

Tungstenmethyl-dimethylsilanols $\text{Cp}(\text{OC})_2(\text{R}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{OH}$ ($\text{R} = \text{Me}, \text{Ph}$) – Synthesis *via* Oxygenation or Hydrolysis*

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The tungstenmethyl-dimethylsilanols $\text{Cp}(\text{OC})_2(\text{R}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{OH}$ [$\text{R} = \text{Me}$ (**6a**), Ph (**6b**)] have been synthesized by oxofunctionalization of the tungstenmethyl-silanes $\text{Cp}(\text{OC})_2(\text{R}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ [$\text{R} = \text{Me}$ (**3a**), Ph (**3b**)] with dimethyldioxirane. **6a** has been additionally obtained by Et_3N -assisted hydrolysis of the tungstenmethyl-chlorosilane $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{Cl}$ (**5**). Compounds **6a,b** are stable with respect to self-condensation, but controlled condensation of **6a** with $\text{Me}_2\text{Si}(\text{H})\text{Cl}$ in the presence of triethylamine has been realized to give the tungstenmethyl-substituted disiloxane $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{O}-\text{SiMe}_2\text{H}$ (**7**). The new compounds have been identified IR- and NMR-spectroscopically and, in the case of **3a**, by X-ray analysis.

Key words: Tungsten, Silanol, Oxygenation

Introduction

The synthesis of transition metal-substituted silanols of the general type $\text{L}_n\text{M}-\text{Si}(\text{R})_{3-n}(\text{OH})_n$ ($n = 1-3$) [2–7] and their condensation with chlorosilanes offer an efficient approach to metallo-siloxanes with a direct metal to silicon bond. In context with the studies concerning tungsten-substituted silanols it has been shown that ligands with a high σ -donor/ π -acceptor property at the tungsten center, like tertiary phosphines, are helpful to guarantee sufficient stability of the $\text{W}-\text{Si}$ bond [4]. However, in these cases, the most useful method for the generation of silanols – hydrolysis of the corresponding chlorosilanes in the presence of an auxiliary base – usually fails due to the strong electron-releasing effect of the metal fragment which leads to a reduced electrophilicity of the silicon atom. A more efficient alternative for the synthesis of $\text{C}_5\text{R}_5(\text{OC})_2(\text{R}'_3\text{P})\text{W}$ -substituted silanols ($\text{R} = \text{H}, \text{Me}$; $\text{R}' = \text{Me}, \text{Ph}$) is offered by the oxygenation of $\text{Si}-\text{H}$ functionalized tungsten-silanes with dimethyldioxirane [8], which gives access to

even a tungsten-silanediol [5] and a -silanetriol [6]. More recently, a catalytic oxygenation procedure has been worked out [7] using the urea/hydrogen peroxide adduct in the presence of catalytic amounts of MeReO_3 [9].

Our interest has now focused on silanols having the $\text{Si}-\text{OH}$ moiety separated from the metal fragment by a methylene group in order to investigate the “transition metal effect” on silanol units which are not directly bound to the metal. Metal complexes with a silylmethyl ligand bearing one or more functional groups are rare in the literature [10–14]. Some of the few examples described so far have been used as precursors in the synthesis of transition metal silene complexes, which were originally proposed by Pannell [10]. Spectroscopical proof has been provided by Wrighton *et al.* for $\text{C}_5\text{R}_5(\text{OC})_2(\text{H})\text{W}-(\eta^2-\text{CH}_2-\text{SiMe}_2)$, generated by low-temperature near-UV photolysis of $\text{C}_5\text{R}_5(\text{OC})_3\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ ($\text{R} = \text{H}, \text{Me}$) [11]. A more stable tungsten silene complex has been synthesized by Berry *et al.* via reductive dechlorination of the chlorofunctional silylmethyl tungsten complex $\text{Cp}_2\text{W}(\text{Cl})-\text{CH}_2-\text{SiMe}_2\text{Cl}$ with magnesium [12].

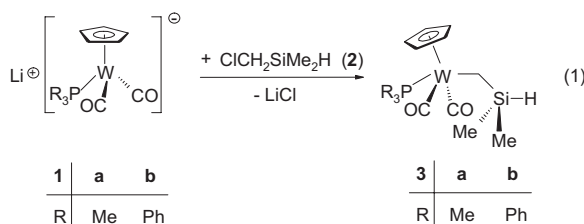
However, no attempts have been made to convert these $\text{Si}-\text{H}$ or $\text{Si}-\text{Cl}$ functional complexes via nu-

* Synthesis and Reactivity of Silicon Transition Metal Complexes, Part 57. In addition, Metallo-Silanols and Metallo-Siloxanes, Part 29. For Part 56/28 see Lit. [1].

cleophilic ligand exchange at the silicon atom [15] into the silanols $\text{L}_n\text{M}-\text{CH}_2-\text{SiMe}_2\text{OH}$, which can be considered as derivatives of trimethylsilanol with a methyl hydrogen substituted by the transition metal fragment. These silanols should be characterized by a higher tendency towards self-condensation compared to the analogous derivatives without methylene bridge, as was shown by us for $\text{Cp}(\text{OC})_2\text{Fe}-\text{CH}_2-\text{SiMe}_2\text{OH}$, which is slowly transformed into the disiloxane $[\text{Cp}(\text{OC})_2\text{Fe}-\text{CH}_2-\text{SiMe}_2]_2\text{O}$ [16]. In the present work, the synthesis of $\text{Si}-\text{H}$ and $\text{Si}-\text{Cl}$ functional tungstenmethyl dimethyl-silanes is presented as well as their conversion into the corresponding silanols.

Results and Discussion

The $\text{Si}-\text{H}$ functional tungstenmethyl-silanes **3a**, **b**, which serve as starting materials for the synthesis of tungstenmethyl-silanols, are most easily prepared by the nucleophilic metalation of the chloromethylsilane **2** with the phosphine-substituted tungsten metalates **1a**, **b** in THF or cyclohexane at room temperature [eq. (1)].



3a, **b** are isolated after reaction periods of 20–24 h as yellow to ochre microcrystalline solids in yields of 68 and 59%, respectively, showing good solubility in aromatic or ethereal solvents. The compounds are only slightly soluble in non polar solvents like *n*-pentane. **3a**, **b** can be stored under N_2 -atmosphere at temperatures below -20°C in the dark for several weeks without decomposition. At room temperature, especially under exposure to light, slow decomposition is observed leading to the respective tungsten hydride complexes $\text{Cp}(\text{OC})_2(\text{R}_3\text{P})\text{W}-\text{H}$ ($\text{R} = \text{Me}, \text{Ph}$), presumably the result of a β -H elimination reaction with extrusion of the silene $\text{CH}_2=\text{SiMe}_2$. This tendency is more pronounced for the triphenylphosphane-substituted derivative **3b**.

The identity of **3a**, **b** has been established spectroscopically by the $\nu(\text{SiH})$ absorption band in the IR spectrum in THF at 2115 (**3a**) and 2122 cm^{-1} (**3b**), re-

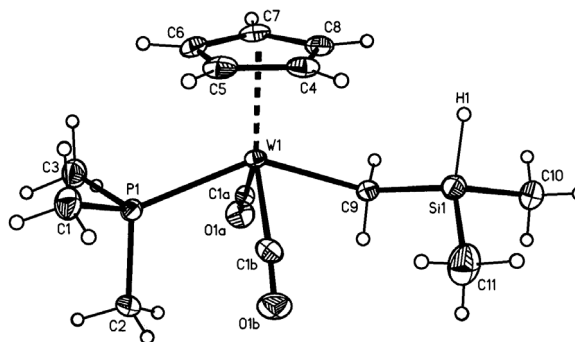


Fig. 1. ORTEP-Plot of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ (**3a**). Selected bond distances (\AA) and -angles ($^\circ$): $\text{W}(1)-\text{C}(9)$ 2.325(3), $\text{W}(1)-\text{P}(1)$ 2.4436(7), $\text{W}(1)-\text{Z}(\text{cp})$ 2.0137(11), $\text{C}(9)-\text{Si}(1)$ 1.853(3), $\text{Si}(1)-\text{C}(11)$ 1.860(3), $\text{Si}(1)-\text{C}(10)$ 1.876(3), $\text{Si}(1)-\text{H}(1)$ 1.462(17); $\text{C}(1\text{B})-\text{W}(1)-\text{C}(1\text{A})$ 102.78(11), $\text{C}(1\text{B})-\text{W}(1)-\text{C}(9)$ 82.60(10), $\text{C}(1\text{A})-\text{W}(1)-\text{C}(9)$ 71.81(10), $\text{Z}(\text{cp})-\text{W}(1)-\text{C}(1\text{A})$ 131.0(1), $\text{Z}(\text{cp})-\text{W}(1)-\text{C}(1\text{B})$ 126.2(1), $\text{Z}(\text{cp})-\text{W}(1)-\text{C}(9)$ 109.6(1), $\text{Z}(\text{cp})-\text{W}(1)-\text{P}(1)$ 112.5(1), $\text{C}(1\text{B})-\text{W}(1)-\text{P}(1)$ 78.56(8), $\text{C}(1\text{A})-\text{W}(1)-\text{P}(1)$ 75.55(8), $\text{C}(9)-\text{W}(1)-\text{P}(1)$ 137.32(7), $\text{C}(3)-\text{P}(1)-\text{W}(1)$ 117.68(10), $\text{Si}(1)-\text{C}(9)-\text{W}(1)$ 120.15(13), $\text{C}(9)-\text{Si}(1)-\text{C}(11)$ 113.40(14), $\text{C}(10)-\text{Si}(1)-\text{H}(1)$ 105.5(11). Selected torsion angles ($^\circ$): $\text{C}(1\text{B})-\text{W}(1)-\text{C}(9)-\text{Si}(1)$ $-67.41(15)$, $\text{C}(1\text{A})-\text{W}(1)-\text{C}(9)-\text{Si}(1)$ $-173.51(17)$, $\text{P}(1)-\text{W}(1)-\text{C}(9)-\text{Si}(1)$ $-131.57(10)$, $\text{W}(1)-\text{C}(9)-\text{Si}(1)-\text{C}(11)$ $70.96(19)$, $\text{W}(1)-\text{C}(9)-\text{Si}(1)-\text{C}(10)$ $-167.73(13)$.

spectively. In the ^1H NMR spectrum the Si-bound proton is detected at 4.71 (**3a**) and 4.74 ppm (**3b**), showing a “nine line pattern” originating from the coupling with the Si-bound methyl- and methylene protons. The signal of the bridging methylene group is found as a pseudo-triplet at 0.04 (**3a**) and 0.28 ppm (**3b**), respectively, due to the approximately equal value of the $^3J(\text{HCSiH})$ and $^3J(\text{HCWP})$ coupling constants. The mutually *trans* position of the CO ligands is proven IR-spectroscopically by the typical intensity ratio of the two $\nu(\text{CO})$ absorption bands $I[\nu(\text{CO})_{\text{as}}]:I[\nu(\text{CO})_{\text{s}}] < 1$ [17]. Additionally, in the ^{13}C NMR spectra, only one doublet signal for the carbonyl carbon atoms at 229.73 (**3a**) and 229.20 (**3b**) ppm is detected, respectively. The doublet signal of the bridging methylene carbon atom is observed at characteristic high field at -39.56 (**3a**) and -36.98 ppm (**3b**).

Yellow crystals of **3a**, suitable for X-ray analysis, could be obtained from a saturated solution of **3a** in a 2:1-mixture of *n*-pentane/toluene at -78°C .

The molecular structure of **3a** [Fig. (1)] shows a pseudo-tetragonal pyramidal piano stool arrangement of the ligands at the central tungsten atom with the cyclopentadienyl ligand in the apical position. The CO

ligands adopt a mutually *trans* position (*vide supra*) [C1B-W1-C1A 102.78(11)°; C9-W1-P1 137.32(7)°]. The angles between the ligands in *cis* position lie between 71.81(10)° [C1A-W1-C9] and 82.60(10)° [C1B-W1-C9].

The W1-P1 bond length with a value of 2.4436(7) Å is in the normal range of other tungsten silyl complexes with a $\text{C}_5\text{R}_5(\text{OC})_2(\text{Me}_3\text{P})\text{W}$ transition metal fragment [4, 18].

The W1-C9 bond length [2.325(3) Å] is comparatively long (sum of covalent radii W-C 2.142 Å) and is at the high end of the values determined for structures with a $\text{CpW}-\text{CH}_2-\text{Si}$ fragment (mean 2.17 Å). It is comparable to the W-C bond lengths in the tungstenmethyl disilane $\text{Cp}(\text{OC})_3\text{W}-\text{CH}_2-\text{SiMe}_2-\text{SiMe}_3$ (2.336 Å) [19] and in the tungsten-substituted ethyl acetate $\text{Cp}(\text{OC})_3\text{W}-\text{CH}_2-\text{CO}_2\text{Et}$ (2.32 Å) [20].

The W1-C9-Si1 angle [120.15(13)°] is significantly widened up from the tetrahedral angle and shows the higher steric demand of the tungsten and the silyl group compared to the hydrogen atoms at the bridging carbon atom. But in contrast to $\text{Cp}(\text{OC})_3\text{W}-\text{CH}_2-\text{SiMe}_2-\text{SiMe}_3$ [19] the W-C-Si angle is significantly reduced (126.1° vs. 120.2°), presumably a consequence of the lower steric demand of the hydrogen substituent at the β -silicon atom of **3a** compared to a trimethylsilyl group.

The silicon atom reveals a tetrahedral arrangement of the substituents with angles between 105.5(11)° [C10-Si1-H1] and 113.40(14)° [C9-Si1-C11]. Although the silicon-bonded hydrogen atom H1 could be located, the Si-H bond length was fixed and refined with soft restraints, making a discussion of this value unreasonable.

Looking along the W1-C9 bond [Fig. (2a)], the silyl group is positioned between the cyclopentadienyl ring and the CO ligand [C1B-W1-C9-Si1 – 67.41(15)°] and adopts an *anti*-position to the C1A-O1A ligand [C1A-W1-C9-Si1 – 173.51(17)°]. The view along the C9-Si1 bond [Fig. (2b)] reveals a pseudo-ethane conformation with a mutually *anti*-position of the tungsten fragment and one of the methyl groups at the silicon atom [W1-C9-Si1-C10 – 167.73(13)°] with a deviation from the ideal conformation of about 12°.

Weak interactions between Cp hydrogen atoms and oxygen atoms of the carbonyl ligands in the solid state are suggested by intermolecular $(\text{Cp})\text{C}^{\cdots}\text{O}(\text{C})$ distances up to 3.433(4) Å.

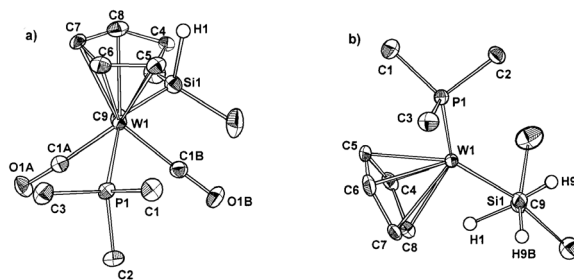
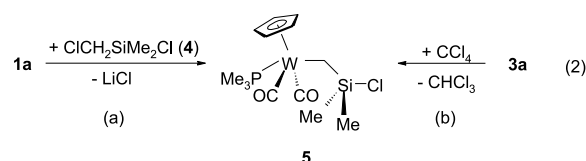


Fig. 2. a) Newman projection of the W1-C9 bond; b) Newman projection of the C9-Si1 bond

The tungstenmethyl-chlorosilane **5** is obtained either by metalation of the chloromethylchlorosilane **4** with **1a** in cyclohexane [eq. (2a)] or by Si-H/Si-Cl exchange at **3a** with CCl_4 in benzene [eq. (2b)].



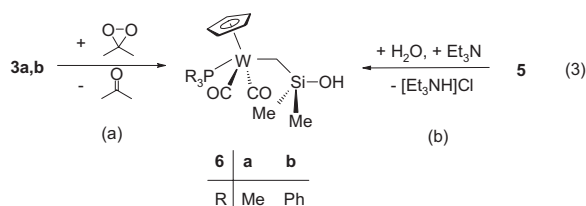
The metalation route provides **5** after a reaction period of 24 h in a yield of 52%. In the case of the chlorination reaction, ten equivalents of CCl_4 and a reaction temperature of 60 °C are necessary to guarantee rapid conversion of **3a**. Using this method, **5** is obtained in 60% yield after 4 h.

5 is isolated as an ochre-yellow solid, which is only slightly soluble in *n*-pentane, but shows good solubility in aromatic and ethereal solvents. It decomposes on contact with air within 1 min quantitatively into the tungsten chloro complex $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{Cl}$. This process also takes place under an N_2 -atmosphere within 1–2 weeks in solution as well as in the solid state. Formally, elimination of the silene $\text{CH}_2=\text{SiMe}_2$ occurs, however, the fate of the silicon moiety is unknown.

The good accessibility and the comparatively high stability of the Si-H functional tungstenmethyl-dimethylsilanes **3a, b** suggested attempts of oxo-functionalization using the “established” oxygenation reagent dimethyldioxirane.

The tungstenmethyl-dimethylsilanol **6a, b** are obtained upon treatment of **3a, b** with dimethyldioxirane after a reaction period of 1–1.5 h at –78 °C and 1 h at room temperature in 55–60% yield [eq. (3a)].

6a, b are isolated as ochre solids, which show good solubility in toluene and diethyl ether. Storage of the

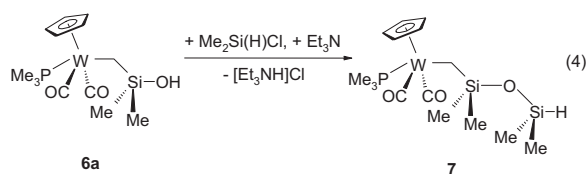


solids at room temperature for two weeks neither leads to self-condensation nor to significant decomposition.

6a, b are characterized by the $\nu(\text{OH})$ stretching band at 3663 cm^{-1} (**6a**, toluene solution) and 3655 cm^{-1} (**6b**, THF solution) in the IR spectra and by a broad signal for the hydroxylic proton at $\delta = 1.63$ (**6a**) and 0.86 (**6b**) ppm in the ^1H NMR spectra (C_6D_6). The characteristic upfield signal of the CH_2 protons is detected as a doublet at $\delta = 0.09$ (**6a**) and 0.38 (**6b**) ppm. In the ^{13}C NMR spectra the signals for the CH_2 group are observed at -34.30 (**6a**) and -31.81 (**6b**) ppm. The $\delta^{29}\text{Si}$ NMR values [23.86 (**6a**); 23.43 ppm (**6b**)] reveal a decreased influence of the transition metal fragment on the silicon atom in the β -position. For example, in the case of **6b**, the signal is shifted approximately 26 ppm to higher field compared to its counterpart without methylene bridge $\text{Cp}(\text{OC})_2(\text{Ph}_3\text{P})\text{W}-\text{SiMe}_2\text{OH}$ (49.6 ppm) [7] and lies in the range of triorganosilanols (Et_3SiOH : 19.3 ppm) [21].

In the oxygenation of **3b**, formation of significant amounts of triphenyl phosphane oxide is also observed. The products can be separated by fractional crystallization at $-78\text{ }^\circ\text{C}$ from toluene/*n*-pentane. This undesirable ligand oxidation is probably a result of the comparatively high reaction temperature of $20\text{--}25\text{ }^\circ\text{C}$ necessary for smooth oxygenation. At $-78\text{ }^\circ\text{C}$ no significant conversion of **3a, b** is detected, whereas the dimethyldioxirane oxygenation of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{SiMe}_2\text{H}$, the analogous compound to **3a** without methylene bridge, into $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{SiMe}_2\text{OH}$ proceeds quantitatively at $-78\text{ }^\circ\text{C}$ within 15 min [22]. This finding also reveals a strongly decreased influence of the metal fragment on the silicon unit in β position.

Attempts to obtain the silanol **6a** via oxygenation of **3a** with H_2O_2 /urea in toluene in the presence of catalytic amounts of MeReO_3 (3 mol %) led to no detectable conversion of **3a** even after 7 d at room temperature. In contrast to tungsten-chlorosilanes of the type $\text{C}_5\text{R}_5(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{SiR}'_2\text{Cl}$ ($\text{R} = \text{H}, \text{Me}$; $\text{R}' = \text{alkyl}, \text{aryl}$), for which hydrolysis fails due



to insufficient electrophilicity of the silicon atom, the tungstenmethyl-silanol **6a** is available by this method from the tungstenmethyl-dimethylchlorosilane **5**. Et_3N -assisted hydrolysis of **5** in diethyl ether affords **6a** after a reaction period of 14 h in a yield of 54% after removal of significant amounts of the tungsten chloro complex $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{Cl}$ – the decomposition product of **5** – via fractional crystallization at $-78\text{ }^\circ\text{C}$ [eq. (3b)]. Therefore, the hydrolysis reaction is inferior to the oxygenation route with respect to the yield of isolated **6a**.

The tungstenmethyl-silanols **6a, b** show the typical reactivity of silanols concerning condensation with organochlorosilanes. In a first experiment, Et_3N -assisted condensation of **6a** with dimethylchlorosilane leads to the formation of the tungstenmethyl-disiloxane **7** [eq. (4)].

The SiH-functional disiloxane **7** can be isolated after a reaction period of 3 d after removal of precipitated $[\text{Et}_3\text{NH}]\text{Cl}$ and the by-product $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{Cl}$ as a dark yellow viscous oil in a yield of 77%. **7** shows good solubility in all common organic solvents and can be stored at $-20\text{ }^\circ\text{C}$ under N_2 -atmosphere for several months. At room temperature, slow decomposition is observed leading to a complex mixture of unknown compounds. Compared to the silanol **6a**, the ^{29}Si NMR signal of the β -Si atom of **7** ($\delta = 18.39$ ppm) is shifted ca. 5.5 ppm to higher field, which is in good accordance with the resonances of triorganosilanols and the corresponding disiloxanes [21]. The signal for the Si atom in δ -position is detected at $\delta = -9.18$ ppm.

Future studies will deal with the synthesis of analogous tungstenmethyl-silanedioles and -silanetriols, which promise to be attractive precursors for the generation of metal-substituted oligo- and polysiloxanes.

Experimental Section

All operations were performed under an atmosphere of pure and dry nitrogen using Schlenk-type techniques. Solvents were dried according to conventional procedures, distilled and saturated with N_2 prior to use. – NMR: Jeol Lambda 300 (300.4 MHz, ^{1}H), 75.5 MHz, ^{13}C), and 59.6 MHz for

^1H , ^{13}C , and ^{29}Si , respectively). [D_6]-benzene as a solvent: $\delta_{\text{H}} = 7.15$, $\delta_{\text{C}} = 128.0$; for ^{29}Si rel. to TMS external. – IR: Perkin-Elmer 283 grating spectrometer. – Melting points: Differential thermoanalysis (Du Pont 9000 Thermal Analysis System). – Elemental analyses were performed in the laboratories of the *Institut für Anorganische Chemie der Universität Würzburg*. – Starting materials were prepared according to literature procedures: $\text{Li}[\text{W}(\text{CO})_2(\text{PR}_3)\text{Cp}]$ ($\text{R} = \text{Me}$ [18a], Ph [22]), $\text{ClCH}_2-\text{SiMe}_2\text{H}$ [23] and dimethyldioxirane [8]. $\text{ClCH}_2\text{SiMe}_2\text{Cl}$ and ClSiMe_2H were purchased and distilled prior to use.

Synthesis of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ (**3a**)

A solution of 1610 mg (4.14 mmol) of $\text{Li}[\text{W}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ (**1a**) in 40 ml of tetrahydrofuran was treated with 714 mg (6.57 mmol) of $\text{ClCH}_2\text{SiMe}_2\text{H}$ (**2**). After stirring for 20 h at room temperature in the dark all volatiles were removed, the brown residue treated with 20 ml of toluene and insoluble material removed by filtration through a Celite pad. The filtrate was reduced in volume to 5 ml and treated with 15 ml of petroleum ether. **3a**, which crystallized at -78°C , was separated, washed two times with *n*-pentane (each 3 ml) and dried in vacuo. Yield 1229 mg (68%). Ochre microcrystalline powder. M. p. 66°C . – IR (THF): $\nu = 2115$ (w, br, SiH), 1918 (s, CO), 1831 (vs, CO) cm^{-1} . – ^1H NMR (300.4 MHz, [D_6]-benzene): $\delta = 4.71$ [n, $^3J(\text{HSiCH}) = 3.7$ Hz, 1 H, HSi], 4.56 [d, $^3J(\text{HCWP}) = 2.0$ Hz, 5 H, H_5C_5], 1.08 [d, $^2J(\text{HCP}) = 9.2$ Hz, 9 H, Me_3P], 0.47 [d, $^3J(\text{HCSiH}) = 3.7$ Hz, 6 H, H_3C], 0.04 ppm [t, $^3J(\text{HCSiH}) \approx ^3J(\text{HCWP}) = 3.7$ Hz, 2 H, H_2C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, [D_6]-benzene): $\delta = 229.73$ [d, $^2J(\text{PWC}) = 17.1$ Hz, CO], 89.11 (s, C_5H_5), 20.97 [d, $^1J(\text{CP}) = 34.2$ Hz, $(\text{CH}_3)_3\text{P}$], 1.27 [s, $(\text{CH}_3)_2\text{Si}$], -39.56 ppm [d, $^2J(\text{CWP}) = 9.1$ Hz, CH_2]. – ^{29}Si NMR (59.6 MHz, [D_6]-benzene): $\delta = -2.53$ ppm [dnd, $^1J(\text{SiH}) = 176.4$ Hz, $^2J(\text{SiCH}) = 6.7$ Hz, $^3J(\text{SiCWP}) = 2.7$ Hz]. – $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, [D_6]-benzene): $\delta = -16.95$ ppm [s, $^1J(\text{PW}) = 218.7$ Hz]. – $\text{C}_{13}\text{H}_{23}\text{O}_2\text{PSiW}$ (454.23): calcd. C 34.37, H 5.10; found C 34.30, H 5.06.

Synthesis of $\text{Cp}(\text{OC})_2(\text{Ph}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ (**3b**)

A suspension of 254 mg (0.42 mmol) of $\text{Li}[\text{W}(\text{CO})_2(\text{PPh}_3)\text{Cp}]$ (**1b**) in 20 ml of cyclohexane was treated with 196 mg (1.81 mmol) of $\text{ClCH}_2\text{SiMe}_2\text{H}$ (**2**) and stirred for 25 h at room temperature in the dark. Insoluble material was removed by filtration through a Celite pad and the filtrate evaporated to dryness in vacuo. The residue was extracted two times with toluene (each 10 ml) and the combined extracts reduced in vacuo to a volume of 1 ml. After addition of 5 ml of *n*-pentane **3b** was crystallized at -78°C , washed two times with *n*-pentane at -78°C (each

1 ml) and dried in vacuo. Yield 159 mg (59 %). Yellow, microcrystalline solid. M. p. 113°C (dec.). – IR (THF): $\nu = 2122$ (w, br, SiH), 1934 (vs, CO), 1852 (s, CO) cm^{-1} . – ^1H NMR (300.4 MHz, [D_6]-benzene): $\delta = 7.54$ [m, 6 H, $(\text{H}_5\text{C}_6)_3\text{P}$], 6.99 [m, 9 H, $(\text{H}_5\text{C}_6)_3\text{P}$], 4.74 [n, $^3J(\text{HSiCH}) = 3.7$ Hz, 1 H, HSi], 4.62 [d, $^3J(\text{HCWP}) = 1.7$ Hz, 5 H, H_5C_5], 0.46 [d, $^3J(\text{HCSiH}) = 3.7$ Hz, 6 H, H_3CSi], 0.28 ppm [t, $^3J(\text{HCSiH}) \approx ^3J(\text{HCWP}) = 3.5$ Hz, 2 H, H_2C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, [D_6]-benzene): $\delta = 229.20$ [d, $^2J(\text{CWP}) = 17.6$ Hz, CO], 137.32 [d, $^1J(\text{CP}) = 47.9$ Hz, C-1, $(\text{C}_6\text{H}_5)_3\text{P}$], 133.88 [d, $^2J(\text{CCP}) = 9.6$ Hz, C-2, C-6, $(\text{C}_6\text{H}_5)_3\text{P}$], 130.13 [d, $^3J(\text{CCCP}) = 2.1$ Hz, C-3, C-5, $(\text{C}_6\text{H}_5)_3\text{P}$], 128.44 [s, C-4, $(\text{C}_6\text{H}_5)_3\text{P}$], 90.95 (s, C_5H_5), 1.25 (s, CH_3Si), -36.98 ppm [d, $^2J(\text{CWP}) = 7.9$ Hz, CH_2]. – $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, [D_6]-benzene): $\delta = -3.02$ ppm [d, $^3J(\text{SiCWP}) = 2.1$ Hz]. – $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, [D_6]-benzene): $\delta = 41.55$ ppm [s, $^1J(\text{PW}) = 238.1$ Hz]. – $\text{C}_{28}\text{H}_{29}\text{O}_2\text{PSiW}$ (640.45): calcd. C 52.51, H 4.56; found C 52.52, H 4.62.

Synthesis of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{Cl}$ (**5**)

a) by metalation of $\text{ClCH}_2\text{SiMe}_2\text{Cl}$ (**4**) with $\text{Li}[\text{W}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ (**1a**)

Analogously to the preparation of **3b** from 783 mg (2.02 mmol) of $\text{Li}[\text{W}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ (**1a**) and 652 mg (4.56 mmol) of $\text{ClCH}_2\text{SiMe}_2\text{Cl}$ (**4**) in 35 ml of cyclohexane after stirring for 24 h at r. t. in the dark. The yellow-brown residue was treated with a mixture of 2 ml of toluene and 15 ml of petroleum ether, and **5** was crystallized at -30°C , washed two times with *n*-pentane (each 2 ml) and dried in vacuo. Yield 513 mg (52%). Ochre microcrystalline powder. M. p. 60°C (dec.).

b) by chlorination of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ (**3a**) with CCl_4

A solution of 199 mg (0.44 mmol) of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ (**3a**) in 10 ml of benzene was treated with 680 mg (4.42 mmol) of CCl_4 and stirred for 4 h at 60°C , whereupon the colour of the solution turned to a dark brown. Insoluble material was removed by filtration through a Celite pad and the filtrate evaporated to dryness in vacuo. The ochre, oily residue was treated with a mixture of 1.5 ml of toluene and 7 ml of *n*-pentane, and **5** was crystallized at -78°C , washed two times with *n*-pentane (each 1 ml) and dried in vacuo. Yield 128 mg (60 %). – IR (cyclohexane): $\nu = 1931$ (s, CO), 1839 (vs, CO) cm^{-1} . – ^1H NMR (300.4 MHz, [D_6]-benzene): $\delta = 4.43$ [d, $^3J(\text{HCWP}) = 2.0$ Hz, 5 H, H_5C_5], 1.01 [d, $^2J(\text{HCP}) = 9.3$ Hz, 9 H, Me_3P], 0.79 (s, 6 H, H_3C), 0.29 ppm [d, $^3J(\text{HCWP}) = 3.3$ Hz, 2 H, H_2C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, [D_6]-benzene): $\delta = 231.23$ [d, $^2J(\text{CWP}) = 18.1$ Hz, CO], 89.42 (s, C_5H_5), 20.34 [d, $^1J(\text{CP}) = 35.2$ Hz, $(\text{CH}_3)_3\text{P}$], 6.15 (s, CH_3Si), -34.28 ppm [d, $^2J(\text{CWP}) =$

9.1 Hz, CH_2]. – $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, $[\text{D}_6]$ -benzene): $\delta = 39.09$ ppm [d, $^3J(\text{SiCWP}) = 5.2$ Hz]. – $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]$ -Benzol): $\delta = -16.61$ ppm [s, $^1J(\text{PW}) = 207.8$ Hz]. – $\text{C}_{13}\text{H}_{22}\text{ClO}_2\text{PSiW}$ (488.67): calcd. C 31.95, H 4.54; found C 29.83, H 3.66*

Synthesis of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{OH}$ (**6a**)

a) by oxygenation of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ (**3a**) with dimethyldioxirane

A solution of 264 mg (0.58 mmol) of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ (**3a**) in 9 ml of acetone was treated dropwise with 6.7 ml (0.60 mmol) of a 0.09 M solution of dimethyl dioxirane in acetone at -78°C and stirred for 1.5 h at this temperature and an additional hour at room temperature. All volatiles were removed in vacuo and the ochre, oily residue washed two times at -20°C with *n*-pentane (each 5 ml). The residue was treated with 10 ml of toluene, and insoluble material was removed by filtration through a Celite pad. The filtrate was reduced in vacuo to a volume of 1 ml and treated with 8 ml of *n*-pentane, whereupon **6a** crystallized, which was separated, washed two times with *n*-pentane (each 1 ml) and dried in vacuo. Yield 164 mg (60 %). Ochre solid. M. p. 68°C (dec.).

b) by hydrolysis of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{Cl}$ (**5**)

A solution of 194 mg (0.40 mmol) of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{Cl}$ (**5**) and 292 mg (2.88 mmol) of Et_3N in 20 ml of Et_2O was treated with 50 mg (2.78 mmol) of H_2O and stirred for 14 h at room temperature. All volatiles were removed in vacuo, the yellow-orange residue was suspended in a mixture of 20 ml of toluene and 20 ml of petroleum ether and filtered over Na_2SO_4 . The filtrate was evaporated in vacuo and the residue was dissolved in 2 ml of toluene, treated with 8 ml of *n*-pentane and **6a** crystallized at -78°C , washed with 5 ml of *n*-pentane at this temperature and dried in vacuo. Yield 102 mg (54 %). – IR (toluene): $\nu = 3663$ (w, br, OH), 1919 (s, CO), 1832 (vs, CO) cm^{-1} . – ^1H NMR (300.4 MHz, $[\text{D}_6]$ -benzene): $\delta = 4.60$ [d, $^3J(\text{HCWP}) = 1.8$ Hz, 5 H, H_5C_5], 1.63 (s, br, 1 H, HO), 1.06 [d, $^2J(\text{HCP}) = 9.2$ Hz, 9 H, Me_3P], 0.50 (s, 6 H, H_3CSi), 0.09 ppm [d, $^3J(\text{HCWP}) = 3.5$ Hz, 2 H, H_2C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $[\text{D}_6]$ -benzene): $\delta = 230.80$ [d, $^2J(\text{PWC}) = 17.2$ Hz, CO], 89.28 (s, C_5H_5), 20.91 [d, $^1J(\text{CP}) = 34.2$ Hz, $(\text{CH}_3)_3\text{P}$], 4.32 (s, CH_3Si), -34.30 ppm [d, $^2J(\text{CWP}) = 9.5$ Hz, CH_2]. – $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.6 MHz, $[\text{D}_6]$ -benzene): $\delta = 23.86$ ppm [d, $^3J(\text{SiCWP}) = 3.3$ Hz]. – $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]$ -benzene): $\delta = -16.78$ ppm [s, $^1J(\text{PW}) = 218.7$ Hz]. –

$\text{C}_{13}\text{H}_{23}\text{O}_3\text{PSiW}$ (470.22): calcd. C 33.21, H 4.93; found C 33.10, H 4.72.

Synthesis of $\text{Cp}(\text{OC})_2(\text{Ph}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{OH}$ (**6b**)

Analogously to the preparation of **6a** (route a) from 60 mg (0.09 mmol) of $\text{Cp}(\text{OC})_2(\text{Ph}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ (**3b**) and 1 ml (0.09 mmol) of a 0.09 M solution of dimethyl dioxirane in 4 ml of acetone after stirring for 1 h at -78°C and 1 h at r. t. All volatiles were removed in vacuo and the ochre, oily residue washed two times at -20°C with *n*-pentane (each 1 ml). The residue was treated with a mixture of 1 ml of toluene and 4 ml of *n*-pentane and stored at -78°C , whereupon **6b** crystallized. **6b** was separated, washed with 0.5 ml of *n*-pentane and dried in vacuo. Yield 32 mg (55 %). Ochre solid. – IR (THF): $\nu = 3655$ (w, br, OH), 1934 (vs, CO), 1852 (s, CO) cm^{-1} . – ^1H NMR (300.4 MHz, $[\text{D}_6]$ -benzene): $\delta = 7.54$ [m, 6 H, $(\text{H}_5\text{C}_6)_3\text{P}$], 7.00 [m, 9 H, $(\text{H}_5\text{C}_6)_3\text{P}$], 4.74 [d, $^3J(\text{HCWP}) = 1.7$ Hz, 5 H, H_5C_5], 0.86 (s, br, 1 H, HO), 0.49 [s, 6 H, H_3CSi], 0.38 ppm [d, $^3J(\text{HCWP}) = 3.1$ Hz, 2 H, H_2C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, $[\text{D}_6]$ -benzene): $\delta = 230.13$ [d, $^2J(\text{CWP}) = 17.6$ Hz, CO], 137.29 [d, $^1J(\text{CP}) = 47.9$ Hz, C-1, $(\text{C}_6\text{H}_5)_3\text{P}$], 133.80 [d, $^2J(\text{CCP}) = 9.9$ Hz, C-2, C-6, $(\text{C}_6\text{H}_5)_3\text{P}$], 130.14 [d, $^3J(\text{CCCP}) = 2.0$ Hz, C-3, C-5, $(\text{C}_6\text{H}_5)_3\text{P}$], 128.60 [s, C-4, $(\text{C}_6\text{H}_5)_3\text{P}$], 91.08 (s, C_5H_5), 4.57 (s, CH_3Si), -31.81 ppm [d, $^2J(\text{CWP}) = 7.6$ Hz, CH_2]. – ^{29}Si NMR (59.6 MHz, $[\text{D}_6]$ -benzene): $\delta = 23.43$ ppm [dm, $^3J(\text{SiCWP}) = 1.8$ Hz]. – $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]$ -benzene): $\delta = 41.23$ ppm [s, $^1J(\text{PW}) = 236.9$ Hz]. – $\text{C}_{28}\text{H}_{29}\text{O}_3\text{PSiW}$ (656.44): calcd. C 51.23, H 4.45; found C 50.89, H 4.51.

Synthesis of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{O}-\text{SiMe}_2\text{H}$ (**7**)

A solution of 197 mg (0.43 mmol) of $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{OH}$ (**6a**) and 219 mg (2.16 mmol) of Et_3N in 30 ml of Et_2O was treated with 174 mg (1.83 mmol) of ClSiMe_2H and stirred for 3 d at r. t. All volatiles were removed in vacuo, the residue was treated with 20 ml of petroleum ether and insoluble material was removed by filtration through a Celite pad. The filtrate was evaporated in vacuo, the residue treated with 2 ml of *n*-pentane and the by-product $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{Cl}$ crystallized at -80°C and removed. The supernatant liquid was evaporated in vacuo, leaving **7**. Yield 156 mg (77 %). Dark yellow, viscous oil. – IR (petroleum ether): $\nu = 2107$ (w, br, SiH), 1932 (s, CO), 1847 (vs, CO) cm^{-1} . – ^1H NMR (300.4 MHz, $[\text{D}_6]$ -benzene): $\delta = 5.22$ [sept, $^3J(\text{HSiCH}) = 2.8$ Hz, 1 H, HSi], 4.60 [d, $^3J(\text{HCWP}) = 1.8$ Hz, 5 H, H_5C_5], 1.07 [d, $^2J(\text{HCP}) = 9.2$ Hz, 9 H, Me_3P], 0.54 (s, 6 H, H_3CSiCH_2), 0.33 [d, $^3J(\text{HCSiH}) = 2.8$ Hz, 6 H, H_3CSiH], 0.14 ppm [d, $^3J(\text{HCWP}) = 3.5$ Hz, 2 H, H_2C]. – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $[\text{D}_6]$ -benzene): $\delta = 230.01$ [d, $^2J(\text{CWP}) = 18.3$ Hz, CO], 89.07 (s, C_5H_5), 20.85 [d,

*No satisfactory elemental analysis possible due to a very high decomposition tendency to $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{Cl}$.

$^1\text{J}(\text{CP}) = 35.6$ Hz, $(\text{CH}_3)_3\text{P}$, 4.47 [s, $(\text{CH}_3)_2\text{Si}$], 1.37 [s, $(\text{CH}_3)_2\text{SiH}$], -34.61 ppm [d, $^2\text{J}(\text{CWP}) = 9.2$ Hz, CH_2]. $-^{29}\text{Si}$ NMR (59.6 MHz, $[\text{D}_6]-\text{benzene}$): $\delta = 18.39$ [m, $\text{Si}(\text{CH}_3)_2\text{CH}_2\text{W}$], -9.18 ppm [dsept, $^1\text{J}(\text{SiH}) = 199.9$ Hz, $^2\text{J}(\text{SiCH}) = 7.0$ Hz, SiH]. $-^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]-\text{benzene}$): $\delta = -16.52$ ppm [s, $^1\text{J}(\text{PW}) = 216.3$ Hz]. $-\text{C}_{13}\text{H}_{23}\text{O}_3\text{PSiW}$ (470.22): calcd. C 34.10, H 5.53; found C 34.42, H 5.64.

*Crystal data for $\text{Cp}(\text{OC})_2(\text{Me}_3\text{P})\text{W}-\text{CH}_2-\text{SiMe}_2\text{H}$ (**3a**)*

The intensities were measured with a Nonius-Kappa CCD diffractometer (Mo-K α radiation, $\lambda = 0.71073$ Å, graphite monochromator) at $T = 123(2)$ K. The structure was solved by the Patterson method [24] (SHELXS-97) and refined by least-square methods based on F^2 with all measured reflections (SHELXL-97) (full-matrix least-squares on F^2) [25]. Non-hydrogen atoms were refined anisotropically, H atoms localized by difference maps and refined using a riding model. An empirical absorption correction was applied.

$\text{C}_{13}\text{H}_{23}\text{O}_3\text{PSiW}$, $M = 454.22$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.9977(3)$, $b = 10.1487(3)$, $c =$

$14.2951(3)$ Å, $\beta = 109.306(2)^\circ$, $V = 1642.71(7)$ Å³, $D_c = 1.837$ Mg m⁻³, $Z = 4$, absorption coefficient μ (MoK α) = 7.195 mm⁻¹, crystal size $0.20 \times 0.15 \times 0.10$ mm, $F(000) = 880$; reflections measured: 28661, independent reflections: 4041, $1.93^\circ < \theta < 28.28^\circ$, $\text{GooF} = 1.055$, residual electron density = $0.896 / -1.883$ e.Å⁻³, $R_1 = 0.0204$, $wR2 = 0.0479$ (all data).

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-186240. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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