Synthesis and Reactivity of Silicon Transition Metal Complexes, 44[◇]
Metallosilanols and Metallosiloxanes, 17[◇◇]

Regiospecific Hydroxylation of Metallodisilanes of the Iron Group – An Impressive Example of the Transition Metal Effect

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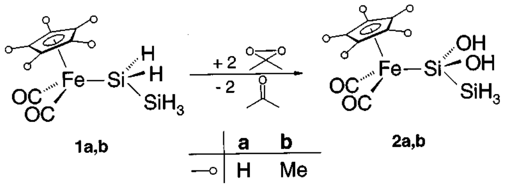
Reaction of the ferriodisilanes $C_5R_5(OC)_2Fe–Si_2H_5$ [R = H (**1a**), Me (**1b**)] with dimethyldioxirane leads to selective insertion of oxygen into the α-Si–H bonds to yield the ferriodihydroxydisilanes $C_5R_5(OC)_2Fe–Si(OH)_2–SiH_3$ [R = H (**2a**), Me (**2b**)]. Another access to yield **2a** is opened by hydrolysis of the dichloro(ferrio)disilane $Cp(OC)_2Fe–SiCl_2–SiH_3$ (**3a**). Treatment of the pentachloro(metallo)disilanes $C_5H_5(OC)_2Fe–Si_2Cl_5$ (**4a**) and $C_5Me_5(OC)_2Ru–Si_2Cl_5$ (**4b**) with water results in regiospecific hydroxylation of the β-silicon atom to generate metallodisilanetriols $C_5R_5(OC)_2M–SiCl_2–Si(OH)_3$ [M = Fe, R = H (**5a**); M = Ru, R = Me (**5b**)]. Controlled condensation of **5b** with $Me_2Si(H)Cl$ leads to the novel rutheniosiloxane $C_5Me_5(OC)_2Ru–SiCl_2–Si(OSiMe_2H)_3$ (**6**).

Introduction

Due to their important role as intermediates in the technical synthesis of silicones[1] organosilanoles have been the subject of extensive studies over several decades[2]. Recently, in context with our studies on the reactivity of functionalized silicon transition metal complexes we have established a new type of silanol containing an Si-bonded transition metal fragment. Access to these metallosilanols is opened by the hydrolysis of halo(metallo)silanes[3] and by the oxygenation of metallosilanes with dimethyldioxirane[4]. Especially the second approach which even allows transformation of metal-bound SiH_3 groups to $Si(OH)_3$ moieties is favored by the strong electron donor capacity of the transition metal fragment which in addition guarantees high stability with respect to condensation. We now focused our interest on metallodisilanes and pentachloro(metallo)disilanes $L_nM-SiX_2-SiX_3$ (X = H, Cl) where two extremely different types of Si−X units are present and which can be regarded as attractive model compounds for the demonstration of the directing effect of transition metal fragments. We have examined this possibility using the metallodisilanes of the iron group [$L_nM = C_5R_5(OC)_2Fe/Ru$ (R = H, Me)] accessible by simple routes[5]. We now report that the transition metal effect can create novel types of disilanyl ligands in which either the α- or the β-silicon atom is fully substituted by hydroxy groups.

Results and Discussion

Treatment of the ferriodisilanes **1a−b** with a solution of dimethyldioxirane in acetone at −78°C results in the formation of the ferriodihydroxydisilanes **2a**, **b**, the first complexes with an $H_3Si-Si(OH)_2$ ligand (Eq. 1).



(1)

The dihydroxydisilanes **2a**, **b** are isolated as pale yellow solids in excellent yields [89% (**2a**), 83% (**2b**)] within hours and are barely soluble in aliphatic or aromatic solvents. The solubility in THF or acetone is reasonable but light-induced decomposition occurs in these solutions within 12−16 h. However, unlimited storage under nitrogen at −20°C is possible. Further hydroxylation of **2a**, **b** with a large excess of dimethyldioxirane does not lead to the expected metallopentahydroxydisilane due to extensive decomposition.

Another approach to **2a**, **b** starting from the ferriodisilanes applies in the first step the regiospecific transformation of **1a**, **b** into the corresponding dichloro(ferrio)disilanes **3a**, **b** by H/Cl exchange with CCl_4 as described recently[6], followed by treatment with water. Hydrolysis of **3a**, **b** in the presence of Et_3N as an auxiliary base takes place only in

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[◇◇] Part 16: S. Möller, H. Jehle, W. Malisch, W. Seelbach in: *Organosilicon Chemistry III: From Molecules to Materials* (Eds.: N. Auner, J. Weis), VCH, Weinheim **1998**, p. 267−270.

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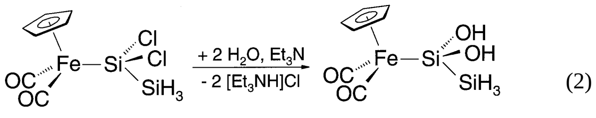
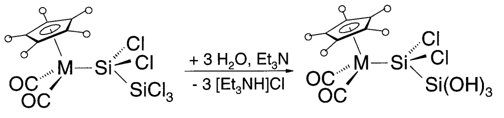
the case of **3a** (Eq. 2). Generated **2a** is isolated after 14 hours in 81% yield.



3a **2a**

The dichloro(ferrio)disilane **3b** does not show an analogous tendency for Cl/OH exchange according to Eq. (2), indicating that the electron-releasing capability of the Cp*(OC)$_2$Fe fragment, which exceeds that of the Cp(OC)$_2$Fe fragment, too strongly reduces the electrophilicity of the α-silicon atom.

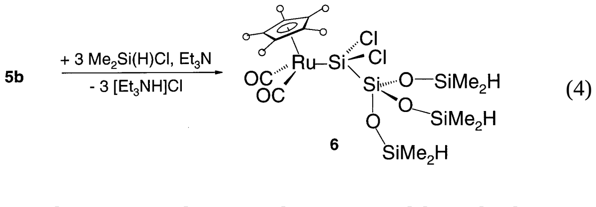
In contrast to the reactions of Eq. (1) in which the metal fragment activates the α-silicon atom with respect to electrophilic attack, nucleophilic exchange activity of this silicon atom is extremely reduced. This fact allows regiospecific hydroxylation in the β-position of the pentachloro(metallo)disilanes **4a**, **b** by base-assisted hydrolysis. Cl/OH exchange is complete within 12 hours at room temperature yielding the dichloro(metallo)trihydroxydisilanes **5a**, **b** as beige, rather air-stable solids (Eq. 3).



4a,b **5a,b** (3)

	a	b
—∘	H	Me
M	Fe	Ru

Remarkable is the stability of the metallodisilanetrioles **5a**, **b** with respect to self-condensation. Apparently, the Si−OH group stabilization by the "transition metal effect" is working even at the β-silicon atom. This property renders **5a**, **b** useful as precursors for selective formation of unusual siloxane arrangements at the β-silicon atom. A first example is realized by base-assisted condensation of **5b** with chlorodimethylsilane to give the novel (ruthenio-silyl)(siloxy)trisiloxane **6** as a deep yellow solid after recrystallization from *n*-pentane at −78°C (yield: 74%) (Eq. 4).



The ruthenio complex **6** is characterized by a high number of Si functionalities which can be used for further hydroxylation or introduction of transition metal fragments by oxidative addition.

In forthcoming publications we will report on these transformations and further regiospecific reactions of metallodisilanes using the "transition metal effect".

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Experimental Section

All operations were performed under purified and dried nitrogen with the Schlenk-type technique. Solvents were dried according to conventional procedures, distilled, and saturated with N_2 prior to use. − NMR: Bruker AMX 400 (400.1 MHz, 100.6 MHz, and 79.5 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively). [D$_6$]Benzene as a solvent (unless otherwise stated): $\delta_H = 7.15$, $\delta_C = 128.0$; [D$_6$]acetone: $\delta_H = 2.04$, $\delta_C = 206, 29.8$; for ^{29}Si ^{2}H-lock internal, rel. to TMS external. − IR: Perkin-Elmer 283. − Melting points: Du Pont 9000 Thermal Analysis System. − Starting materials: $C_5R_5(OC)_2Fe{-}SiH_2{-}SiH_3$ (R = H, Me)[5], $C_5Me_5(OC)_2Ru{-}SiH_2{-}SiH_3$[5].

1. *1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1-dihydroxydisilane* (**2a**)

A) *Dimethyldioxirane Route:* A solution of 150 mg (0.62 mmol) of $Cp(OC)_2Fe{-}Si_2H_5$ (**1a**) in 5 ml of toluene was combined with 16.5 ml (1.24 mmol) of a 1.4 M solution of dimethyldioxirane in acetone at −78°C leading to a rapid change of colour from yellow to orange. The reaction mixture was warmed up to room temperature within 50 min, unsoluble material separated, and volatiles were removed in vacuo. Remaining **2a** was washed with pentane and dried in vacuo. − Yield 146 mg (89%).

B) *Hydrolysis Route:* A solution of 537 mg (1.70 mmol) of $Cp(OC)_2Fe{-}SiCl_2{-}SiH_3$ (**3a**) in 15 ml of Et_2O was combined with 63 mg (3.5 mmol) of H_2O and 353 mg (3.4 mmol) of Et_3N at 0°C and the reaction mixture stirred for 10 h in the dark. Following the work-up procedure of A) **2a** was obtained in 81% yield. − Yellow microcrystalline powder. − M.p. 66°C (decomp.). − $C_7H_{10}FeO_4Si_2$ (264.92): calcd. C 27.32, H 2.49; found C 27.38, H 2.63. − ^{1}H NMR: $\delta = 3.95$ (s, H_5C_5), 3.88 (s, br., 2 H, HO), 3.76 [s, ^1J(SiH) = 196.0 Hz, 3 H, H_3Si]. − ^{13}C NMR: $\delta = 214.6$ (s, CO), 85.07 (s, C_5H_5). − ^{29}Si NMR: $\delta = 99.88$ (s, α-Si), −100.1 (s, β-Si). − IR (toluene): $\tilde{\nu} = 3372$ cm^{-1} [m, br., ν(OH)]; 2135 [m, ν(SiH)]; 2000 (vs), 1953 (vs) [ν(CO)].

2. *1-[Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio]-1,1-dihydroxydisilane* (**2b**): According to 1. A) from 130 mg (0.42 mmol) of **1b** and 11 ml (0.84 mmol) of a 1.3 M solution of dimethyldioxirane in acetone after 80 min. − Yield: 98 mg (89%). − Yellow, microcrystalline powder. − M.p. 65°C (decomp.). − $C_{12}H_{20}FeO_4Si_2$ (340.31): calcd. C 42.35, H 5.92; found C 42.26, H 6.01. − ^{1}H NMR: $\delta = 3.57$ [s, ^1J(SiH) = 182.0 Hz, 3 H, H_3Si], 2.28 (s, br., 2 H, HO), 1.58 [s, 15 H, $(H_3C)_5C_5$]. − ^{13}C NMR: $\delta = 215.9$ (s, CO), 95.70 [s, $C_5(CH_3)_5$], 9.69 [s, $(CH_3)_5C_5$]. − ^{29}Si NMR: $\delta = 96.70$ [s, $Si(OH)_2$], −95.26 (s, SiH_3). − IR (toluene): $\tilde{\nu} = 3479$ cm^{-1} [m, br., ν(OH)]; 2107 [m, ν(SiH)], 1986 (vs), 1931 (vs) [ν(CO)].

3. *1,1-Dichloro-1-dicarbonyl(η^5-cyclopentadienyl)ferrio]-2,2,2-trihydroxydisilane* (**5a**): A solution of 1.01 g (2.46 mmol) of $Cp(OC)_2Fe{-}Si_2Cl_5$ (**4a**) in 50 ml of Et_2O was combined with 132 mg (7.38 mmol) of H_2O and 747 mg (7.38 mmol) of Et_3N. The reaction mixture was stirred for 12 h at room temperature, followed by separation of insoluble material. After removal of volatiles, the remaining residue was washed with 15 ml of *n*-pentane, filtered, and dried in vacuo. − Yield: 740 mg (84%). − Pale yellow, microcrystalline powder. − M.p. 64°C (decomp.). − $C_7H_8Cl_2FeO_5Si_2$ (355.06): calcd. C 23.68, H 2.27; found C 23.81, H 2.39. − ^{1}H

NMR: δ = 4.48 (s, 5 H, H_5C_5), 3.96 (s, br, 3 H, HO). − ^{13}C NMR: δ = 212.9 (s, CO), 84.51 (s, C_5H_5). − IR (THF): $\tilde{\nu}$ = 3481 cm^{-1} [s, br., ν(OH)]; 2000 (vs), 1946 (vs) [ν(CO)].

4. *1,1-Dichloro-1-dicarbonyl(η^5-pentamethylcyclopentadienyl)ruthenio]-2,2,2-trihydroxydisilane* (**5b**): According to 3. from 260 mg (0.49 mmol) of **4b**, 26.5 mg (1.47 mmol) of H_2O and 150 mg (1.47 mmol) of Et_3N in 50 ml of Et_2O after stirring for 12 h. − Yield: 110 mg (47%). − Pale yellow, microcrystalline powder. − M.p. 57°C (decomp.). − $C_{12}H_{18}Cl_2O_5RuSi_2$ (470.42): calcd. C 30.69, H 3.87; found C 30.64, H 3.86. − ^{1}H NMR ([D$_6$]acetone): δ = 2.20 (s, 3 H, HO), 1.92 [s, 15 H, $(H_3C)_5C_5$]. − ^{13}C NMR ([D$_6$]acetone): δ = 204.47 (s, CO), 100.58 [s, $C_5(CH_3)_5$], 10.64 [s, $(CH_3)_5C_5$]. − IR (Et_2O): $\tilde{\nu}$ = 3473 cm^{-1} [s, br., ν(OH)]; 2001 (vs), 1944 (vs) [ν(CO)].

5. *3-{[Dicarbonyl(η^5-pentamethylcyclopentadienyl)ruthenio]-dichlorosilyl}-3-(dimethylsiloxy)-1,1,5,5-tetramethyltrisiloxane* (**6**): 321 mg (3.40 mmol) of $Me_2Si(H)Cl$ and 343 mg (3.39 mmol) of Et_3N in 20 ml of Et_2O were added dropwise to a solution of 402 mg (1.13 mmol) of $C_5Me_5(OC)_2Ru{-}SiCl_2{-}Si(OH)_3$ (**5b**) in 10 ml of Et_2O. After stirring for 8 h, volatiles were removed in vacuo. The residue was extracted with 15 ml of *n*-pentane and **6** crystallized at −78°C. − Yield: 113 mg (74%). − Yellow waxy solid. − M.p.: 77°C (decomp.). − $C_{18}H_{36}Cl_2O_5Si_5Ru$ (644.85): calcd. C 33.52, H 5.63; found C 33.21, H 5.50. − ^{1}H NMR: δ = 5.19 [sept, ^3J(HSiCH) = 2.8 Hz, ^1J(HSi) = 202.5 Hz, 3 H, HSi], 1.86 [s, 15 H, $(H_3C)_5C_5$], 0.51 [d, ^3J(HSiCH) = 2.8 Hz, 18 H, (H_3C)Si]. − ^{13}C NMR: δ = 203.3 (s, CO), 99.7 [s, $C_5(CH_3)_5$] 10.2 [s, $(CH_3)_5C_5$], 1.4 (s, CH_3). − ^{29}Si NMR: δ = −10.14 (s, β-Si), −27.00 (s, δ-Si) [α-silicon signal was not observed]. − IR (toluene): $\tilde{\nu}$ = 2117 cm^{-1} [s, ν(SiH)]; 1995 (vs), 1936 (vs) [ν(CO)].

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