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Communications

$C_5R_5(OC)_2(Me_3P)M$-Substituted Silanetriols of Molybdenum and Tungsten (R = H, Me). Synthesis via Oxofunctionalization of Metallotrihydridosilanes and Transformation into the Multifunctionalized Metallotetrasiloxane $C_5Me_5(OC)_2(Me_3P)WSi(OSiMe_2H)_3$[1]

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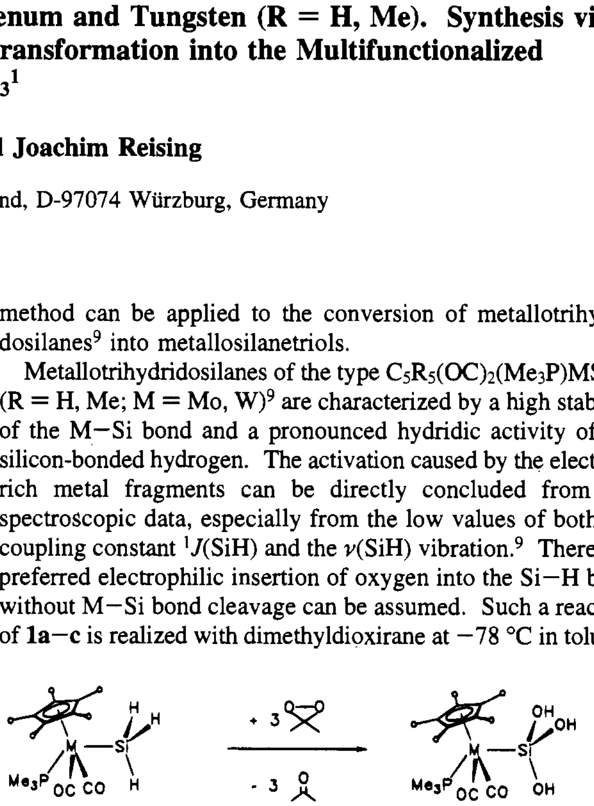
Hydrolysis of organotrichlorosilanes $RSiCl_3$ leads to organosilanetriols $RSi(OH)_3$, which usually undergo rapid condensation to siloxanes.[2] When bulky ligands are attached to the silicon, it is possible to isolate and characterize organosilanetriols.[3] Recently, the first silanetriols attached to transition metals $L_nM-Si(OH)_3$ [$L_nM = (OC)(Cl)(Ph_3P)_2Os$[4] and $Cp(OC)_2Fe$[5]] have been obtained from hydrolysis of the corresponding trichlorosilyl complexes, indicating that metal fragments can stabilize silanetriols. The stabilization is derived not only from steric effects of the metal group but also from its electron donation to the silicon. The hydrolysis route is limited by the fact that electron-rich metal fragments reduce substitution rates at silicon, a situation observed for the metallotrichlorosilanes $C_5R_5(OC)_2(Me_3P)M-SiCl_3$ (M = Cr, Mo, W; R = H, Me).[6] An alternative synthetic strategy however is offered by the electrophilic oxygenation of the Si−H bond with dimethyldioxirane[7] as was proved for the ferrio- and rutheniosilanes $C_5R_5(OC)_2M\text{-}SiR'_2H$ (R = H, Me; M = Fe, Ru; R′ = alkyl, aryl).[8] This communication demonstrates for the first time that this method can be applied to the conversion of metallotrihydridosilanes[9] into metallosilanetriols.

Metallotrihydridosilanes of the type $C_5R_5(OC)_2(Me_3P)MSiH_3$ (R = H, Me; M = Mo, W)[9] are characterized by a high stability of the M−Si bond and a pronounced hydridic activity of the silicon-bonded hydrogen. The activation caused by the electron-rich metal fragments can be directly concluded from the spectroscopic data, especially from the low values of both the coupling constant $^1J(SiH)$ and the $\nu(SiH)$ vibration.[9] Therefore preferred electrophilic insertion of oxygen into the Si−H bond without M−Si bond cleavage can be assumed. Such a reaction of **1a−c** is realized with dimethyldioxirane at −78 °C in toluene leading within 2 h to the formation of the metallosilanetriols **2a−c**. After workup **2a−c** can be isolated in 34−71% yield as beige to yellow crystalline powders which can be stored at room temperature for weeks.



1 2 (1)

	a	b	c
-○	H	Me	Me
M	Mo	Mo	W

As a consequence of the high number of hydroxy functions, **2a−c** show only moderate solubility in strong polar solvents (e.g. acetonitrile). There is no condensation involving the hydroxy groups in solution nor in the solid state. The structure assignments of the metal-coordinated $Si(OH)_3$ moieties is deduced from the broad OH signals in the ^1H NMR at δ = 2.97−3.82 ppm and the $\nu(OH)$ band at 3645−3490 cm^{-1} in the IR. While the $\nu(OH)$ vibrations in the 3600 cm^{-1} region exclude the formation of hydrogen bonding in solution for **2b,c**, the significantly lower value for **2a** (3490 cm^{-1}) suggests such

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(1) Part 12 of the series Metallo-silanols and Metallo-siloxanes. In addition, part 38 of the series Synthesis and Reactivity of Silicon Transition Metal Complexes. Part 11/37: Lankat, R.; Fey, O.; Malisch, W. In press.

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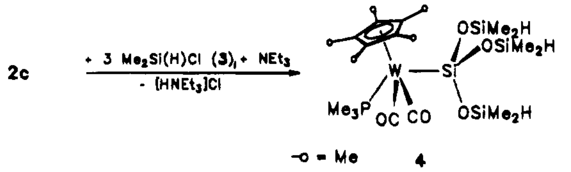
an interaction.[10] This point needs to be clarified by structure determination.

Treatment of **2c** with excess $Me_2Si(H)Cl$ (**3**) gives a first idea concerning the synthetic potential of **2a**–**c**. Conducting the reaction in toluene/diethyl ether (1/2) in the presence of Et_3N results within 10 h in the formation of the multifunctionalized tungsten tetrasiloxane **4**, crystallized from petroleum ether at −78 °C in 78% yield.



(2)

4, the first example for a metal-fragment-substituted branched tetrasiloxane, is isolated as a yellow microcrystalline powder, showing a high solubility in nonpolar solvents. Due to the low value of the $^1J(SiH)$ coupling of 201.2 Hz and the ^{29}Si NMR chemical shift of −11.61 ppm, comparable to that of $HMe_2SiOSiMe_2H$ (204.3 Hz, −4.42 ppm),[11] an influence of the metal fragment on the terminal $SiMe_2H$ groups can be excluded. The three SiH units of the siloxy ligand promise valuable transformations, e.g. oxidative addition to metal fragments leading to cyclic metallosiloxanes, which are subject of further investigations.

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Supporting Information Available: Text presenting all experimental and spectroscopic data for **2a**–**c** and **4** (3 pages). Ordering information is given on any current masthead page.

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