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Hydroxysilylene-Bridged Dinuclear Iron Complexes $[Cp(OC)_2Fe]_2Si(X)OH$ (X = H, Cl, OH): Synthesis, Structural Characterization, and Condensation with Chlorodimethylsilane

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The novel bis(ferrio)silanols $[Cp(OC)_2Fe]_2Si(X)OH$ [X = H (**2**), OH (**4**), Cl (**7**)] are obtained via hydrolysis of $[Cp(OC)_2Fe]_2Si(H)Cl$ (**1**) or via oxygenation of the bis(ferrio)hydridosilanes $[Cp(OC)_2Fe]_2Si(H)X$ [X = Cl (**1**), H (**6**)] with dimethyldioxirane. Subsequent condensation reactions with chlorodimethylsilane yield the bis(ferrio)siloxanes $[Cp(OC)_2Fe]_2Si(X)(OSiMe_2H)$ [X = H (**12**), $OSiMe_2H$ (**13**), OH (**15**)]. In an analogous manner the hetero-bismetalated silanol $[Cp(OC)_2Fe][Cp(OC)_2(Me_3P)W]Si(Me)OH$ (**11**) and the disiloxane $[Cp(OC)_2Fe][Cp(OC)_2(Me_3P)W]Si(Me)(OSiMe_2H)$ (**14**) have been prepared. The influence of the transition metal substituents on the chemical and spectroscopic properties of these compounds has been investigated. The X-ray structure analyses of the bis(ferrio)silanol $[Cp(OC)_2Fe]_2Si(H)OH$ and the bis(ferrio)dimethoxysilane $[Cp(OC)_2Fe]_2Si(OCH_3)_2$ (**5**)—generated via methanolysis of $[Cp(OC)_2Fe]_2SiCl_2$ (**3**)—are presented.

Introduction

Transition metal substituted compounds of silicon have drawn great attention in recent years mainly due to their pivotal role in several important catalytic conversions, e.g., hydrosilylation of olefins,[2] dehydrogenative coupling of primary and secondary silanes,[3] or the ring-opening metathesis polymerization of cyclic organodisilanes.[4] Consequently, a huge number of compounds containing a metal−silicon bond have been prepared in the past decades by various synthetic methods, and special attention has been given to the effect of transition metal fragments to the reactivity of the silicon atom.[5] Among the most outstanding findings concerning the "transition metal effect" the significant stabilization of silanols, -diols, and -triols must be pointed out,[6] which makes them attractive precursors for the designed buildup of metallo-siloxanes, including examples with stereogenic silicon and transition metal centers, e.g., $Cp(OC)(Ph_3P)Fe{-}Si(Me)(Ph)OH$.[7]

In most cases the introduction of an Si−OH function into metallo-silanes has been accomplished either by hydrolysis of Si−halogen moieties or by oxygen insertion into Si−H bonds using dimethyldioxirane. Whereas several metallo-silanols $L_nM{-}SiR_{3-n}(OH)_n$ and even metallo-disilanols, e.g., $L_nM{-}SiCl_2Si(OH)_3$ or $L_nM{-}Si(OH)_2SiH_3$, have been prepared mainly with transition metal substituents of the chromium and iron group,[8] the knowledge concerning hydroxysilylene-bridged dinuclear metal complexes is limited to the iron derivatives $[Cp(OC)_2Fe]_2Si(R)OH$ (R = Me, *p*Tol) and $Cp_2(OC)_3Fe_2Si(Mes)(OH)$ (Mes = mesityl).[9] The most important aspect concerning this class of compounds lies mainly in the cumulative electronic effect of the two transition metal substituents attached to one Si atom. This effect

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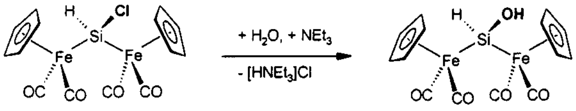
not only can be used to prepare stable bis(metallo)silanols but might also be crucial for the stabilization of the "unusual" silanols of the type $R_2Si(X)OH$ ($X = H$, Cl) containing a silicon-bound hydrogen or a chlorine atom, for which $(tBu)_2SiCl(OH)$ is the only fully characterized example known to date.[10]

Results and Discussion

The novel hydroxysilylene- and bis(hydroxy)silylene-bridged dinuclear iron complexes $[Cp(OC)_2Fe]_2Si(X)OH$ [$X = H$ (**2**), OH (**4**), Cl (**7**)] have been synthesized making use of two different synthetic routes. Hydrolysis of the bis(ferrio)chlorosilane **1** in diethyl ether in the presence of triethylamine as an auxiliary base yields the corresponding bis(ferrio)silanol **2**, which can be obtained as a yellow crystalline solid showing good solubility in polar and aromatic solvents (eq 1).

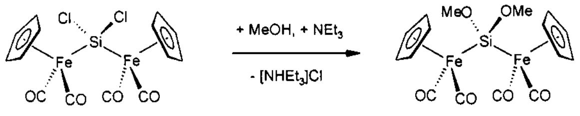


(1)

1 **2**

The bis(ferrio)silanol **2** exhibits no tendency toward self-condensation, obviously a result of the greatly reduced acidity of the Si(OH) group compared to organosilanols originating from the transition metal effect. The high degree of electron transfer from the transition metal substituents to the bridging silicon can also be estimated from the low Si−H stretching frequency (2027 cm^{-1}) as well as from the comparably small $^1J_{SiH}$ coupling constant of 179 Hz, which indicate an electron-rich Si−H bond.[11]

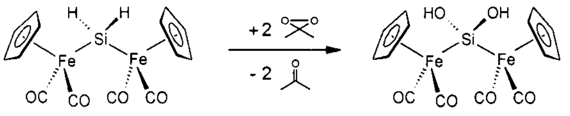
The analogous synthesis of the bis(ferrio)silanediol $[Cp(OC)_2Fe]_2Si(OH)_2$ (**4**) failed due to insufficient reactivity of the starting material $[Cp(OC)_2Fe]_2SiCl_2$ (**3**) in the presence of H_2O/NEt_3. Even after treating **3** for 2 days with KOH/H_2O in THF at 50 °C no Cl/OH exchange could be observed. This is probably a result of the π back-bonding of two Cl substituents to the silicon atom, which strengthens the Si−Cl bonds and reduces the electrophilicity of **3**. However, the methanolysis of **3** can be realized under mild conditions in the presence of triethylamine as an auxiliary base. We assume that in this case the "softer" nucleophilic character of methanol compared to water allows the reaction with **3**. The resulting bis(ferrio)dimethoxysilane **5** is obtained in good yields (77%) as a yellow crystalline solid (eq 2).



(2)

3 **5**

The lack of reactivity of **3** toward hydrolysis prompts as an alternative approach the oxygenation of the bis(ferrio)silane **6** with dimethyldioxirane (DMD). This procedure had proved particularly efficient with electron-rich SiH bonds of mononuclear ferrio-silanes[6] and is expected to be even more productive with respect to the conversion of a SiH unit activated by two transition metal fragments. The oxygenation of **6** was carried out under standard conditions in acetone at −78 °C (eq 3) and monitored IR-spectroscopically by the disappearance of the Si−H absorption ($\tilde{\nu} = 2037$ cm^{-1}) and the simultaneous formation of a broad OH band ($\tilde{\nu} = 3520$ cm^{-1}) within 45 min.

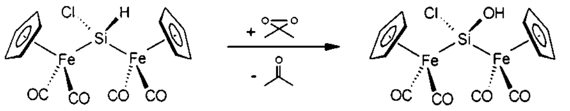


(3)

6 **4**

After removing the solvent in vacuo and washing the residue with *n*-pentane the resulting bis(ferrio)silanediol **4** could be isolated in 75% yield as a light yellow solid showing good solubility in diethyl ether or acetonitrile. The ^{29}Si NMR resonance of **4** can be found at 86.8 ppm and is in good accordance with the downfield shifts typical of other μ_2-silylenediiron complexes.[12] The silanediol **4** shows high stability with respect to self-condensation in solution and in the solid state, characteristic of metal fragment substituted derivatives.

Taking advantage of the stabilizing effect of two iron fragments on Si(OH) units even the bis(metallo)chlorosilanol **7** can be prepared by treating the bis(ferrio)chlorosilane **1** with DMD (eq 4).



(4)

1 **7**

7 was obtained as a light yellow solid in moderate yield (57%) and to our knowledge is the second isolated chlorosilanol (vide supra).[10] Despite the doubled transition metal effect, **7** rapidly decomposes at room temperature into $Cp(OC)_2Fe{-}Cl$ and insoluble silica. We assume **7** to be a highly attractive starting material for the generation of the silanone $[Cp(OC)_2Fe]_2Si{=}O$. Experiments aiming at the generation of this species via dehydrohalogenation of **7** are currently in progress. Silanones have so far only been observed in gas phase or in an argon matrix at low temperatures.[13]

The oxofunctionalization of an SiH bond using DMD also proved successful for the synthesis of the first hetero-bismetalated silanol **11**. The required SiH functional precursor **10** could be prepared from the tungsten-substituted chlorosilane **8** and the sodium metalate **9** (eq 5).

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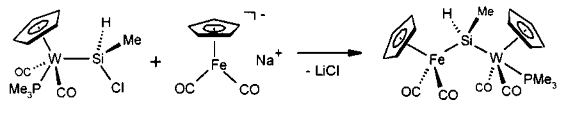
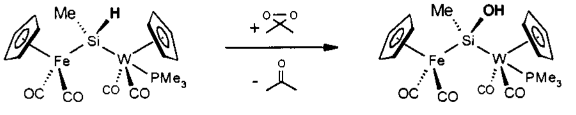


(5)

8 **9** **10**

As byproducts of this metalation reaction, the binuclear complexes $[Cp(OC)_2Fe]_2$ and $[Cp(OC)_2Fe-W(CO)_2(PMe_3)Cp]$ were formed in significant amounts. These could not be separated completely by recrystallization, and therefore **10** was not obtained in analytically pure form. However, further conversion of **10** with DMD produced the iron- and tungsten-substituted silanol **11** (eq 6).



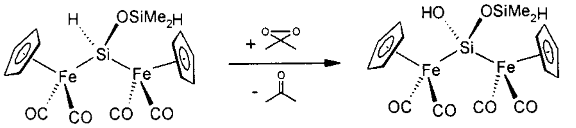
(6)

10 **11**

Pure **11** was isolated as a yellow solid that can be kept at −20 °C for several months. In solution it is stable at room temperature with respect to self-condensation, but decomposes within several days to $[Cp(OC)_2Fe]_2$ and $Cp(OC)_2(Me_3P)W-H$.

Despite their reduced reactivity with respect to self-condensation, the Si(OH) units in the stable bis(ferrio)silanols **2**, **4**, and **11** can be used to carry out the typical condensation reactions of silanols with chlorodimethylsilane. Condensation with chlorodimethylsilane in diethyl ether in the presence of Et_3N yields the bis(metallo)siloxanes **12**−**14**, which are obtained as light brown oils or waxy solids soluble in *n*-pentane or benzene. The ^{29}Si NMR shifts of the Si atoms in γ-position of the transition metal fragments can be found in the typical region of comparable organosiloxanes[11] from 12.5 to −7.9 ppm, whereas the α-Si atoms experience a significant downfield shift (57.7−84.1 ppm).

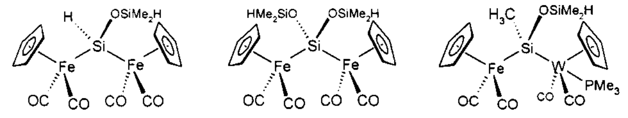
The disiloxanol **15** could be observed as an intermediate in the formation of the bismetalated trisiloxane **13**, but it proved impossible to isolate the monocondensation product **15** since it is always formed in a mixture with **13**. However, pure **15** could be easily prepared by treatment of **12** with DMD at −78 °C in acetone (eq 7).



(7)

12 **15**

The bis(ferrio)disiloxanol **15** can be isolated as a tan solid in excellent yields. The exclusive formation of **15** shows that electrophilic attack of DMD at the metal-activated α-SiH bond is strongly favored. The γ-SiH moiety remains unaffected even when an excess of DMD is employed. This result is in accordance with the pronounced electronic activation of the α-SiH moiety by the electron-releasing metal fragments, which can also be deduced from the low values of the $\tilde{\nu}$(SiH) absorption of 2016 cm^{-1} and $^1J_{SiH}$ coupling constant of 178 Hz. In comparison, the metal effect on the γ-SiH bond is insignificant ($\tilde{\nu}$(SiH) = 2112 cm^{-1}, $^1J_{SiH}$ = 207 Hz).



12 **13** **14**

Figure 1.

The example of **12** demonstrates impressively how the regioselectivity of the electrophilic oxygenation of a metallo-siloxane can be determined by transition metal substituents, especially if these are bonded to the same Si center.

X-ray Structure Determination of $[Cp(OC)_2Fe]_2Si(H)OH$ (2) and $[Cp(OC)_2Fe]_2Si(OMe)_2$ (5). Suitable single crystals of **2** and **5** were obtained by slow evaporation of a saturated solution of the respective compound in diethyl ether. The crystal structures were solved and refined using the ShelX-TL 6.1 program package;[14] hydrogen atoms in both compounds were calculated according to ideal geometry. The $Cp(OC)_2Fe$-fragments of **2** show the typical pseudooctahedral arrangement of the ligands, with the largest angles between the carbonyl groups (96.37° and 93.70°). The coordination around the Si atom shows a significant deviation from the ideal tetrahedral geometry, especially with respect to the angle Fe−Si−Fe of 123.70(2)° involving the iron fragments. This expansion can be explained not only by the repulsion of the two bulky organometallic substituents but also—according to Bent's rule[15]—by the increased contribution of s-orbitals to the hybridization of those Si-valence orbitals directed to the electron-donating $Cp(OC)_2Fe$-substituents. The second key feature of this structure is the Fe−Si bond distance of 2.3359(6) Å [2.3374(6) Å], which is nearly the sum of covalent radii of iron and silicon (2.34 Å). This value is significantly higher than that of the Fe−Si distances observed in mono(ferrio)silanes $CpL_2Fe-SiR_3$ (L = CO, PR_3) (e.g., 2.29 Å in the case of $C_5Me_5(OC)_2Fe-SiH_3$[16]). In the present case the stabilizing d−σ* interaction between iron and silicon[17] is diminished by the competition of two iron substituents on the same Si atom. In contrast, the Si−O bond (1.683 Å) shows no significant elongation. Molecules of **2** are linked to pairs by hydrogen bonds between the Si(OH) moieties of the individual monomers [d(H1O···O1) = 2.197 Å].

In addition, each dimeric unit of **2** is forming weak interactions involving hydrogen of the C_5H_5 ligands and the oxygen of neighboring silanol and carbonyl units, thus resulting in a double-chain arrangement of **2** in the solid state (Figure 3). The interactions of O1−H8, O1B−H5, and O1B−H9 are directed along the double chain, while H5 forms an additonal hydrogen bridge to O2A, which connects the two strains. In the solid state two different conformers of **5** of C_2- and C_1-symmetry are found. The following pairs of substituents adopt a *trans* position when viewed along the Fe−Si axis: CO/Fe, CO/OMe, Cp/OMe in conformer 1 and Cp/Fe, CO/

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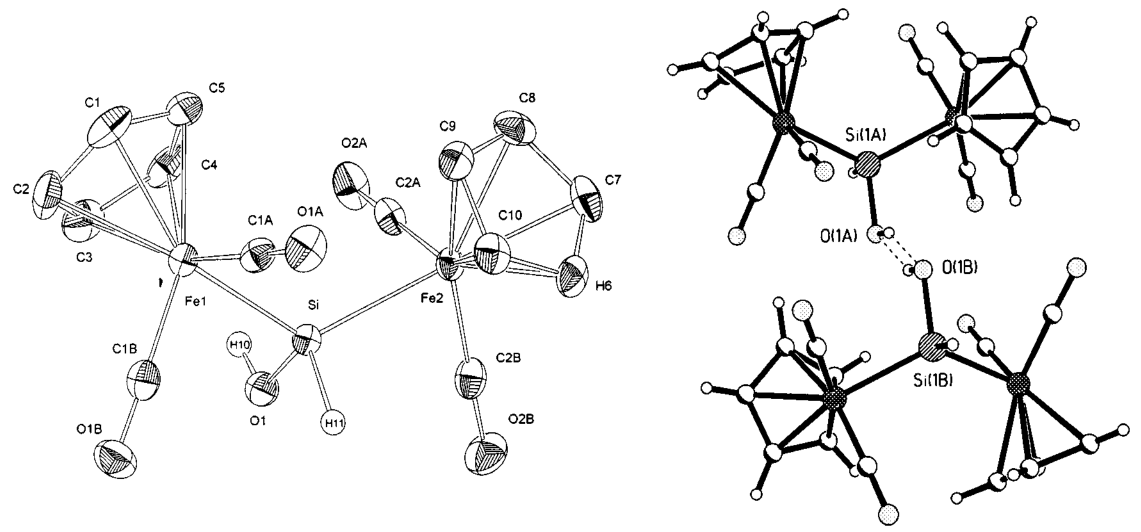

Figure 2. Molecular structure and hydrogen-bonded dimer of $[Cp(OC)_2Fe]_2Si(H)OH$ (**2**). The atoms O1, H1O, and H11 are positionally disordered. Only the major disorder component (90% occupancy) is shown.

Table 1. Crystal Data and Data Collection Parameters for 2 and 5

	$[Cp(OC)_2Fe]_2Si(H)OH$ (**2**)	$[Cp(OC)_2Fe]_2Si(OMe)_2$ (**5**)
empirical formula	$C_{14}H_{12}Fe_2O_5Si$	$C_{16}H_{16}Fe_2O_6Si$
fw	400.03	444.08
temperature	123(2) K	173(2) K
wavelength (Mo Kα)	0.71073 Å	0.71073 Å
cryst syst	monoclinic	triclinic
space group	$P2(1)/n$ (No.14)	$P\bar{1}$ (No.2)
unit cell dimens	$a = 7.6430(1)$ Å	$a = 8.3043(4)$
	$b = 16.9101(2)$ Å	$b = 14.2272(7)$
	$c = 11.6528(1)$ Å	$c = 15.2937(8)$
	$\alpha = 90°$	$\alpha = 91.439(3)°$
	$\beta = 99.307(1)°$	$\beta = 105.325(3)°$
	$\gamma = 90°$	$\gamma = 93.885(3)°$
volume	1486.23(3) $Å^3$	1736.91(15) $Å^3$
Z	4	5
calcd density	1.788 Mg/m^3	1.698 Mg/m^3
abs coeff	2.051 mm^{-1}	1.768 mm^{-1}
F(000)	808	904
cryst size (mm)	0.50 × 0.30 × 0.15	0.2 × 0.25 × 0.1
θ range	$2.96° < \theta < 25.00°$	$1.38° < \theta < 30.60°$
no. of reflns (collected/unique)	27 223/2603	27 157/9667
R(int)	0.0681	0.0273
abs corr	empirical	empirical
no. of data/restraints/params	2603/7/197	9667/0/455
GooF on F^2	1.071	0.978
R Indices $[I>2\sigma(I)]$	R1 = 0.0224	R1 = 0.0567
	wR2 = 0.0581	wR2 = 0.0917
largest diff peak and hole	0.468/−0.400 e/$Å^3$	0.860/−0.448 e/$Å^3$

Table 2. Selected Bond Length (Å) and Angles (deg) of 2

Fe(1)−Si(1)	2.3359(6)	Fe(2)−C(2A)	1.742(2)
Fe(2)−Si(1)	2.3374(6)	Fe(2)−C(2B)	1.751(2)
Fe(1)−Z(cp1)	1.728(1)	C(1A)−O(1A)	1.152(2)
Fe(2)−Z(cp2)	1.730(1)	C(1B)−O(1B)	1.154(3)
Si(1)−O(1)	1.6829(15)	C(2A)−O(2A)	1.156(2)
Fe(1)−C(1B)	1.751(2)	C(2B)−O(2B)	1.148(3)
Fe(1)−C(1A)	1.756(2)	O(1)···(H1O)	2.197
O(1)···H(8)	2.533	O(1B)···H(5)	2.707
O(1B)···H(9)	2.705	(O2A)···H(5)	2.611

Fe(1)−Si(1)−Fe(2)	123.70(2)	O(1B)−C(1B)−Fe(1)	177.97(18)
O(1)−Si(1)−H(11)	105.5	C(2A)−Fe(2)−C(2B)	93.70(9)
C(1B)−Fe(1)−C(1A)	96.37(9)	C(2A)−Fe(2)−Si(1)	86.83(6)
C(1B)−Fe(1)−Si(1)	82.58(7)	C(2B)−Fe(2)−Si(1)	81.66(7)
C(1)−Fe(1)−Si(1)	88.11(6)	O(2A)−C(2A)−Fe(2)	179.13(19)
O(1)−C(1A)−Fe(1)	177.53(18)	O(2B)−C(2B)−Fe(2)	178.15(18)

OMe, CO/OMe in conformer 2. Both conformers display the typical distorted tetrahedral geometry at the Si atoms with large Fe−Si−Fe-bond angles of 119.91(3)° and 121.56(3)°. The Fe−Si bond distances of 2.3372(7) and 2.3494(6) Å are similar to **2** and are elongated in comparison to mono(ferrio)silanes.[16] Two molecules of each conformer are linked via hydrogen bonds to tetrameric units involving the C_5H_5 ligands and the Si-bonded oxygen atoms [d(H13···O10) = 2.547 Å] or the oxygen atoms of the carbonyl groups [d(H20···O6) = 2.517 Å], respectively (Figure 5).

Conclusion

This paper describes the synthesis of four novel homo- and heterobinuclear complexes with Si(H)OH, $Si(OH)_2$, or Si(Cl)OH bridges between the transition metal centers. The introduction of an OH moiety into a μ_2-silylene bridge can be achieved either by hydrolytic Cl/OH conversion or by oxygenation of SiH functional precursors depending on the specific substitution environment of the silicon center. The chemical properties of the bis(metallo)silanols, especially the high stability toward self-condensation, are strongly determined by the electron-releasing effect of the two metal substitu-

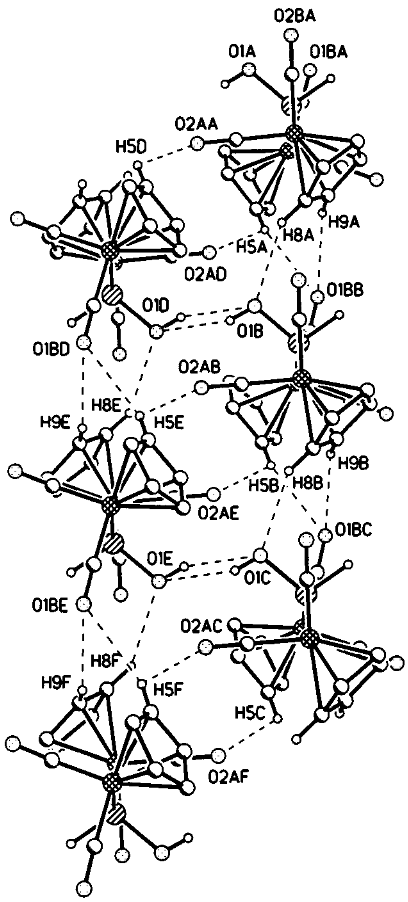

Figure 3. Double-chain structure of **2**.

ents, giving access to rare examples of silanols $R_2Si(X)OH$ (X = H, Cl), with the chlorosilanols representing promising precursors for the generation of transition metal substituted silanones. The bis(ferrio)silanols undergo facile condensation with chlorodimethylsilane to generate the metal-substituted siloxanes $[Cp(OC)_2Fe]_2Si(X)(OSiMe_2H)$ (X = H, OH, $OSiMe_2H$). Due to the influence of the neighboring transition metal, the α-silicon differs considerably both in chemical and in spectroscopic properties from the "normal" γ-silicon. This aspect can be used, as the example of $[Cp(OC)_2Fe]_2Si(H)OSiMe_2H$ demonstrates, for the regioselective oxygenation of the α-SiH function resulting in siloxanol formation. The γ-SiH bond in the new bis(metallo)siloxanes provides numerous possibilities for further modification, including halogenation, oxygenation, or metalation reactions.

Experimental Section

General Procedures. All manipulations were performed in an inert atmosphere of purified and dried nitrogen by using standard Schlenk techniques. Solvents were appropriately dried and purified using standard procedures. NMR spectra were recorded at room temperature on a JEOL JNM-LA 300 spectrometer. All chemical shifts are in ppm referenced to solvent signals (^1H and ^{13}C) or to the external standards H_3PO_4 (^{31}P) and TMS (^{29}Si). IR spectra were recorded using a Perkin-Elmer 283 spectrophotometer. Samples were prepared as solutions in a NaCl cell. The starting materials $[Cp(OC)_2Fe]_2SiHCl$,[12a] $[Cp(OC)_2Fe]_2SiCl_2$,[12a] $[Cp(OC)_2Fe]_2SiH_2$,[18] and $Cp(OC)_2(Me_3P)W-SiMeClH$[19] were prepared according to literature procedures.

$[Cp(OC)_2Fe]_2Si(H)OH$ (2). A solution of $[Cp(OC)_2Fe]_2Si(H)Cl$ (**1**) (480 mg, 1.15 mmol) in 10 mL of diethyl ether was treated with 0.1 mL of NEt_3 and 0.2 mL of H_2O. After stirring for 16 h at room temperature the solution was filtered through a Celite pad and condensed in vacuo to a volume of 1 mL. Adding 10 mL of *n*-pentane and cooling to 0 °C precipitated the product, which was filtered off and dried in vacuo. Light yellow solid: yield 332 mg (72%); mp 53 °C (dec). ^1H NMR (C_6D_6): δ 7.24 ($^1J_{HSi}$ = 179 Hz, 1H, SiH); 4.32 (s, 5H, H_5C_5); 1.83 (s, 1H, OH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 216.42/215.88 (CO); 84.55 (C_5H_5). ^{29}Si NMR (C_6D_6): δ 97.21 (d, $^1J_{SiH}$ = 179 Hz). IR (cyclohexane): $\tilde{\nu}$(OH) = 3662 (w); $\tilde{\nu}$(SiH) = 2027(m); $\tilde{\nu}$(CO) = 1991 (vs), 1952 (vs), 1942 (vs) cm^{-1}. Anal. Calcd for $C_{14}H_{12}Fe_2O_5Si$ (400.04): C 42.04; H 3.02. Found: C 42.10; H 2.96.

$[Cp(OC)_2Fe]_2Si(OCH_3)_2$ (5). A solution of 320 mg (0.707 mmol) of $[Cp(OC)_2Fe]_2SiCl_2$ (**3**) was combined with 0.3 mL (2.16 mmol) of NEt_3 and 5 mL of methanol. After stirring for 24 h at 20 °C the solution was filtered through a Celite pad and condensed in vacuo. The remaining brown residue was redissolved in 1 mL of diethyl ether. Solid **5** was precipitated by dropwise additon of *n*-pentane at 0 °C. Yellow microcrystalline solid: yield 241 mg (77%); mp 57 °C (dec). ^1H NMR (C_6D_6): δ 4.41 (s, 10H, H_5C_5); 3.64 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 216.14 (CO); 84.43 (C_5H_5); 51.97 (CH_3). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 92.43. IR (cyclohexane): $\tilde{\nu}$(CO) = 2004 (m), 1993 (vs), 1945 (vs) cm^{-1}. Anal. Calcd for $C_{16}H_{16}Fe_2O_6Si$ (444.08): C 43.28; H 3.63. Found: C 42.97; H 3.88.

$[Cp(OC)_2Fe]_2Si(OH)_2$ (4). A solution of 640 mg (1.66 mmol) of $[Cp(OC)_2Fe]_2SiH_2$ (**6**) was combined at −78 °C with 50 mL of a 0.076 M solution (3.80 mmol) of dimethyldioxirane in acetone. After 45 min the solvent was evaporated in vacuo and the remaining residue was washed twice with 5 mL of *n*-pentane. Yellow solid: yield 540 mg (83%); mp 62 °C (dec). ^1H NMR (CD_3CN): δ 4.92 (s, 10 H, C_5H_5); 4.08 (s, 2 H, OH). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 217.2 (CO); 118.6 (C_5H_5). $^{29}Si\{^1H\}$ NMR (CD_3CN): δ 86.8. IR (acetonitrile): $\tilde{\nu}$(OH) = 3520 (br); $\tilde{\nu}$(CO) = 1996 (s), 1983 (vs), 1932 (vs) cm^{-1}. Anal. Calcd for $C_{14}H_{12}Fe_2O_6Si$ (392.0): C 40.42; H 2.91. Found: C 39.96; H 2.83.

$[Cp(OC)_2Fe]_2Si(Cl)OH$ (**7**). A solution of 360 mg (0.86 mmol) of $[Cp(OC)_2Fe]_2Si(H)Cl$ (**1**) in 5 mL of acetone was treated at −78 °C with 11 mL of a 0.08 M solution of DMD in acetone. After stirring for 1 h the solution was condensed in vacuo to 1 mL. Addition of 5 mL of *n*-pentane precipitated solid **7**, which was filtered off, washed with 5 mL of cold *n*-pentane, and dried in vacuo. Light yellow solid: yield 212 mg (57%); mp 44 °C (dec). ^1H NMR (C_6D_6): δ 4.32 (s, 10 H, C_5H_5); 3.12 (s, br, 1 H, OH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 215.36, 215.24 (CO); 85.26 (C_5H_5). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 120.51. IR (cyclohexane): $\tilde{\nu}$(OH) = 3640 (w); $\tilde{\nu}$(CO) = 2002 (s), 1996 (vs) 1955 (vs) cm^{-1}. Anal. Calcd for $C_{14}H_{11}ClFe_2O_5Si$ (434.47): C 38.70; H 2.55. Found: C 37.42; H 2.98.

$[Cp(OC)_2Fe][Cp(OC)_2(Me_3P)W]Si(Me)H$ (10). A solution of 692 mg (1.502 mmol) of $Cp(OC)_2(Me_3P)W-SiMeClH$ (**8**) was added to a suspension of 300 mg (1.50 mmol) of $Na[Fe(CO)_2Cp]$ (**9**) in 10 mL of cyclohexane. After stirring for 48 h the solution was filtered and condensed in vacuo to 3 mL. Then 10 mL of *n*-pentane was added and the solution was cooled to 0 °C. A light brown solid precipitated which contained **10** and 30−40% of $[Cp(OC)_2Fe]_2$ and $Cp(OC)_2(Me_3P)WH$. By recrystallizing several times from toluene/*n*-pentane at −78 °C some of the impurities could be removed. Yield: 337 mg, light brown solid. ^1H NMR (C_6D_6): δ 5.58 (q, $^3J_{HSiCH}$ = 4.0 Hz, 1H, SiH); 4.77 (d, 5H, $^3J_{HCWP}$ = 3.3 Hz, C_5H_5W); 4.54 (s, 5H, C_5H_5Fe); 1.54 (d, $^3J_{HCSiH}$ = 3.8 Hz, 3H, CH_3Si); 1.14 (d, $^2J_{HCP}$ = 9.4 Hz, 9H, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 226.52 (d, $^2J_{CWP}$ = 17.6

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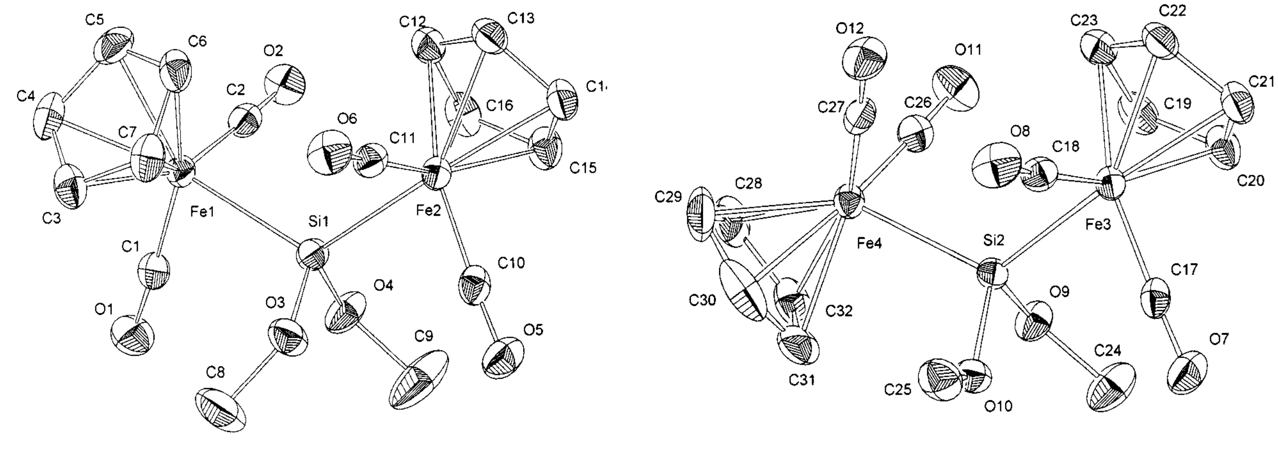

Conformer 1 (C_2-symmetry) Conformer 2 (C_1-symmetry)

Figure 4. ORTEP plots of different conformers of $[Cp(OC)_2Fe]_2Si(OCH_3)_2$ (**5**).

Table 3. Selected Bond Lengths (Å) and Angles (deg) of 5

conformer 1		conformer 2	
Fe(1)−Si(1)	2.3372(7)	Fe(3)−Si(2)	2.3494(6)
Fe(2)−Si(1)	2.3409(7)	Fe(4)−Si(2)	2.3520(7)
O(3)−Si(1)	1.6731(16)	O(9)−Si(2)	1.6659(15)
O(4)−Si(1)	1.6626(16)	O(10)−Si(2)	1.6728(15)
Fe(1)−Si(1)−Fe(2)	119.91(3)	Fe(3)−Si(2)−Fe(4)	121.56(3)
O(4)−Si(1)−O(3)	106.74(9)	O(9)−Si(2)−O(10)	100.37(8)
O(3)−Si(1)−Fe(1)	110.14(6)	O(9)−Si(2)−Fe(3)	110.58(6)
O(3)−Si(1)−Fe(2)	104.86(6)	O(9)−Si(2)−Fe(4)	103.43(6)
C(11)−Fe(2)−C(10)	93.40(10)	C(18)−Fe(3)−C(17)	94.24(10)
C(2)−Fe(1)−C(1)	92.01(10)	C(26)−Fe(4)−C(27)	94.10(10)

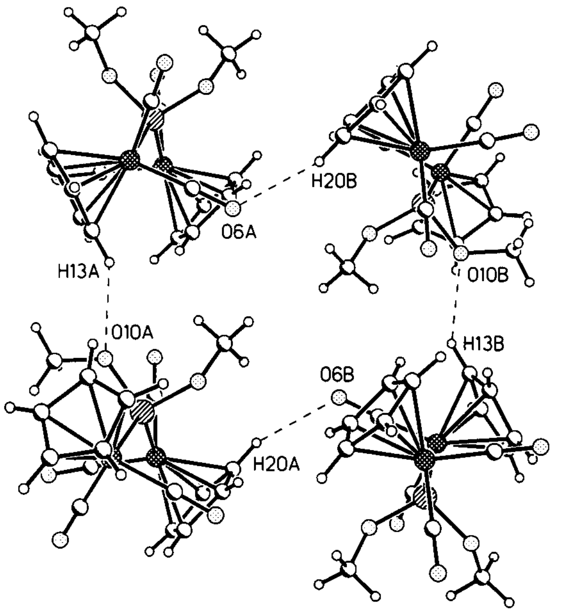

Figure 5. Tetrameric unit of **5**.

Hz, WCO); 224.88 (d, $^2J_{CWP}$ = 18.0 Hz, WCO); 217.96, 217.67 (s, FeCO); 89.25 (s, C_5H_5W); 84.19 (s, C_5H_5Fe); 21.08 (d, $^1J_{CP}$ = 34.5 Hz, CH_3P); 10.48 ppm (s, CH_3Si). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −12.54 ppm ($^1J_{PW}$ = 272.2 Hz). ^{29}Si NMR (C_6D_6): δ 27.40 ppm (d, $^2J_{SiWP}$ = 14.2 Hz). IR (cyclohexane): $\tilde{\nu}$(SiH) = 2040 (w) cm^{-1}, $\tilde{\nu}$(FeCO) = 1989 (s), 1942 (w), $\tilde{\nu}$(WCO) = 1869 (s), 1829 (m) cm^{-1}.

$[Cp(OC)_2Fe][Cp(OC)_2(Me_3P)W]Si(Me)OH$ (11). To a solution of 270 mg of **10** in 10 mL of acetone was added 2.8 mL of a 0.08 M solution (0.224 mmol) of DMD in acetone at −78 °C. After stirring for 1 h the solvent was removed in vacuo and the remaining residue was redissolved in 5 mL of toluene. The solution was filtered, treated with 10 mL of *n*-pentane, and cooled to −78 °C. A yellow solid precipitated, which was filtered from the solution, washed with 5 mL of *n*-pentane, and dried in vacuo. Yield: 110 mg (0.178 mmol), yellow microcrystalline solid; mp 46 °C (dec). ^1H NMR (C_6D_6): δ 4.86 (d, $^3J_{HCWP}$ = 1.0 Hz, 5 H, WC_5H_5); 4.57 (s, 5 H, FeC_5H_5) 2.48 (s, 1 H, OH); 1.78 (s, 3 H, $SiCH_3$); 1.10 (d, $^2J_{HCP}$ = 9.3 Hz, 9 H, PCH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −11.10 ($^1J_{PW}$ = 269.4 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 227.66 (d, $^2J_{CWP}$ = 17.6 Hz, W−CO); 226.01 (d, $^2J_{CWP}$ = 18.0 Hz, W−CO); 217.90, 217.81 (s, Fe−CO); 89.84 (s, WC_5H_5); 84.23 (s, FeC_5H_5); 20.75 (d, $^1J_{CP}$ = 19.7 Hz, PCH_3); 14.24 (s, $SiCH_3$). IR (benzene): $\tilde{\nu}$(OH) = 3623 (w) cm^{-1}, $\tilde{\nu}$(CO) = 1988 (s), 1930 (s), 1902 (m), 1862 (m), 1818 (vs), 1808 (vs) cm^{-1}.

$[Cp(OC)_2Fe]_2Si(H)(OSiMe_2H)$ (12). $ClSiMe_2H$ (307 mg, 3.21 mmol) and 324 mg (3.21 mmol) of Et_3N were added to a solution of 856 mg (2.14 mmol) of $[Cp(OC)_2Fe]_2SiH(OH)$ (**2**) in 20 mL of Et_2O. After stirring for 2 h at 20 °C the solution was filtered over Celite and condensed in vacuo, leaving a residue of pure **12**. Light brown oil: yield 914 mg (93%). ^1H NMR (C_6D_6): δ 7.30 (s, $^1J_{SiH}$ = 178.6 Hz, 1 H, FeSiH); 5.10 (sept, $^3J_{HCSiH}$ = 2.8 Hz, $^1J_{SiH}$ = 208.5 Hz, 1 H, $OSi(CH_3)_2H$); 4.38 (s, 10 H, C_5H_5); 0.37 (d, $^3J_{HCSiH}$ = 2.8 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 215.77 (s, CO); 84.60 (s, C_5H_5); 0.44 (s, CH_3). ^{29}Si NMR (C_6D_6): δ 84.10 (d, $^1J_{SiH}$ = 178.3 Hz, FeSiH); −7.90 (d, $^1J_{SiH}$ = 208.5 Hz, $OSiMe_2H$). IR (cyclohexane): $\tilde{\nu}$(SiH) = 2112 (w, br), 2016 (m); $\tilde{\nu}$(CO) = 1990 (br, s), 1953 (s), 1943 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{18}Fe_2O_5Si_2$ (458.18): C 41.94; H 3.96. Found: C 41.68; H 4.15.

$[Cp(OC)_2Fe]_2Si(OSiMe_2H)_2$ (13). A solution of 243 mg (0.620 mmol) of $[Cp(OC)_2Fe]_2Si(OH)_2$ (**4**) in 20 mL of Et_2O was combined at 20 °C with 291 mg (2.88 mmol) of Et_3N and 348 mg (3.64 mmol) of $ClSiMe_2H$. After stirring for 20 h all volatiles were removed in vacuo and the remaining residue was redissolved in 10 mL of *n*-pentane. The solution was filtered over Celite and condensed in vacuo, leaving a residue of **13**. Orange-brown oil: yield 289 mg (88%). ^1H NMR (C_6D_6): δ 5.21 (sept, $^3J_{HSiCH}$ = 2.8 Hz,$^1J_{HSi}$ = 201.3 Hz, 2H, SiH); 4.39 (s, 10 H, C_5H_5); 0.41 (d, $^3J_{HCSiH}$ = 2.8 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 216.2 (CO); 84.7 (C_5H_5); 0.84 (CH_3). $^{29}Si\{^1H\}$ NMR (C_6D_6): 57.7 (SiFe); −11.2 (SiH). IR (*n*-pentane): $\tilde{\nu}$(SiH) = 2132 (w); $\tilde{\nu}$(CO) = 2004 (s), 1991 (vs), 1943 (vs) cm^{-1}. Anal. Calcd for $C_{18}H_{24}Fe_2O_6Si_3$ (532.34): C 40.61; H 4.54. Found: C 39.35; H 4.74.

$[Cp(OC)_2Fe][Cp(OC)_2(PMe_3)W]Si(Me)(OSiMe_2H)$ (14). A solution of 110 mg (0.178 mmol) of **11** in 10 mL of diethyl ether was treated at room temperature with 210 mg (2.16 mmol) of triethylamine and 170 mg (0.178 mmol) of chlorodimethylsilane. After stirring for 2 h all volatiles were removed in vacuo and the remaining oily residue was dissolved in 10 mL of *n*-pentane. The solution was filtered through Celite and condensed in vacuo. Yield: 163 mg (92%), brown oil. ^{1}H NMR (C_6D_6): δ 5.39 (sept, $^3J_{HSiCH} = 2.5$ Hz, 1 H, SiH); 4.93 (d, $^3J_{HCWP}$ = 1.1 Hz, 5 H, WC_5H_5); 4.60 (s, 5 H, FeC_5H_5); 1.80 (s, 3 H, $WSiCH_3$); 1.11 (d, $^2J_{HCP} = 9.4$ Hz, 9 H, PCH_3); 0.53 ppm (d, $^3J_{HSiCH} = 2.5$ Hz, 6 H, $SiCH_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ − 10.42 ($^1J_{PW} = 264.4$ Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 227.59 (d, $^2J_{CWP}$ = 18.1 Hz, W−CO); 226.01 (d, $^2J_{CWP} = 18.3$ Hz, W−CO); 218.15, 217.95 (s, Fe−CO); 89.97 (s, WC_5H_5); 84.23 (s, FeC_5H_5), 20.65 (d, $^1J_{CP} = 34.8$ Hz, PCH_3); 20.19 (s, $WSiCH_3$); 1.09, 1.08 ppm (s, $SiCH_3$). ^{29}Si NMR (C_6D_6): δ 76.92 (d, $^2J_{SiWP} = 15.9$ Hz); 12.51 (s, SiH). IR (*n*-pentane): $\tilde{\nu}$(SiH) = 2120 (br) cm^{-1}, $\tilde{\nu}$(FeCO) = 1990 (s), 1936 (s) cm^{-1}, $\tilde{\nu}$(WCO) = 1897 (m), 1821 (s) cm^{-1}.

[Cp(OC)$_2$Fe]$_2$Si(OH)(OSiMe$_2$H) (15). A 0.04 M solution (16.2 mL, 0.65 mmol) of dimethyldioxirane in acetone was added dropwise to a cooled solution (−78 °C) of 297 mg (0.65 mmol) of [Cp(OC)$_2$Fe]$_2$Si(H)(OSiMe$_2$H) (**12**) in 5 mL of acetone. After the reaction mixture had warmed to room temperature (1 h) the solvent was removed in vacuo. The remaining residue was washed with 5 mL of cold *n*-pentane and dried in vacuo. Tan solid: yield 293 mg (95%); mp 56 °C (dec). ^{1}H NMR (C_6D_6): δ 5.23 (sept, $^3J_{HCSiH} = 2.8$ Hz, $^1J_{SiH} = 201.3$ Hz, 1 H, SiH); 4.37 (s, 10 H, C_5H_5); 2.72 (s, 1H, OH); 0.41 (d, $^3J_{HCSiH}$ = 2.8 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 216.19 (s, CO); 84.64 (s, C_5H_5); 0.88 (s, CH_3). ^{29}Si{^{1}H} NMR (C_6D_6): δ 92.46 (SiFe); −10.60 (SiH). IR (cyclohexane): $\tilde{\nu}$(OH) = 3368 (w, br) cm^{-1}; $\tilde{\nu}$(SiH) = 2114 (w, br); $\tilde{\nu}$(CO) = 2004 (s), 1990 (s), 1942 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{18}Fe_2O_6Si_2$ (474.18): C 40.53; H 3.83. Found: C 40.14; H 3.68.

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Supporting Information Available: Full crystallographic data for the compounds [Cp(OC)$_2$Fe]$_2$Si(H)OH (**2**) and [Cp(OC)$_2$Fe]$_2$Si(OMe)$_2$ (**5**). This material is available free of charge via the Internet at http://pubs.ac.org.

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