Journal of Organometallic Chemistry 566 (1998) 259–262

A catalytic pathway for the conversion of tungsten-silanes into tungsten-silanols[1]

Wolfgang Malisch [a],*, Heinrich Jehle [a], Catherine Mitchel [b], Waldemar Adam [b]

[a] *Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*
[b] *Institut für Organische Chemie der Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

Received 28 April 1998

Abstract

Tungsten substituted silanes $C_5H_5(OC)_2(Ph_3P)W{-}SiMe_2H$ (**3a**), $C_5Me_5(OC)_2(Me_3P)W{-}SiMe_2H$ (**3b**) and $C_5Me_5(OC)_2(Me_3P)W{-}SiH_3$ (**6**) are converted with urea hydrogenperoxide in the presence of catalytic amounts of $MeReO_3$ to the corresponding metallo-silanols $C_5H_5(OC)_2(Ph_3P)W{-}SiMe_2OH$ (**4a**), $C_5Me_5(OC)_2(Me_3P)W{-}SiMe_2OH$ (**4b**) and $C_5Me_5(OC)_2(Me_3P)W{-}Si(OH)_3$ (**7**). Condensation of **4b** with R_3SiCl yields the tungsten-substituted disiloxanes $C_5Me_5(OC)_2(Me_3P)W{-}SiMe_2OSiR_3$ ($SiR_3 = SiMe_2H$ (**5a**), $SiCl_3$ (**5b**)). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Metallo-silanes; Metallo-silanols; Oxofunctionalization; $MeReO_3$–UHP

1. Introduction

Metallo-silanoles represent a special class of silanoles, which are characterized by a remarkably high stability with respect to self condensation. This property, which is even valid for silanetriole derivatives [1], and the generally stable metal–silicon bond makes these compounds useful precursors towards controlled condensation with chlorosilanes to build up unusual arrangements of functionalized siloxanes at metal centres. Studies concerning the synthesis of metal-fragment-substituted silanols have shown that the usual access via hydrolysis of the corresponding metallo-chlorosilanes is strongly limited due to the reduced electrophilicity of the silicon caused by the electron releasing transition metal [2]. On the other hand the metal fragment is responsible for highly hydridic Si–H units, creating the conditions for electrophilic oxygenation via oxygen insertion with dimethyldioxirane [3]. This method offers for the first time access to $Cp(OC)_2Fe(Ru)$-, or $C_5Me_5(OC)_2(Me_3P)Mo(W)$-substituted silanols [4]. In order to enlarge this class of compounds we have looked for possibilities to avoid the time consuming and lavish preparation of dimethyldioxirane. Moreover, the use of a common oxidation reagent should be realized in a catalytic procedure. In this context methylrheniumtrioxide (MTO) was preferentially taken into account, whose catalytic activity in diverse oxygenation processes has been impressively demonstrated by Herrmann and others [5]. This communication reports about an efficient catalytic pathway for the oxidation of tungsten-substituted silanes using urea-hydrogenperoxide in the presence of MTO.

2. Results

To provide the utmost clear conditions in context with a catalytic procedure we synthesized model compounds bearing only one Si–H-unit. We focused on

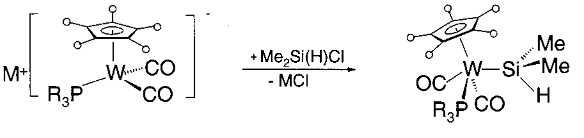
---

* Corresponding author. Tel.: +49 931 8885277; fax: +49 931 8884618; e-mail: Wolfgang.Malisch@mail.uni-wuerzburg.de

[1] Preliminary communications: Synthesis and reactivity of silicon transition metal complexes, 45 (part 44); Metallo-silanoles and metallo-siloxanes, 18 (part 17). W. Malisch, H. Jehle, S. Möller, Ch. Saha-Möller, W. Adam, Eur. J. Inorg. Chem. 1998, in press.

0022-328X/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S0022-328X(98)00727-X

tungsten-silanes, since these species have shown high reactivity with respect to oxygen insertion. Metallo-dimethylsilanes of this type were obtained by the reaction of the alkaline metalates **1a**,**b** with dimethylchlorosilane **2** in cyclohexane at room temperature in the absence of light. Nucleophilic ligand exchange at the silicon [6] generates **3a**,**b**, isolated as beige microcrystalline solids in good yields after 16 h (Eq. 1).



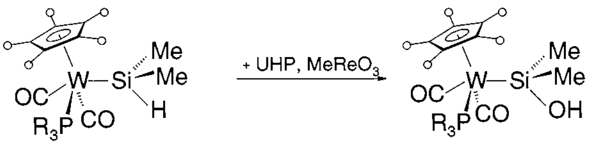
(1)

1a,b **2** **3a,b**

	a	b
R	Ph	Me
—o	H	Me

The influence of the metal fragment is established by the low-field ^{29}Si chemical shift [$\delta = 1.7$ ppm (**3a**), 7.4 ppm (**3b**)], as well as by the reduced value of the ^{1}J(SiH) coupling constant [179.6 Hz (**3a**), 173.7 Hz (**3b**)]. In addition the ν(Si–H) stretching band is shifted considerably to lower wavenumbers [2026 (**3a**), 2031 cm^{-1}(**3b**)] compared to Me$_2$Si(H)Cl (2278 cm^{-1}).

Treatment of **3a**,**b** with urea-hydrogenperoxide in the presence of (3–4 mol%) MeReO$_3$ in acetone at −78°C leads to the formation of the metallo-silanols **4a**,**b** within 12–14 h (Eq. 2). Completeness of oxygenation is monitored by the disappearence of the ν(Si–H) band at 2026/2031 cm^{-1}. In order to establish the catalytic activity of MTO, an analogous experiment was run with **3a** using exclusively urea hydrogen peroxide. Besides decomposition of **3a** after 12 h no formation of **4a** was observed.



(2)

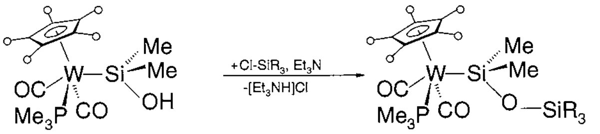
3a,b **4a,b**

	a	b
R	Ph	Me
—o	H	Me

The metallo-silanols are isolated in good yields [71% (**4a**), 78% (**4b**)] as yellow microcrystalline solids, which are air stable for a short period of time and can be stored under nitrogen at room temperature without decomposition. **4a**,**b** exhibit rather good solubility in acetone and toluene.

The ^{29}Si-NMR resonance of the OH substituted silicon atoms shows a typical downfield shift of 49.6 ppm (**4a**) and 51.5 (**4b**) ppm compared with **3a** (1.7 ppm) and **3b** (7.4 ppm).

In addition, chemical proof is obtained for the formation of a Si-bonded hydroxyl group by treatment of **4b**, dissolved in toluene, with dimethylchlorosilane and silicontetrachloride, respectively, in the presence of Et$_3$N as an auxiliary base. After a reaction period of 48 h the corresponding metallo-siloxanes **5a**,**b** are isolated in excellent yields as pale yellow microcrystalline powders (Eq. 3).



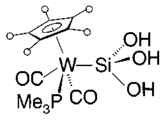
(3)

4b **5a,b**

5a: SiR$_3$ = SiMe$_2$H
5b: SiR$_3$ = SiCl$_3$
—o = Me

5a,**b** represent further interesting examples of metallo-disiloxanes with a functionalized γ-silicon atom, offering the possibility for various derivatizations.

The catalytic oxygenation procedure used in Eq. (2) is also efficient for Si–H tungsten species having more than one hydrogen at the silicon. Cp*(OC)$_2$(Me$_3$P)W–SiH$_3$ (**6**) is converted in an analogous manner using MTO/UHP after 14 h into the tungsten-silanetriol **7**. This compound is now obtained in higher yield (94%) compared to the dioxirane oxidation applied by us to prepare **7** for the first time (71%) [1].



7

This paper presents an attractive catalytic pathway for the oxygenation of metallo-silanes. Characteristic of this type of process are the extremely mild conditions (oxidation starts at −78°C) and the good yields. Forthcoming publications will present further examples of the application of the catalytic system MeReO$_3$/UHP for the formation of metallo-silanols as well as for the oxofunctionalization of other transition metal substituted element–hydrogen bonding systems.

3. Experimental section

All operations were performed under an atmosphere of purified and dried nitrogen using Schlenk-type technique. Solvents were dried according to conventional procedures, distilled and saturated with N$_2$ prior to use. ^{1}H-, ^{13}C{^{1}H}- and ^{29}Si{^{1}H}-NMR spectra were obtained with Bruker AMX 400, Jeol LA 300, Jeol FX 90Q or Bruker AMX 200 spectrometers. δ(^{1}H)/(^{13}C) chemical shifts are reported downfield from $Si(CH_3)_4$, referenced to the residual proton signal (^{1}H) or natural abundance carbon signal (^{13}C) of the deuterated solvent. $\delta(^{29}Si)$ chemical shifts are measured relative to external $Si(CH_3)_4$. IR spectra were recorded on a Perkin-Elmer 283 grating spectrometer in NaCl cells of 0.1 mm path length. Starting materials: $K[W(PPh_3)(CO)_2Cp]$ [7], $Li[W(PMe_3)(CO)_2C_5R_5]$ (R = H, Me) [7].

3.1. 1-[Dicarbonyl(η^5-cyclopentadienyl)(triphenylphosphane)tungsten]-dimethylsilane (**3a**)/1-[Dicarbonyl-(η^5-pentamethylcyclopentadienyl-(trimethylphosphane)tungsten]-dimethylsilane (**3b**)

To a suspension of finely powdered **1a** (300 mg (0.51 mmol))/**1b** (515 mg (1.33 mmol)) in 40 ml of cyclohexane $Me_2Si(H)Cl$ (180 mg (1.94 mmol)/366 mg (3.87 mmol)) is added dropwise and the reaction mixture stirred at room temperature for 18 h/2 h. After removal of the solvent and excessive silane in vacuo, the residue is treated three times with 5 ml toluene till the extract shows no IR-spectroscopic evidence for the presence of **3a**/**3b**. The toluene extracts were combined in vacuo, evaporated to dryness, the remaining **3a**/**3b** washed at − 30°C with petrolether and dried in vacuo. Yield: 204 mg (64%) (**3a**)/280 mg (48%) (**3b**). Ochre microcrystalline powders. M.p. 73°C/73°C. **3a:** $C_{27}H_{27}O_2PSiW$ (626.41): calc. C 51.77, H 4.34; found C 51.38, H 4.13. ^{1}H-NMR (400.1 MHz, [D_6]-benzene): $\delta = 7.78$ (m, 15 H, phenyl), 5.35 [septd, ^3J(HCSiH) = 3.6 Hz, ^3J(PWSiH) = 1.0 Hz, ^1J(SiH) = 179.6 Hz, 1H, HSi], 4.55 [d, ^3J(PWCH) = 0.9 Hz, 5 H, H_5C_5], 0.95 [d, ^3J(HSiCH) = 3.6 Hz, 6H, $(H_3C)_2Si$]. ^{13}C-NMR (100.6 MHz, [D_6]-benzene): $\delta = 228.3$ [d, ^2J(PWC) = 18.9 Hz, CO], 143.6 − 125.5 [$(H_5C_6)_3P$], 88.3 (s, C_5H_5), 1.9 ppm [s, $(H_3C)_2Si$]. ^{31}P-NMR (162 MHz [D_6]-benzene): $\delta = 41.9$ ppm [s, ^1J(WP) = 288.1 Hz]. ^{29}Si-NMR (79.5 MHz, [D_6]-benzene): $\delta = 1.7$ ppm [d, ^2J(PWSi) = 12.3 Hz].-IR (pentane): ν(SiH) = 2026 (w) cm^{-1}; ν(CO) = 1933 (s), 1842 (vs) cm^{-1}. **3b:** $C_{17}H_{31}O_2PSiW$ (510.34): calc. C 40.01, H 6.27; found C 39.86, H 6.15. ^{1}H-NMR (200 MHz, [D_6]-benzene): $\delta = 4.76$ [septd, ^3J(HCSiH) = 3.6Hz, ^3J(PWSiH) = 2.0 Hz, ^1J(SiH) = 173.7 Hz, 1 H, HSi], 1.74 [s, 15 H, $(H_3C)_5C_5$], 1.26 [d, ^2J(PCH) = 8.9 Hz, 9 H, $(H_3C)_3P$], 0.89 ppm [d, ^3J(HSiCH) = 3.6 Hz, 6 H, $(H_3C)_2Si$]. ^{31}P-NMR (36 MHz, [D_6]-benzene): $\delta = -13.45$ ppm [s, ^1J(WP) = 294.9 Hz]. ^{13}C-NMR (50 MHz, [D_6]-benzene): $\delta = 231.10$ [d, ^2J(PWC) = 20.0 Hz, ^1J(WC) = 152.9 Hz, CO], 100.40 [s, $(H_3C)_5\underline{C}_5$], 20.42 [d, ^1J(PC) = 33.4 Hz, $(H_3C)_3P$], 11.12 [s, $(H_3\underline{C})_5C_5$], 1.83 ppm [s, $(H_3C)_2Si$]. ^{29}Si-NMR (18 MHz, [D_6]-benzene): $\delta = 7.40$ ppm [d, ^2J(PWSi) = 11.7 Hz, ^1J(WSi) = 41.8 Hz]. IR (cyclohexane): ν(SiH) = 2031 (vw) cm^{-1}; ν(CO) = 1893 (s), 1821 (vs) cm^{-1}.

3.2. 1-[Dicarbonyl(η^5-cyclopentadienyl)(triphenylphosphane)tungsten]-dimethylsilanole (**4a**)

A solution of 432 mg (0.68 mmol) of $Cp(OC)_2(Ph_3P)W{-}SiMe_2H$ (**3a**) in 10 ml of acetone is combined with 5.1 mg (0.020 mmol) of $MeReO_3$ and 65 mg (0.69 mmol) of urea-hydrogenperoxide at −78°C. After stirring for 3 h, the reaction mixture is warmed up to room temperature and stirred for another 12 h. Insoluble material is separated and the filtrate evaporated to dryness in vacuo. Remaining **4a** is washed with 5 ml of *n*-pentane and dried in vacuo. Yield: 314 mg (71%). Yellow microcrystalline powder. M.p.: 78°C. $C_{27}H_{27}O_3PSiW$ (642.41): calc. C 50.48, H 4.23; found C 50.26, H 4.17. ^{1}H-NMR (400.1 MHz, [D_6]-benzene): $\delta = 7.81$ (m, 15 H, phenyl), 4.64 [d, ^4J(PWCH) = 0.5 Hz, 5 H, H_5C_5] 2.2 (s, br, 1 H, OH), 1.08 [s, $(H_3C)_2Si$]. ^{13}C-NMR (100.6 MHz, [D_6]-benzene): $\delta = 227.9$ [d, ^2J(PWC) = 18.2 Hz, CO], 143.7 − 125.6 [$(H_5C_6)_3P$], 88.7 (s, C_5H_5), 2.0 ppm [s, $(H_3C)_2Si$]. ^{31}P-NMR (162 MHz [D_6]-benzene): $\delta = 41.8$ ppm [s, ^1J(WP) = 285.3 Hz]. ^{29}Si-NMR (79.5 MHz, [D_6]-benzene): $\delta = 49.6$ ppm [d, ^2J(PWSi) = 14.2 Hz]. IR (pentane): ν(OH) = 3665 (w) cm^{-1}; ν(CO) = 1898 (s), 1821 (vs) cm^{-1}.

3.3. Treatment of **3a** with urea-hydrogenperoxide (in the absence of MTO)

A solution of 216 mg (0.34 mmol) of $Cp(OC)_2(Ph_3P)W{-}SiMe_2H$ (**3a**) in 13 ml of acetone is combined with 33 mg (0.35 mmol) of urea-hydrogenperoxide at − 78°C. After stirring for 3 h, the reaction mixture is warmed up to room temperature and stirred for another 9 h. After this time no generation of **4a** was observed in the reaction mixture by IR- and NMR-spectroscopy.

3.4. 1-[Dicarbonyl(η^5-pentamethylcyclopentadienyl(trimethylphosphane)tungsten]-dimethylsilanole (**4b**)

According to Section 3.2 from 280 mg (0.55 mol) of $C_5Me_5(OC)_2(Me_3P)W{-}SiMe_2H$ (**3b**), 5.5 mg (0.022 mmol) of $MeReO_3$ and 51.6 mg (0.55 mmol) of urea-hydrogenperoxide after 12 h. Yield: 225 mg (78%). Yellow microcrystalline powder. M.p.: 121°C. $C_{17}H_{31}O_3PSiW$ (526.32): calc. C 38.79, H 5.93; found C 38.53, H 5.79. ^{1}H-NMR (400.1 MHz, [D_6]-benzene): $\delta = 2.65$ (s, br, 1 H, HO), 1.89 [s, 15 H, $(H_3C)_5C_5$], 1.29 [d, ^{2}J (PCH) = 9.1 Hz, 9H, $(H_3C)_3P$], 0.97 ppm [s, 6 H, $(H_3C)_2Si$]. ^{13}C-NMR (100.6 MHz, [D_6]-benzene): $\delta = 231.8$ [d, ^2J(PWC) = 21.0 Hz, ^1J(WC) = 154.1 Hz, CO], 101.1 [s, $(H_3C)_5\underline{C}_5$], 20.0 [d, ^1J(PC) = 33.8 Hz, $(H_3C)_3P$], 11.5 [s, $(H_3\underline{C})_5C_5$], 9.5 ppm [s, ^1J(SiC) = 51.5 Hz, $(H_3C)_2Si$]. ^{31}P-NMR (162 MHz [D_6]-benzene): $\delta = -12.7$ ppm [s, ^1J(WP) = 290.6 Hz]. ^{29}Si-NMR (79.5

MHz, [D$_6$]-benzene): $\delta = 51.5$ ppm [d, ^2J(PWSi) $= 13.6$ Hz, ^1J(WSi) $= 42.5$ Hz]. IR (THF): ν(OH) $= 3676$ (vw), 3640 (w, br) cm^{-1}; ν(CO) $= 1895$ (s), 1809 (vs) cm^{-1}.

*3.5. 1-[Dicarbonyl(η^5-pentamethylcyclopentadienyl)(trimethylphosphane)tungsten]-1,1,3,3-tetramethyldisiloxane (**5a**)*

A solution of 85 mg (0.16 mmol) Cp*(OC)$_2$(Me$_3$P)W-SiMe$_2$OH (**4a**) in 8 ml of toluene is combined with 73 mg (0.72 mmol) of Et$_3$N and 85 mg (0.90 mmol) of Me$_2$Si(H)Cl and the reaction mixture stirred for 2 days at room temperature. Volatile material is removed in vacuo and the residue extracted with 20 ml of *n*-pentane. **5a** is isolated after crystallization at -78°C. Yield: 87 mg (92%). Pale yellow microcrystalline powder. M.p.: 114°C. $C_{19}H_{37}O_3PSi_2W$ (584.49): calc. C 39.04, H 6.38; found C 38.58, H 6.40. ^{1}H-NMR (60 MHz, [D$_6$]-benzene): $\delta = 5.30$ [sept, ^3J(HCSiH) $= 2.8$ Hz, ^1J(SiH) $= 200.0$ Hz, 1 H, HSi], 1.74 [s, 15 H, (H$_3$C)$_5$C$_5$], 1.15 [d, ^2J(PCH) $= 9.3$ Hz, 9 H, (H$_3$C)$_3$P], 0.85 [s, 6 H, (H$_3$C)$_2$SiW], 0.25 ppm [d, ^3J(HSiCH) $= 2.8$ Hz, 6 H, (H$_3$C)$_2$Si]. ^{31}P-NMR (162 MHz, [D$_6$]-benzene): $\delta = -12.46$ ppm [s, ^1J(WP) $= 285.1$ Hz]. ^{13}C-NMR (100.6 MHz, [D$_6$]-benzene): $\delta = 233.01$ [d, ^2J(PWC) $= 20.4$ Hz, CO], 101.12 [s, (H$_3$C)$_5\underline{C}_5$], 19.85 [d, ^1J(PC) $= 33.9$ Hz, (H$_3$C)$_3$P], 11.47 [s, (H$_3\underline{C}$)$_5$C$_5$], 9.67 [s, ^1J(SiC) $= 51.5$ Hz, (H$_3$C)$_2$SiW], 1.50 ppm [s, (H$_3$C)$_2$Si]. ^{29}Si-NMR (18 MHz, [D$_6$]-benzene): $\delta = 46.48$ [d, ^2J(PWSi) $= 13.9$ Hz, ^1J(WSi) $= 46.9$ Hz, (H$_3$C)$_2$SiW], -9.88 ppm [s, (H$_3$C)$_2$Si]. IR (cyclohexane): ν(SiH) $= 2106$ (w) cm^{-1}; ν(CO) $= 1896$ (s), 1823 (vs) cm^{-1}. IR (benzene): ν(SiH) $= 2100$ (w) cm^{-1}; ν(CO) $= 1889$ (s), 1811 (vs) cm^{-1}; ν(SiMe) $= 1284$ (w), 1248 (m) cm^{-1}; ν(SiOSi) $= 1025$ (s, br), 591 (w) cm^{-1}.

*3.6. 1-[Dicarbonyl(η^5-pentamethylcyclopentadienyl)(trimethylphosphane)tungsten]-1,1-dimethyl-3,3,3-trichlorodisiloxane (**5b**)*

According to Section 3.5 from 147 mg (0.28 mmol) of C$_5$Me$_5$(OC)$_2$(Me$_3$P)W–SiMe$_2$OH (**4a**), 85 mg (0.84 mmol) of Et$_3$N and 60 mg (0.35 mmol) of SiCl$_4$ after 30 min. Yield: 168 mg (91%). Pale yellow microcrystalline powder. M.p.: 76°C. $C_{17}H_{30}Cl_3O_3PSi_2W$ (659.78): calc. C 30.95, H 4.85; found C 31.10, H 4.87. ^{1}H-NMR (400 MHz, [D$_6$]-benzene): $\delta = 1.65$ [d, ^4J(PWCCH) $= 0.5$ Hz, 15 H, (H$_3$C)$_5$C$_5$], 1.08 [d, ^2J(PCH) $= 9.1$ Hz, 9 H, (H$_3$C)$_3$P), 0.93 ppm (s, 6 H, (H$_3$C)$_2$Si]. ^{31}P-NMR (162 MHz, [D$_6$]-benzene): $\delta = -13.58$ ppm [s, ^1J(WP) $=$ 277.0 Hz]. ^{13}C-NMR (100.6 MHz, [D$_6$]-benzene): $\delta =$ 232.21 [d, ^2J(PWC) $= 21.0$ Hz, ^1J(WC) $= 148.8$ Hz, CO], 101.48 [s, (H$_3$C)$_5$C$_5$), 19.59 (d, ^1J(PC) $= 34.4$Hz, (H$_3$C)$_3$P), 11.37 (s, (H$_3\underline{C}$)$_5$C$_5$], 9.50 ppm [s, ^1J(SiC) $=$ 50.5 Hz, (H$_3$C)$_2$Si]. ^{29}Si-NMR (79 MHz, [D$_6$]-benzene): $\delta = 63.47$ ppm [d, ^2J(PWSi) $= 14.3$ Hz, ^1J(WSi) $= 56.7$ Hz, (H$_3$C)$_2$SiCl$_3$ not observed]. IR (toluene): ν(CO) $=$ 1903 (s), 1824 (vs) cm^{-1}.

*3.7. 1-[Dicarbonyl(η^5pentamethylcyclopentadienyl)(trimethylphosphane)tungsten]-silanetriol) (**4c**)*

According to Section 3.2 from 50 mg (0.12 mmol) of C$_5$Me$_5$(OC)$_2$(Me$_3$P)W–SiH$_3$ **3c**, 3.6 mg (0.014 mmol) of MeReO$_3$ and 34 mg (0.36 mmol) of urea-hydrogenperoxide after 14 h. Yield: 52 mg (94%). Pale yellow microcrystalline powder. M.p. 103°C. $C_{15}H_{27}O_5PSiW$ (530.29): calc. C 33.98, H 5.13; found C 33.58, H 4.91. **4c** was characterized by comparison with authentic material [1].

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 347: 'Selective Reactions of Metal-Activated Molecules') as well as from the Fonds der Chemischen Industrie.

References

[1] W. Malisch, R. Lankat, S. Schmitzer, J. Reising, Inorg. Chem. 34 (1995) 5702.

[2] W. Malisch, S. Schmitzer, G. Kaupp, K. Hindahl, H. Käb, U. Wachtler, in: N. Auner, J. Weis (Eds), Organosilicon Chemistry, VCH, Weinheim, 1994, p. 185.

[3] (a) W. Adam, U. Azzena, F. Prechtl, K. Hindahl, W. Malisch, Chem. Ber. 125 (1992) 1409. (b) W. Malisch, K. Hindahl, H. Käb, J. Reising, W. Adam, F. Prechtl, Chem. Ber. 128 (1995) 963. (c) S. Möller, H. Jehle, W. Malisch, W Seelbach, in: N. Auner, J. Weis (Eds), Organosilicon Chemistry III: From Molecules to Materials, VCH, Weinheim, 1998, p. 267.

[4] (a) S. Möller, O. Fey, W. Malisch, W. Seelbach, J. Organomet. Chem. 507 (1996) 239. (b) W. Malisch, S. Schmitzer, R. Lankat, M. Neumayer, F. Prechtl, W. Adam, Chem. Ber. 128 (1995) 1251.

[5] (a) W.A. Herrmann, F.E. Kühn, Acc. Chem. Res. 13 (1997) 169. (b) A.M. Al-Ajlouni, J.H. Espenson, J. Am. Chem. Soc. 117 (1995) 9243. (c) J. Rudolph, K.L. Reddy, J.P. Chiang, K.B. Sharpless, J. Am. Chem. Soc. 119 (1997) 6189. (d) F.G.A. Stone, R. West, Adv. Organomet. Chem. 41 (1997) 127.

[6] S. Schmitzer, U. Weis, H. Käb, W. Buchner, W. Malisch, T. Polzer, U. Posset, W. Kiefer, Inorg. Chem. 32 (1993) 303.

[7] K[W(PPh$_3$)(CO)$_2$Cp] is prepared via K/benzophenone reduction of Cp(OC)$_2$(Ph$_3$P)W–Cl according to the method described in: T.A. George, R.A. Kovar, Inorg. Chem. 20 (1981) 285.