there were no indications for any decay. The structures were solved by  
51  
52 direct methods (SHELXS97 [53]) and successive difference Fourier syntheses. Refinements  
53  
54 applied full-matrix least-squares methods (SHELXL97 [54]).  
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The H atoms were placed in geometrically calculated positions using a riding model with isotropic temperature factors constrained at 1.2 for non-methyl and at 1.5 for methyl groups

1  
2  
3 times  $U_{eq}$  of the carrier C atom. The solvent molecule toluene was isotropically refined with  
4  
5 an occupancy of 0.25 and a common  $U_{eq}$  as a regular hexagon and a fixed aryl-methyl  
6  
7 distance. One *i*-propyl group is disordered over two positions with occupancy of 0.5 (C32,  
8  
9 C32', C33, C33'). Si1, W1, two CO-groups and the *t*-butyl-group are disordered over two  
10  
11 positions with occupancies of 0.4 (Si1', W1', C13', O13', C15' O15', C8' C9', C10') and 0.6  
12  
13 (Si1, W1, C13, O13, C15 O15, C8 C9, C10). All disordered atoms were refined isotropically.  
14  
15 Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were  
16  
17 taken from International Tables for X-ray Crystallography [55]. The figures were created by  
18  
19 SHELXTL [56]. Selected bond distances and angles are given in Table 1.  $R_I = 0.0485$  for  
20  
21 3236 [ $I > 2\sigma(I)$ ] and  $wR_2 = 0.1119$  for 7541 independent reflections. The max. and min.  
22  
23 residual electron densities were 0.743 and  $-0.596 \text{ e}\cdot\text{\AA}^{-3}$ , respectively. Crystallographic data  
24  
25 for the structure reported in this paper have been deposited with the Cambridge  
26  
27 Crystallographic Data Centre as supplementary material publication no. CCDC 726151.  
28  
29 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road,  
30  
31 Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).  
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41 **{[2,6-Bis(diisopropoxyphosphonyl)-4-*tert*-butyl]phenyl}phenylsilicon(II)·tungsten penta-**  
42 **carbonyl, [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>2</sub>](Ph)SiW(CO)<sub>5</sub> (2):** A solution of {[2,6-bis-  
43  
44 (diisopropoxyphosphonyl)-4-*tert*-butyl]phenyl}dihydridophenylsilane (3.500 g, 6.15 mmol)  
45  
46 and tungsten hexacarbonyl (3.580 g, 9.23 mmol) in tetrahydrofuran (270 mL) was exposed  
47  
48 to UV-radiation for 40 min at room temperature. The volume of gaseous products was  
49  
50 258 mL. From this solution a sample of 600  $\mu\text{L}$  was collected and a  $^{31}\text{P}$  NMR spectrum  
51  
52 (THF / D<sub>2</sub>O-capillary) was recorded. UV-radiation was continued for another 45 min during  
53  
54 which additional 60 mL of gaseous products were collected. The solution thus obtained was  
55  
56 stirred for further 50 min. From this solution a sample 600  $\mu\text{L}$  was collected and a second  $^{31}\text{P}$   
57  
58 NMR spectrum (THF / D<sub>2</sub>O-capillary) was recorded. After the solvent had been evaporated  
59  
60

1  
2  
3 the residue was extracted with toluene (2 x 75 mL). The combined extracts were concentrated  
4  
5 in vacuo and *n*-hexane was added. Crystallization at 4 °C afforded 0.550 g (23%) of [2·0.25  
6  
7 C<sub>7</sub>H<sub>8</sub>] as yellow crystals of mp 135 °C. <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.79 (d, <sup>3</sup>J(<sup>1</sup>H -  
8  
9 <sup>1</sup>H) = 6.2 Hz, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)'), 0.97 (d, <sup>3</sup>J(<sup>1</sup>H - <sup>1</sup>H) = 5.7 Hz, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)'), 1.06  
10  
11 (s, 9H; C(CH<sub>3</sub>)<sub>3</sub>), 1.20 (d, <sup>3</sup>J(<sup>1</sup>H - <sup>1</sup>H) = 6.2 Hz, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)'), 1.30 (d, <sup>3</sup>J(<sup>1</sup>H -  
12  
13 <sup>1</sup>H) = 5.7 Hz, 6H, CH(CH<sub>3</sub>)(CH<sub>3</sub>)'), 4.18 (unresolved, 2H; OCH), 5.06 (unresolved, 2H;  
14  
15 OCH), 7.19-7.28 (unresolved, 3H; H<sub>m/p</sub>), 8.08 (unresolved, 2H; H<sub>3/5</sub>), 8.04-8.10 (unresolved,  
16  
17 2H; H<sub>o</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.63 MHz, C<sub>6</sub>D<sub>6</sub>): δ 23.3 (unresolved; C(CH<sub>3</sub>)<sub>2</sub>), 23.5 (C(CH<sub>3</sub>)<sub>2</sub>),  
18  
19 23.9 (C(CH<sub>3</sub>)<sub>2</sub>), 30.6 (s, 3C; C(CH<sub>3</sub>)<sub>3</sub>), 34.6 (s, 1C; C(CH<sub>3</sub>)<sub>3</sub>), 73.6 (2C) and 74.5 (2C) (OCH),  
20  
21 127.3 (s, 1C; C<sub>p</sub>), 127.9 (s, 2C; C<sub>m</sub>), 131.8 (dd, <sup>1</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 188 Hz, <sup>3</sup>J(<sup>13</sup>C - <sup>31</sup>P) = 21 Hz,  
22  
23 2C; C<sub>2,6</sub>), 132.0 (dd, <sup>2</sup>J(<sup>13</sup>C - <sup>31</sup>P) = 16 Hz, <sup>4</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 6 Hz, 2C; C<sub>3,5</sub>), 135.3 (s, 1C; C<sub>o</sub>),  
24  
25 145.4 (s, 1C; C<sub>i</sub>), 152.5 (t, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 13 Hz, 1C; C<sub>4</sub>), 163.1 (t, <sup>2</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 31 Hz, 1C; C<sub>1</sub>),  
26  
27 202.6 (s, <sup>1</sup>J(<sup>13</sup>C-<sup>183</sup>W) = 123 Hz, 4C; CO), 204.0 (s, 1C; CO). <sup>29</sup>Si NMR (79.49 MHz, C<sub>6</sub>D<sub>6</sub>):  
28  
29 δ 58.1 (t, <sup>1</sup>J(<sup>29</sup>Si-<sup>31</sup>P) = 10 Hz, <sup>1</sup>J(<sup>29</sup>Si-<sup>183</sup>W) = 129 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, C<sub>6</sub>D<sub>6</sub>): δ  
30  
31 27.9. IR (KBr):  $\tilde{\nu}$  (CO) 2050, 1962, 1908, 1880 cm<sup>-1</sup>. Electrospray-MS (M = [4-*t*-Bu-2,6-  
32  
33 {P(O)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>2</sub>](Ph)SiW(CO)<sub>5</sub>): m/z 863.1 [M - CO + H]<sup>+</sup>, m/z 807.0 [M - 3CO + H]<sup>+</sup>,  
34  
35 m/z 567.8 [M - W - 5CO + H]<sup>+</sup>. Elemental Analysis: C<sub>34.75</sub>H<sub>46</sub>O<sub>11</sub>P<sub>2</sub>SiW (913.56); C 45.4  
36  
37 (calcd. 45.68); H 5.3 (5.08)%.

38  
39 **In situ generation of benzoxasilaphosphol [1(P), 3(Si)-P(O)-(O-*i*-Pr)OSi(H)Ph-6-*t*-Bu-4-  
40  
41 P(O)(O-*i*-Pr)<sub>2</sub>]C<sub>6</sub>H<sub>2</sub> (mixture of diastereomers 3a, 3b).**

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51 A solution of tungsten hexacarbonyl (1.240 g, 3.52 mmol) in tetrahydrofuran (270 mL) was  
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53 exposed to UV-radiation for 15 min at room temperature. The volume of gaseous products  
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55 collected was 87 mL. The resulting solution was transferred into a two-necked flask. To this  
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57 reaction mixture [{2,6-bis-(diisopropoxyphosphonyl)-4-*t*-butyl}phenyl]dihydridophenylsilane  
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59 (1.000 g, 1.76 mmol) was added. After the solution had been stirred for 60 min at room  
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temperature a <sup>31</sup>P-NMR spectrum was recorded. <sup>31</sup>P{<sup>1</sup>H} (121.49 MHz, THF/C<sub>6</sub>D<sub>6</sub>): δ 18.1 (s,

starting material), 25.7 (s, unknown by-product), 28.3 (s). The solvent was removed in vacuo and the resulting residue was re-dissolved in toluene followed by addition of Ph<sub>4</sub>PBr (0.67 g, 1.6 mmol). After stirring the reaction mixture for two hours at 40 °C a <sup>31</sup>P NMR spectrum was recorded. <sup>31</sup>P{<sup>1</sup>H} (121.49 MHz, toluene/C<sub>6</sub>D<sub>6</sub>): δ 16.5 (d, <sup>4</sup>J(<sup>31</sup>P-<sup>31</sup>P) = 7.2 Hz), 17.1 (d, <sup>4</sup>J(<sup>31</sup>P-<sup>31</sup>P) = 7.2 Hz), 19.3 (d, <sup>4</sup>J(<sup>31</sup>P-<sup>31</sup>P) = 7.2 Hz), 19.6 (d, <sup>4</sup>J(<sup>31</sup>P-<sup>31</sup>P) = 7.2 Hz), 24.1 (s, Ph<sub>4</sub>P<sup>+</sup>).

**In situ generation of {[2,6-bis(diisopropoxyphosphonyl)-4-*tert*-butyl]phenyl}-fluorosilicon(II)-tungsten pentacarbonyl, [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>2</sub>](F)SiW(CO)<sub>5</sub>**

(4). To a suspension of triphenylcarbonium hexafluorophosphate (0.054 g, 0.14 mmol) in toluene (10 mL) was added dropwise, at 0 °C, a solution of {[2,6-Bis(diisopropoxyphosphonyl)-4-*tert*-butyl]phenyl}phenylsilicon(II)·[W(CO)<sub>5</sub>] (2; 0.120 g, 0.14 mmol) in toluene (5 mL). After stirring the reaction mixture for 4.5 h at 0 °C, the colour of the solution turned brown, and a pale yellow precipitate of tetraphenylmethane (Ph<sub>4</sub>C) was observed. For <sup>31</sup>P-, <sup>19</sup>F- and <sup>29</sup>Si-NMR spectroscopy, 600 μL of the supernatant solution was collected and 50 μL of C<sub>6</sub>D<sub>6</sub> was added to the latter. From this mixture time-dependent NMR spectra were recorded. a) t = 4.5 h: <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, toluene/C<sub>6</sub>D<sub>6</sub>): δ 26.4 (d, <sup>1</sup>J(<sup>31</sup>P-<sup>19</sup>F) = 9.4 Hz, 4), 27.7 (2), 29.4 (the corresponding hexafluorophosphate of [2-Ph]<sup>+</sup>, [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]SiW(CO)<sub>5</sub><sup>+</sup>), -142.5 (septett, <sup>1</sup>J(<sup>31</sup>P-<sup>19</sup>F)=711 Hz, PF<sub>6</sub><sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (282.38 MHz, toluene/C<sub>6</sub>D<sub>6</sub>): δ -154.7 (t, <sup>1</sup>J(<sup>19</sup>F-<sup>31</sup>P) = 9.4 Hz, <sup>1</sup>J(<sup>19</sup>F-<sup>29</sup>Si) = 256 Hz, 4), -74.4 (d, <sup>1</sup>J(<sup>19</sup>F-<sup>31</sup>P) = 711 Hz, PF<sub>6</sub><sup>-</sup>). <sup>29</sup>Si{<sup>1</sup>H} NMR (59.63 MHz, toluene/C<sub>6</sub>D<sub>6</sub>): δ 59.7 (t, <sup>1</sup>J(<sup>29</sup>Si-<sup>31</sup>P) = 10 Hz), -87.3 (dt, <sup>1</sup>J(<sup>29</sup>Si-<sup>19</sup>F) = 256 Hz, <sup>3</sup>J(<sup>29</sup>Si-<sup>31</sup>P) = 12.5 Hz). b) t = 12 h: <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, toluene/C<sub>6</sub>D<sub>6</sub>): δ 26.2 (d, <sup>1</sup>J(<sup>31</sup>P-<sup>19</sup>F) = 9.5 Hz, integral 94, 4), 24.2 (s, integral 6, not assigned), -142.3 (septett, <sup>1</sup>J(<sup>31</sup>P-<sup>19</sup>F)=711 Hz, PF<sub>6</sub><sup>-</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (282.38 MHz, toluene/C<sub>6</sub>D<sub>6</sub>): δ -152.3 (t, <sup>1</sup>J(<sup>19</sup>F-<sup>31</sup>P) = 10 Hz, <sup>1</sup>J(<sup>19</sup>F-<sup>29</sup>Si) = 255 Hz, 4).

**Synthesis of [{2,6-bis(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]diphenylsiliconium-ditungstendecacarbonyl hydride, [4-*t*-Bu-2,6-{P(O)(Oi-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]SiPh<sub>2</sub><sup>+</sup> [W<sub>2</sub>(CO)<sub>10</sub>H]<sup>-</sup>**

(6). A solution of [{2,6-bis-(diisopropoxyphosphonyl)-4-*tert*-butyl}phenyl]diphenylsilane (1.450 g, 2.17 mmol) and tungsten hexacarbonyl (1.410 g, 4.00 mmol) in tetrahydrofuran (270 mL) was exposed to UV-radiation for 30 min at room temperature. The gaseous products (90 mL) were collected. After the solution had been concentrated in vacuo to a volume of approximately 100 mL it was heated at reflux for 70 minutes followed by complete removal of the solvent in vacuo. The residue was dissolved in toluene (15 mL). Addition of *n*-hexane (15 mL) to the clear solution caused precipitation of an amorphous solid. The latter was filtered, washed with *n*-hexane and dried in vacuo (9 x 10<sup>-3</sup> Torr, 90 min) to give 1.090 g (0.86 mmol, 40%) of **5** as a yellow powder, mp 105 °C. <sup>1</sup>H NMR (400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -11.70 (s, <sup>1</sup>J(<sup>1</sup>H-<sup>183</sup>W) = 42.0 Hz, 1H; W<sub>2</sub>H), 1.18 (d, <sup>3</sup>J(<sup>1</sup>H-<sup>1</sup>H) = 6.1 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.26 (d, <sup>3</sup>J(<sup>1</sup>H-<sup>1</sup>H) = 6.1 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.48 (s, 9H; C(CH<sub>3</sub>)<sub>3</sub>), 4.44 (doublet of septets, <sup>3</sup>J(<sup>1</sup>H-<sup>31</sup>P) = 6.5 Hz, <sup>3</sup>J(<sup>1</sup>H-<sup>1</sup>H) = 6.4 Hz, 4H; OCH), 7.39 (complex pattern, 4H; H<sub>m</sub>), 7.45 (complex pattern, 2H; H<sub>p</sub>), 7.65 (complex pattern, 4H; H<sub>o</sub>), 8.21 (complex pattern, 2H; H<sub>Ar</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 23.25 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 1.9 Hz, 2C) and 23.27 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 1.9 Hz, 2C) and 23.32 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 1.9 Hz, 2C) and 23.34 (d, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 1.9 Hz, 2C) (C(CH<sub>3</sub>)<sub>2</sub>), 30.9 (s, 3C; C(CH<sub>3</sub>)<sub>3</sub>), 36.0 (s, 1C; C(CH<sub>3</sub>)<sub>3</sub>), 77.7 (complex pattern, 4C; OCH), 127.9 (s, 2C; C<sub>m</sub>), 130.3 (s, 4C; C<sub>p</sub>), 131.9 (dd, <sup>1</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 184.1 Hz, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 18.3 Hz, 2C; C<sub>2,6</sub>), 132.0 (complex pattern, 2C; C<sub>3,5</sub>), 134.4 (s, 4C; C<sub>o</sub>), 135.2 (t, <sup>4</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 4.9 Hz, 2C; C<sub>i</sub>), 152.8 (t, <sup>3</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 22.4 Hz, 1C; C<sub>4</sub>), 159.1 (t, <sup>2</sup>J(<sup>13</sup>C-<sup>31</sup>P) = 12.6 Hz, 1C; C<sub>1</sub>), 199.1 (s, <sup>1</sup>J(<sup>13</sup>C-<sup>183</sup>W) = 124 Hz, 8C; CO), 201.7 (s, <sup>1</sup>J(<sup>13</sup>C-<sup>183</sup>W) = 162 Hz, 2C; CO). <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 26.6. <sup>29</sup>Si{<sup>1</sup>H} NMR (59.63 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -67.2. Electrospray-MS (positive mode): m/z = 643.4 ([4-*t*-Bu-2,6-{P(O)(Oi-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]SiPh<sub>2</sub><sup>+</sup>); negative mode m/z = 480.9 ([W<sub>2</sub>(CO)<sub>4</sub>H]<sup>-</sup>).

Elemental Analysis: C<sub>44</sub>H<sub>50</sub>O<sub>16</sub>P<sub>2</sub>SiW<sub>2</sub> (1292.53); C 40.8 (Calcd. 40.88); H 4.0 (3.90)%.

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3 **Reaction of [{2,6-bis(diisopropoxyphosphonyl)-4-tert-butyl}phenyl]triphenylsilane with**  
4 **W(CO)<sub>6</sub>.** A solution of [{2,6-bis-(diisopropoxyphosphonyl)-4-tert-  
5 butyl}phenyl]triphenylsilane (1.000 g, 1.39 mmol) and tungsten hexacarbonyl  
6 (0.490 g, 1.39 mmol) in tetrahydrofuran (270 mL) was UV-irradiated for 20 min at room  
7 temperature. The volume of gaseous products collected was 31 mL. After stirring the reaction  
8 mixture for 30 min, 600  $\mu$ L of the solution were collected for <sup>31</sup>P NMR spectroscopy and  
9 then the solvent was evaporated in vacuo. For <sup>29</sup>Si-NMR spectroscopy the residue was  
10 dissolved in C<sub>6</sub>D<sub>6</sub>. <sup>31</sup>P{<sup>1</sup>H} NMR (161.98 MHz, THF / C<sub>6</sub>D<sub>6</sub>):  $\delta$  17.1. <sup>29</sup>Si NMR (79.49 MHz,  
11 C<sub>6</sub>D<sub>6</sub>):  $\delta$  -13.5 (s, <sup>1</sup>J(<sup>29</sup>Si-<sup>13</sup>C) = 80 Hz).

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25 **Reaction of diphenylsilane with W(CO)<sub>6</sub>.** A solution of diphenylsilane (0.550 g, 3.0 mmol)  
26 and tungsten hexacarbonyl (1.750 g, 4.5 mmol) in tetrahydrofuran (270 mL) was UV-  
27 irradiated for 20 min at room temperature. The volume of gaseous products collected during  
28 this time was 110 mL (66% of calculated volume). A NMR sample was taken from this  
29 solution and time-dependent <sup>1</sup>H spectra were recorded. <sup>1</sup>H NMR (599.83 MHz, THF / D<sub>2</sub>O-  
30 capillary) a) t = 3 h:  $\delta$  -3.85 (s, <sup>1</sup>J(<sup>1</sup>H-<sup>183</sup>W) = 15 Hz; integral 0.4), 4.86 (s, <sup>1</sup>J(<sup>1</sup>H-  
31 <sup>29</sup>Si) = 198 Hz; Ph<sub>2</sub>SiH<sub>2</sub>; integral: 1.0). b) t = 19 h:  $\delta$  -3.85 (s, <sup>1</sup>J(<sup>1</sup>H-<sup>183</sup>W) = 15 Hz; integral  
32 1.0), 4.86 (s, <sup>1</sup>J(<sup>1</sup>H-<sup>29</sup>Si) = 197.5 Hz; Ph<sub>2</sub>SiH<sub>2</sub>; integral 0.5).

### 33 34 35 36 37 38 39 40 41 42 43 44 45 46 **Acknowledgements**

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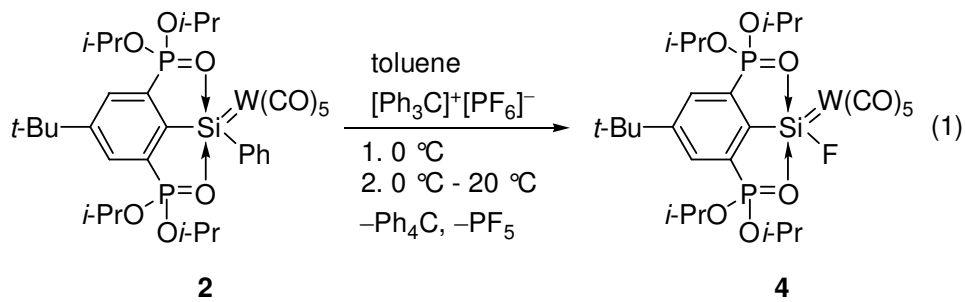
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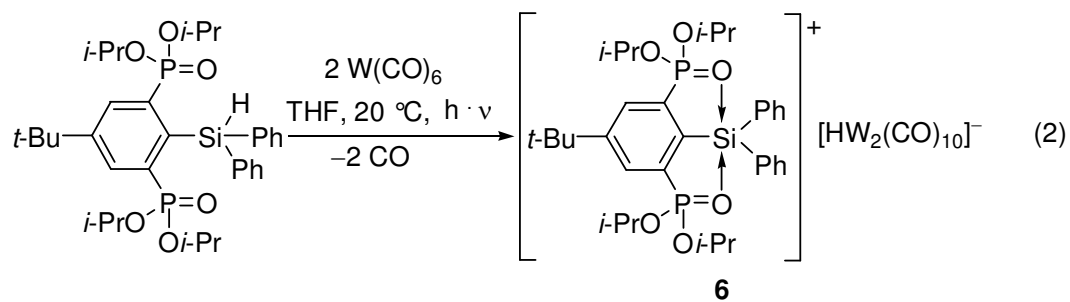
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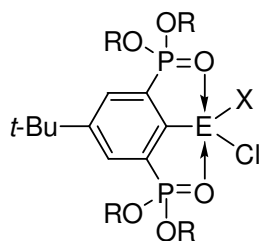
**Table 1.** Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) for **2** with standard deviations given in parentheses.

Si(1)-W(1)	2.636(7)	P(2)-O(2)	1.481(5)
Si(1)-O(1)	1.986(7)	W(1)-C(11)	1.874(17)
Si(1)-O(2)	2.670(7)	W(1)-C(12)	2.065(14)
Si(1)-C(1)	1.910(9)	W(1)-C(13)	1.73(2)
Si(1)-C(21)	1.906(11)	W(1)-C(14)	1.926(12)
P(1)-O(1)	1.480(5)	W(1)-C(15)	1.97(2)
O(1)-Si(1)-O(2)	162.2(3)	W(1)-Si(1)-C(21)	124.5(4)
W(1)-Si(1)-O(1)	107.1(3)	C(1)-C(6)-P(2)	118.5(6)
C(1)-Si(1)-O(1)	91.9(3)	C(1)-C(2)-P(1)	116.2(6)
C(21)-Si(1)-O(1)	96.9(4)	Si(1)-C(1)-C(2)-P(1)	4.2(7)
W(1)-Si(1)-C(1)	122.5(4)	Si(1)-C(1)-C(6)-P(2)	-8.5(10)
C(1)-Si(1)-C(21)	105.4(4)		



**Equation 1**

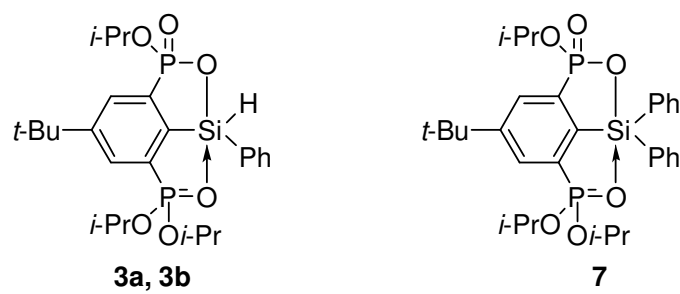
**Equation 2**

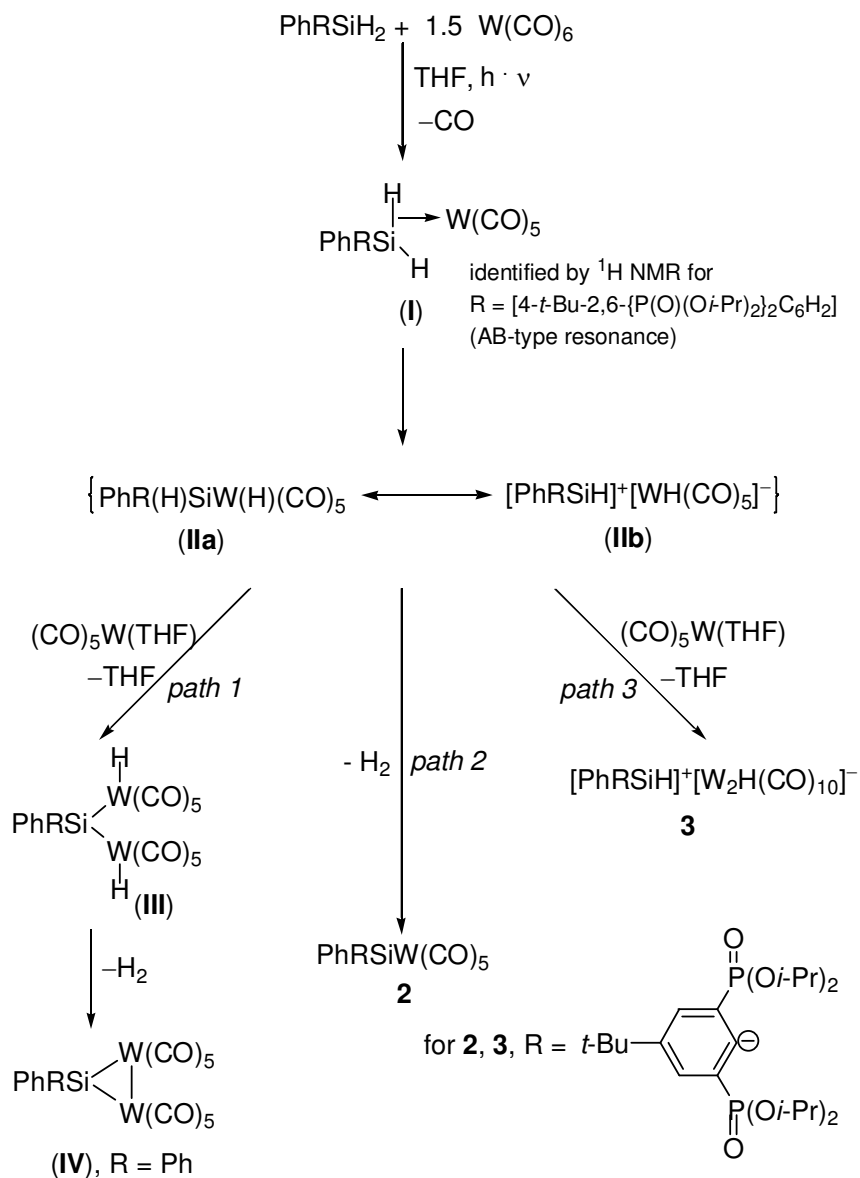


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- (A) E = Pb, R = Et, *i*-Pr, X = I.p.  
 (B) E = Sn, R = Et, *i*-Pr, X = I.p.  
 (C) E = Sn, R = Et, *i*-Pr, X = Cr(CO)<sub>5</sub>,  
 Mo(CO)<sub>5</sub>, W(CO)<sub>5</sub>, Ru(C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>  
 (D) E = Ge, R = *i*-Pr, X = I.p.  
 (E) E = Ge, R = *i*-Pr, X = Cr(CO)<sub>5</sub>

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**Figure 1.**

**Figure 3.**



Scheme 1.

## Captions for Figures and Scheme

**Figure 1.** Organoelement compounds that contain the intramolecularly O,C,O-coordinating pincer-type ligand [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]<sup>−</sup>.

**Figure 2.** <sup>31</sup>P{<sup>1</sup>H} NMR spectra (121.49 MHz, THF/D<sub>2</sub>O-capillary, room temperature) of a solution in THF containing [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]SiH<sub>2</sub>Ph (**1**) and W(CO)<sub>6</sub> which had been UV-irradiated for 40 min (lower part) and for 85 min (upper part).

**Figure 3.** The benzoxasilaphosphole derivatives **3a**, **3b**, and **7**.

**Figure 4.** <sup>1</sup>H NMR spectrum (599.83 MHz, THF/D<sub>2</sub>O-capillary, room temperature, Si-H part) of a solution in THF containing [4-*t*-Bu-2,6-{P(O)(*Oi*-Pr)<sub>2</sub>}<sub>2</sub>C<sub>6</sub>H<sub>2</sub>]SiH<sub>2</sub>Ph (**1**) and W(CO)<sub>6</sub> which had been UV-irradiated for 40 min. ○ <sup>1</sup>J(<sup>1</sup>H-<sup>29</sup>Si) = 243 Hz, J(<sup>1</sup>H-<sup>1</sup>H) 9 Hz, □ <sup>1</sup>J(<sup>1</sup>H-<sup>29</sup>Si) = 206 Hz.

**Figure 5.** General view (SHELXTL) of the molecular structure of compound **2** showing 30% probability displacement ellipsoids.

**Scheme 1.** Proposed reaction pathways that account for the formation of the silylene complex **2** and the organosiliconium salt **3**.

