Metallosilanediols of Molybdenum and Tungsten. Synthesis and Transformation to Functionalized Metallotrisiloxanes. Hydrogen-bonded Structure of [$(C_5Me_5)(OC)_2(Me_3P)Mo–SiMe(OH)_2$]

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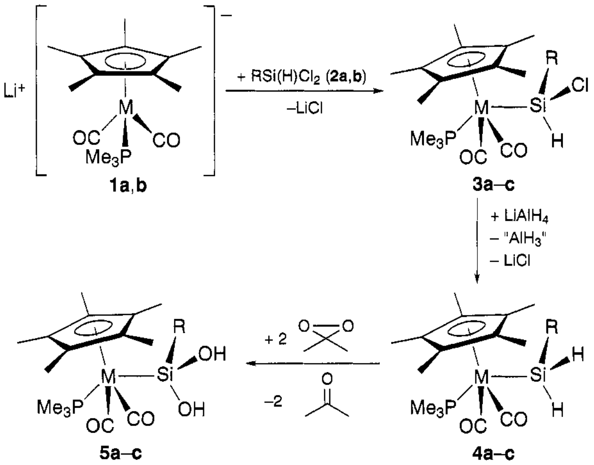
Metallosilanediols [$(C_5Me_5)(OC)_2(Me_3P)M–SiR(OH)_2$] (M = Mo, W; R = Me, Ph) react with $Me_2Si(H)Cl$ to form metallotrisiloxanes [$(C_5Me_5)(OC)_2(Me_3P)Mo–Si(R)(OSiMe_2H)_2$] (R = Me, Ph) which are converted to the cyclic bis(metallo)trisiloxanes [$(C_5Me_5)(OC)_2(Me_3P)Mo–SiR(OSiMe_2)Fe(SiMe_2O)(H)(CO)(C_5H_5)$] (R = Me, Ph) on irradiation in the presence of [$(C_5H_5)(OC)_2Fe–Me$]; the structures of [$(C_5Me_5)(OC)_2(Me_3P)Mo–SiMe(OH)_2$] and [$(C_5Me_5)(OC)_2(Me_3P)Mo–Si(Ph)(OSiMe_2)Fe(SiMe_2O)(H)(CO)(C_5H_5)$] are determined by X-ray diffraction analysis.

The condensation of organosilanols is the basis of the synthesis of siloxanes and silicones.[2] This process can be supressed by bulky organic groups, which in some cases offers access to compounds of the type $R_{4-n}Si(OH)_n$ (n = 1–3).[3] Eaborn and coworkers[4] have demonstrated structural diversity especially for organosilanediols $R_2Si(OH)_2$, arising through hydrogen bonding, with layer structures for compounds with small ligands and association into chains or discrete oligomers, favoured by bulky ligands. Our interest in this field is focused on transition metal substituted silanols, since these compounds promise condensation of the silanol ligand under the electronic and stereochemical control of the metal fragment. However, when the metal fragment acts as a powerful electron donor, these species are not available *via* hydrolysis of the corresponding metallochlorosilanes[5] due to strongly reduced Cl–OH exchange activity of the silicon. Recently, we have found that in such a case oxygenation of metallohydridosilanes with dimethyldioxirane[6] provides a versatile and convenient route, generating a hydroxy group at silicon *via* oxygen insertion into the Si–H bond under extremely mild conditions. According to this procedure metallosilanols $L_nM–SiR_2(OH)$ of iron [L_nM = $C_5H_5(OC)_2Fe$],[7] chromium, molybdenum and tungsten [L_nM = $(C_5R_5)(OC)_2(Me_3P)M$, M = Cr, Mo, W][8] have been obtained. Now we report for the first time the use of this method for the generation of metallosilanediols of the chromium series, the structure of such a species and the transformation to chained and cyclic metallosiloxanes.

The synthesis of these silanols starts with the lithium metallates **1a,b**[9] reacting with the organodichlorosilanes $RSi(H)Cl_2$ [R = Me (**2a**), Ph (**2b**)] in cyclohexane to give the corresponding metallochlorosilanes **3a–c**† after 18–24 h. On treatment with $LiAlH_4$ (−78 °C, 1 h, then 2.5 h room temp.) **3a–c** are converted to the metallodihydridosilanes **4a–c**.† Reaction of **4a–c** in toluene at −78 °C with a solution of dimethyldioxirane in acetone affords, after warming to room temp., the corresponding metallosilanediols **5a–c**† in good yields. **5a–c** show high stability with respect to oxygen and moisture and are characterized by a limited solubility in aromatic solvents (Scheme 1).

The X-ray crystal structure‡ of **5a** (Fig. 1) reveals pseudo square pyramidal coordination at the molybdenum atom with the Me_3P ligand and the silyl ligand in a mutually *trans* position. The silyl ligand adopts a staggered conformation to the $C_5Me_5(OC)_2(Me_3P)Mo$-fragment with C(3) in the sterically favoured *anti* position to the C_5Me_5 moiety. The distances Si–O(3) (1.667 Å) and Si–O(4) (1.643 Å) are quite similar to those of organosilanols and disiloxanes (averaged 1.63–1.66 Å[10]). The angle Mo–Si–C(3) (117.9°) is significantly widened due to the steric requirement of the metal fragment. In the solid state **5a** forms discrete dimers held together by two hydrogen bridges, as the characteristic distances of the oxygen atoms indicate [O(3)–O(4) 2.84 Å].[11] The six-membered cycle, composed of silicon and oxygen atoms, adopts a chair conformation. There is no indication for further hydrogen bridging,[4] presumably a result of the steric requirement of the transition metal group.

The metallosilanediols **5a,b** allow specially designed synthesis of metallosiloxanes bearing functionality. This possibility is demonstrated by the γ-SiH-functionalized molybdenum-trisiloxanes **7a,b**,† obtained from **5a,b** and dimethylchloro-silane **6** in benzene–diethyl ether in the presence of triethylamine in 85 (**7a**) and 88% (**7b**) yield (Scheme 2).



1 a M = Mo; **b** M = W
2 a R = Me; **b** R = Ph
3–5 a M = Mo, R = Me; **b** M = Mo, R = Ph; **c** M = W, R = Me

Scheme 1

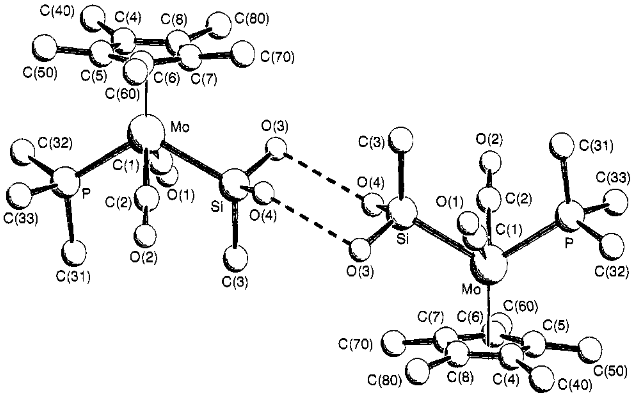
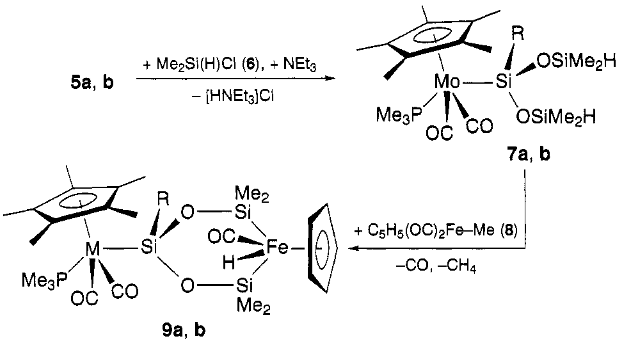


Fig. 1 Crystal structure of **5a**. Selected bond distances (Å) and angles (°): Mo–P 2.433(1), Mo–Si 2.571(1), Si–O(3) 1.643(4), Mo–Si–O(3) 109.7(1), Mo–Si–O(4) 114.7(1), Mo–Si–C(3) 117.9(2), O(3)–Si–O(4) 104.7(2); Mo–C(1)–O(1) 175.8(4), P–Mo–Si 121.08(5), P–Mo–C(1) 78.7(2), Si–Mo–C(1) 69.1(1), C(1)–Mo–C(2) 106.6(2). Selected torsion angles (°): Si–Mo–P–C(31), 8.1(3), P–Mo–Si–O(3) −130.5(1), P–Mo–Si–O(4) 112.1(2), Si–Mo–P–C(31), 8.1(3), C(3)–Si–Mo–P −6.7(2), C(1)–Mo–Si–O(4) 173.7(2).

Photoinduced oxidative addition of **7a,b** to $(C_5H_5)(OC)_2$-Fe–Me[12] leads, after elimination of CO and methane, to the cyclic Si-metallated metallotrisiloxanes **9a,b**, formed as a 1 : 1 (**9a**) or 4 : 1 (**9b**) mixture of isomers, originating from the arrangement of the iron-bound carbonyl and the phenyl group at the silicon either on the same side of the siloxane cycle (see structure of **9b**) or on opposite sides. **9a,b** represent the first cyclo(metalla)siloxanes,[13] which in addition contain an exocyclic Si-bonded metal fragment.

The X-ray structure determination‡ of **9b** (Fig. 2) reveals pseudo square pyramidal coordination at the iron and the molybdenum atoms with the most bulky ligands CO and phenyl in the sterically favoured *anti* position. The phenyl group at Si(1) is also located *anti* to the C_5Me_5 ligand and staggered with respect to the CO ligands at molybdenum. The ferra-siloxane cycle Fe–Si(2)–O(4)–Si(1)–O(5)–Si(3) attains a chair conformation with Si(2)–O(4)–Si(1)/Si(3)–O(5)–Si(1) angles of 138.8 and 139.16°. The most remarkably feature is the agostic coordination of the Si–H bond indicated by the unusually long Fe–H(1) distance (1.457 Å) and the short Si(3)–H(1) distance (1.870 Å). These values are comparable with those of the η^2-SiH-complex $(MeC_5H_4)(OC)(Me_3P)Mn(H)SiPh_2H$ (Mn–H/Si–H: 1.49/1.78 Å).[14] The view perpendicular to the siloxane ring-plane shows H(1) to be distinctly inclined towards Si(3), proved by the Si(2)–Fe–H(1)/Si(3)–Fe–H(1) angles of 61.10 and 53.24°.§

The metallosilandiols presented in this paper are synthetically valuable precursors for the synthesis of unusual metallosiloxanes, suitable for the incorporation of further metal fragments. The resulting compounds are interesting model compounds with respect to SiO_2-supported transition metal catalysts.



5, **7**, **9** **a** R = Me; **b** R = Ph

Scheme 2

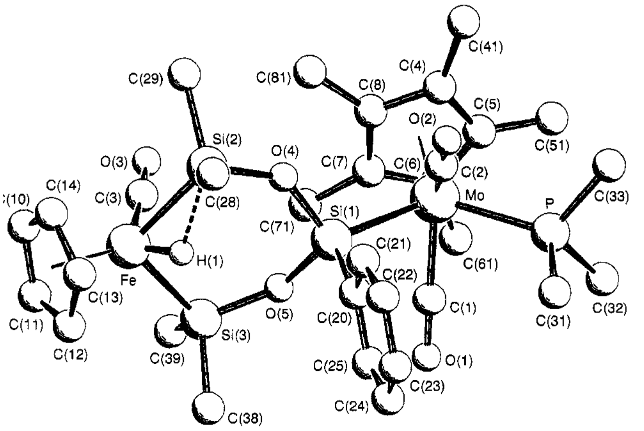


Fig. 2 Crystal structure of **9b**. Selected bond distances (Å) and angles (°): Fe–Si(3) 2.337(2), Fe–H(1) 1.457(3), Si(3)–H(1) 1.870(3), Si(1)–O(4) 1.657(3), Fe–C(3) 1.722(5), Mo(1)–P 2.439(1), Mo(1)–Si(1) 2.547(1), Si(2)–O(4) 1.641(3), Si(3)–O(5) 1.645(3), C(3)–Fe–H(1) 105.8(2), O(4)–Si(1)–O(5) 105.0(2), Si(2)–O(4)–Si(1) 138.8(2), Si(2)–Fe–Si(3) 101.35(5), Si(3)–O(5)–Si(1) 139.16(14), Si(3)–Fe–H(1) 53.24(14), Si(2)–Fe–H(1) 61.10(14), Fe–Si(3)–H(1) 38.57(9). Selected torsion angles (°): Fe–Si(2)–O(4)–Si(1) −32.0(3), Fe–Si(3)–O(5)–Si(1) 31.5(3), P–Mo–Si(1)–C(20) 3.7(2), Mo– Si(1)–C(20)–C(21) 92.5(4), H(1)–Fe–C(3)–O(3) −171(7), Si(3)– Fe–C(3)–O(3) 122(7), Si(2)–Fe–C(3)–O(3) −134(7).

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Footnotes

† All new compounds gave satisfactory elemental analyses and were characterized by ^1H, ^{13}C, ^{31}P and ^{29}Si NMR and IR spectra. **3c** and **4c** were described previously.[11]

‡ *Crystal data* for **5a**: $C_{16}H_{29}MoO_4PSi$; M = 440.40, monoclinic, space group $C2/c$ (No. 15), a = 28.27(2), b = 8.543(3), c = 17.018(8) Å, α = 90.0(0)°, β = 96.0069(4)°, γ = 90.0(0)°, V = 4086.7(59) Å^3, Z = 8, D_c = 1.432 g cm^{-3}, T = 293 K, absorption coefficient (ψ scan): μ(Mo-Kα) = 7.747 mm^{-1}, Enraf-Nonius CAD4-diffractometer, $2\theta_{max}$ = 44°, 4990 reflections measured, 2352 symmetry-independent reflections (R = 0.026, R_w = 0.0295). The intensity data were collected using a CAD4 diffractometer using $\omega - \theta$ scans. The unit-cell parameters were determined by a least-squares refinement on diffractometer angles for 25 automatically centred reflections. The structure was solved by the Patterson heavy atom method using the SHELXS-86 program package (G. M. Sheldrick).[15] All non-hydrogens were refined anisotropically by least-squares fourier-method. The H atoms were found and refined by the riding method. For **9b**: $C_{31}H_{47}FeMoO_5PSi_3$, M = 766.72, monoclinic, space group $P2_1/n$ (No. 1014), a = 11.194(1), b = 21.598(3), c = 14.664(2) Å, α = 90.0(0)°, β = 96.20(2)°, γ = 90.0(0)°, V = 3545.3(7) Å^3, Z = 4, D_c = 1.436 g cm^{-3}, T = 233 K, absorption coefficient (ψ scan): μ(Mo-Kα) = 9.45 mm^{-1}, Enraf-Nonius CAD4-diffractometer, $2\theta_{max}$ = 46°, 5209 reflections measured, 4514 symmetry-independent reflections (R = 0.0298, R_w = 0.0658). The intensity data were collected using a CAD4 diffractometer using $\omega - \theta$ scans. The unit cell parameters were determined by a least-squares refinement on diffractometer angles for 25 automatically centred reflections. The structure was solved by the direct methods using the SHELXS-86 program package and refined anisotropically by full-matrix least-squares using the SHELXL-93 program package (G. M. Sheldrick).[16] H(1) was found and isotropically refined, the other H atom positions were calculated geometrically by using the AFIX command on SHELXL-93. The program SCHAKAL-92 (E. Keller[17]) was used for drawing the molecules. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ In solution an agostic Fe–H(1)–Si(3) bonding appears to be less likely due to the low $^2J_{SiFeH}$ coupling constants of 20.4, respectively, 22.4 Hz for the Fe–H proton in the NMR.

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