Synthesis, Structural Characterization and Reactivity of the (Ferriomethyl)silanols $C_5R_5(OC)_2Fe{-}CH_2{-}SiMe(R')OH$ (R = H, Me; R′ = Me, Ph)[‡]

Wolfgang Malisch,*[a] Marco Hofmann,[a] Martin Nieger,[b] Wolfgang W. Schöller,[c] and Andreas Sundermann[c]

Keywords: Silicon / Iron / Oxygenation / (Metalloalkyl)silanols / Density functional calculations

The novel (ferriomethyl)-substituted silanols $C_5R_5(OC)_2Fe–CH_2–SiMe(R')OH$ [R = H, R′ = Me (**4a**), Ph (**4b**); R = Me, R′ = Me (**4c**)] are obtained by hydrolysis of the chloro(ferriomethyl)silanes $C_5R_5(OC)_2Fe–CH_2–SiMe(R')Cl$ [R = H, R′ = Me (**3a**), Ph (**3b**); R = Me, R′ = Me (**3c**)] in the presence of Et_3N. Another access to this class of compounds is offered by the oxygenation of Si–H-functional (ferriomethyl)silanes with dimethyldioxirane, as shown for **4a** by the oxo-functionalization of the (ferriomethyl)silane $Cp(OC)_2Fe–CH_2–SiMe_2H$ (**3d**). **4a**–**c** have been characterized spectroscopically and by X-ray structure analyses showing the formation of tube- or chain-like arrangements in the solid state caused by hydrogen bonding. In addition, the bonding situation in the related (ferriomethyl)silanol $Cp(OC)_2Fe–CH_2–SiH_2OH$ has been analyzed on the basis of density functional calculations. **4a** shows self-condensation to give the 1,3-bis(ferriomethyl)disiloxane $[Cp(OC)_2Fe–CH_2–SiMe_2]_2O$ (**5**), which is also obtained by the reaction of **4a** with **3a**. Analogous treatment of **4a** with the chloro(organo)silanes $R(R')Si(Me)Cl$ (R = H, R′ = Me, *p*-Tol; R = R′ = Me) yields the monometalated disiloxanes $Cp(OC)_2Fe–CH_2–Si(Me)_2OSi(Me)(R)R'$ [R = H, R′ = Me (**6a**), *p*-Tol (**6b**); R = R′ = Me (**6c**)].

Introduction

Transition metal substituted siloxanes represent attractive model compounds for catalytically active transition metal complexes anchored on silica surfaces.[2−5] They offer an opportunity to determine the reaction mechanisms of heterogeneous catalyzed reactions on a molecular level in order to improve the selectivity, activity and lifetime of a heterogeneous catalyst. As a consequence many of those model compounds have been synthesized in the last few years often starting from stable organosilanetriols[6−10] or incompletely condensed silsesquioxanes[11−18] which can react with various metal complexes resulting in the formation of metallosiloxanes with the structural unit $L_nM{-}O{-}Si$, i.e. a silanolate ligand sphere around the transition metal centre.

Another approach to transition metal substituted siloxanes involves the synthesis of metallosilanols of the general type $L_nM{-}Si(R)_{3-n}(OH)_n$ ($n = 1{-}3$)[19−34] and their extensive condensation with chlorosilanes giving access to metallosiloxanes with a direct metal−silicon bond. In this context, metallosilanols containing the metal fragments $C_5R_5(OC)_2(Me_3P)M$ (M = Mo, W; R = H, Me),[19−24] $C_5R_5(OC)_2M$ (M = Fe, Ru; R = H, Me),[23−27] $(Ph_3P)_2(OC)(Cl)Os$,[28] $(OC)_5Cr$,[29] (dcpe)(Ph)Pt,[30] $(Et_3P)_2(Cl)(H)Ir$[33] and $Cp_2(H)Mo$[34] have been realized. Due to the strong electron-releasing effect of the metal fragment the acidity of the Si−OH proton and the tendency towards self-condensation are strongly decreased. This situation offers the possibility of isolating metal derivatives with an $Si(OH)_3$ unit,[20,28] which are synthetically useful for the generation of well-defined metallosiloxanes by controlled co-condensation processes.

In recent years, two routes − hydrolysis of chloro(metallo)silanes in the presence of an auxiliary base[23−25] and oxo-functionalization of hydrido(metallo)silanes with the mild oxidizing agent dimethyldioxirane[31,32,35−37] − proved to be most efficient for the generation of metallosilanols. The electrophilic oxygen insertion is especially productive for metallosilanes with electron-rich Si−H bonds provided by metal fragments with high donor capacity. For these sys-

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[‡] Synthesis and Reactivity of Silicon Transition Metal Complexes, 52. Metallosilanols and Metallosiloxanes, 24. Part 51/23: Ref.[1]

[a] Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, 97074 Würzburg, Germany
Fax: (internat.) + 49-(0)931/888-4618
E-mail: Wolfgang.Malisch@mail.uni-wuerzburg.de

[b] Institut für Anorganische Chemie der Universität Bonn,
Gerhard-Domagk-Straße 1, 53121 Bonn, Germany

[c] Fakultät für Chemie der Universität Bielefeld,
Postfach 100131, 33501 Bielefeld, Germany
E-mail: Wolfgang.Schoeller@uni-bielefeld.de

tems the hydrolysis of the analogous chloro(metallo)silanes fails since the electrophilicity of the silicon atom is too weak.

Our interest has now turned to silanols having the Si−OH moiety separated from the metal fragment by a methylene group in order to check the "transition metal effect" on silanol units that are not directly bound to the transition metal atom. The spacer group should also help to suppress undesirable decomposition reactions involving "β-hydrogen abstraction" from the Si−OH group, observed for ferriosilanols of the type $Cp(OC)_2Fe-Si(R)(R')OH$ (R, R′ = alkyl, aryl).[38]

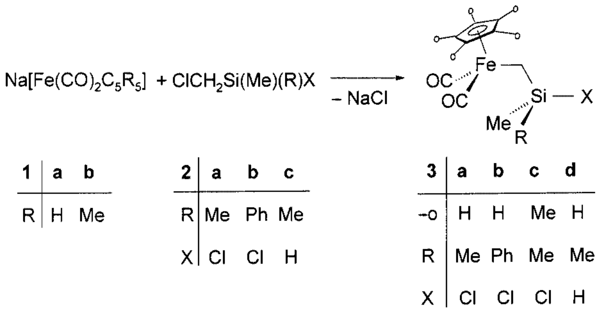
Although the Me_3SiCH_2 ligand has found wide application in transition metal chemistry due to its inertness with respect to β-hydride abstraction,[39−41] only a few examples exist in the literature with a silylmethyl ligand having one or more functional groups at the silicon atom.[42−52] These compounds have been used as precursors in the synthesis of silene transition metal complexes, which were originally proposed by Pannell[42] as intermediates in the β-elimination reaction of $Cp(OC)_2Fe-CH_2-SiMe_2H$ and were spectroscopically observed by Wrighton et al. by low-temperature near-UV photolysis of $C_5R_5(OC)_3W-CH_2-SiMe_2H$ (R = H, Me)[46] and $C_5Me_5(OC)_2Fe-CH_2-SiMe_2H$.[47] The chloro-functional (silylmethyl)tungsten complex $Cp_2W(Cl)-CH_2-SiMe_2Cl$ has been used by Berry et al. to generate a stable silene transition metal complex by reductive dechlorination with magnesium.[48]

No attempts so far have been made to generate or isolate any (metallomethyl)-substituted silanols from these silicon-functional complexes. Here we report on the synthesis of the first (ferriomethyl)-substituted silanols bearing a methylene group between the silanol and the iron fragment.

Results and Discussion

Synthesis of Si−Cl- and Si−H-Functional (Ferriomethyl)silanes (3a−d)

The chloro-functional (ferriomethyl)silanes $C_5R_5(OC)_2Fe-CH_2-SiMe(R')Cl$ [R = H, R′ = Me (**3a**), Ph (**3b**); R = Me, R′ = Me (**3c**)] are obtained by nucleophilic metallation of the organosilanes $ClCH_2SiMe(R')Cl$ [R′ = Me (**2a**); Ph (**2b**)] with the sodium ferrates $Na[Fe(CO)_2C_5R_5]$ [R = H (**1a**), Me (**1b**)] in THF or cyclohexane after reaction periods of 16−36 h at room temperature (Scheme 1).[53] The heterogeneous method using cyclohexane as a solvent proved to be advantageous over the homogeneous one using THF because of the formation of considerable amounts of undesirable by-products in the latter case.



Scheme 1. Synthesis of the (ferriomethyl)silanes **3a−d**

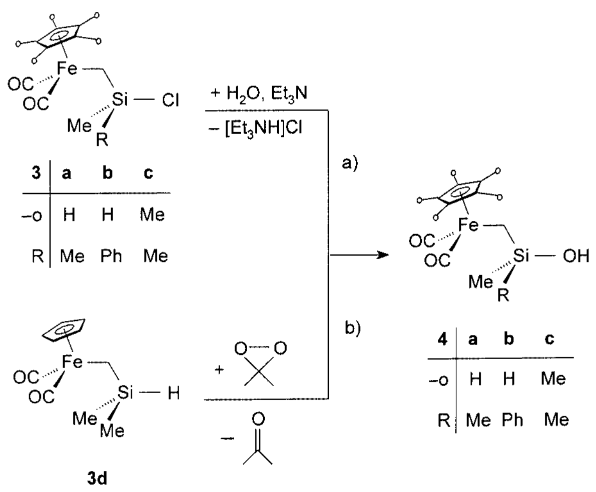
In the synthesis of **3a**,**b** metallation of **2a**,**b** occurs primarily at the silicon atom. The initially formed ferriosilanes $Cp(OC)_2Fe-SiMe(R')(CH_2Cl)$ [R′ = Me (**3a′**), Ph (**3b′**)] can be subsequently converted into the chloro(ferriomethyl)silanes **3a**,**b** by thermal rearrangement at 120 °C. In the case of **3a** this rearrangement is nearly quantitative after 1 h,[44,45] whereas in the other case a mixture of the two isomers is produced after heating for 3 h (**3b**/**3b′** ≈ 80:20), from which **3b** can be separated by crystallization at −78 °C from *n*-pentane. Prolonged heating and a higher temperature lead to extensive decomposition of **3b**.

In the metallation of **2a** with the pentamethylcyclopentadienyl-substituted ferrate **1b** no isomer of **3c** is detected; **3c** is obtained directly at room temperature after appropriate workup in a moderate yield of 33% due to the formation of considerable amounts of $C_5Me_5(OC)_2Fe-Cl$, which are removed by repeated fractional crystallization at −20 °C.

The Si−H-functional (ferriomethyl)silane **3d** is obtained analogously by nucleophilic metallation of $ClCH_2SiMe_2H$ (**2c**) with **1a** in THF.[42,43]

Synthesis of (Ferriomethyl)silanols (4a−c)

The (ferriomethyl)silanol $Cp(OC)_2Fe-CH_2-SiMe_2OH$ (**4a**) is available by hydrolysis of **3a** in diethyl ether in the presence of the auxiliary base Et_3N. It can be isolated after 2 h at room temperature in 89% yield (Scheme 2, route a). A second approach to **4a** involves oxygenation of **3d** with dimethyldioxirane in acetone after 2 h (−78 °C to room temp.) in 67% yield (Scheme 2, route b). The oxygenation route guarantees a more convenient workup procedure but proved to be inferior to the hydrolysis route with respect to the lower yield of the resulting silanol **4a**, presumably due to oxidative decomposition reactions at the metal fragment.



Scheme 2. Synthesis of the (ferriomethyl)silanols **4a−c** by hydrolysis or oxygenation

For the synthesis of the (ferriomethyl)silanols $C_5R_5(OC)_2Fe-CH_2-Si(Me)(R')OH$ [R = H, R′ = Ph (**4b**); R = Me, R′ = Me (**4c**)] only the hydrolysis route (Scheme 2, route a) has been applied; **4b**,**c** can be isolated after reaction periods of 4 h at room temperature in the presence of Et_3N in yields of 74% (**4b**) and 40% (**4c**), respectively.

The (ferriomethyl)silanols **4a**−**c** are obtained as slightly air-sensitive yellow-brown waxy solids [m.p. 38 °C (**4a**), to 89 °C (**4c**)], which show good solubility in diethyl ether and aromatic solvents like benzene and toluene and are rather soluble even in aliphatic solvents like *n*-pentane. They are characterized in the IR spectrum by the OH stretching band at $\tilde{\nu} = 3698\ cm^{-1}$ (**4a**), $3682\ cm^{-1}$ (**4b**) and $3703\ cm^{-1}$ (**4c**) (*n*-pentane solution), and in the ^1H NMR spectrum (C_6D_6) by a broad signal for the hydroxy proton at $\delta = 0.95$ (**4a**), 1.28 (**4b**) and 0.92 (**4c**) ppm. The characteristic upfield signal of the CH_2 protons is detected at $\delta = -0.42$ (**4a**) and -0.62 (**4c**) ppm. In the case of **4b**, the asymmetric silicon atom leads to diastereotopic CH_2 protons which are detected as pair of doublets at $\delta = -0.09$ and -0.38 ppm. In the ^{13}C NMR spectra the signals for the CH_2 group are observed between $\delta = -12.4$ (**4c**) and -24.5 (**4b**) ppm. The chemical shifts in the ^{29}Si NMR spectra [$\delta = 21.8$ (**4a**), 11.7 (**4b**), 21.1 (**4c**) ppm] reveal a decreased influence of the transition metal fragment on the silicon atom in the β-position. For example, in the case of **4a**, the signal is shifted by approximately 44 ppm to a higher field compared with its counterpart $Cp(OC)_2Fe-SiMe_2OH$ ($\delta = 66.1$ ppm)[1] without a methylene bridge.

X-ray Analyses of 4a−c

Final evidence for the structural assignments of **4a**−**c** is given by single-crystal X-ray structure determinations (Figures 1−3). In the case of **4a**, two crystallographically independent molecules have been found in the asymmetric unit.

The crystal structures of **4a**−**c** reveal a pseudo-octahedral coordination sphere at the iron atom, indicated by the ligand−iron−ligand angles close to 90°. The largest one is in all cases found between the carbonyl carbon atoms lying between 97.52(9)° (**4c**) and 93.15(7)° (**4a**), while the angles between the methylene carbon atom and the CO ligands are slightly smaller [92.00(8)° (**4c**), to 85.94(7)° (**4a**)].

The conformation along the iron−methylene bond reveals a distorted staggered pseudo-ethane arrangement. In the case of **4a**,**b** the SiR_3 substituent adopts a nearly "*anti*" position to one of the CO groups [C2−Fe1−C8−Si1 164.21(11)/150.30(11)° (**4a**), −161.32(11)° (**4b**)] and is positioned between the cyclopentadienyl and the other carbonyl ligand, but as the dihedral angles indicate in the case of **4a**, that a major difference exists concerning the orientation in the two different molecules of the asymmetric unit (see also below).

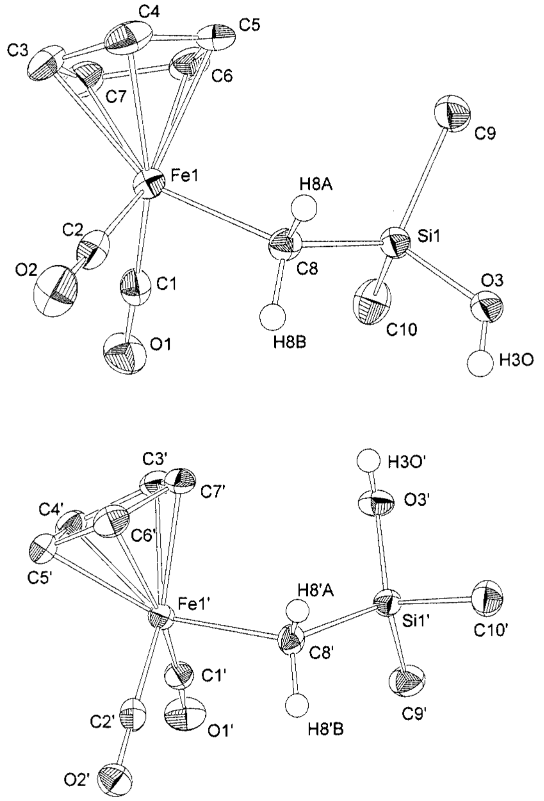


Figure 1. ORTEP view of $Cp(OC)_2Fe-CH_2-SiMe_2OH$ (**4a**), showing the two crystallographically independent molecules; hydrogen atoms have been omitted for clarity (except for those at C8 and O3); selected bond lengths [Å] and angles [°]: Fe1−Cp(Z) 1.728(2)/1.730(2), Fe1−C8 2.0896(16)/2.0863(17), C8−Si1 1.8451(17)/1.8508(16), Si1−O3 1.6599(13)/1.6558(13), Si1−C10 1.8596(19)/1.8686(19), Si1−C9 1.8668(17)/1.8508(18); C1−Fe1−C2 93.61(8)/93.15(7), C1−Fe1−C8 89.38(8)/92.32(8), C2−Fe1−C8 87.20(7)/85.94(7), Cp(Z)−Fe1−C1 126.8(2)/126.3(2), Cp(Z)−Fe1−C2 125.1(1)/126.5(1), Cp(Z)−Fe1−C8 123.4(1)/121.6(1), Fe1−C8−Si1 120.36(8)/120.51(8), C8−Si1−O3 108.41(7)/114.90(7), C9−Si1−O3 102.63(7)/104.03(8); selected torsion angles [°]: Fe1−C8−Si1−O3 −174.24(8)/40.09(12), C1−Fe1−C8−Si1 70.57(11)/57.31(11), Fe1−C8−Si1−C9 71.72(12)/−77.92(12)

Looking at **4c**, the silanol group is positioned between the two carbonyl ligands [C1B−Fe1−C11−Si1 41.70(12)°; C1A−Fe1−C11−Si1 −55.91(12)°] in a mutually "*anti*" position to the pentamethylcyclopentadienyl group, which is in sharp contrast to **4a**,**b** and probably a consequence of the higher steric demand of the C_5Me_5 ligand.

The lengths of the iron−methylene bonds lie in a close range between 2.0931(18) (**4b**) and 2.0775(16) Å (**4c**) and are similar to other $C_5R_5(OC)_2Fe-CR_3$ complexes bearing an sp^3-carbon atom at the iron atom.[54−56]

The Fe−C−Si bond angle is in all cases wider than the tetrahedral angle and is up to 124.89(9)° for **4c**, which is in agreement with a higher s-character of the carbon orbital interactions with the more electropositive iron and silicon atoms according to Bent's rule,[57,58] but also shows the higher steric demand of the iron and silanol groups in comparison to the H atoms at the methylene carbon atom. This finding parallels that for the complexes $Cp(OC)(Ph_3P)Fe-CH_2-SiMe_3$ [Fe−C−Si 122.8(2)°],[59] $Cp(OC)_2Fe-CH_2-SiMe_2-SiMe_2-Fe(CO)_2Cp$ [Fe−C−Si 123.4(2)°][60] and *meso*-$[Cp(OC)_2Fe-CH_2-Si(Me)(Ph)]_2$ [Fe−C−Si 120.5(1)°][61] which, to the best of our know-

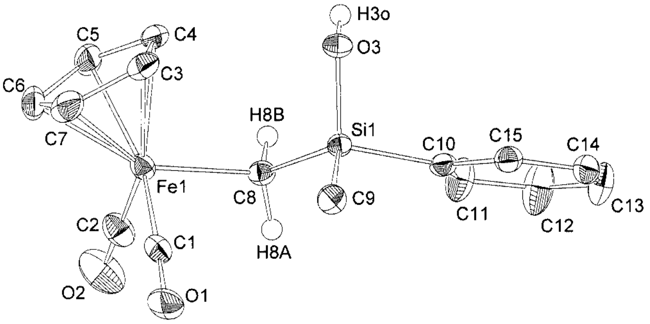


Figure 2. ORTEP view of $Cp(OC)_2Fe-CH_2-Si(Me)(Ph)OH$ (**4b**); hydrogen atoms have been omitted for clarity (except for those at C8 and O3); selected bond lengths [Å] and angles [°]: Fe1−Cp(Z) 1.734(1), Fe1−C8 2.0931(18), C8−Si1 1.8464(18), Si1−O3 1.6645(13), Si1−C9 1.8598(18), Si1−C10 1.8825(19); C1−Fe1−C2 93.38(9), C1−Fe1−C8 90.98(8), C2−Fe1−C8 86.42(8), Cp(Z)−Fe1−C1 126.2(1), Cp(Z)−Fe1−C2 126.2(1), Cp(Z)−Fe1−C8 122.4(1), Fe1−C8−Si1 116.14(9), C8−Si1−O3 112.18(7), C9−Si1−O3 104.72(8), C8−Si1−C9 114.89(8), O3−Si1−C10 105.80(7); selected torsion angles [°]: Fe1−C8−Si1−O3 −67.89(10), Fe1−C8−Si1−C10 173.59(8), C1−Fe1−C8−Si1 −68.00(10), Fe1−C8−Si1−C9 51.55(12)

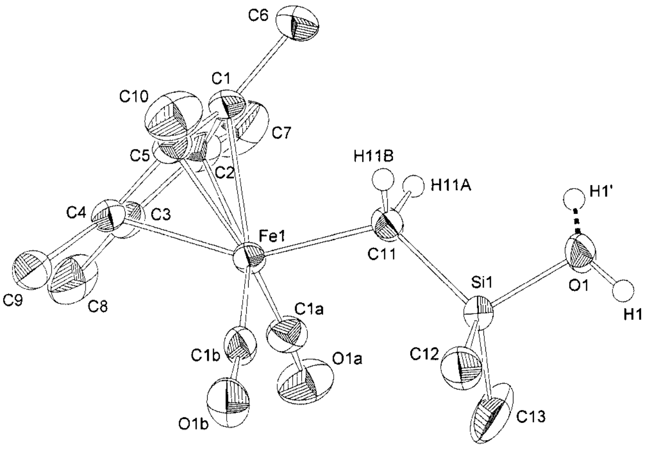


Figure 3. ORTEP view of $C_5Me_5(OC)_2Fe-CH_2-SiMe_2OH$ (**4c**); hydrogen atoms have been omitted for clarity (except for those at C11 and O1); selected bond lengths [Å] and angles [°]: Fe1−C_5Me_5(Z) 1.759(2), Fe1−C11 2.0775(16), C11−Si1 1.8477(17), Si1−O1 1.6589(12), Si1−C12 1.859(2), Si1−C13 1.865(2); C1B−Fe1−C1B 97.52(9), C1B−Fe1−C11 92.17(7), C1A−Fe1−C11 92.00(8), C_5Me_5(Z)−Fe1−C1A 122.2(1), C_5Me_5(Z)−Fe1−C1B 124.1(1), C_5Me_5(Z)−Fe1−C11 120.7(1), Fe1−C11−Si1 124.89(9), C11−Si1−O1 106.66(7), C12−Si1−O1 106.39(8), C11−Si1−C12 113.72(9), O1−Si1−C13 107.53(10), C11−Si1−C13 114.29(10), C12−Si1−C13 107.78(13); selected torsion angles [°]: C1B−Fe1−C11−Si1 41.70(12), C1A−Fe1−C11−Si1 −55.91(12), Fe1−C11−Si1−O1 169.61(10), Fe1−C11−Si1−C12 −73.43(13), Fe1−C11−Si1−C13 50.93(16)

ledge, are the only other structurally characterized compounds with a $CpL_2Fe-CH_2-SiR_3$ (L = CO, PPh_3) moiety.

The Si−O bond lengths with values between 1.6645(13) (**4b**) and 1.6558(13) Å (**4a**) are nearly identical and lie within the range of other organo- and metallo-substituted silanols.[19−34,62−65] The silicon atom shows in all cases a distorted tetrahedral arrangement of substituents with the expected smaller angle between the OH and CH_3 group[57,58] [106.39(8) (**4c**) to 102.63(7)° (**4a**)] and enlarged ones to the methylene carbon atom [114.89(8) (**4b**) to 114.29(10)° (**4c**)].

Looking at the arrangement of the substituents along the methylene−silicon bond, in the case of **4b** there is a nearly ideal "*anti*" arrangement of the iron fragment and the phenyl group, with a small deviation of only about 6° [Fe1−C8−Si1−C10 173.59(8)°], whereas in the case of **4c** the hydroxy group adopts the "*anti*" position to the iron fragment [Fe1−C11−Si1−O1 169.61(10)°] with a deviation of about 10°.

The situation in the case of **4a** is a bit more complex. The two different molecules are characterized by a nearly ideal "*anti*" position of the iron atom and the hydroxy group [Fe1−C8−Si1−O3 −174.24(8)] in the one case and a "*gauche*" position of these ligands with a more significant deviation from ideal conformation of about 20° [Fe1−C8−Si1−O3 40.09(12)°] in the other. This situation is clearly a consequence of the formation of a polymeric arrangement of the molecular subunits based on hydrogen bonding (see also below).

Triorganosilanols often show interesting hydrogen-bonded superstructures, the pattern of which depends on the nature of the organic substituents.[65] In contrast to the structures of other diorgano(metallo)silanols L_nM-SiR_2OH, which prefer hydrogen-bonded "dimerization", e.g. $C_5Me_5(OC)_2Fe-SiMe_2OH$[1] and C_5Me_5-$(OC)_2Ru-Si(o\text{-}Tol)_2OH$,[26] in the case of the (ferriomethyl)silanols **4a**,**b** strong intermolecular OH···O bridges lead to the formation of discrete tetrameric units in the solid state, indicated by O···O distances of 2.7320(16)/2.7410(17) (**4a**) and 2.6965(17) Å (**4b**). This arrangement is similar to that found for Ph_3SiOH.[62]

Looking at **4a**, the tetramers consist of the two types of staggered conformers, concerning the C8−Si bond (see above). They are formed by an alternating arrangement of

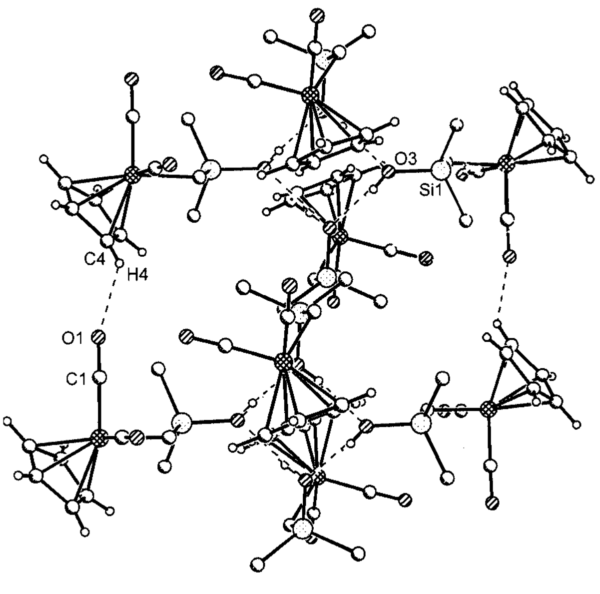


Figure 4. Ladder-type connection of **4a** between the "*anti*" conformers of neighboring tetramers via CH···OC bridges

the "*anti*" and "*gauche*" conformers and exhibit a centre of symmetry.

The tetrameric units are connected to each other in a ladder-type fashion by weak CH···OC interactions of the Cp and one CO ligand [C4···O1 3.358(3) Å] between two "*anti*" conformers of neighbouring units, as depicted in Figure 4. This kind of hydrogen bonding, although very rare, has recently been found by Braga et al. in the structures of $[Cp(CO)_2Fe]_2$ and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)$.[66,67]

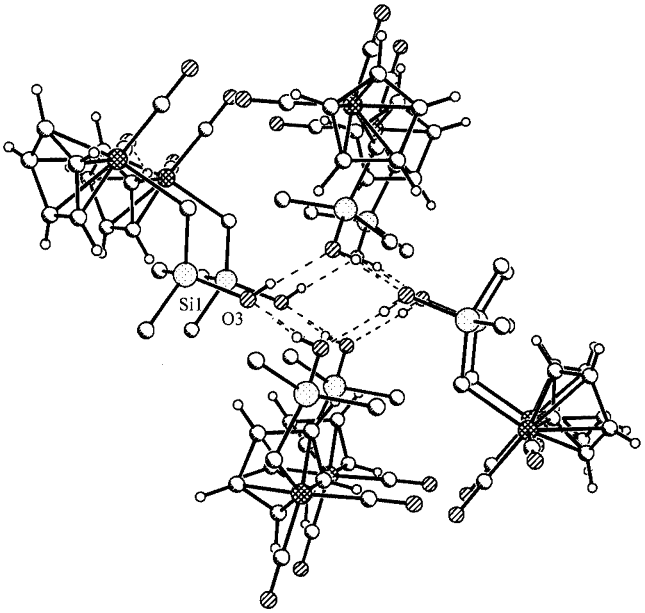


Figure 5. View inside the tube-like arrangement of the tetrameric units of **4a**

The tetrameric units are stacked on top of each other in the same way, resulting in a tube-like arrangement of the Si−OH moieties, which can be seen from Figure 5. The tubes can be considered as hydrophilic channels inside a lipophilic shape of the remaining (ferriomethyl) fragments. Between atoms of different tubes there are no or only marginal interactions, indicated by C···O distances of more than 3.70 Å.

In the case of **4b**, the situation is similar, but in contrast to **4a** there are no conformational isomers in the crystal structure, but two pairs of enantiomers which form the tetramer. The enantiomers are linked in an alternate fashion by hydrogen bonding to produce the centrosymmetric tetra-

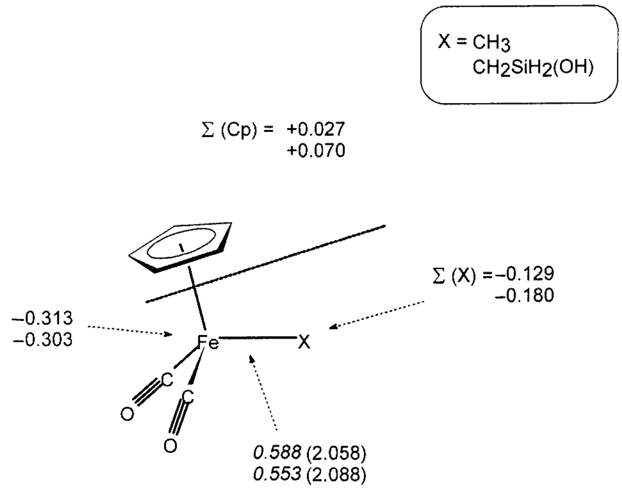


Figure 9. Population analysis of $Cp(OC)_2Fe-X$ ($X = CH_3$, CH_2SiH_2OH), NBO charges and Wiberg bond indices (in italics); in parentheses are Fe−X equilibrium distances

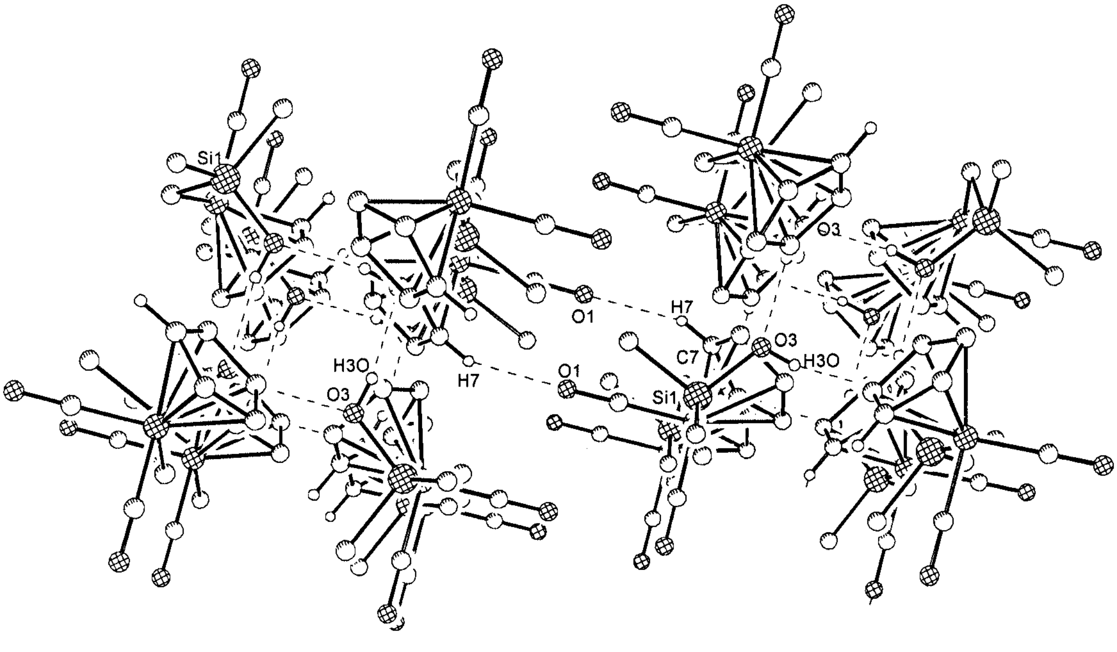


Figure 6. View inside the tube-like arrangement of the tetrameric units of **4b** with connection of the tubes via CH···OC bridges; hydrogen atoms (except for those involved in hydrogen bonding) as well as the phenyl carbon atoms (except for the *ipso* carbon atom) have been omitted for clarity

mer. Like **4a**, the tetramers are stacked on top of each other to produce a tube-like arrangement (Figure 6). These tubes are linked by weak CH···OC interactions of the Cp and one CO ligand of two enantiomers with the same configuration of neighboring tubes [C7···O1 3.406(2) Å].

The situation for the (ferriomethyl)silanol **4c** is somehow different. The molecules are connected by OH···O bridges giving rise to the formation of an infinite chain structure. This arrangement is a result of a "flip mechanism" of the disordered Si−OH proton[68] which guarantees the linkage of the molecules in two directions (intermolecular O···O distance 2.751/2.789 Å). This connection via hydrogen bonding is repeated in an infinite fashion to result in the formation of a linear chain structure, as depicted in Figure 7.

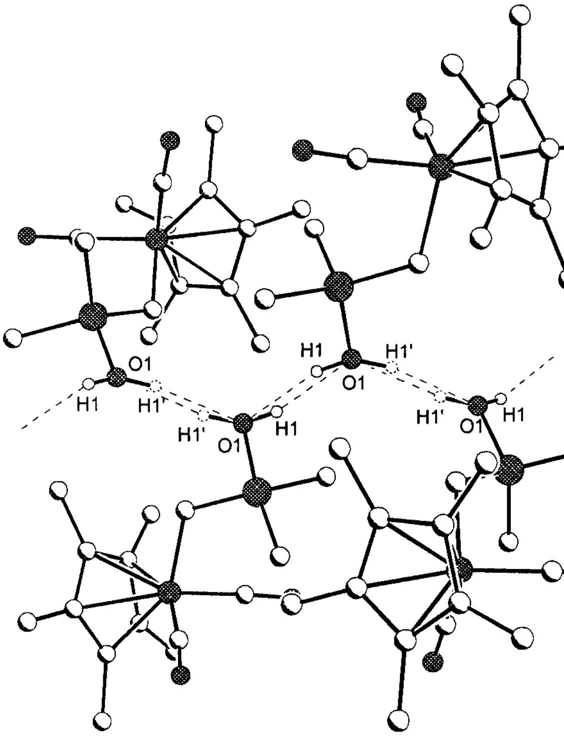


Figure 7. Chain structure of **4c** via OH···O bridges of the disordered SiOH proton

These chains interact by weak CH···OC contacts of the C_5Me_5 and one CO ligand with intermolecular C···O distances lying between 3.409(2) and 3.632(3) Å (Figure 8).

DFT Calculations

In order to analyze the bonding situation in the (ferriomethyl)silanol **4a** in more detail, we performed density functional calculations[69] on the model compounds $Cp(OC)_2Fe-X$ ($X = CH_3$, CH_2SiH_2OH). Plots of their equilibrium structures, determined at BP86/SBK(d) level,[70−73] are shown in Figure 9, together with the results of a natural bond orbital population analysis (NBO).[74]

The bonding parameters for $X = CH_2SiH_2OH$ are in agreement with the X-ray investigation on **4a** (Fe−C: computed 2.088 Å, experimental 2.089 Å). The calculations also predict a widened valent angle at the carbon atom [$X = CH_2SiH_2(OH)$: Fe−C−Si = 115.7°], in agreement with the expectations from Bent's rule.[57,58] It is of interest to analyze the electron density distributions within the calculated structures. The substituent X (CH_3, CH_2SiH_2OH) is only weakly bound to the metal atom (Wiberg bond index for Fe−C 0.59 vs. 0.55), as compared with a stronger coordination of the carbonyl units (bond index 0.89 vs. 0.90). Interestingly, the iron atom accumulates negative charge, although the overall metal fragment releases electron density to X. The electron-withdrawing effect of X (−I) is more strongly pronounced for $X = CH_2SiH_2OH$ than for $X = CH_3$.

Condensation Behavior of 4a

Although **4a** can be stored at −20 °C for several months without any self-condensation, at room temperature, this process slowly starts even in the solid state, leading to the 1,3-bis(ferriomethyl)disiloxane **5**.[43] The disiloxane formation also occurs in solution, which was proven by monitoring a C_6D_6 solution by NMR spectroscopy. In this case, **5** is formed in 33% yield after 30 d.

The disiloxane **5** is additionally obtained by the reaction of **4a** with the chloro(ferriomethyl)silane **3a** in diethyl ether in the presence of the auxiliary base Et_3N after a reaction period of 3 d at room temperature (Scheme 3).

Disiloxanes with only one iron fragment are available in the same manner using the chlorosilanes R(R′)Si(Me)Cl (R = H, R′ = Me, *p*-Tol; R = R′ = Me) (Scheme 4). The (ferriomethyl)-substituted disiloxanes **5** and **6a−c** are obtained in good yields of 76−85% as orange-brown (**5**) and yellow-brown oils (**6a−c**), respectively, which can be stored under nitrogen at room temperature for several months without decomposition.

The dinuclear disiloxane **5** shows a characteristic upfield shift of $\delta = 9$ ppm in the ^{29}Si NMR spectrum compared to the silanol **4a** [$\delta = 12.8$ (**5**) versus 21.8 (**4a**) ppm], which finds its counterpart in the resonances of triorganosilanols and the corresponding disiloxanes.[75]

In accordance with this finding, the ^{29}Si NMR resonances of the β-Si atom of **6a−c** are observed at $\delta = 15.9$ (**6a**), 17.0 (**6b**) and 13.8 (**6c**) ppm. The Si−H-functionalized disiloxanes **6a**,**b** offer the possibility of further functionalization. In this context, experiments to effect Si−H/Si−OH transformation are under investigation, as well as oxidative addition reactions to electronically unsaturated metal fragments.

Conclusion

The results of this paper demonstrate that (ferriomethyl)-substituted silanols are accessible either by Cl/OH exchange at the silicon atom of chloro(ferriomethyl)silanes or by oxygen insertion into the Si−H bond of the corresponding (ferriomethyl)silanes. They show interesting structural features, like aggregation to tetramers and the formation of tube- or

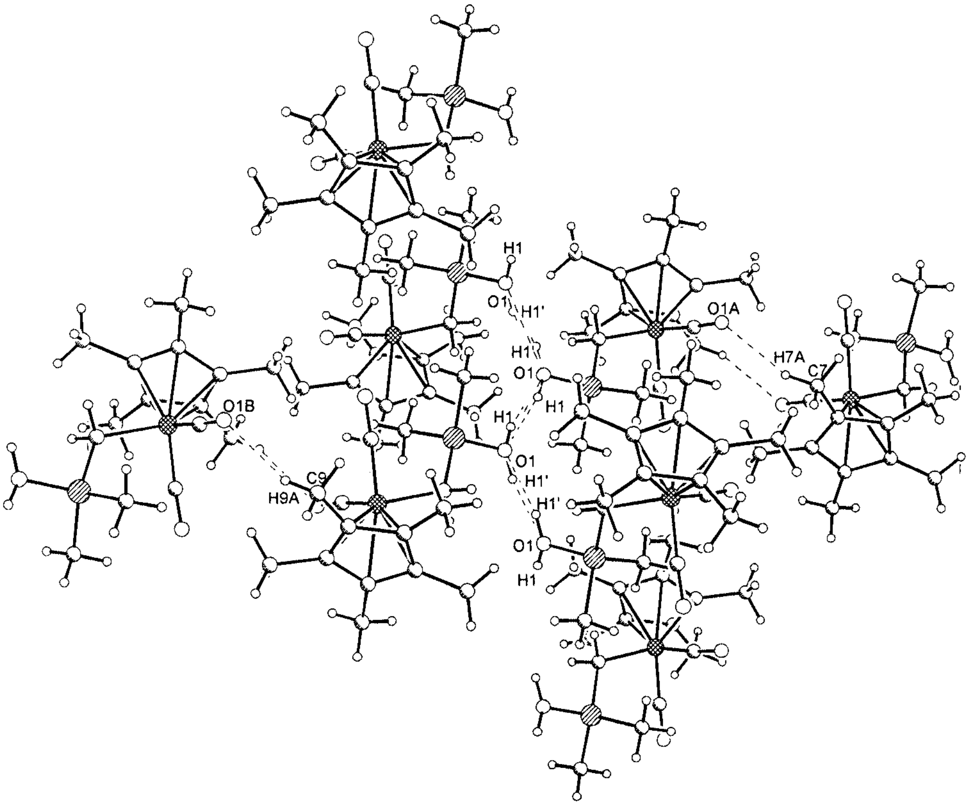
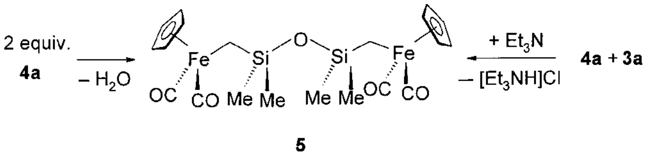
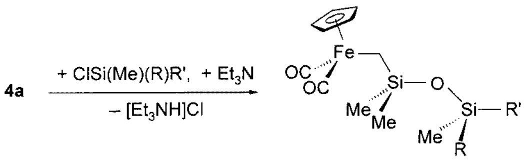


Figure 8. Connection of the chains of **4c** via CH···OC interactions



Scheme 3. Synthesis of the 1,3-bis(ferriomethyl)disiloxane **5**



6	a	b	c
R	H	H	Me
R'	Me	*p*-Tol	Me

Scheme 4. Synthesis of the (ferriomethyl)disiloxanes **6a–c**

chain-like arrangements, which is a consequence of intermolecular hydrogen bonding.

The stability of this type of metal fragment substituted silanols with respect to self-condensation is reduced, compared with the ferriosilanols $C_5R_5(OC)_2Fe-SiMe_2OH$ (R = H, Me)[1] bearing the Si–OH unit directly at the transition metal atom. As a consequence, the silanol **4a** undergoes condensation to a disiloxane, which is well known from triorganosilanols. Apart from that, these compounds are ideal precursors to perform controlled reactions with chlorosilanes to generate novel transition metal containing siloxanes.

Current work deals with the generation of (ferriomethyl)-substituted silanediols and silanetriols in order to check the capability of these species to create metal-substituted oligo- or polysiloxanes by controlled self-condensation reactions.

Experimental Section

General Remarks: All operations were performed under purified and dried 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, 75.5 MHz, and 59.6 MHz for ^1H, ^{13}C, and ^{29}Si, respectively). [D$_6$]Benzene as a solvent: $\delta_H = 7.15$ ppm, $\delta_C = 128.0$ ppm; for ^{29}Si rel. to TMS external. IR: Perkin–Elmer 283 grating spectrometer. Melting points: differential thermo analysis (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: $Na[Fe(CO)_2Cp]$,[76] $Na[Fe(CO)_2C_5Me_5]$,[77] $ClCH_2Si(Me)(Ph)Cl$,[78] $Cp(OC)_2Fe-CH_2-SiMe_2H$,[43] $Cp(OC)_2Fe-CH_2-SiMe_2Cl$,[45] ClSi(Me)(*p*-Tol)H[79] and dimethyldioxirane.[37] $ClCH_2SiMe_2Cl$, $ClSiMe_2H$ and $ClSiMe_3$ were purchased commercially and distilled prior to use.

1. Chloro{[dicarbonyl(η^5-cyclopentadienyl)ferrio]methyl}methyl(phenyl)silane (3b): A stirred suspension of $Na[Fe(CO)_2Cp]$ (**1a**)

(1329 mg, 6.65 mmol) in cyclohexane (40 mL) was treated with ClCH$_2$Si(Me)(Ph)Cl (**2b**) (2157 mg, 10.51 mmol) and stirred for 36 h at room temperature in the dark. The reaction mixture was filtered through a Celite pad and the filtrate concentrated in vacuo. Excess **2b** was distilled off at 90 °C (10^{-2} Torr) and the remaining dark brown oil was heated to 120 °C for 3 h. After cooling to room temperature, the mixture was suspended in *n*-pentane (20 mL) and filtered off from insoluble decomposition products through a Celite pad. The filtrate was reduced to a volume of 8 mL and **3b** was crystallized at −78 °C and dried in vacuo. Yield: 1093 mg (47%). Orange-brown, waxy solid. M.p. 55 °C. ^{1}H NMR: δ = 7.69 (m, 2 H, H$_5$C$_6$Si), 7.20 (m, 3 H, H$_5$C$_6$Si), 3.97 (s, 5 H, H$_5$C$_5$), 0.75 (s, 3 H, H$_3$C), −0.02 (d, $^2J_{\mathrm{H,H}}$ = 12.9 Hz, 1 H, H$_2$C), −0.05 ppm (d, $^2J_{\mathrm{H,H}}$ = 12.9 Hz, 1 H, H$_2$C). ^{13}C{^{1}H} NMR: δ = 216.99 (s, CO), 216.96 (s, CO), 139.7 (s, C-1 of C$_6$H$_5$), 133.7 (s, C-2, C-6 of C$_6$H$_5$), 129.9 (s, C-4 of C$_6$H$_5$), 128.2 (s, C-3, C-5 of C$_6$H$_5$), 84.8 (s, C$_5$H$_5$), 3.3 (s, CH$_3$), −24.9 (s, CH$_2$) ppm. ^{29}Si{^{1}H} NMR: δ = 27.9 (s) ppm. IR (*n*-pentane): ṽ = 1999 (s, CO), 1962 cm^{-1} (vs, CO). C$_{15}$H$_{15}$ClFeO$_2$Si (346.75): calcd. C 51.97, H 4.36; found C 51.60, H 4.64.

2. Chloro{[dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio]methyl}dimethylsilane (3c): A stirred suspension of Na[Fe(CO)$_2$C$_5$Me$_5$] (**1b**) (1315 mg, 4.87 mmol) in cyclohexane (40 mL) was treated with ClCH$_2$SiMe$_2$Cl (**2a**) (1087 mg, 7.60 mmol) and stirred for 20 h at room temperature in the dark. The reaction mixture was filtered through a Celite pad and the filtrate concentrated in vacuo. The orange-red residue was treated with *n*-pentane (15 mL) and stored at −20 °C overnight to crystallize the by-products [C$_5$Me$_5$(OC)$_2$Fe]$_2$ and C$_5$Me$_5$(OC)$_2$FeCl. The supernatant liquid was separated and the volume reduced in vacuo to 10 mL. Remaining C$_5$Me$_5$(OC)$_2$FeCl was crystallized at −20 °C and filtered off. The filtrate was reduced in vacuo to 5 mL and **3c** was crystallized at −78 °C, washed twice with *n*-pentane (each 1 mL) at this temperature and dried in vacuo. Yield: 571 mg (33%). Orange-brown, waxy solid. M.p. 60 °C (decomp.). ^{1}H NMR: δ = 1.25 [s, 15 H, (H$_3$C)$_5$C$_5$], 0.66 (s, 6 H, H$_3$CSi), −0.43 (s, 2 H, H$_2$C) ppm. ^{13}C{^{1}H} NMR: δ = 219.5 (s, CO), 95.7 [s, *C*$_5$(CH$_3$)$_5$], 9.1 [s, (*C*H$_3$)$_5$C$_5$], 4.7 (s, CH$_3$Si), −12.0 (s, CH$_2$) ppm. ^{29}Si NMR: δ = 35.5 (non, $^2J_{\mathrm{Si,H}}$ = 6.7 Hz) ppm. IR (cyclohexane): ṽ = 1983 (s, CO), 1931 cm^{-1} (vs, CO). C$_{15}$H$_{23}$ClFeO$_2$Si (354.75): calcd. C 50.79, H 6.53; found C 50.51, H 6.30.

3. {[Dicarbonyl(η^5-cyclopentadienyl)ferrio]methyl}dimethylsilanol (4a). a) Hydrolysis of Cp(OC)$_2$FeCH$_2$SiMe$_2$Cl (3a) in the Presence of Et$_3$N: A stirred solution of **3a** (237 mg, 0.83 mmol) in Et$_2$O (30 mL) was treated with Et$_3$N (730 mg, 7.21 mmol) and H$_2$O (100 mg, 5.55 mmol). After addition, stirring was continued for 2 h at room temperature. Precipitated [Et$_3$NH]Cl and excess H$_2$O were removed by filtration through Na$_2$SO$_4$. The filtrate was concentrated in vacuo, leaving yellow-brown oily **4a**, which was crystallized from *n*-pentane (3 mL) at −78 °C and dried in vacuo. Yield: 197 mg (89%). **b) Oxygenation of Cp(OC)$_2$FeCH$_2$SiMe$_2$H (3d) with Dimethyldioxirane:** A stirred solution of **3d** (238 mg, 0.95 mmol) in acetone (10 mL) was treated dropwise at −78 °C with a solution of dimethyldioxirane (1.22 mmol,16 mL, 0.076 M) in acetone. After addition, the reaction mixture was stirred for 1 h at this temperature and an additional 1 h at room temperature. All volatiles were removed in vacuo, leaving brown oily **4a**, which was crystallized from *n*-pentane (3 mL) at −78 °C and dried in vacuo. Yield: 170 mg (67%). Yellow-brown, waxy solid. M.p. 38 °C. ^{1}H NMR: δ = 4.24 (s, 5 H, H$_5$C$_5$), 0.95 (br. s, 1 H, HO), 0.23 (s, 6 H, H$_3$C), −0.42 (s, 2 H, H$_2$C) ppm. ^{13}C{^{1}H} NMR: δ = 218.0 (s, CO), 84.8 (s, C$_5$H$_5$), 3.2 (s, CH$_3$), −23.1 (s, CH$_2$) ppm. ^{29}Si{^{1}H} NMR: δ = 21.8 (s) ppm. IR (*n*-pentane): ṽ = 3698 (w, OH), 2000 (s, CO), 1959 cm^{-1} (vs, CO). C$_{10}$H$_{14}$FeO$_3$Si (266.15): calcd. C 45.13, H 5.30; found C 45.11, H 5.21.

4. {[Dicarbonyl(η^5-cyclopentadienyl)ferrio]methyl}methyl(phenyl)silanol (4b): According to 3.a) obtained from **3b** (352 mg, 1.02 mmol), Et$_3$N (219 mg, 2.16 mmol) and H$_2$O (100 mg, 5.56 mmol) in Et$_2$O (20 mL) after 4 h at room temperature. Yield: 247 mg (74%). Yellow-orange, crystalline solid. M.p. 60 °C. ^{1}H NMR: δ = 7.63 (m, 2 H, H$_5$C$_6$Si), 7.26 (m, 3 H, H$_5$C$_6$Si), 4.18 (s, 5 H, H$_5$C$_5$), 1.28 (br. s, 1 H, HO), 0.44 (s, 3 H, H$_3$CSi), −0.09 (d, $^2J_{\mathrm{H,H}}$ = 12.8 Hz, 1 H, H$_2$C), −0.38 (d, $^2J_{\mathrm{H,H}}$ = 12.8 Hz, 1 H, H$_2$C) ppm. ^{13}C{^{1}H} NMR: δ = 217.8 (s, CO), 217.6 (s, CO), 142.9 (s, C-1 of C$_6$H$_5$), 133.5 (s, C-2, C-6 of C$_6$H$_5$), 129.1 (s, C-3, C-5 of C$_6$H$_5$), 128.0 (s, C-4 of C$_6$H$_5$), 84.8 (s, C$_5$H$_5$), 1.8 (s, CH$_3$), −24.9 (s, CH$_2$) ppm. ^{29}Si{^{1}H} NMR: δ = 11.7 (s) ppm. IR (*n*-pentane): ṽ = 3682 (w, br, OH), 1995 (s, CO), 1952 cm^{-1} (vs, CO). C$_{15}$H$_{16}$FeO$_3$Si (328.23): calcd. C 54.89, H 4.91; found C 54.60, H 5.06.

5. {[Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio]methyl}dimethylsilanol (4c): According to 3.a) obtained from **3c** (126 mg, 0.36 mmol), Et$_3$N (365 mg, 3.60 mmol) and H$_2$O (200 mg, 11.1 mmol) in Et$_2$O (20 mL) after 4 h at room temperature. Precipitated [Et$_3$NH]Cl and excess H$_2$O were removed by filtration through Na$_2$SO$_4$. The filtrate was concentrated in vacuo and treated with *n*-pentane (5 mL). The by-products C$_5$Me$_5$(OC)$_2$FeCl and [C$_5$Me$_5$(OC)$_2$Fe]$_2$ were crystallized at 0 °C and separated by filtration through a Celite pad. The filtrate was reduced to 2 mL and **6c** was crystallized at −78 °C and dried in vacuo. Yield: 48 mg (40%). Yellow-orange solid. M.p. 89 °C (decomp.). ^{1}H NMR: δ = 1.35 [s, 15 H, (H$_3$C)$_5$C$_5$], 0.92 (br. s, 1 H, HO), 0.40 (s, 6 H, H$_3$CSi), −0.62 (s, 2 H, H$_2$C) ppm. ^{13}C{^{1}H} NMR: δ = 220.1 (s, CO), 95.2 [s, *C*$_5$(CH$_3$)$_5$], 9.2 [s, (*C*H$_3$)$_5$C$_5$], 3.2 (s, CH$_3$Si), −12.4 (s, CH$_2$) ppm. ^{29}Si{^{1}H} NMR: δ = 21.1 (s) ppm. IR (*n*-pentane): ṽ = 3703 (w, OH), 1988 (s, CO), 1936 cm^{-1} (vs, CO). C$_{15}$H$_{24}$FeO$_3$Si (336.29): calcd. C 53.57, H 7.19; found C 53.82, H 7.05.

6. 1,3-Bis{[dicarbonyl(η^5-cyclopentadienyl)ferrio]methyl}-1,1,3,3-tetramethyldisiloxane (5). a) Self Condensation of Cp(OC)$_2$FeCH$_2$SiMe$_2$OH (4a): In an NMR sample tube **4a** (20 mg, 0.08 mmol) was dissolved in C$_6$D$_6$ (0.6 mL). After 30 d at room temperature, **5** was formed in 33% yield as determined by ^{1}H NMR spectroscopy. **b) Reaction of Cp(OC)$_2$FeCH$_2$SiMe$_2$OH (4a) with Cp(OC)$_2$FeCH$_2$SiMe$_2$Cl (3a):** **3a** (103 mg, 0.48 mmol) in Et$_2$O (20 mL) was added dropwise to a stirred solution of **4a** (108 mg, 0.41 mmol) in Et$_2$O (20 mL). After stirring for 3 d in the dark at room temperature, all volatiles were removed in vacuo. The residue was suspended in *n*-pentane (15 mL) and filtered through a Celite pad. The volume of the filtrate was reduced in vacuo to 3 mL and **5** crystallized at −78 °C. Solid **5** melts upon warming to room temperature. Yield: 163 mg (77%). Orange-brown oil. ^{1}H NMR: δ = 4.24 (s, 10 H, H$_5$C$_5$), 0.36 (s, 12 H, H$_3$C), −0.25 (s, 4 H, H$_2$C) ppm. ^{13}C{^{1}H} NMR: δ = 218.0 (s, CO), 84.9 (s, C$_5$H$_5$), 4.0 (s, CH$_3$), −22.4 (s, CH$_2$) ppm. ^{29}Si{^{1}H} NMR: δ = 12.8 (s) ppm. IR (*n*-pentane): ṽ = 2003 (s, CO), 1961 cm^{-1} (vs, CO). C$_{20}$H$_{26}$Fe$_2$O$_5$Si$_2$ (514.29): calcd. C 46.71, H 5.09; found C 46.37, H 5.32.

7. 1-{[Dicarbonyl(η^5-cyclopentadienyl)ferrio]methyl}-1,1,3,3-tetramethyldisiloxane (6a): According to 6.b) obtained from **4a** (866 mg, 3.26 mmol), Et$_3$N (1186 mg, 11.50 mmol) and Me$_2$Si(H)Cl (694 mg, 10.26 mmol) in Et$_2$O (60 mL) after stirring in the dark at room temperature for 12 h. The residue was suspended in *n*-pentane (40 mL) and filtered through a Celite pad. The filtrate was concentrated in vacuo, leaving **6a**. Yield: 900 mg (85%). Yellow-brown oil. ^{1}H NMR: δ = 5.05 (sept, $^3J_{H,H}$ = 2.4, $^1J_{H,Si}$ = 201.6 Hz, 1 H, HSi), 4.19 (s, 5 H, H_5C_5), 0.28 [s, 6 H, $(H_3C)_2SiCH_2$], 0.22 [d, $^3J_{H,H}$ = 2.4 Hz, 6 H, $(H_3C)_2SiH$], −0.39 (s, 2 H, H_2C) ppm. $^{13}C\{^1H\}$ NMR: δ = 217.9 (s, CO), 84.8 (s, C_5H_5), 3.4 [s, $(CH_3)_2SiCH_2$], 1.2 [s, $(CH_3)_2SiH$], −23.0 (s, CH_2) ppm. $^{29}Si\{^1H\}$ NMR: δ = 15.9 (s, $SiCH_2Fe$), −8.0 (s, SiH) ppm. IR (*n*-pentane): ṽ = 2116 (w, br, SiH), 2003 (s, CO), 1961 cm^{-1} (vs, CO). $C_{12}H_{20}FeO_3Si_2$ (324.30): calcd. C 44.44, H 6.21; found C 44.09, H 6.21.

8. 1-{[Dicarbonyl(η^5-cyclopentadienyl)ferrio]methyl}-1,1,3-trimethyl-3-(*p*-tolyl)disiloxane (6b): According to 7. obtained from **4a** (296 mg, 1.11 mmol), Et_3N (219 mg, 2.16 mmol) and (*p*-Tol)(Me)(H)SiCl (189 mg, 1.11 mmol) in Et_2O (40 mL) after stirring for 24 h in the dark at room temperature. After workup the crude product was dried for 6 h at 5 × 10^{-5} Torr. Yield: 338 mg (76%). Brown oil. ^{1}H NMR: δ = 7.63 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H_4C_6), 7.08 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H_4C_6), 5.47 (q, $^3J_{H,H}$ = 2.8, $^1J_{H,Si}$ = 206.4 Hz, 1 H, HSi), 4.16 (s, 5 H, H_5C_5), 2.10 (s, 3 H, $H_3CC_6H_4$), 0.47 (d, $^3J_{H,H}$ = 2.8 Hz, 3 H, H_3CSiH), 0.31 [s, 6 H, $(H_3C)_2SiCH_2$], −0.35 (s, 2 H, H_2C) ppm. $^{13}C\{^1H\}$ NMR: δ = 217.8 (s, CO), 139.8 (s, C-1 of C_6H_4), 135.0 (s, C-4 of C_6H_4), 134.0 (s, C-2, C-6 of C_6H_4), 129.1 (s, C-3, C-5 of C_6H_4), 84.8 (s, C_5H_5), 21.5 (s, $CH_3C_6H_4$), 3.5 [s, $(CH_3)_2SiCH_2$], 0.1 (s, CH_3SiH), −23.1 (s, CH_2) ppm. ^{29}Si NMR: δ = 17.0 (m, $SiCH_2Fe$), −14.6 (dsext, $^1J_{Si,H}$ = 206.4, $^2J_{Si,H}$ = 6.4 Hz, SiH) ppm. IR (*n*-pentane): ṽ = 2119 (w, br, SiH), 2002 (s, CO), 1960 cm^{-1} (vs, CO). $C_{18}H_{24}FeO_3Si_2$ (400.41): calcd. C 53.99, H 6.04; found C 54.00, H 5.97.

9. 3-{[Dicarbonyl(η^5-cyclopentadienyl)ferrio]methyl}-1,1,1,3,3-pentamethyldisiloxane (6c): According to 7. obtained from **4a** (213 mg, 0.80 mmol), Et_3N (219 mg, 2.16 mmol) and Me_3SiCl (257 mg, 2.37 mmol) in Et_2O (30 mL) after stirring for 24 h in the dark at room temperature. Yield: 204 mg (79%). Yellow-brown oil. ^{1}H NMR: δ = 4.21 (s, 5 H, H_5C_5), 0.28 [s, 6 H, $(H_3C)_2Si$], 0.18 [s, 9 H, $(H_3C)_3Si$], −0.36 (s, 2 H, H_2C) ppm. $^{13}C\{^1H\}$ NMR: δ = 217.9 (s, CO), 84.9 (s, C_5H_5), 3.8 [s, $(CH_3)_2Si$], 2.3 [s, $(CH_3)_3Si$], −22.5 (s, CH_2) ppm. ^{29}Si NMR: δ = 13.8 (m, $SiCH_2Fe$), 6.2 [dec, $^2J_{Si,H}$ = 7.0 Hz, $Si(CH_3)_3$] ppm. IR (Et_2O): ṽ = 2000 (vs, CO), 1953 cm^{-1} (vs, CO). $C_{13}H_{22}FeO_3Si_2$ (338.33): calcd. C 46.15, H 6.55; found C 46.80, H 6.63.

X-ray Crystal Structure Analyses of 4a−c: Table 1 contains details of the structures. The intensities were measured with a Nonius-Kappa CCD diffractometer (Mo-$K_α$ radiation, λ = 0.71073 Å, graphite monochromator) at *T* = −150 °C. The structures were solved by direct methods (Patterson methods)[80] (SHELXS-97) and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-97) (full-matrix least-squares on F^2,[81]). Non-hydrogen atoms were refined anisotropically, H atoms localized by difference electron density and refined using a "riding" model [H(O) free]. An empirical absorption correction was applied. CCDC-115086 (**4a**), -148145 (**4b**) and -156552 (**4c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm "Spezifische Phänomene in der Siliciumchemie") as well as from the Fonds der Chemischen Industrie. M. N. wants to thank the DAAD for financial support.

Table 1. Data for the crystal structure analyses

	4a	**4b**	**4c**
Empirical formula	$C_{10}H_{14}FeO_3Si$	$C_{15}H_{16}FeO_3Si$	$C_{15}H_{24}FeO_3Si$
Formula mass	266.15	328.22	336.28
Crystal system	triclinic	tetragonal	monoclinic
Space group	$P\bar{1}$ (no. 2)	$I4_1/a$ (no. 88)	$C2/c$ (no. 15)
Unit cell			
a [Å]	8.0351(4)	22.0578(10)	27.2245(2)
b [Å]	11.4028(4)	22.0578(10)	13.8293(1)
c [Å]	13.9508(6)	12.4151(6)	9.3090(1)
α [°]	75.637(2)	90	90
β [°]	79.190(2)	90	101.394(1)
γ [°]	76.894(2)	90	90
Volume [Å^3]	1194.27(9)	6040.5(5)	3435.73(5)
Z	4	16	8
Calcd. density [g/cm^3]	1.480	1.444	1.300
μ [mm^{-1}]	1.347	1.081	0.951
F(000)	552	2720	1424
Crystal size [mm]	0.30 × 0.25 × 0.09	0.40 × 0.35 × 0.30	0.35 × 0.20 × 0.10
θ range [°]	2.85/28.30	1.85/26.35	1.66/25.00
Index ranges (*h*, *k*, *l*)	$-10 \le h \le 9$ $-14 \le k \le 14$ $-17 \le l \le 14$	$-27 \le h \le 27$ $-25 \le k \le 25$ $-12 \le l \le 15$	$-32 \le h \le 32$ $-16 \le k \le 16$ $-11 \le l \le 11$
No. of reflections	11445	13115	34665
No. of unique reflections	5413	3035	3020
Parameters, restraints	277, 4	184, 1	186, 0
*R*1 [$I > 2\sigma_I$]	0.0275	0.0299	0.0255
*wR*2	0.0678	0.0664	0.0690
T [K]	123(2)	123(2)	123(2)
Max. residual electron density [e/Å^3]	0.367/−0.353	0.220/−0.304	0.282/−0.268

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There is a significant gap between those two peaks and the remaining peaks in the difference density map. Using HFIX 87, HFIX 147 and HTAB in the SHELXL-97 refinement two possible H(O) positions, very close to the low localized density peaks, are indicated. This all suggests a disorder (50:50) of the Si−OH group with “flipping” hydrogen bond pattern. In addition, data are collected at 123 K and the quality is “not so bad”, which even improves the possibility of localization of disordered H atoms.

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Received March 15, 2002
[I02131]