Conversion of Ferriosilanes to Ferriosilanols by Selective Oxidation of the SiH Function by Dimethyldioxirane[1]

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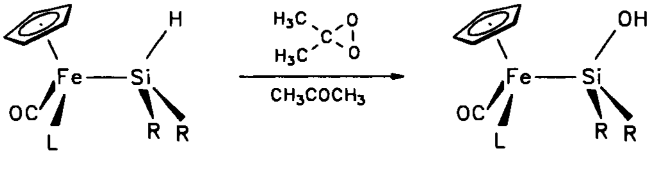
The reaction of ferriohydridosilanes Cp(CO)(L)Fe$-$SiR$_2$H (R = Me, *t*-Bu, Ph, *o*-Tolyl; L = CO, Ph$_3$P) **1a**$-$**e** with dimethyldioxirane (as an acetone solution) leads directly to the corresponding ferriosilanols Cp(CO)(L)Fe$-$SiR$_2$OH **2a**$-$**e** in moderate to excellent yields.

Organosilanols play an important role as intermediates in the technical synthesis of silicones[2]. In contrast to the chemistry of organosilanols, which has been intensively studied[3], there is only limited knowledge on derivatives L$_n$M$-$SiR$_{3-x}$(OH)$_x$ (x = 1$-$3), in which an organometallic fragment is attached to silicon.

In context with systematic studies on exchange reactions at the silicon atom of ferriohalosilanes we found that the ferrio-substituted silanols of the type C$_5$R$_5$(CO)$_2$Fe$-$SiR^{1}R^{2}OH (R = H, Me) can be obtained in good yields by the conventional method of silanol formation, which involves the hydrolysis of the corresponding ferriochlorosilanes in the presence of an auxiliary base[1,4]. This route, however, cannot be applied to ferriochlorosilanes which bear an electron-rich organoiron fragment like Cp(CO)(Ph$_3$P)Fe or sterically demanding organo groups at the silicon atom.

Another potentially convenient way to prepare silanols is by direct oxidation of the corresponding silanes. Recently dimethyldioxirane was shown to be an ideal oxidant for numerous electron-rich as well as electron-poor substrates[5], e.g. the epoxidation of π-systems, oxidation of heteroatoms, and oxygen insertion into C$-$H bonds. Relevant for the present study is the selective transformation of organosilanes into their silanols[6] by dimethyldioxirane without any condensation to disiloxanes. Furthermore, the fact that ruthenium thiolates with electron-rich metal centers can be selectively oxidized by dimethyldioxirane at the sulfur atom to afford the sulfone ligand[7], encouraged us to use this novel oxidant for the synthesis of ferriosilanols from their silanes.

Scheme 1



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Indeed, the reaction of dimethyldioxirane (as an acetone solution) with the ferriohydridosilanes **1a**$-$**e** (Scheme 1) led to the corresponding silanols **2a**$-$**e** in moderate to excellent yields. The results of these transformations are summarized in Table 1, in which the reaction parameters and yields are stated. The preparative procedure consisted of adding rapidly the required amount of oxidant to the dissolved substrates **1a**$-$**e** at low temperature. After removal of the solvents, purification by column chromatography afforded the silanols **2a**$-$**e** in good yields.

Table 1. Hydroxylation of ferriosilanes **1a**$-$**e** with dimethyldioxirane[a,b]

	L	R	Dioxirane [equiv.]	Time [h]	Temp. [°C]	Yield[c,d] (%)
a	CO	Me	1.9	6.0	0	46
b	CO	*t*-Bu	1.9	0.3	-78	98
c	CO	Ph	1.6	2.5	0	86
d	CO	*o*-Tol	1.5	0.5	0	85
e	PPh$_3$	*o*-Tol	1.5	0.5	-78	43

[a] Dimethyldioxirane was used as acetone solution. — [b] All reactions were run under dry N$_2$ (1 at). — [c] Yield after column chromatography. — [d] Conversion >95%.

The ferriosilanols **2a**$-$**e** crystallize from pentane as pale yellow or light brown solids. They show no tendency for self-condensation to the disiloxanes during the preparation nor on standing in solution. The structure assignment of the silanols **2a**$-$**e** rests on the $\tilde{\nu}$-OH vibration at 3700$-$3600 cm^{-1} in the IR spectrum and the signals for this functional group at δ = 1.63$-$2.50 in the ^{1}H-NMR spectrum. From the doubling of the higher $\tilde{\nu}$-CO band the existence of two conformational isomers is evident for **2b**[8]. In the case of the *ortho*-tolyl derivative **2e** two ^{1}H- and ^{13}C-NMR resonances for the diastereotopic methyl groups indicate the chirality of the neighbouring metal center. In addition to the spectral data, satisfactory microanalyses of the new compounds **2b, d, e** support the proposed structures.

For the electron-rich derivatives **1b, e** an increased reactivity towards oxidation by dimethyldioxirane was observed, which allowed the reaction to be carried out even at -78°C (Table 1). This activation of the Si$-$H bond is achieved in two different ways. On one hand, in the case of **1b** the electron density is increased directly at the silicon atom by the $+I$ effect of the *t*-butyl groups, which leads to the highest yield of silanol for all substrates investigated. On the other hand, the same effect can be achieved by increasing the electron density at the metal center as in **1e** by substitution of a carbonyl by a triphenylphosphane ligand, which is characterized by a higher σ-donor/π-acceptor ratio. The oxidation proceeds as fast as in the former case; however, the yield of silanol **2e** is somewhat lower due to partial product loss during column chromatography. Comparison of the dioxirane method (*A*) with the hydrolysis route (*B*) in context with the generation of the silanols **2a, c** demonstrates method *B* to be advantageous for **2a** both with respect to the reaction time and the yield obtained (*A*: 6 h, 46%; *B*: 45 min, 89%), while method *A* is recommended for **2c** (*A*: 2.5 h, 86%; *B*: 72 h, 59%).

In summary, the presented dimethyldioxirane oxidation of ferrio-substituted silanes constitutes a convenient and general way to prepare ferriosilanols, which is complementary to the hydrolysis route in so far as that the formation of ferriosilanols with electron-rich metal centers can be realized for the first time. As **2e** shows that this procedure offers access to derivatives with a chiral iron fragment. Ferriosilanols of this type are of special interest with respect to stereochemically controlled transformations involving the silanol function[9]. The selective oxidation of the Si–H bond without attacking the ligand sphere or oxidizing the metal center provides interesting opportunities for the oxyfunctionalisation of organometallic compounds. Investigations on metallosilanes with other metal fragments, e.g. $Cp(CO)_2(L)M$ (M = Cr, Mo, W; L = CO, Me_3P) are in progress[10].

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Experimental

Instrumentation and Materials: Melting points: Du Pont Thermal Analyser (DSC Cell). – IR: Perkin-Elmer 283. – ^1H and ^{13}C NMR: Bruker WM 200 (200 MHz) or Bruker AMX 400 (400 MHz); chemical shifts refer to TMS. – ^{31}P NMR: Bruker AMX 400 (400 MHz); chemical shifts refer to external 85% H_3PO_4. – All solvents were purified and dried by standard literature procedures. – The substrates **1a, c, d** were prepared according to literature procedures[8]. Compound **1b** (m.p. 132°C) was obtained by the reaction of $Cp(CO_2)FeCH_3$ with $H_2Si(t\text{-}Bu)_2$ in pentane under elimination of methane. Substrate **1e** (m.p. 101°C) was prepared by UV irradiation of **1d** in cyclohexane in the presence of PPh_3. Dimethyldioxirane (as an acetone solution) was prepared according to the published procedure[11] and dried two days over molecular sieves (4 Å) at –20°C before use. – All reactions were carried out under N_2 (1 at).

General Procedure for the Oxidation of Ferriosilanes **1a–e** *by Dimethyldioxirane:* An acetone solution of dimethyldioxirane (1.2 equivalent) was added rapidly to a solution of the ferriosilanes **1a–e** in the appropriate solvent (cf. below) at the temperature specified (Table 1). The reaction mixture was stirred at this temperature until total consumption of the oxidant (negative KI test). For complete conversion of the substrate, the required amount of dimethyldioxirane (usually an excess) was added at the same temperature and progress of the reaction was monitored by TLC or IR. After filtration over Celite, the solvent was removed (–10°C, 0.01 Torr) and the residue purified by column chromatography.

Cp(CO)₂Fe–Si(Me)₂OH (**2a**: According to the general procedure, 98.0 mg (46%) of **2a** were obtained as a brown oil after column chromatography [silica gel, petroleum ether (50–60°C)/AcOEt (10:3), column 50 × 2 cm] by employing 200 mg (0.790 mmol) of **1a** dissolved in 5 ml of acetone at 0°C and a total of 25 ml of a 0.060 M (1.50 mmol) dimethyldioxirane solution. Precipitation with pentane afforded **2a** as a beige, waxy solid, m.p. 43–45°C. – IR (Cyclohexane): $\tilde{\nu}$ = 3688 (w, br, OH) cm^{-1}, 1999 (s, CO), 1952 (s, CO). – ^1H NMR (200 MHz, C_6D_6): δ = 0.65 (s, 6H, CH_3), 2.08 (s, 1H, SiOH), 4.32 (s, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ = 10.6 (CH_3), 83.6 (C_5H_5), 215.7 (CO).

Cp(CO)₂Fe–Si(t-Bu)₂OH (**2b**): According to the general procedure, 223 mg (98%) of **2b** were obtained as a brown oil after column chromatography [silylated silica gel, cyclohexane/toluene 20:1), column 10 × 1 cm] by employing 216 mg (0.680 mmol) of **1d** dissolved in 1 ml of acetone at –78°C and a total of 14.9 ml of a 0.086 M (1.28 mmol) dimethyldioxirane solution. Precipitation with pentane afforded **2b** as a beige powder, m.p. 102°C. – IR (CH_2Cl_2): $\tilde{\nu}$ = 3696 (w, br, OH) cm^{-1}, 2000 (s, CO), 1997 (s, CO), 1949 (vs, CO). – ^1H NMR (400 MHz, C_6D_6): δ = 1.13 (s, 18H, CH_3), 1.63 (s, 1H, SiOH), 4.31 (s, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 30.4 [$C(CH_3)_3$], 30.7 (CH_3), 82.3 (C_5H_5), 216.11 (CO).

$C_{15}H_{20}FeSiO_3$ (336.3) Calcd. C 53.57 H 7.19
Found C 53.75 H 7.47

Cp(CO)₂Fe–Si(Ph)₂OH (**2c**): According to the general procedure, 90.0 mg (86%) of **2c** were obtained as a red-brown oil after column chromatography [silica gel, petroleum ether (50–60°C)/AcOEt (10:3), column 50 × 2 cm] by employing 100 mg (0.280 mmol) of **1c** dissolved in 2.5 ml of acetone at 0°C and a total of 7.7 ml of a 0.060 M (0.460 mmol) dimethyldioxirane solution. Precipitation with pentane afforded **2c** as a beige powder, m.p. 99°C. – IR (Cyclohexane): $\tilde{\nu}$ = 3600 (w, br, SiOH) cm^{-1}, 2000 (s, CO), 1952 (vs, CO). – ^1H NMR (200 MHz, C_6D_6): δ = 2.50 (s, 1H, SiOH), 4.15 (s, 5H, C_5H_5), 7.10–7.87 (m, 10H, C_6H_5). – $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ = 84.4 (C_5H_5), 128.0 (*m*-C aromatic), 128.8 (*p*-C aromatic), 133.8 (*o*-C aromatic), 145.2 (*i*-C aromatic), 215.3 (CO).

Cp(CO)₂Fe–Si(o-Tol)₂OH (**2d**): According to the general procedure, 87.0 mg (82%) of **2d** were obtained as a brown oil after column chromatography [silica gel, petroleum ether (50–60°C)/AcOEt (6:1), column 50 × 2 cm] by employing 100 mg (0.260 mmol) of **1d** dissolved in 1 ml of acetone at 0°C and a total of 5.1 ml of a 0.075 M (0.380 mmol) dimethyldioxirane solution. Precipitation with toluene/pentane afforded **2d** as beige cubes, m.p. 105°C. – IR (CH_2Cl_2): $\tilde{\nu}$ = 3660 (w, br, OH) cm^{-1}, 2010 (s, CO), 1950 (s, CO). – ^1H NMR (200 MHz, C_6D_6): δ = 1.82 (s, 1H, SiOH), 2.36 (s, 6H, CH_3), 4.05 (s, 5H, C_5H_5), 7.10–7.15 (m, 6H, aromatic H), 7.68–7.72 (m, 2H, aromatic H). – $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ = 23.2 (CH_3), 84.6 (C_5H_5), 125.1, 129.1, 130.7, 135.4, 142.7, and 144.0 (*i*-C-CH_3 and *i*-C-Si), 216.0 (CO).

$C_{21}H_{20}FeSiO_3$ (404.3) Calcd. C 62.38 H 4.99
Found C 62.32 H 4.80

Cp(CO)(PPh₃)Fe–Si(o-Tol)₂OH (**2e**): According to the general procedure, 85.0 mg (43%) of **2e** were obtained as a yellow oil after column chromatography [silylated silica gel, cyclohexane/toluene (1:5), column 8 × 1 cm] by employing 194 mg (0.310 mmol) of **1e** dissolved in 10 ml of CH_2Cl_2 at –78°C and a total of 6.9 ml of a 0.067 M (0.470 mmol) dimethyldioxirane solution. Precipitation with pentane afforded **2e** as a yellow powder, mp. 96°C. – IR (CH_2Cl_2): $\tilde{\nu}$ = 3649 (w, br, OH) cm^{-1}, 1921 (s, CO). – ^1H NMR (200 MHz, C_6D_6): δ = 2.10 (s, br, 1H, OH), 2.34 (s, 3H, CH_3), 2.67 (s, 3H, CH_3), 4.24 (s, 5H, C_5H_5), 6.95–7.49 (m, 21H, aromatic H), 7.68–7.72 (m, 2H, aromatic H). – $^{13}C\{^1H\}$ NMR (100 MHz,

C_6D_6): δ = 23.7 (CH_3), 23.8 (CH_3), 84.0 (C_5H_5), 124.3, 124.5, 129.5, 129.6, 130.6, 130.7, 135.0, 137.8 (SiC_6H_4), 143.2 and 143.5 and 146.8 and 147.1 (*i*-C-CH_3 and *i*-C-Si), 128.0 (d, J_{PC} = 23.1 Hz), 128.5 (d, J_{PC} = 22.9 Hz), 133.8 (d, J_{PC} = 9.7 Hz, *p*-C aromatic) 138.9 (d, J_{PC} = 45.0 Hz, *i*-C aromatic) (PC_6H_5), 220.9 (d, J_{PFeC} = 30.5 Hz, CO). – ^{31}P NMR (162 MHz, C_6D_6): δ = 76.1 (s).

$C_{38}H_{35}FeO_2PSi$ (638.8) Calcd. C 71.47 H 5.52
Found C 71.44 H 5.44

CAS Registry Numbers

1a: 32731-69-4 / **1b**: 140149-26-4 / **1c**: 117251-43-1 / **1d**: 140149-27-5 / **1e**: 140149-28-6 / **2a**: 140149-29-7 / **2b**: 140149-30-0 / **2c**: 140149-31-1 / **2d**: 140149-32-2 / **2e**: 140149-33-3 / dimethyldioxirane: 74087-85-7

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