Si−H-Functionalized Ferriodisiloxanes: Synthesis from the Ferriodimethylsilanols $C_5R_5(OC)_2Fe-SiMe_2OH$ (R = H, Me) and Photoinduced Transformation into μ_2-Disiloxanediyl-Bridged Dinuclear Iron Complexes[‡]

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Hydrolysis of the ferriochlorosilanes $C_5R_5(OC)_2Fe–SiMe_2Cl$ [R = H (**1a**), Me (**1b**)] in the presence of Et_3N yields the corresponding ferriosilanols $C_5R_5(OC)_2Fe–SiMe_2(OH)$ (**2a** and **2b**). In addition, **2b** is also obtained by oxo-functionalization of $C_5Me_5(OC)_2Fe–SiMe_2H$ (**3**) with dimethyldioxirane. The ferriosilanol **2a** can be converted into the ferriodisiloxanes $Cp(OC)_2Fe–SiMe_2OSiR_3$ [R_3Si = $Me_2(H)Si$ (**5a**), $p\mathrm{Tol}_2(H)Si$ (**5b**), Me_3Si (**5c**) and $p\mathrm{Tol}(Me)(H)Si$ (**5d**)] by condensation with the chloro(organo)silanes R_3SiCl (**4a**–**d**). Irradiation of **5a** and **5b** results in CO elimination, followed by dimerization to give the cyclic 1,5-diferratetrasiloxanes $[\mu_2\text{-}SiMe_2OSi(R)_2]_2[Fe(H)(CO)Cp]_2$ [R = Me (**6a**) and *p*Tol (**6b**)]. Compounds **2b** and **6b** have been characterized by single-crystal X-ray structure determination.

Introduction

Transition metal substituted silicon compounds have attracted great attention in recent years, especially with regard to the effect of the metal component on the reactivity of the silicon unit.[2−5] In the context of our systematic studies on the reactivity of functionalized silicon−transition metal complexes[6−13] we have shown that metallosilanols with a direct M−Si bond of the general type $L_nM-Si(R)_{3-n}(OH)_n$ (n = 1−3)[14−30] are characterized by remarkably high stability towards self-condensation, due to the electron-releasing effect of the metal fragment. This property has permitted the isolation of a number of transition metal substituted silanols,[14−26] mainly of the chromium and iron groups, including examples with stereogenic metal and silicon atoms[26] and even of metallosilanediols[27,28] and -silanetriols.[29,30]

The reactivity of this special class of silanols has so far not been explored in detail. However, preliminary studies showed facile condensation with chlorosilanes as an efficient route to metallosiloxanes.[22−24,26−30] In particular, those bearing an SiH function at the γ-silicon atom offer high synthetic potential in terms of the oxidative addition of the SiH unit to electronically unsaturated metal centres to provide access to Si−O−Si-bridged dinuclear metal complexes.[27]

This was strong motivation to perform the synthesis of novel metallosilanols, especially with the well-known iron fragments $C_5R_5(OC)_2Fe$ (R = H, Me), and condensation reactions to afford the corresponding disiloxanes. Furthermore, the SiH-functional derivatives were used for photoinduced transformation, providing novel eight-membered cyclic dimetallasiloxanes.

Results and Discussion

Access to the ferriodimethylsilanols **2a** and **2b**, the precursors for synthesis of the ferriodisiloxanes, is given by two procedures − hydrolysis of chloroferriosilanes[14,18] and oxo-functionalization of ferriosilanes.[16,20]

Hydrolysis of the chloroferriodimethylsilanes **1a** and **1b** in diethyl ether in the presence of the auxiliary base Et_3N at room temperature afforded the metallated silanols **2a** and **2b** in good yields [89% (**2a**), 70% (**2b**)] [Equation (1), route a]. The C_5Me_5-substituted complex **1b** undergoes ligand exchange (48 h) significantly more slowly than the Cp compound **1a**. This difference can be associated with the reduced electrophilicity of the silicon atom, deriving from the greater electron-releasing effect of the permethylated Cp ring. Controlled Cl/OH exchange can be performed without an auxiliary base, as demonstrated for **2a**, indicating that the Fe−Si bonds in both **1a** and **2a**, in contrast to those in

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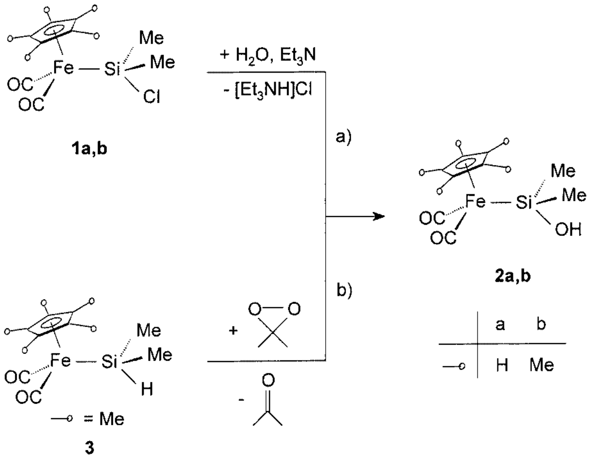
trialkylferriosilanes, are resistant towards cleavage with HCl.

In addition, the C_5Me_5-substituted ferriosilanol **2b** was obtained by oxygenation of the corresponding ferriodimethylsilane **3** with dimethyldioxirane [Equation (1), route b]. This method gave shorter reaction times and a more convenient workup procedure than the hydrolysis route. However, the yield was significantly lower (36%), presumably due to oxidation of the transition metal centre.[31]



(1)

The ferriodimethylsilanols **2a** and **2b** were obtained as slightly air-sensitive, pale yellow solids, showing good solubility in all kinds of organic solvents. Compounds **2a** and **2b** did not undergo self-condensation at room temperature even in the presence of Et_3N.

In order to gain an insight into the solid-state structure of the ferriodimethylsilanols **2a** and **2b**, especially with respect to hydrogen-bonded aggregation, an X-ray structure determination of **2b** was performed. Two molecules were found in the asymmetric unit (Figure 1). For the central iron atom a pseudo-octahedral coordination sphere is indicated by the ligand−iron−ligand angles, which are close to 90°. A larger angle exists between the carbonyl carbon atoms [98.3(3)°], while those between the CO ligands and the silicon atom are diminished [83.1(2)°/84.1(2)° and 83.9(2)°/84.0(2)°]. Newman projection along the Fe−Si bond reveals a staggered conformation of the substituents, with one of the methyl groups *trans* to the C_5Me_5 ring and the OH group consequently occupying the space between the C_5Me_5 ring and one carbonyl ligand. The Fe−Si distances [2.313(2) Å and 2.319(2) Å] lie within the range observed in known iron−silicon compounds.[32,33] The Si−O bond lengths [1.676(9) Å and 1.653(6) Å] are slightly greater than those in organosilanols,[34] indicating some electronic saturation of the silicon atom by the transition metal component. The silicon atoms show a distorted tetrahedral coordination with reduced angles between the methyl and hydroxy substituents [104.8(3)−106.2(4)°] and enlarged ones to the metal component [111.6(4)−115.5(3)°]. Triorganosilanols often show interesting hydrogen-bonded superstructures, forming chains,[35,36] tetramers[37] or dimers,[38−40] depending on the steric demand of the organic substituents. A few examples show that, as far as the formation of hydrogen bonds is concerned, the transition metal components show an effect analogous to that of organic substituents, the difference being that the acidity of the OH hydrogen atom is reduced and the basicity of the oxygen atom is increased.[16,22] Compound **2b**, because of the bulkiness of the metal component, prefers hydrogen-bonded "dimerization", indicated by an oxygen−oxygen distance of 2.889 Å. This arrangement is similar to that found in $C_5Me_5(OC)_2Ru{-}Si(o\text{Tol})_2OH$.[22]

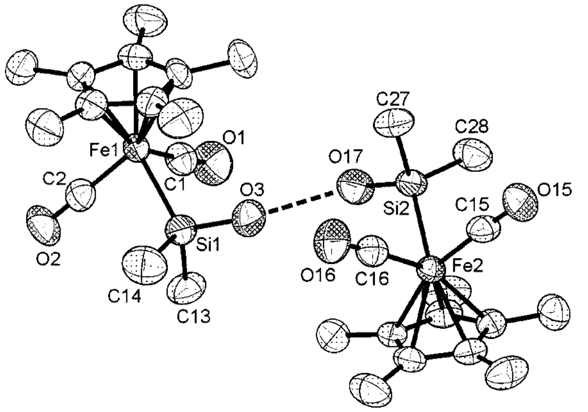
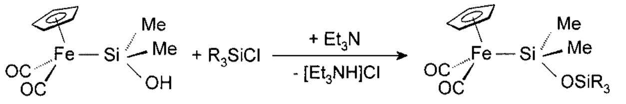


Figure 1. ORTEP Plot of **2b** (O···O bond is dashed); selected bond lengths [Å], angles [°] and torsion angles [°]: Fe1−C1 1.731(8), Fe1−C2 1.755(7), Fe1−Si1 2.313(2), O3−Si1 1.676(9), Si1−C14 1.864(7), Si1−C13 1.871(7), Fe2−C15 1.732(7), Fe2−C16 1.743(8), Fe2−Si2 2.319(2), Si2−O17 1.653(6), Si2−C28 1.864(7), Si2−C27 1.894(7); C1−Fe1−C2 98.3(3), C1−Fe1−Si1 83.1(2), C2−Fe1−Si1 84.1(2), O3−Si1−C14 105.2(5), O3−Si1−C13 106.2(4), C14−Si1−C13 104.9(4), O3−Si1−Fe1 111.6(4), C16−Fe2−C15 98.3(3), C15−Fe2−Si2 83.9(2), C16−Fe2−Si2 84.0(2), O17−Si2−C28 105.1(3), O17−Si2−C27 106.0(3), C28−Si2−C27 104.8(3), O17−Si2−Fe2 113.5(2), C28−Si2−Fe2 113.8(2), C27−Si2−Fe2 112.8(2); C1−Fe1−Si1−O3 74.0(4), C2−Fe1−Si1−O3 173.1(4), C15−Fe2−Si2−O17 −177.0(3), C16−Fe2−Si2−O17 −77.9(3)

Due to their high stabilities with respect to self-condensation, the ferriosilanols **2a** and **2b** are excellent starting materials for further reactions. Among these, condensation with chlorosilanes is of special interest for investigation of the transition metal effect on the Si−O−Si bonding system and the γ-silicon atom of the resulting ferriodisiloxanes. Treatment of **2a** with the chloro(organo)silanes **4a−d** in Et_2O in the presence of the auxiliary base Et_3N at room temperature afforded the ferriodisiloxanes **5a−d** [34% (**5c**) to 95% (**5b**) yield] after 1−12 h, these compounds being isolated as pale yellow (**5c**) or orange (**5a**, **5b**, **5d**) oils displaying high solubility in benzene and *n*-pentane [Equation (2)].

Compounds **5a** and **5d** were also obtained in the absence of triethylamine, but the reaction rate was significantly lower [70% (**5a**)/10% (**5d**) conversion after 7 d].

Comparison of the spectroscopic data of the ferriosilanol **2a** and of the ferriosiloxanes **5a−d** shows no significant effect concerning the $\nu(CO)_{sym}$ and $\nu(CO)_{asym}$ frequencies of the CO ligands, while for the ^{29}Si NMR resonance a highfield shift for the iron-bound silicon atom from $\delta = 66.05$ ppm (**2a**) to $\delta = 58.73$ (**5a**), 61.45 (**5b**) or 59.97 ppm (**5d**) is

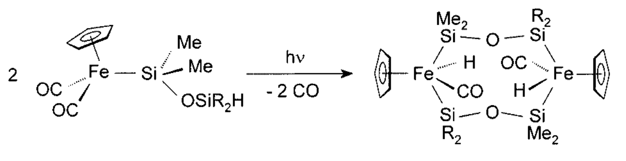


2a **4a-d** **5a-d**

	a	b	c	d
R_3Si	$Me_2(H)Si$	pTol$_2$(H)Si	Me_3Si	pTol(Me)(H)Si

(2)

found. The ṽ(SiH) absorptions of **5a**, **5b** and **5d** (2123−2112 cm^{-1}) lie in the normal range of Si−H functional organosilanes or organosiloxanes, showing that the "transition metal effect" on the silicon atom in the γ-position is negligible. This finding implies that for these systems the known reactivity behaviour of Si−H-functional silanes − photoinduced oxidative addition of SiH functions to coordinatively unsaturated metal centres, for example, resulting in the formation of M(H)−Si units − may be expected.[5] Indeed, irradiation of **5a** and **5b** with UV light in cyclohexane for 7 h/20 h resulted in controlled CO elimination, followed by Si−H addition to the iron atom. The resulting eight-membered cyclic ferriodisiloxanes **6a** and **6b** were obtained as white (**6a**) and beige (**6b**) solids in 19% (**6a**) and 10% (**6b**) yields [Equation (3)].



5a,b **6a,b**

	a	b
R	Me	pTol

(3)

The structures of **6a** and **6b** were confirmed by the Fe−H resonance in the ^1H NMR at $\delta = -13.31$ (**6a**)/-12.54 ppm (**6b**), with ^2J(HFeSi) coupling constants of 23.6 (**6a**)/24.0 Hz (**6b**) excluding agostic FeHSi interaction.[5] In addition, the $^{29}Si\{^1H\}$ NMR spectra show singlets at $\delta = 45.11$ (**6a**) and 46.71 (**6b**) ppm, indicating chemical equivalence of the methyl-substituted silicon atoms.

Intramolecular cyclization to the four-membered *cyclo*-ferradisiloxanes Cp(OC)(H)Fe-(SiMe$_2$OSiR$_2$-κ^2-Si)[41−45] can be ruled out, as shown by the X-ray structure determination of **6b**. This type of siloxane is obviously disfavoured, due to high ring strain.

Figure 2 shows that **6b** can be regarded as deriving from the well-known cyclic organotetrasiloxanes by replacement of the oxygen atoms in the 1- and 5-positions with the isolobal iron fragment Cp(OC)(H)Fe.[46]

The Fe−Si bond lengths of 2.339(1) Å (Fe1−Si1) and 2.311(1) Å (Fe1−Si2) show the expected decrease on going from the methyl- to the tolyl-substituted metal−silicon unit and lie within the range of known bis(silyl)iron complexes.[47,48] The Si−O distances [1.636 (Si1) and 1.635 Å (Si2)] are significantly shorter than those in four-membered *cyclo*-metalladisiloxanes {e.g., $(Ph_3P)_2$(OC)(H)Ir(SiMe$_2$O-SiMe$_2$-κ^2-Si) [d(Si−O) = 1.690/1.678 Å][44] or (dppe)Pt(Si-Me$_2$OSiMe$_2$-κ^2-Si) [d(Si−O) = 1.693/1.689 Å][49]} and imply a partial double bond character for the Si−O bond.[50−55] The value of 153.6(1)° for the Si−O−Si angle is similar to that in cyclic organotetrasiloxanes.[32] The iron atoms show a pseudo-square-pyramidal arrangement, with the Cp ligand in the apical position and the two Si atoms at the tetragonal base arranged *trans* to each other [Si1−Fe1−Si2 109.43(4)°] as well as the CO and H ligands [C1−Fe1−H1 102.4(2)°]. The silicon atoms show distorted tetrahedral coordination with different Fe−Si−C angles depending on the nature of the organic ligand [114.4(1)/111.3(1)° Fe−Si−C(pTol); 116.0(2)/109.2(2)° Fe−Si−C(Me)], with the Fe−Si−C(Me) angles showing stronger deviation from the ideal value.

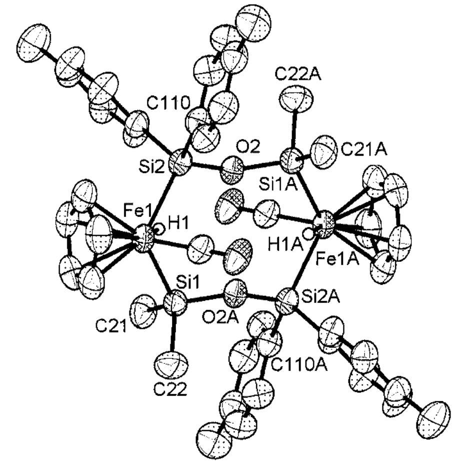


Figure 2. ORTEP Plot of **6b**; selected bond lengths [Å], angles [°] and torsion angles [°]: Fe1−Si1 2.339(1), Fe1−Si2 2.311(1), Fe1−H1 1.4644(5), Si1−O2A 1.636(2), Si2−O2 1.635(2), Si1−C21 1.868(4), Si2−C110 1.891(3); Si1−Fe1−Si2 109.43(4), Si2−Fe1−H1 55.88(3), Si1−Fe1−H1 62.03(3), C1−Fe1−H1 102.4(2), Si2−O2−Si1A 153.6(1), Fe1−Si1−O2A 110.81(9); Fe1−Si2−O2 111.75(9), Fe1−Si1−C21 116.0(2), C21−Si1−C22 107.5(3), Fe1−Si2−C110 114.4(1), Fe1−Si2−O2−Si1A −128.18(8), H1−Fe1−Si2−O2 −51.09(8), Si1−Fe1−Si2−O2 −18.29(7)

For $(R_2SiO)_4$ rings a variety of conformations (C_i chair, C_2 boat, S_4 boat) has been found in the solid state,[32] with $(tBu_2SiOSiMe_2O)_2$ representing an exception, due to the planarity of the ring.[56] The eight-membered $Fe_2Si_4O_2$ arrangement of **6b** adopts a chair conformation with both metal components bent in opposite directions out of the plane defined by the four silicon atoms (Figure 3). An identical situation holds for the oxygen atoms.

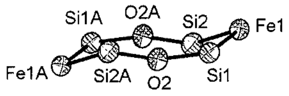


Figure 3. Chair conformation of the eight-membered ring of **6b**

Conclusions

The γ-SiH-functionalized ferriodisiloxanes presented in this paper proved to be synthetically valuable precursors for the simple synthesis of Si−O−Si-bridged homodinuclear iron complexes. Further investigation is currently being directed towards heteronuclear derivatives with metal complexes characterized by a high tendency towards oxidative addition of SiH functions, such as Pt or Ir. Another aspect concerns the introduction of hydroxy groups at the γ-silicon atom, giving access to metallosiloxanols. These compounds are of special interest for further condensation to afford transition metal fragment substituted oligosiloxanes. We regard these species as model compounds for catalytic systems immobilized on a silica surface.

Experimental Section

General Remarks: All reactions were performed under purified nitrogen. Solvents were dried by conventional procedures, distilled and saturated with N_2 prior to use. ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were recorded with Jeol FX 90Q, Bruker AC 200 and Bruker AMX 400 spectrometers; $\delta(^{29}Si)$ chemical shifts are measured relative to external Me_4Si; $\delta(^1H)/(^{13}C)$ are reported downfield from Me_4Si, referenced to the residual proton signal (^1H) or natural-abundance carbon signal of C_6D_6 (^{13}C). Infrared spectra were recorded with a Perkin−Elmer 283 grating spectrometer. The solutions were measured in NaCl cells of 0.1 mm path length with a resolution of about 2 cm^{-1}. Melting points: differential thermal analysis (Du Pont 9000 Thermal Analysis System). Literature procedures were employed to synthesize $Cp(OC)_2Fe-SiMe_2Cl$ (**1a**)[57] and dimethyldioxirane.[58] $Me_2Si(H)Cl$ (**4a**), Me_3SiCl (**4c**), Et_3N and 18-crown-6 were obtained commercially and were distilled prior to use.

1. Chloro[dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio]dimethylsilane (1b): Me_2SiCl_2 (1680 mg, 13.03 mmol) was added to a suspension of $Na[Fe(CO)_2C_5Me_5]$ (880 mg, 3.26 mmol) in 50 mL of cyclohexane and the mixture was vigorously stirred for 40 h at room temperature. After filtration, the solvent was removed in vacuo, the red residue was extracted three times with 10 mL of *n*-pentane, and **1b** crystallized at −78 °C. Yield 410 mg (37%). Orange, microcrystalline powder. M.p. 96 °C. ^1H NMR (60 MHz, [D_6]benzene): δ = 1.60 [s, 15 H, $(H_3C)_5C_5$], 0.97 ppm (s, 6 H, H_3CSi). IR (*n*-pentane): $\tilde{\nu}$ = 1993 cm^{-1} (vs), 1941 (vs) [ν(CO)]. $C_{14}H_{21}ClFeO_2Si$ (340.74): calcd. C 49.35, H 6.23, Cl 10.40; found C 49.07, H 5.91, Cl 10.60.

2. [Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio]dimethylsilane (3): The preparation was as described under 1., from $Na[Fe(CO)_2C_5Me_5]$ (700 mg, 2.59 mmol) and $Me_2Si(H)Cl$ (735 mg, 7.77 mmol) in 100 mL of cyclohexane (20 h). Further purification of **3** was performed by sublimation at 83−85 °C (10^{-2} Torr). Yield 420 mg (53%). Yellow, microcrystalline powder. M.p. 43 °C. ^1H NMR (60 MHz, [D_6]benzene): δ = 4.72 [sept, ^3J(HSiCH) = 3.6 Hz, 1 H, HSi], 1.50 [s, 15 H $(H_3C)_5C_5$], 0.62 ppm [d, ^3J(HCSiH) = 3.6 Hz, 6 H, $(H_3C)_2Si$]. $^{13}C\{^1H\}$ NMR (50 MHz, [D_6]benzene): δ = 217.27 (s, CO), 94.57 [s, $C_5(CH_3)_5$], 9.45 [s, $(CH_3)_5C_5$], 2.79 ppm [s, $(CH_3)_2Si$]. $^{29}Si\{^1H\}$ NMR (18 MHz, [D_6]benzene): δ = 28.36 ppm (s). IR (cyclohexane): $\tilde{\nu}$ = 2043 cm^{-1} [w, ν(SiH)], 1984 (vs), 1931 (vs) [ν(CO)]. $C_{14}H_{22}FeO_2Si$ (306.3): calcd. C 54.90, H 7.24; found C 54.72, H 6.95. MS (30 °C): *m/z* (%) = 306 (3) [M^+], 278 (36) [M − CO^+], 248 (26) [$C_5Me_5(CO)Fe - SiH^+$], 191 (100) [$C_5Me_5Fe^+$].

3. [Dicarbonyl(η^5-cyclopentadienyl)ferrio]dimethylsilanol (2a): $Cp(OC)_2Fe-SiMe_2Cl$ (**1a**, 256 mg, 0.96 mmol), dissolved in 25 mL of Et_2O, was treated with Et_3N (144 mg, 1.44 mmol) and H_2O (100 mg, 5.55 mmol). After 45 min of stirring at room temperature, the precipitate of [Et_3NH]Cl was separated, the orange solution was concentrated to dryness, and the resulting ferriosilanol was washed five times with 2 mL of *n*-pentane and dried in vacuo. Yield 215 mg (89%). Light yellow, microcrystalline powder. M.p. 45 °C (decomp.). ^1H NMR (200 MHz, [D_6]benzene): δ = 4.27 (s, 5 H, H_5C_5), 1.77 (br. s, 1 H, HO), 0.70 ppm (s, 6 H, H_3C). $^{29}Si\{^1H\}$ NMR (18 MHz, [D_6]benzene): δ = 66.05 ppm (s). IR (cyclohexane): $\tilde{\nu}$ = 3690 cm^{-1} [br, w, ν(OH)], 1998 (s), 1947 (vs) [ν(CO)]. $C_9H_{12}FeO_3Si$ (252.13): calcd. C 42.88, H 4.80; found C 42.14, H 4.79.

4. Synthesis of 2a in the Absence of an Auxiliary Base: H_2O (1000 mg, 55.6 mmol) was added to a solution of $Cp(OC)_2Fe-SiMe_2Cl$ (**1a**, 270 mg, 1.00 mmol) in Et_2O (20 mL). After 2 h of stirring at room temperature, the organic layer was separated and concentrated in vacuo. The resulting **2a** was washed twice with 2 mL of *n*-pentane and dried in vacuo. Yield 242 mg (96%).

5. [Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio]dimethylsilanol (2b): The preparation was as described under 3., from $C_5Me_5(OC)_2Fe-SiMe_2Cl$ (**1b**, 235 mg, 0.69 mmol), H_2O (12 mg, 0.69 mmol) and Et_3N (730 mg, 7.2 mmol) (48 h). Yield 155 mg (70%). Yellow microcrystalline powder. M.p. 72 °C (decomp.). ^1H NMR (400 MHz, [D_6]benzene): δ = 1.55 [s, 15 H, $(H_3C)_5C_5$], 1.02 (s, 1 H, HO), 0.67 ppm [s, 6 H, $(H_3C)_2Si$]. $^{13}C\{^1H\}$ NMR (101 MHz, [D_6]benzene): δ = 217.62 (s, CO), 95.13 [s, $C_5(CH_3)_5$], 9.96 [s, $(CH_3)_2Si$], 9.80 ppm [s, $(CH_3)_5C_5$]. $^{29}Si\{^1H\}$ NMR (80 MHz, [D_6]benzene): δ = 66.83 ppm (s). IR (toluene): $\tilde{\nu}$ = 3629 cm^{-1} [w, br, ν(OH)], 1979 (vs), 1922 (vs) [ν(CO)]. $C_{14}H_{22}FeO_3Si$ (322.26): calcd. C 52.18, H 6.88; found C 52.63, H 7.15.

6. Synthesis of 2b by Oxygenation of $C_5Me_5(OC)_2Fe-SiMe_2H$ (3) with Dimethyldioxirane: A solution of dimethyldioxirane in acetone (0.10 M, 10 mL) was added dropwise at −78 °C to a solution of $C_5Me_5(OC)_2Fe-SiMe_2H$ (**3**, 265 mg, 0.87 mmol) in 20 mL of toluene. After 1 h of stirring, the mixture was allowed to warm to room temperature and the solvent was evaporated in vacuo. The orange residue was extracted with 10 mL of *n*-pentane, and **2b** crystallized at −78 °C. Yield 100 mg (36%).

7. Chlorobis(4-methylphenyl)silane (4b): A Grignard solution, freshly prepared from Mg (2.43 g, 0.1 mol) and 4-bromotoluene (1.71 g, 0.1 mol) in 50 mL of diethyl ether, was added dropwise over 1 h to a cooled solution (0 °C) of $HSiCl_3$ (6.77 g, 0.05 mol) in 100 mL of Et_2O. After the mixture had been stirred for 1 h at room temperature, the precipitate was filtered off and the resulting dark brown, oily residue was fractionally distilled. Yield 12.69 g (51%). Colourless liquid. B.p. 105−107 °C/0.01 Torr. ^1H NMR (60 MHz, [D_6]benzene): δ = 7.53 [d, $^3J_{HCCH}$ = 8.0 Hz, 4 H, H-3/5 of H_4C_6], 6.97 [d, $^3J_{HCCH}$ = 8.0 Hz, 4 H, H-2/6 of H_4C_6], 5.90 (s, 1 H, HSi), 1.92 ppm (s, 6 H, H_3C). IR (cyclohexane): $\tilde{\nu}$ = 2159 cm^{-1} [s, ν(SiH)].

8. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1,3,3-tetramethyldisiloxane (5a)

a) From $Cp(OC)_2Fe-SiMe_2OH$ (2a), $Me_2Si(H)Cl$ (4a) and Et_3N: A solution of $Cp(OC)_2Fe-SiMe_2OH$ (**2a**, 224 mg, 0.89 mmol) in 20 mL of Et_2O was treated with Et_3N (101 mg, 1.00 mmol) and $Me_2Si(H)Cl$ (**4a**, 308 mg, 2.84 mmol). After the mixture had been stirred for 1 h at room temperature, the precipitate of [Et_3NH]Cl was filtered off and all volatiles were removed in vacuo. The red oily residue was extracted with 3 mL of *n*-pentane, the solvent was removed, and **5a** was dried in vacuo. Yield 218 mg (79%).

b) From Cp(OC)$_2$Fe−SiMe$_2$OH (2a), NaH and Me$_2$Si(H)Cl (4a): A cooled solution (−78 °C) of Cp(OC)$_2$Fe−SiMe$_2$OH (**2a**, 100 mg, 0.40 mmol) in 10 mL of toluene was treated with NaH (10 mg, 0.40 mmol) and 18-crown-6 (10 mg) and stirred for 30 min. After addition of Me$_2$Si(H)Cl (**4a**, 47 mg, 0.50 mmol) the mixture was allowed to warm to room temperature and stirred for another 10 min. After filtration through a Celite pad, the solvent was removed and **5a** was washed at −78 °C with 3 mL of *n*-pentane and dried in vacuo. Yield 104 mg (84%). Orange oil. M.p. −37 °C. ^{1}H NMR (400.1 MHz, [D$_6$]benzene): δ = 5.04 [sept, ^3J(HSiCH) = 2.7, $^1J_{\text{SiH}}$ = 202.0 Hz, 1 H, HSi], 4.12 (s, 5 H, H$_5$C$_5$), 0.63 (s, 6 H, H$_3$CSiFe), 0.23 ppm [d, ^3J(HSiCH) = 2.7 Hz, 6 H, H_3CSiH]. ^{29}Si{^{1}H} NMR (79.5 MHz, [D$_6$]benzene): δ = 58.73 (s, SiFe), −8.27 ppm (s, SiH). IR (*n*-pentane): $\tilde{\nu}$ = 2117 cm^{-1} [w, ν(SiH)], 1998 (s), 1957 (vs) [ν(CO)]. C$_{11}$H$_{18}$FeO$_3$Si$_2$ (310.28): calcd. C 42.58, H 5.85; found C 42.29, H 5.82.

9. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1-dimethyl-3,3-bis(4-methylphenyl)disiloxane (5b): The preparation was as described under 8a., from Cp(OC)$_2$Fe−SiMe$_2$OH (**2a**, 699 mg, 2.77 mmol), Et$_3$N (722 mg, 7.14 mmol) and (*p*Tol)$_2$Si(H)Cl (**4b**, 1026 mg, 4.16 mmol) in 60 mL of diethyl ether (5 h). Yield 1214 mg (95%). Orange oil. M.p. −20 °C. ^{1}H NMR (400.1 MHz, [D$_6$]benzene): δ = 7.69 [d, $^3J_{\text{HCCH}}$ = 6.8 Hz, 2 H, H-3/H-5 of H$_4$C$_6$], 7.07 [d, $^3J_{\text{HCCH}}$ = 6.8 Hz, 2 H, H-2/H-6 of H$_4$C$_6$], 5.87 [s, $^1J_{\text{SiH}}$ = 211.3 Hz, 1 H, HSi], 4.13 (s, 5 H, H$_5$C$_5$), 2.11 (s, 6 H, H_3CC$_6$H$_4$), 0.71 ppm (s, 6 H, H$_3$CSi). ^{13}C{^{1}H} NMR (100.6 MHz, [D$_6$]benzene): δ = 215.42 (s, CO), 140.00 (s, C-1 of C$_6$H$_4$), 134.76 (s, C-3/C-5 of C$_6$H$_4$), 133.48 (s, C-4 of C$_6$H$_4$), 129.11 (s, C-2/C-6 of C$_6$H$_4$), 83.64 (s, C$_5$H$_5$), 21.52 (s, CH$_3$C$_6$H$_4$), 11.08 ppm (s, CH$_3$Si). ^{29}Si{^{1}H} NMR (79.5 MHz, [D$_6$]benzene): δ = 61.45 (s, SiFe), −22.76 ppm [s, Si(*p*Tol)$_2$H]. IR (*n*-pentane): $\tilde{\nu}$ = 2123 cm^{-1} [w, ν(SiH)], 2000 (vs), 1949 (vs) [ν(CO)], 1252 [vw, ν(SiCH$_3$)], 1042 [m, br, ν$_{\text{as}}$(SiOSi)], 597 [s, ν$_{\text{s}}$(SiOSi)]. C$_{23}$H$_{26}$FeO$_3$Si$_2$ (462.474): calcd. C 59.73, H 5.67; found C 59.84, H 5.80.

10. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1,3,3,3-pentamethyldisiloxane (5c): The preparation was as described under 8a., from Cp(OC)$_2$Fe−SiMe$_2$OH (**2a**, 366 mg, 1.43 mmol), Et$_3$N (211 mg, 2.09 mmol) and Me$_3$SiCl (**4c**, 244 mg, 2.25 mmol) in 15 mL of Et$_2$O (12 h). Further purification of **5c** was performed by distillation at 50 °C (10^{-4} Torr). Yield 153 mg (34%). Pale yellow oil. M.p. −32 °C. ^{1}H NMR (60 MHz, [D$_6$]benzene): δ = 4.21 (s, 5 H, H$_5$C$_5$), 0.63 [s, 6 H, (H$_3$C)$_2$SiFe], 0.19 ppm [s, 9 H, (H$_3$C)$_3$Si]. ^{29}Si{^{1}H} NMR (79.5 MHz, [D$_6$]benzene): δ = 55.50 (s, SiFe), 5.44 ppm (s, SiMe$_3$). IR (benzene): $\tilde{\nu}$ = 1994 cm^{-1} (vs), 1936 (vs) [ν(CO)]. C$_{12}$H$_{20}$FeO$_3$Si$_2$ (324.31): calcd. C 44.44, H 6.22; found C 44.90, H 5.77. MS: *m*/*z* = 324 [M$^+$].

11. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1,3-trimethyl-3-(4-methylphenyl)disiloxane (5d): The preparation was as described under 8a., from Cp(OC)$_2$Fe−SiMe$_2$OH (**2a**, 302 mg, 1.20 mmol), Et$_3$N (203 mg, 2.01 mmol) and *p*Tol(Me)Si(H)Cl (**4d**, 420 mg, 2.46 mmol) in 20 mL of Et$_2$O (1 h). Further purification of **5d** was performed by column chromatography (20 × 2 cm, Al$_2$O$_3$, activity IV, cyclohexane). Yield 270 mg (70%). Orange oil. M.p. 4 °C. ^{1}H NMR (60 MHz, [D$_6$]benzene): δ = 7.64 [d, $^3J_{\text{HCCH}}$ = 8.5 Hz, 2 H, H-3/5 of H$_4$C$_6$], 7.12 [d, $^3J_{\text{HCCH}}$ = 8.5 Hz, 2 H, H-2/6 of H$_4$C$_6$], 5.47 [q, ^3J(HSiCH) = 2.8, $^1J_{\text{SiH}}$ = 207.0 Hz, 1 H, HSi], 4.08 (s, 5 H, H$_5$C$_5$), 2.10 (s, 3 H, H_3CC$_6$H$_4$), 0.68, 0.67 (2 s, 6 H, H$_3$CSiFe), 0.49 ppm [d, ^3J(HSiCH) = 2.8 Hz, 3 H, H_3CSiH]. ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = 215.49 (s, CO), 139.75 (s, C-1 of C$_6$H$_4$), 134.98 (s, C-4 of C$_6$H$_4$), 133.91 (s, C-2/6 of C$_6$H$_4$), 129.06 (s, C-3/5 of C$_6$H$_4$), 83.55 (s, C$_5$H$_5$), 21.48 (s, CH$_3$C$_6$H$_4$), 11.03 (s, CH$_3$SiFe), 1.02 ppm (s, CH$_3$SiH). ^{29}Si{^{1}H} NMR (18 MHz, [D$_6$]benzene): δ = 59.97 (s, SiFe), −15.39 ppm (s, SiH). IR (cyclohexane): $\tilde{\nu}$ = 2112 cm^{-1} [w, ν(SiH)], 1999 (s), 1947 (vs) [ν(CO)]. C$_{17}$H$_{22}$FeO$_3$Si$_2$ (386.38): calcd. C 52.85, H 5.74; found C 52.17, H 5.78.

12. Treatment of Cp(OC)$_2$Fe−SiMe$_2$OH (2a) with Me$_2$Si(H)Cl (4a) or *p*Tol(Me)Si(H)Cl (4d) in the Absence of an Auxiliary Base: A solution of Cp(OC)$_2$Fe−SiMe$_2$OH (**2a**, 151 mg, 0.60 mmol) and either Me$_2$Si(H)Cl (**4a**, 300 mg, 3.17 mmol) or *p*Tol(Me)Si(H)Cl (**4d**, 258 mg, 1.51 mmol) in 15 mL of Et$_2$O was stirred at room temperature. After 7 d, conversion into **5a**/**5d** was 70%/10% complete.

13. Bis(μ-1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis[carbonyl(η^5-cyclopentadienyl)hydridoiron(IV)] (6a): A solution of Cp(OC)$_2$Fe−SiMe$_2$OSiMe$_2$H (**5a**, 581 mg, 1.87 mmol) in 40 mL of cyclohexane was irradiated with UV light (quartz lamp TQ 718, 700 W, Hanau) for 7 h. After removal of the solvent in vacuo, the residue was purified by column chromatography (20 × 1 cm, silica gel, 0.063−0.2 mm, 20 °C, cyclohexane/benzene, 2:1). The eluate from the yellow zone was concentrated to dryness, the residue was stirred with 2 mL of ice-cold *n*-pentane, and the precipitate of **6a** separated and dried in vacuo. Yield: 100 mg (19%). White microcrystalline powder. M.p. 126 °C (decomp.). ^{1}H NMR (60 MHz, [D$_6$]benzene): δ = 3.94 (s, 10 H, H$_5$C$_5$), 0.80 (s, 12 H, H$_3$C), 0.65 (s, 12 H, H$_3$C), −13.31 ppm [s, ^2J(HFeSi) = 23.6 Hz, 2 H, HFe]. ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = 212.98 (s, CO), 82.46 (s, C$_5$H$_5$), 13.37 (s, CH$_3$), 12.97 ppm (s, CH$_3$). ^{29}Si{^{1}H} NMR (18 MHz, [D$_6$]benzene): δ = 45.31 ppm (s). IR (cyclohexane): $\tilde{\nu}$ = 1955 cm^{-1} [vs, ν(CO)], 1257 (m), 1247 (m) [ν(SiCH$_3$)], 1070 (s), 1065 (m, sh) [ν$_{\text{as}}$(SiOSi)], 576 (m), 565 (m) [ν$_{\text{s}}$(SiOSi)]. C$_{20}$H$_{36}$Fe$_2$O$_4$Si$_4$ (564.542): calcd. C 42.55, H 6.43; found C 42.24, H 6.50.

14. Bis[μ-1,1-dimethyl-3,3-bis(4-methylphenyl)disiloxane-1,3-diyl]bis[carbonyl(η^5-cyclopentadienyl)hydridoiron(IV)] (6b): The preparation was as described under 13., from Cp(OC)$_2$Fe−SiMe$_2$OSi(*p*Tol)$_2$H (**5b**, 998 mg, 2.16 mmol) in 40 mL of cyclohexane (20 h). Crystallization of **6b** occurred at −78 °C in *n*-pentane. Yield: 90 mg (10%). Beige, microcrystalline powder. M.p. 179 °C (decomp.). ^{1}H NMR (60 MHz, [D$_6$]benzene): δ = 8.01, 7.90 [2 d, $^3J_{\text{HCCH}}$ = 7.7/7.6 Hz, 8 H, H-3/H-5 of H$_4$C$_6$], 7.25, 7.19 [2 d, $^3J_{\text{HCCH}}$ = 7.6/7.7 Hz, 8 H, H-2/H-6 of H$_4$C$_6$], 3.93 (s, 10 H, H$_5$C$_5$), 2.26, 2.19 (2 s, 12 H, H_3CC$_6$H$_4$), 0.70, 0.63 (2 s, 12 H, H$_3$C), −12.54 ppm [s, ^2J(HFeSi) = 24.0 Hz, 2 H, HFe]. ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene): δ = 213.17 (s, CO), 142.97, 142.22 (2 s, C-1 of C$_6$H$_4$), 138.14, 138.03 (2 s, C-4 of C$_6$H$_4$), 135.38, 134.61 (2 s, C-3/C-5 of C$_6$H$_4$), 128.72, 128.37 (2 s, C-2/C-6 of C$_6$H$_4$), 83.99 (s, C$_5$H$_5$), 21.47, 21.43 (2 s, CH$_3$C$_6$H$_4$), 13.57, 13.17 ppm (2 s, CH$_3$Si). ^{29}Si{^{1}H} NMR (18 MHz, [D$_6$]benzene): δ = 46.71 ppm [s, Si(CH$_3$)$_2$], Si(*p*Tol)$_2$ signal not detected. IR (cyclohexane): $\tilde{\nu}$ = 1956 cm^{-1} (vs), 1945 (m, sh) [ν(CO)], 1258 [m, br, ν(SiCH$_3$)], 1051 (s, br), 1020 (m, br) [ν$_{\text{as}}$(SiOSi)], 574 (m), 565 (w) [ν$_{\text{s}}$(SiOSi)]. C$_{44}$H$_{52}$Fe$_2$O$_6$Si$_2$ (868.929): calcd. C 60.82, H 6.03; found C 60.85, H 5.88.

15. X-ray Crystal Structure Determination of 2b: Colourless crystals of **2b** suitable for X-ray diffraction were grown by slow diffusion of *n*-pentane into a benzene solution of **2b** at room temperature. Crystal data: C$_{28}$H$_{44}$Fe$_2$O$_6$Si$_2$, *M* = 644.52, monoclinic, space group *P*2$_1$ (no. 5), *a* = 9.042(10) Å, *b* = 13.941(5) Å, *c* = 13.125(9) Å, β = 104.14(4)°, *V* = 1604.2(22) Å^3, *Z* = 4, $d_{\text{calcd.}}$ = 1.334

g·cm^{-3}, CAD4 diffractometer (Enraf−Nonius), radiation type: Mo-K_{α}, wavelength: $\lambda = 0.71073$ Å, graphite monochromator, crystal size: $0.19 \times 0.10 \times 0.07$ mm, temperature: 293 K, ω/Θ-scan, scale range: $1.60° < \Theta < 22.50°$, $F(000) = 680$, total reflections: 2373, independent reflections: 2211 with $I > 2.0\sigma(I)$, absorption coefficient: $\mu = 1.018$ mm^{-1}, empirical absorption correction ($T_{\mathrm{min.}}/T_{\mathrm{max.}} = 0.8779/0.9978$), structure solution: SHELXS-86[59] by direct methods, structure refinement: SHELXL-93[60] (369 parameters), $R_1 = 0.0293$, $wR_2 = 0.0683$. The positions of the OH hydrogen atoms were located and isotropically refined, while the remaining hydrogen atoms were geometrically positioned and subsequently refined with a riding model. CCDC-158196 contains the supplementary crystallographic data for this compound. 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].

16. X-ray Crystal Structure Determination of 6b: Pale yellow crystals of **6b** suitable for X-ray diffraction were grown by slow diffusion of *n*-pentane into a toluene solution of **6b** at −35 °C. Crystal data: $C_{26}H_{31}FeO_2Si_2$, $M = 487.54$, triclinic, space group: $P\bar{1}$ (no. 2), $a = 8.882(3)$ Å, $b = 9.241(6)$ Å, $c = 15.243(9)$ Å, $\alpha = 87.423(12)°$, $\beta = 79.07(2)°$, $\gamma = 86.49(2)°$, $V = 1225.5(11)$ Å^3, $Z = 2$, $d_{\mathrm{calcd.}} = 1.321$ g·cm^{-3}, CAD4 diffractometer (Enraf−Nonius), radiation type: Mo-K_{α}, wavelength: $\lambda = 0.71073$ Å, graphite monochromator, crystal size: $0.50 \times 0.40 \times 0.20$ mm, temperature: 293 K, ω/Θ-scan, scale range: $2.20° < \Theta < 26.91°$, $F(000) = 514$, total reflections: 5545, independent reflections: 4314 with $I > 2\sigma(I)$, absorption coefficient: $\mu = 0.735$ mm^{-1}, empirical absorption correction ($T_{\mathrm{min}}/T_{\mathrm{max}} = 0.9433/0.9965$), structure solution: SHELXS-86[59] by direct methods, structure refinement: SHELXL-93[60] (371 parameter), $R_1 = 0.0405$, $wR_2 = 0.1189$. The positions of all hydrogen atoms except those of the *p*Tol methyl groups were located and isotropically refined, while the remaining hydrogen atoms were geometrically positioned and subsequently refined with a riding model. In addition, one toluene molecule with a disordered CH_3 group was found in the unit cell. CCDC-158197 contains the supplementary crystallographic data for this compound. 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].

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