

Syntheses of tungsten-substituted oligosilanes

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Abstract

By way of alkali halide elimination, monotungsten- and ditungsten-substituted oligosilanes can be obtained. The polarity of the solvent used and the leaving groups at silicon have a strong influence on the syntheses. Heterogeneous reactions (apolar solvent) result in monotungsten compounds, whereas homogeneous conditions (mixture of solvents) shorten the reaction time and lead to α, ω -ditungsten-silanes. Using this modified alkali halide elimination method, the new permethylated silicon–tungsten compounds $\text{Cl}-(\text{SiMe}_2)_n-\text{Wp}$ and $\text{Wp}-(\text{SiMe}_2)_n-\text{Wp}$ ($n = 3, 4$; $\text{Wp} = \text{W}(\text{CO})_3\text{cp}$) were isolated. In addition, the synthesis of the first perhydrogenated α, ω -ditungsten oligosilanes $\text{Wp}-(\text{SiH}_2)_n-\text{Wp}$ ($n = 2, 3$) is reported. Cyclic silanes with a tungsten substituent and further reactive groups in the molecule are obtained by selective reaction of the triflate group at silicon.

1. Introduction

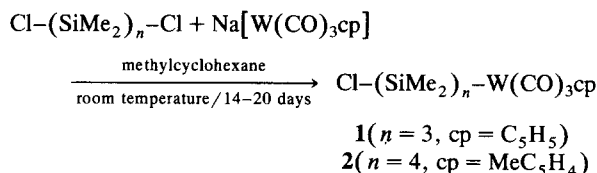
The elimination of alkali halides is a very useful method to obtain transition metal–silicon compounds. Many applications of this reaction, in particular for earlier transition metals with low electron densities at the central atom, have been found [1–3]. Only a small number of compounds containing transition metal–oligosilane bonds are known, mainly with the late transition metals iron and cobalt [4,5]. The first compounds with tungsten substituents on disilanes were prepared by Malisch in 1972 [6] in the reaction of $\text{Na}[\text{W}(\text{CO})_3\text{cp}]$ with permethylated halosilanes in apolar solvents (e.g. cyclohexane). In the reaction of α, ω -dihalosilanes with 2 eq. $[\text{W}(\text{CO})_3\text{cp}]^-$, monosubstituted tungsten compounds were obtained only for thermodynamic reasons [7]. Recently, we reported the syntheses of perhydrogenated silicon complexes of iron and molybdenum [8], which could be suitable precursors in MOCVD processes [9] to deposit stoichiometric metal silicides. In this work, we attempted to apply these reactions to perhydrogenated silanes bearing tungsten substituents.

2. Syntheses

2.1. Permethylated species

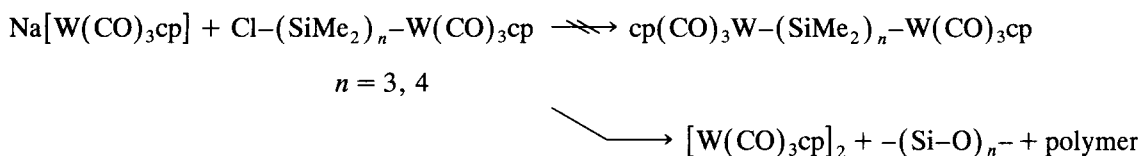
Silicon–tungsten compounds are rather unstable towards temperature or light. To avoid decomposition of

the substances, it is necessary to observe defined conditions such as the polarity of the solvent used. By reaction of $\text{Na}[\text{W}(\text{CO})_3\text{cp}]$ with α, ω -dichlorosilanes ($n = 3, 4$) in methylcyclohexane, α -chloro- ω -tungsten-silanes (**1**, **2**) were achieved, according to the results of Malisch [6] on disilanes.

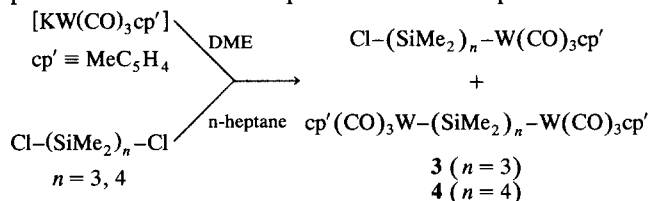


The reaction is very slow because of the insolubility of the metal salt and the low reactivity of chlorosilanes. The flask was treated with ultrasound repeatedly to accelerate the reaction by better suspension of the undissolved reagents. Subsequent reaction with another eq. $\text{Na}[\text{W}(\text{CO})_3\text{cp}]$ did not result in disubstitution, but led to the formation of the transmetallation product.

Thereby a large amount of Si–O derivatives was isolated. Oxygen in these siloxanes probably originated from the solvent or from decomposed CO ligands. However, there was a large amount of non-isolable polymers containing Si, O and W. A more effective way to obtain disubstitution was to modify the conditions of the reaction. Using the more soluble and therefore more nucleophilic salt $\text{K}[\text{W}(\text{CO})_3\text{cp}']$ ($\text{cp}' \equiv \text{MeC}_5\text{H}_4$) and homogeneous conditions, it was possible to isolate α, ω -ditungsten compounds (**3**, **4**). To obtain a homoge-



neous solution, the anion was dissolved in 1,2-dimethoxyethane (DME) and added to the silane compound dissolved in *n*-heptane at room temperature.



The transformation was finished within 2 days, but the yields decreased because of the formation of byproducts and a small amount of transmetalation product. The monosubstituted byproducts (**1**, **2**) could be removed due to their different solubility in *n*-pentane.

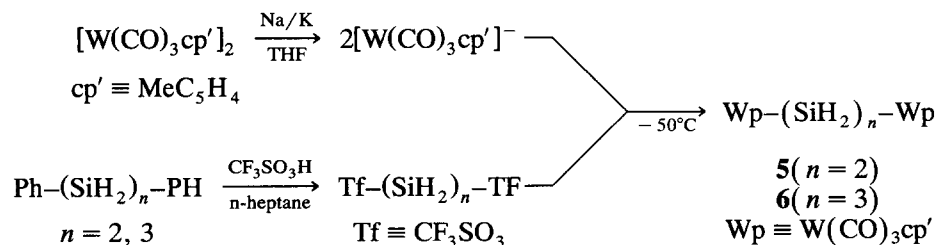
2.2. Perhydrogenated species

So far, no perhydrogenated oligosilane compounds involving tungsten substituents have been prepared. In a similar manner to the synthesis of **3** and **4**, the preparation of the first α,ω -ditungsten-perhydrooligosilanes was undertaken. α,ω -Diphenylsilanes are liquids and stable at room temperature for longer periods. Phenyl groups are split off easily using trifluoromethanesulphonic acid to give bistriflic silanes. The triflate group is very useful for the synthesis of transition metal–silicon compounds, because transmetalation reactions are avoided. The use of freshly prepared $\text{K}[\text{W}(\text{CO})_3\text{cp}']$ was necessary. The preparation of $\text{K}[\text{W}(\text{CO})_3\text{cp}']$ from $[\text{W}(\text{CO})_3\text{cp}']_2$ was performed as described in Ref. [10].

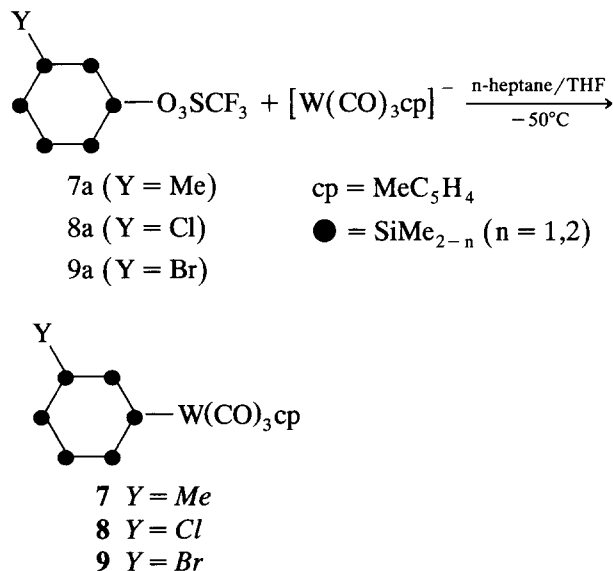
The hydrogenated complexes (**5**, **6**) were far more stable than the methylated complexes, as indicated by the increased yields. Compounds **5** and **6** could be suitable precursors for the deposition of stoichiometric thin metal silicide layers.

2.3. Cyclic systems

Cyclohexasilanes with transition metal substituents (Fe, Co, Mo) have been synthesized previously [11] by



reaction of the cyclohexasilane derivatives $\text{Si}_6\text{Me}_{11}\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with the highly nucleophilic metallates $\text{Na}[\text{Co}(\text{CO})_3(\text{PPh}_3)]$ and $\text{Na}[\text{Fe}(\text{CO})_2\text{cp}]$. To act against the inclination of silicon–metal compounds to decompose, transformations were performed in apolar medium, but the halogen derivatives of cyclohexasilane showed poor reactivity in these solvents. To avoid long reaction times and higher temperatures, it was necessary to use more reactive sila compounds and solvents of lower polarity than pure tetrahydrofuran (THF). Silanes bearing a triflate group were more appropriate. Transmetalations could be avoided and side reactions were almost suppressed (**7**). The selectivity of the reaction of triflic-silanylestere with complex metal anions can be seen in the syntheses of **8** and **9**. Because of the higher reactivity, the triflic group reacted much faster than the halogen function.



Despite the high reactivity of the bromo group in molecule **9a**, the main product of the reaction was **9**. Thus the selectivity of the triflate group in the reaction of 1,3-mixed substituted cyclohexasilanes offers a wide field of synthetic variations.

3. Experimental section

3.1. General

All transformations involving air- or moisture-sensitive materials were carried out under dry nitrogen or argon using a modified Schlenk technique. Solvents were dried over Na/K alloy under nitrogen and distilled prior to use. Metallates [12,13] and silicon starting materials [14–17] were prepared according to literature methods. NMR spectra were recorded with a Bruker MSL 300 (^1H , 300.13 MHz; ^{13}C , 75.47 MHz; ^{29}Si , 59.627 MHz); the compounds were dissolved in C_6D_6 or spectra were obtained from the reaction solution with a capillary filled with D_2O (^{29}Si spectra only). IR spectra were recorded with a Perkin–Elmer 883 IR spectrometer using an NaCl IR cuvette (0.05 mm). GC/MS analyses were performed on an HP 5890 Series II (capillary column HP-1, $15\text{ m} \times 0.2\text{ mm} \times 0.1\text{ }\mu\text{m}$, MSD/HP 5971 A). Mass spectra were recorded with a Kratos profile spectrometer.

3.2. Synthesis of $\text{Cp}(\text{CO})_3\text{W}-(\text{SiMe}_2)_n-\text{Cl}$ (1: $n = 3$, $\text{cp} \equiv \text{C}_5\text{H}_5$; 2: $n = 4$; $\text{cp} \equiv \text{MeC}_5\text{H}_4$)

$\text{Na}[\text{W}(\text{CO})_3\text{cp}]$ (1, 1.0 g/2.8 mmol; 2, 1.08 g/2.9 mmol) and $\text{Cl}(\text{SiMe}_2)_n\text{Cl}$ (1 mmol) were suspended in 50 ml of dry methylcyclohexane and stirred for 14 ($n = 3$) and 20 ($n = 4$) days at room temperature. Because the product is sensitive to light, the flask was enveloped in aluminium foil. When the IR spectrum showed no further reaction, the salts were filtered off and the solvent was removed. The product was extracted with *n*-pentane ($5 \times$) from the brown residue and then recrystallized from *n*-pentane at -70°C .

1-Chloro-3-(η^5 -cyclopentadienyltricarbonyltungsten)hexamethyltrisilane (1): yield, less than 30%; ^{29}Si NMR (ppm/TMS): 27.59, -7.67 , -34.53 , $^1J_{\text{Si-W}} = 22.3\text{ Hz}$; ^1H NMR (ppm/TMS): 4.61 (5H), 0.71 (6H), 0.50 (6H), 0.33 (6H); IR ($\text{cm}^{-1}/\text{n-pentane}$): 2026, 1937; $\text{C}_{14}\text{H}_{23}\text{ClO}_3\text{Si}_3\text{W}$, $M_R = 542.89$.

1-Chloro-4-(η^5 -methylcyclopentadienyltricarbonyltungsten)octamethyltetrasilane (2): yield, 0.2 g (32.5%); ^{29}Si NMR (ppm/TMS): 27.94, -5.26 , -32.80 , -42.75 , $^1J_{\text{Si-W}} = 21.0\text{ Hz}$; ^1H NMR (ppm/TMS): 4.60 (q, 4H), 1.41 (s, 3H), 0.62–0.25 (m, 24H); IR ($\text{cm}^{-1}/\text{n-pentane}$): 2026, 1936; $\text{C}_{17}\text{H}_{31}\text{ClO}_3\text{Si}_4\text{W}$, $M_R = 615.08$.

3.3. Synthesis of $\text{cp}'(\text{CO})_3\text{W}-(\text{SiMe}_2)_n-\text{W}(\text{CO})_3\text{cp}'$ (3, $n = 3$; 4, $n = 4$; $\text{cp}' \equiv \text{MeC}_5\text{H}_4$)

$\text{Cl}(\text{SiMe}_2)_n\text{Cl}$ (1 mmol, $n = 3, 4$) was dissolved in 50 ml of dry *n*-pentane, and a solution of $\text{K}[\text{W}(\text{CO})_3\text{cp}']$ (1 g/2.5 mmol) dissolved in 30 ml of dry 1,2-dimethoxyethane was added dropwise at room tempera-

ture with the exclusion of light. After stirring for 2 days at room temperature, no further reaction was detected by IR. All solids were separated by filtration and the solvent was removed. The brown residue was dissolved in 50 ml of dry *n*-pentane and filtered again. The solvents and unreacted starting materials were removed at room temperature in vacuo (10^{-4} bar) in about 2 h. *n*-Pentane (15 ml) was added to the brown residue and the suspension was treated with ultrasound for 10 min to dissolve all the product. The product was crystallized at -70°C .

1,3-Bis(η^5 -methylcyclopentadienyltricarbonyltungsten)hexamethyltrisilane (3): yield, 0.12 g (14%); ^{29}Si NMR (ppm/TMS): -6.94 , -39.82 ; IR ($\text{cm}^{-1}/\text{n-pentane}$): 2031, 1929; $\text{C}_{24}\text{H}_{32}\text{O}_6\text{Si}_3\text{W}_2$, $M_R = 868.47$.

1,4-Bis(η^5 -methylcyclopentadienyltricarbonyltungsten)octamethyltetrasilane (4): yield, 0.08 g (9%); ^{29}Si NMR (ppm/TMS): -4.07 , -21.47 ; IR ($\text{cm}^{-1}/\text{n-pentane}$): 2021, 1931; $\text{C}_{26}\text{H}_{38}\text{O}_6\text{Si}_4\text{W}_2$, $M_R = 926.63$; MS (selected, M/I): 897 ($\text{M}-\text{CO}/21.5\%$), 73 ($\text{SiMe}_3/100\%$), 263 ($\text{Wcp}'/63.0\%$).

3.4. Synthesis of $\text{cp}'(\text{CO})_3\text{W}-(\text{SiH}_2)_n-\text{W}(\text{CO})_3\text{cp}'$ (5, $n = 2$, $\text{cp}' = \text{MeC}_5\text{H}_4$; 6, $n = 3$, $\text{cp}' = \text{C}_5\text{H}_5$)

$\text{Ph}(\text{SiH}_2)_n\text{Ph}$ (1.8 mmol, $n = 2, 3$) was dissolved in 30 ml of dry *n*-heptane, cooled to -40°C and treated with 4 mmol/0.6 g $\text{CF}_3\text{SO}_3\text{H}$. After 2 h, no $\text{Ph}(\text{SiH}_2)_n\text{Ph}$ could be detected by GC/MS. The solution was decanted into a flask. In a parallel reaction, $[\text{W}(\text{CO})_3\text{cp}']_2$ (0.62 g/0.9 mmol) was dissolved in dry THF and treated with 0.2 ml of Na/K alloy ($1 : 3/\rho \approx 0.9$) at room temperature. When the carbonyl stretching frequencies of the starting material disappeared from the IR spectrum, excess alloy was filtered off over celites (ROTH) and the solution was transferred into a dropping funnel. The solution was added dropwise to a stirred solution of $\text{Tf}-(\text{SiH}_2)_n-\text{Tf}$ ($\text{Tf} \equiv \text{CF}_3\text{SO}_3$) at -60°C . After the reaction had finished (observation with IR spectroscopy), the solvent was removed and the residue was suspended in dry *n*-pentane. After filtration from the formed salts, the solution was reduced to 10 ml. The product was crystallized at -70°C .

1,2-Bis(η^5 -methylcyclopentadienyltricarbonyltungsten)disilane (5): yield, 0.7 g (55%); ^{29}Si NMR (ppm/TMS): -65.78 , $^1J_{\text{Si-H}} = 184\text{ Hz}$, $^1J_{\text{Si-W}} = 22.3\text{ Hz}$; ^1H NMR (ppm/TMS): 4.65 (q, 4H), 4.22 (s, 4H), 0.88 (s, 3H); ^{13}C NMR (ppm/TMS): 221.02, 215.17 (CO), 89.81, 88.56, 86.84 ($\text{Me}-\text{cp}$), 32.13 ($\text{Me}-\text{cp}$); IR ($\text{cm}^{-1}/\text{n-pentane}$): 2016, 1922; $\text{C}_{18}\text{H}_{18}\text{O}_6\text{Si}_2\text{W}_2$, $M_R = 754.21$; MS (selected M/I): 726 ($\text{M}-\text{CO}/8.5\%$), 722 ($\text{M}-\text{SiH}_4/15.0\%$), 44 (100%), 302 (65.3%).

1,3-Bis(η^5 -cyclopentadienyltricarbonyltungsten)trisilane (6): yield, 0.25 g (45%); ^{29}Si NMR (ppm/TMS): -74.06 (tt), -95.29 (pt), $^1J_{\text{Si1-H1}} = 185.85\text{ Hz}$, $^1J_{\text{Si2-H2}} = 177.95\text{ Hz}$, $^2J_{\text{Si1-H2}} = 4.2\text{ Hz}$, $^2J_{\text{Si2-H1}} = 7.4$

Hz, $^1J_{\text{Si-W}} = 24.1$ Hz; ^1H NMR (ppm/TMS): 4.68 (q, 4H), 4.02 (s, 6H), 3.82 (s, 1H); ^{13}C NMR (ppm/TMS): 224.7, 219.0 (CO), 92.4 (cp); IR (cm^{-1} /THF–n-heptane): 2020, 2003, 1927; $\text{C}_{16}\text{H}_{16}\text{O}_6\text{Si}_3\text{W}_2$, $M_R = 756.26$.

3.5. Synthesis of $\text{cp}'(\text{CO})_3\text{W-Si}_6\text{Me}_{11}$ (7)

$\text{Tf-Si}_6\text{Me}_{11}$ ($\text{Tf} \equiv \text{CF}_3\text{SO}_3$) (1.0 mmol), freshly prepared from $\text{PhSi}_6\text{Me}_{11}$, was dissolved in n-heptane and cooled to -50°C . A solution of $\text{K}[\text{W}(\text{CO})_3\text{cp}']$ (0.5 g/1.3 mmol) in 50 ml 1,2-dimethoxyethane was added dropwise. After the addition, reaction was allowed at room temperature for 2 h. The solvent was removed and dry petrolether was added. After filtration, the solution was reduced to 15 ml. The product was crystallized at -70°C .

(η^5 -Methylcyclopentadienyltricarbonyltungsten)undecamethylcyclohexasilane (7): yield, 0.4 g (58%); ^{29}Si NMR (ppm/TMS): 7.02, -39.23 , -42.21 , -42.58 , $^1J_{\text{Si-W}} = 34.92$ Hz; ^{13}C NMR (ppm/TMS): 217.67 (CO), 109.33 (Me- C_1), 88.82, 86.92 (Me-cp), 14.57 (Me-cp), -5.12 to -6.42 (Si-Me); IR (cm^{-1} /petrolether): 2018, 1989, 1924; $\text{C}_{20}\text{H}_{40}\text{O}_3\text{Si}_6\text{W}$, $M_R = 680.90$; MS (selected M/I): 682 (M^+ /23.4%), 73 (SiMe_3 /100%), 264 (71.1%).

3.6. Synthesis of 1-X-3-($\text{cp}'(\text{CO})_3\text{W}$) $\text{Si}_6\text{Me}_{10}$ (8, X $\equiv$ Cl; 9, X $\equiv$ Br)

A solution of 2.88 mmol of freshly prepared $[\text{W}(\text{CO})_3\text{cp}']^-$ in THF was added to a stirred solution of 1-Cl-3-(CF_3SO_3) $\text{Si}_6\text{Me}_{10}$ (2.90 mmol) in n-heptane at -50°C . To complete the transformation, the solution was stirred for 2 h at 0°C . After the solvents had been removed at room temperature, 100 ml of dry n-pentane was added. The flask was treated with ultrasound for 15 min and the solids were removed by filtration. The yellow solution was reduced to 20 ml and the product was crystallized at -70°C .

1-Chloro-3-(η^5 -methylcyclopentadienyltricarbonyltungsten)decamethylcyclohexasilane (8): yield, 1.1 g (59%); ^{29}Si NMR (ppm/TMS): 15.37, -28.50 , -30.44 , -41.31 , -41.40 , -53.08 , $^1J_{\text{Si-W}} = 23.51$ Hz; ^{13}C NMR (ppm/TMS): 220.06, 215.64, 215.35 (CO), 108.27 (Me- C_1), 91.14, 86.66 (Me-cp), 16.06 (Me-

cp), 1.33 to -6.13 (Me); IR (cm^{-1} /n-pentane): 2021, 1916, 1895; $\text{C}_{19}\text{H}_{37}\text{ClO}_3\text{Si}_6\text{W}$, $M_R = 701.32$.

1-Bromo-3-(η^5 -methylcyclopentadienyltricarbonyltungsten)decamethylcyclohexasilane (9): yield, 0.4 g (19%); ^{29}Si NMR (ppm/TMS): 13.07, -27.99 , -31.15 , -40.37 , -40.95 , -52.69 , $^1J_{\text{Si-W}} = 24.3$ Hz; ^{13}C NMR (ppm/TMS): 221.22, 216.37, 215.98 (CO), 110.20 (Me- C_1), 92.65, 88.73 (Me-cp); 18.30 (Me-cp); 2.54 to -5.86 (Me); IR (cm^{-1} /n-pentane): 2019, 1925, 1896; $\text{C}_{19}\text{H}_{37}\text{BrO}_3\text{Si}_6\text{W}$, $M_R = 745.78$.

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