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Polychlorinated metallo-siloxanes of iron, molybdenum and tungsten - structure of 1-[dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1,3,3,3-pentachlorodisiloxane☆

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Abstract

Reaction of the metalates Na[Fe(CO)$_2$C$_5$R$_5$] [R = H (**1a**); Me (**1b**)] and Li[M(CO)$_2$(PMe$_3$)Cp] [M = Mo (**1c**); W (**1d**)] with the chlorosiloxanes Cl$_3$SiOSiCl$_3$ (**2a**) and Cl$_3$SiOSiCl$_2$OSiCl$_3$ (**2b**) leads to the metallo-siloxanes L$_n$M–SiCl$_2$OSiCl$_3$ [L$_n$M = Cp(OC)$_2$Fe (**3a**), Cp(OC)$_2$(Me$_3$P)Mo (**4a**), Cp(OC)$_2$(Me$_3$P)W (**4b**)] and C$_5$R$_5$(OC)$_2$Fe–SiCl$_2$OSiCl$_2$OSiCl$_3$ [(R = H (**3b**), Me (**3c**)], respectively. Cp(OC)$_2$Fe–SiCl$_2$OSiCl$_2$OSiCl$_3$ (**3b**) has been converted to the bis-metalated polychlorinated siloxane Cp(OC)$_2$Fe–SiCl$_2$OSiCl$_2$O-SiCl$_2$Fe(CO)$_2$Cp (**8**) by reaction with a second equivalent of Na[Fe(CO)$_2$Cp] (**1a**). The structure of Cp(OC)$_2$Fe–SiCl$_2$OSiCl$_3$ (**3a**) was obtained by X-ray diffraction.

Keywords: Silicon; Metalation; Metallo-siloxane; Alcoholysis

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1. Introduction

The condensation of organosilanols is a well known key step in the synthesis of siloxanes and silicones [1,2]. Recently, it has been demonstrated that transition metal substituted silanols are easily accessible via hydrolysis of metallo-chlorosilanes [3] and by oxygenation of metallo-silanes with dimethyldioxirane [4] or the catalytic system MTO/UHP [5], provided that the starting material contains a stable metal–silicon bond. The outstanding feature of metallo-silanols is their strongly reduced tendency towards self-condensation compared with organosilanols. This property makes them useful precursors towards controlled, base assisted condensation with diverse chlorosilanes [5–7] to build up siloxane ligands at the metal center. Especially SiH-functionalized metallo-siloxanes, as it has been proved recently, are ideal for the straight forward generation of dinuclear, siloxane-bridged complexes [8], characterized by a metal–silicon bond. This contrasts with the extensively investigated metallasiloxanes, where the metal and the silicon are separated by oxygen [9,10]. In this communication we present the synthesis of multifunctionalized metallo-polychlorosiloxanes via metalation of perchlorinated siloxanes [11]. Additionally, the metalation of isoelectronic methylene bridged silanes is investigated.

☆ Synthesis and reactivity of silicon transition metal complexes, **58**. In addition, metallo-silanols and metallo-siloxanes, **30**. Part 57/29: Ref. [8].

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2. Experimental

2.1. General remarks

NMR: Bruker AMX 400 (400.1, 100.6 and 79.5 MHz for ^{1}H, ^{13}C and ^{29}Si, respectively). [D$_6$]-benzene as a solvent (used unless otherwise stated) $\delta_H = 7.15$, $\delta_C = 128.0$; for ^{29}Si ^{2}H-Lock internal, rel. TMS external. IR: Perkin–Elmer 283. MS: Finnigan MAT SSQ 7000 (EI, 70 eV) unless otherwise stated. Results are presented as follows: m/z (isotope with maximum intensity) (% {total of all isotopic mass values}, [fragment]$^+$). GC: Varian Star 3400cx, column 25 m × 0.22 mm ID; HT8 (SGE, Germany) T-program: 10 min 140–250 °C, 10 min 250 °C; solvent: n-pentane. DTA: Du Pont 9000. All reactions were performed under an atmosphere of purified nitrogen. Solvents were dried according to conventional procedures, distilled and saturated with N$_2$ prior to use. Starting materials: Na[Fe(CO)$_2$Cp] (**1a**) [12], Na[Fe(CO)$_2$Cp*] (**1b**) [13], Li[Mo(CO)$_2$(PMe$_3$)Cp] (**1c**) [14], Li[W(CO)$_2$(PMe$_3$)Cp] (**1d**) [15], Si$_2$OCl$_6$ (**2a**), Si$_3$O$_2$Cl$_8$ (**2b**) and Si$_4$O$_4$Cl$_8$ (**6**) [16–19] were prepared according to the literature.

2.1.1. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1,3,3,3-pentachlorodisiloxane (*3a*)

A suspension of 1.41 g (7.06 mmol) Na[Fe(CO)$_2$Cp] (**1a**) in 50 ml cyclohexane is combined with 2.21 g (7.77 mmol) Si$_2$OCl$_6$ (**2a**). The reaction mixture is stirred for 48 h at ambient temperature under exclusion of light, insoluble material (unreacted metalate and formed NaCl) is separated by filtration and the solvent is removed in vacuum. The remaining residue is washed with 5 ml n-pentane at −78 °C to separate traces of [Cp(OC)$_2$Fe]$_2$ and dried in vacuum. Yield 2.04 g (62%). Beige solid. M.p. (dec.) 63 °C. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 3.95$ ppm (s, 5H, C$_5$H$_5$). ^{13}C{^{1}H}-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 210.6$ (s, CO), 84.9 ppm (s, C$_5$H$_5$). ^{29}Si{^{1}H}-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = 38.5$ (s, α-Si), −59.1 ppm (s, γ-Si). IR (cyclohexane): $\tilde{\nu}$(CO) = 2025 (s), 1987 (vs) cm^{-1}. GC ret. time: 9:09 min. MS: 425.8 (1.0, [M]$^+$), 397.8 (10.5, [M−CO]$^+$), 390.8 (5.7, [M−Cl]$^+$), 369.8 (100.0, [M−2CO]$^+$). C$_7$H$_5$Cl$_5$FeO$_3$Si$_2$ (426.84). Calc. C, 19.72; H, 1.18. Found: C, 20.24; H, 1.32%.

2.1.2. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1,3,3,5,5,5-heptachlorotrisiloxane (*3b*)

According to Section 2.1.1. from 500 mg (2.51 mmol) Na[Fe(CO)$_2$Cp] (**1a**) in 50 ml cyclohexane and 1.04 g (2.60 mmol) Si$_3$O$_2$Cl$_8$ (**2b**). The remaining residue is washed with 10 ml n-pentane each at −78 °C five times and dried in vacuum. Yield 784 mg (58%). Beige microcrystalline solid. M.p. (dec.) 69 °C. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 4.24$ ppm (s, 5H, C$_5$H$_5$). ^{13}C{^{1}H}-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 204.0$ (s, CO), 88.7 ppm (s, C$_5$H$_5$). ^{29}Si{^{1}H}-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta =$ 51.7 (s, α-Si), −43.3 (s, ε-Si), −67.6 ppm (s, γ-Si). IR (cyclohexane): $\tilde{\nu}$(CO) = 2029 (s), 1991 (vs) cm^{-1}. C$_7$H$_5$Cl$_7$FeO$_4$Si$_3$ (541.20). Calc. C, 15.52; H, 0.93. Found: C, 15.91; H, 1.06%.

2.1.3. 1-[Dicarbonyl(η^5-pentamethylcyclopentadienyl)-ferrio]-1,1,3,3,5,5,5-heptachlorotrisiloxane (*3c*)

According to Section 2.1.1 from 1.50 g (5.55 mmol) Na[Fe(CO)$_2$C$_5$Me$_5$] (**1b**) in 50 ml cyclohexane and 2.66 g (6.65 mmol) Si$_3$O$_2$Cl$_8$ (**2b**) after 16 h. Yield 1.90 g (56%). Beige microcrystalline solid. M.p. (dec.) 68 °C. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 1.26$ ppm [s, 15H, (H$_3$C)$_5$C$_5$]. ^{13}C{^{1}H}-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 215.1$ (s, CO), 96.5 [s, $(H_3C)_5\underline{C}_5$], 9.5 ppm [s, $(H_3\underline{C})_5C_5$]. ^{29}Si{^{1}H}-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = 39.6$ (s, α-Si), −42.7 (s, ε-Si), −65.9 ppm (s, γ-Si). IR (cyclohexane): $\tilde{\nu}$(CO) = 2017 (s), 1927 (vs) cm^{-1}. C$_{12}$H$_{15}$Cl$_7$FeO$_4$Si$_3$ (611.52). Calc. C, 23.57; H, 2.47. Found: C, 23.59; H, 2.53%.

2.1.4. 1-[Dicarbonyl(η^5-cyclopentadienyl)-(trimethylphosphine)molybdo-]1,1,3,3,3-pentachlorodisiloxane (*4a*)

According to Section 2.1.1 from 4.40 g (14.68 mmol) Li[Mo(CO)$_2$(PMe$_3$)Cp] (**1c**) in 50 ml benzene and 6.24 g (21.9 mmol) Si$_2$OCl$_6$ (**2a**) after 20 h. Yield 4.40 g (56%). Beige microcrystalline solid. M.p. (dec.) 45 °C. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta =$ 5.12 (s, 5H, C$_5$H$_5$), 1.53 ppm [d, ^2J(PCH) = 9.3 Hz, 9H, (H$_3$C)$_3$P]. ^{13}C{^{1}H}-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 229.9$ (d, ^2J(PMoC) = 26.7 Hz, CO), 91.1 (s, C$_5$H$_5$), 21.1 ppm [d, ^1J(PC) = 32.4 Hz, (H$_3$C)$_3$P]. ^{31}P{^{1}H}-NMR [(D$_6$]-benzene, 121.5 MHz): $\delta = 20.4$ ppm. ^{29}Si{^{1}H}-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = 51.7$ [d, ^2J(PMoSi) = 21.5 Hz, α-Si], −52.14 ppm (s, γ-Si). IR (benzene): $\tilde{\nu}$ (CO) = 1945 (s), 1871 (vs) cm^{-1}. C$_{10}$H$_{14}$Cl$_5$MoO$_3$PSi$_2$ (542.57). Calc. C, 22.14; H, 2.60. Found: C, 22.23; H, 2.85%.

2.1.5. 1-[Dicarbonyl(η^5-cyclopentadienyl)-(trimethylphosphine)tungsto-]1,1,3,3,3-pentachlorodisiloxane (*4b*)

According to Section 2.1.1 from 1.02 g (2.62 mmol) Li[W(CO)$_2$(PMe$_3$)Cp] (**1d**) in 20 ml benzene and 0.82 g (2.89 mmol) Si$_2$OCl$_6$ (**2a**) after 20 h. Yield 572 mg (35%). Beige microcrystalline solid. M.p. (dec.) 72 °C. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 4.58$ (s, 5H, C$_5$H$_5$), 0.91 ppm [d, ^2J(PCH) = 9.7 Hz, 9 H, (H$_3$C)$_3$P]. ^{13}C{^{1}H}-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 223.00$ [d, ^2J(PWC) = 21 Hz, CO], 89.79 (s, C$_5$H$_5$), 20.32 ppm [d, ^1J(PC) = 35.9 Hz, (H$_3$C)$_3$P]. ^{31}P{^{1}H}-NMR [(D$_6$]-benzene, 121.5 MHz): $\delta = 17.35$ ppm [^1J(PW) = 238 Hz]. ^{29}Si{^{1}H}-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta =$ 26.44 [d, ^2J(PWSi) = 20.9 Hz, α-Si], −52.29 ppm (s, γ-Si). IR (benzene): $\tilde{\nu}$(CO) = 1940 (s), 1861 (vs) cm^{-1}. MS:

629.8 (49.3, $[M]^+$), 601.8 (22.0, $[M-CO]^+$), 594.8 (22.0, $[M-Cl]^+$), 573.8 (42.9, $[M-2CO]^+$), 571.8 (100.0, $[M-CO-2Me]^+$). $C_{10}H_{14}Cl_5O_3PSi_2W$ (630.48). Calc. C, 19.05; H, 2.24. Found: C, 19.32; H, 2.47%.

2.1.6. [Dicarbonyl(η^5-cyclopentadienyl)ferrio]-dichlorosilyl-(trichlorosilyl)methane (*5*)

According to Section 2.1.1 from 2.49 g (12.45 mmol) $Na[Fe(CO)_2Cp]$ (**1a**) in 70 ml cyclohexane and 2.49 ml (13.69 mmol) $Cl_3SiCH_2SiCl_3$ after 14 h. Unreacted $Cl_3SiCH_2SiCl_3$ is removed by crystallization of the product from petroleum ether at −78 °C. Yield 2.45 g (46%). Beige microcrystalline solid. M.p. (dec.) 44 °C. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 3.89$ (s, 5H, C_5H_5), 1.68 ppm (s, 2H, H_2C). $^{13}C\{^1H\}$-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 211.6$ (s, CO), 85.1 (s, C_5H_5), 29.6 ppm (s, CH_2). ^{29}Si-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = 80.8$ [t, $^2J(SiCH) = 8.2$ Hz, α-Si], 5.0 ppm [t, $^2J(SiCH) = 12.1$ Hz, γ-Si]. IR (cyclohexane): $\tilde{\nu}(CO) =$ 2015 (s), 1970 (vs) cm^{-1}. $C_8H_7Cl_5FeO_2Si_2$ (424.43). Calc. C, 22.64; H, 1.66. Found: C, 22.57; H, 1.71%.

2.1.7. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,3,3,3′,3′,5,5,-heptachlorocyclotetrasiloxane (*7a*)

According to Section 2.1.1 from 850 mg (4.25 mmol) $Na[Fe(CO)_2Cp]$ (**1a**) in 30 ml cyclohexane and 2.55 g (5.54 mmol) $Si_4O_4Cl_8$ (**6**) after 16 h. Yield 1.61 g (63%). Beige microcrystalline solid. M.p. (dec.) 68 °C. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta =$ 3.95 ppm (s, 5H, C_5H_5). $^{13}C\{^1H\}$-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 210.74$ (s, CO), 84.39 ppm (s, C_5H_5). $^{29}Si\{^1H\}$-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = 15.7$ (s, α-Si), −69.5 (s, γ-Si), −72.3 ppm (s, ε-Si). IR (cyclohexane): $\tilde{\nu}(CO) =$ 2026 (s), 1982 (vs) cm^{-1}. MS: 573.6 (3.0, $[M-CO]^+$), 564.7 (7.1, $[M-Cl]^+$), 545.7 (100.0, $[M-2CO]^+$), 507.7 (22.2, $[M-2CO, -Cl]^+$). $C_7H_5Cl_7FeO_6Si_4$ (601.47). Calc. C, 13.98; H, 0.84. Found: C, 14.37; H, 1.08%.

2.1.8. 1-[Dicarbonyl(η^5-pentamethylcyclopentadienyl)-(trimethylphosphine)molybdo]-1,3,3, 3′,3′,5,5,-heptachlorocyclotetrasiloxane (*7b*)

According to Section 2.1.1 from 304 mg (0.82 mmol) $Na[Mo(CO)_2(PMe_3)C_5Me_5]$ (**1c**) in 20 ml cyclohexane and 433 mg (0.94 mmol) $Si_4O_4Cl_8$ (**6**) after 16 h. Yield 440 mg (54%). Beige microcrystalline solid. M.p. (dec.) 40 °C. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 1.64$ [s, 15H, $(H_3C)_5C_5$], 0.99 ppm [d, $^2J(PCH) = 8.8$ Hz, 9H, $(H_3C)_3P$]. $^{13}C\{^1H\}$-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 236.3$ [d, $^2J(PMoC) = 29.1$ Hz, CO], 103.7 [s, $(H_3C)_5\underline{C}_5$], 18.6 [d, $^1J(PC) = 31.2$ Hz, CH_3P], 11.1 ppm [s, $(\underline{C}H_3)_5C_5$]. $^{31}P\{^1H\}$-NMR [(D$_6$]-benzene, 121.5 MHz): $\delta = 18.6$ ppm. $^{29}Si\{^1H\}$-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = 32.2$ (s, α-Si), −70.1 (s, γ-Si), −72.9 ppm (s, γ-Si). IR (cyclohexane): $\tilde{\nu}(CO) = 1935$ (s), 1862 (vs) cm^{-1}. MS [Varian MAT 112 S (EI, 70 eV)]: 787.7 (49.9, $[M]^+$), 752.8 (100, $[M-Cl]^+$), 731.7 (68.2, $[M-2CO]^+$), 661.8 (94.1, $[M-2CO, -2Cl]^+$). $C_{15}H_{24}Cl_7MoO_6PSi_4$ (787.78). Calc. C, 22.87; H, 3.07. Found: C, 22.56; H, 2.84%.

2.1.9. 1,5-Bis[dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1,3,3,5,5-hexachlorotrisiloxane (*8*)

According to Section 2.1.1 from 320 mg (1.60 mmol) $Na[Fe(CO)_2Cp]$ (**1a**) in 15 ml hexane and 768 mg (1.92 mmol) $Cp(CO)_2Fe-Si_3O_2Cl_7$ (**3b**) after 48 h. Yield 382 mg (35%). Beige microcrystalline solid. M.p. 38 °C. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 4.12$ ppm (s, 5H, H_5C_5). $^{13}C\{^1H\}$-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta =$ 210.9 (s, CO), 84.9 ppm (s, C_5H_5). $^{29}Si\{^1H\}$-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta =$ 36.7 (s, α-Si), −72.84 ppm (s, γ-Si). IR (cyclohexane): $\tilde{\nu}(CO) = 2028$ (vs), 1991 (vs) cm^{-1}. $C_{14}H_{10}Cl_6Fe_2O_6Si_3$ (682.9). Calc. C, 24.62; H, 1.47. Found: C, 25.31; H, 1.77%.

2.1.10. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1-dichloro-3,3,3−trimethoxydisiloxane (*9a*)

A solution of 209 mg (0.49 mmol) $Cp(OC)_2Fe-SiCl_2OSiCl_3$ (**3a**) in 10 ml diethylether is combined with 1 ml Et_3N and 60 μl MeOH (1.47 mmol) at −78 °C. The reaction mixture is stirred for 1 h, warming up to ambient temperature. Insoluble material is separated by filtration and volatiles are removed in vacuum. Yield 167 mg (83%). Brownish oil. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 4.23$ (s, 5H, H_5C_5), 3.56 ppm (s, 9H, OCH_3). $^{13}C\{^1H\}$-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 211.71$ (s, CO), 85.15 (s, C_5H_5), 51.23 ppm (s, OCH_3). $^{29}Si\{^1H\}$-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = 32.74$ (s, α-Si), −87.17 ppm [s, γ-Si]. IR (diethylether): $\tilde{\nu}(CO) = 2028$ (vs), 1980 (vs) cm^{-1}. $C_{10}H_{14}Cl_2FeO_6Si_2$ (413.14). Calc. C, 29.07; H, 3.42. Found: C, 29.72; H, 1.77%.

2.1.11. [Dicarbonyl(η^5-cyclopentadienyl)ferrio]-dichlorosilyl-trimethoxysilyl-methane (*9b*)

According to Section 2.1.10 from 242 mg (0.57 mmol) $Cp(OC)_2Fe-SiCl_2CH_2SiCl_3$ (**5**) in 20 ml toluene, 0.5 ml Et_3N and 69.4 μl (1.71 mmol) MeOH in 14 h at ambient temperature. The resulting residue is washed three times each with 7 ml petroleum ether and dried in vacuum. Yield 160 mg (76%). Brownish solid. M.p. (dec.) 56 °C. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 4.19$ (s, 5H, C_5H_5), 3.45 [s, 9H, OCH_3], 1.22 ppm (s, 2H, H_2C). $^{13}C\{^1H\}$-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 212.4$ (s, CO), 85.1 (s, C_5H_5), 50.4 (s, OCH_3), 17.1 ppm (s, CH_2). ^{29}Si-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = 90.3$ [t, $^2J(SiCH) = 9.6$ Hz, α-Si], −46.4 ppm [dec t, $^2J(SiCH) = 12.8$ Hz, $^3J(SiOCH) = 3.4$ Hz, γ-Si]. IR (cyclohexane): $\tilde{\nu}(CO) = 2014$ (s), 1973 (vs) cm^{-1}. $C_{11}H_{16}Cl_2FeO_5Si_2$ (411.17). Calc. C, 32.13; H, 3.92. Found: C, 31.65; H, 3.98%.

2.1.12. *1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1,3,3,3–pentamethoxydisiloxane (**10a**)*

A solution of 59 mg (0.14 mmol) $Cp(OC)_2Fe-SiCl_2OSi(OMe)_3$ (**9b**) in 5 ml diethylether is combined with 0.5 ml Et_3N and 0.5 ml MeOH and the resulting reaction mixture is stirred 1 h at ambient temperature. Insoluble material is separated by filtration, volatiles are removed in vacuum and the resulting residue is washed with 2 ml *n*-pentane and dried in vacuum. Yield 42 mg (73%). Brownish oil. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 4.38$ (s, 5H, H_5C_5), 3.65 (s, 6H, $FeSiOCH_3$), 3.59 ppm (s, 9H, $SiOSiOCH_3$). $^{13}C\{^1H\}$-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 214.19$ (s, CO), 83.40 (s, C_5H_5), 51.02 (s, $FeSiOCH_3$), 50.33 ppm ($SiOSiOCH_3$). $^{29}Si\{^1H\}$-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = 0.62$ (s, Fe–Si), −86.65 ppm [s, $Si(OCH_3)_3$]. IR (Et_2O): $\tilde{\nu}$(CO) = 2014 (vs), 1961 (vs) cm^{-1}. MS: 376.0 (17.7, $[M-CO]^+$), 373.0 (4.4, $[M-OMe]^+$), 348.0 (100.0, $[M-2CO]^+$), 345.0 (50.0, $[M-CO, -OMe]^+$), 341.0 (16.7, $[M-2OMe]^+$), 316.0 (58.9, $[M-2CO, -OMe]^+$) 314.0 (6.5, $[M-CO, -2OMe]^+$). $C_{12}H_{20}FeO_8Si_2$ (404.30). Calc. C, 35.65; H, 4.99. Found: C, 35.96; H, 5.21%.

2.1.13. *[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-dimethoxysilyl-trimethoxysilyl-methane (**10b**)*

A solution of 154 mg (0.36 mmol) $Cp(OC)_2Fe-SiCl_2CH_2SiCl_3$ (**5**) in 10 ml MeOH is treated with 0.3 ml Et_3N and the resulting reaction mixture is stirred for 10 h at ambient temperature. Insoluble material is separated by filtration, volatiles are removed in vacuum, the resulting residue is washed three times with 7 ml petroluem ether each and dried in vacuum. Yield 92 mg (75%). Brownish oil. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 4.33$ (s, 5H, C_5H_5), 3.51 [s, 6H, $Si(OCH_3)_2$], 3.49 [s, 9H, $Si(OCH_3)_3$], 0.52 ppm (s, 2H, H_2C). $^{13}C\{^1H\}$-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta = 214.9$ (s, CO), 83.7 (s, C_5H_5), 50.6 [s, $Si(OCH_3)_2$], 50.3 [s, $Si(OCH_3)_3$], 5.8 ppm (s, CH_2). ^{29}Si-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = 48.5$ [sept t, ^2J(SiCH) = 9.1 Hz, ^3J(SiOCH) = 4.5 Hz, α-Si], −42.5 ppm [dec t, ^2J(SiCH) = 13.2 Hz, ^3J(SiOCH) = 3.9 Hz, γ-Si]. IR (cyclohexane): $\tilde{\nu}$(CO) = 2000 (s), 1930 (vs) cm^{-1}. $C_{13}H_{22}FeO_7Si_2$ (402.33). Calc. C, 38.81; H, 5.51. Found: C, 38.09; H, 5.40%.

2.1.14. *1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,3,3,3′,3′,5,5–heptamethoxycyclotetrasiloxane (**11**)*

According to Section 2.1.10 from 102 mg (0.17 mmol) $Cp(OC)_2Fe-Si_4O_4Cl_7$ (**7a**) in 10 ml diethylether, 0.5 ml Et_3N and 13.5 μl MeOH (0.34 mmol) at −78 °C after 2 h. NMR-spectra show a mixture of several methanolysis of products. The residue is solved in 10 ml diethylether and the procedure according to Section 2.1.13 is repeated. Yield 58 mg (60%). Brownish oil. ^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): $\delta = 4.37$ (s, 5H, C_5H_5), 3.71 (s, 3H, α-OCH_3), 3.61 (s, 6H, γ-OCH_3), 3.59 (s, 6H, γ-OCH_3), 3.57 (s, 3H, ε-OCH_3), 3.57 ppm (s, 3H, ε-OCH_3). $^{13}C\{^1H\}$-NMR ([D$_6$]-benzene, 75.45 MHz): $\delta =$ 213.84 (s, CO), 83.56 (s, C_5H_5), 51.21 (s, OCH_3), 51.03 (s, OCH_3), 51.02 (s, OCH_3), 50.97 (s, OCH_3), 50.20 ppm (s, OCH_3). $^{29}Si\{^1H\}$-NMR ([D$_6$]-benzene, 59.58 MHz): $\delta = -7.20$ ppm (s, FeSi), −92.50 (s, γ-Si), −94.13 ppm (s, ε-Si). IR (diethylether): $\tilde{\nu}$(CO) = 2009(vs), 1965 (vs) cm^{-1}. MS: 542.0 (1.6, $[M-CO]^+$), 539.0 (3.6, $[M-OMe]^+$), 514.0 (100.0, $[M-2CO]^+$), 512.0 (5.3, $[M-CO, -OMe]^+$), 482.0 (19.6, $[M-2CO, -OMe]^+$), 467.0 (26.2, $[M-2CO, -2OMe]^+$). $C_{14}H_{26}FeO_{13}Si_4$ (570.54). Calc. C, 29.47; H, 4.59. Found: C, 29.62; H, 4.68%.

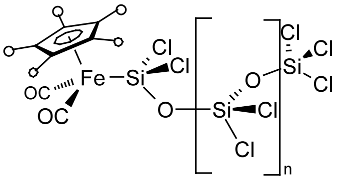
2.1.15. *Crystal structure determination of $Cp(OC)_2Fe-SiCl_2OSiCl_3$ (**3a**)*

Suitable colorless crystals were obtained by slow evaporation of a saturated solution of **3a** in *n*-pentane at 25°C. The data were collected from shockcooled crystals on a BRUKER SMART-APEX diffractometer with D8 goniometer (graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) equipped with a low temperature device in omega-scan mode at 173(2) K [20]. The data was integrated with SAINT [21] and an empirical absorption correction [22] was applied. The structure was solved by direct methods (SHELXS-97) [23] and refined by full-matrix least-squares methods against F^2 (SHELXL-97) [24]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms were calculated by an idealized geometry. Compound **3a**: $C_7H_5Cl_5FeO_3Si$, M = 426.39; triclinic; space group: $P\bar{1}$ (No. 2); $a = 8.6022(19)$ Å, $b = 9.809(2)$ Å, $c = 10.416(2)$ Å; $\alpha = 100.028(4)°$, $\beta = 111.835(18)°$, $\gamma = 97.185(4)°$; $V = 785.8(3)$ Å^3; $Z = 2$; $D_{calc} = 1.802$ g cm^{-3}; crystal size: 0.3 × 0.2 × 0.15 mm^3; μ(Mo–K$_\alpha$) = 1.955 mm^{-1}, scale range: $2.16 < \theta < 25.05°$; total reflections: 13 874; independent reflections: 2782; $R_{int} = 0.0271$; Goodness-of-fit = 1.133, residual electron density: 0.461/−0.280 e·Å^{-3}, $R_1 = 0.0411$, $wR_2 = 0.0920$.

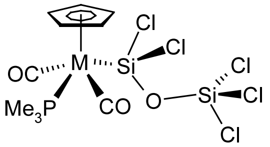
3. Results and discussion

3.1. *Synthesis of polychlorinated metallo-siloxanes*

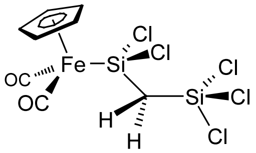
In accordance with the established heterogeneous metalation of chlorosilanes [25], a suspension of the metalates $Na[Fe(CO)_2C_5R_5]$ [R = H (**1a**), Me (**1b**)] and $Li[M(CO)_2PMe_3Cp]$ [M = Mo (**1c**), W (**1d**)] is combined with the chlorosiloxanes $Si_nO_{n-1}Cl_{2n+2}$ [$n = 2$ (**2a**); 3 (**2b**)] in an equimolar ratio. The reaction mixture is stirred at ambient temperature under exclusion of light for 16 to 72 h to give the ferrio-pentachlorodisiloxane (**3a**), ferrio-heptachlorotrisiloxanes (**3b**,**c**) and the tungsten–molybdenum-pentachlorodisiloxanes (**4a**,**b**), respectively, in yields up to 62%. In an analogous manner the methylene bridged-hexachlorosilane $Cl_3Si{-}CH_2{-}SiCl_3$ is converted into the mono-metalated species **5** by reaction with the sodium ferrate (**1a**) in benzene after 20 h.



3	a	b	c
n	0	1	1
-o	H	H	Me



4	a	b
M	Mo	W



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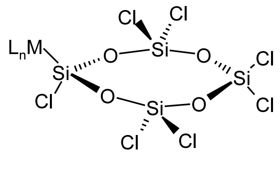
Compounds **3**–**5** are isolated as beige, moisture and air sensitive solids which can be stored under an atmosphere of nitrogen at −20 °C. After 30 days only slight decomposition is observed. The transition metal fragment substitution of one silicon atom is evident by the characteristic low field resonance of the metal bound silicon in the ^{29}Si-NMR spectra data [38.5 (**3a**), 51.7 (**3b**), 51.7 (**4a**), 26.4 ppm (**4b**)], compared with −46.0 ppm for hexachlorodisiloxane (**2a**).

Suitable colorless crystals were obtained by slow evaporation of a saturated solution of **3a** in *n*-pentane at room temperature. The single crystal X-ray diffraction analysis of **3a** reveals a pseudooctahedral coordinated iron atom. The angles C6–Fe1–Si1 and C12–Fe1–Si1 with 86.50 and 87.27°, respectively, are slightly reduced compared to the ideal value of 90°. In contrast, the angle C12–Fe1–C6 is expanded to 94.35°. The angles at the metalated silicon atom involving the metal fragment are widened up to 113.28° (Fe1–Si1–O3), 115.16° (Fe1–Si1–Cl5) and 116.21° (Fe1–Si1–Cl4), while the others are upset to 103.11° (Cl4–Si1–Cl5), 103.36° (Cl4–Si1–O3) and 104.19° (Cl5–Si1–O3). The iron–silicon bond length Fe1–Si1 (221.0 pm) lies in the lower range of this value, indicating an interaction of populated metal d-orbitals with Si–Cl-σ*-orbitals [26]. As a consequence two different Si–O-bond lengths are observed. The metalated silicon atom Si1 has a distance of 164.1 pm to O3 {$[Cp(OC)_2FeSiMeF]_2O$ 160.3 pm [27]}, while the bond length O3–Si2 (156.2 pm) appears significantly shorter ($SiCl_3OSiCl_3$ 159.3 pm [28]). The angle Si1–O3–Si2 (159.16°) can be classified as large ($SiCl_3OSiCl_3$ 146.0° [28]). A *Newman* projection along the Si1–Fe1–bond shows *anti*-position of the $OSiCl_3$-group to the Cp-ligand (Cp_z–Fe1–Si1–O3 179.1°). The bond angles and bond lengths of the $SiCl_3$-group cannot be discussed due to a disorder of the chlorine atoms (Fig. 1).

The treatment of the cyclic octachlorotetrasiloxane (**6**) with **1a** as well as with $Li[Mo(CO)_2(PMe_3)C_5Me_5]$ (**1d**) yields the ferrio/molybdenum-heptachloro-cyclotetrasiloxane **7a**,**b**. The Si_4O_4-network of **6** is not affected in this reaction, that means, that the metalate does not induce any ring-opening reaction.

The spectroscopic properties of the γ-Si-atom in the siloxane-network of **7a** are not influenced by the iron fragment, which is indicated by the high-field resonance in the ^{29}Si-NMR spectrum (−69.5 ppm) which is comparable to the one of the ε-Si-atom (−72.3 ppm).



L_nM = $Cp(OC)_2Fe$ (**7a**), $Cp^*(OC)_2(Me_3P)Mo$ (**7b**)

The obtained open-chain ferrio-siloxane (**3b**) can be transformed into the corresponding bis-metalated species **8** by treatment with another equivalent of sodium ferrate (**1a**) under heterogeneous reaction conditions in cyclohexane after 48 h at 25 °C.

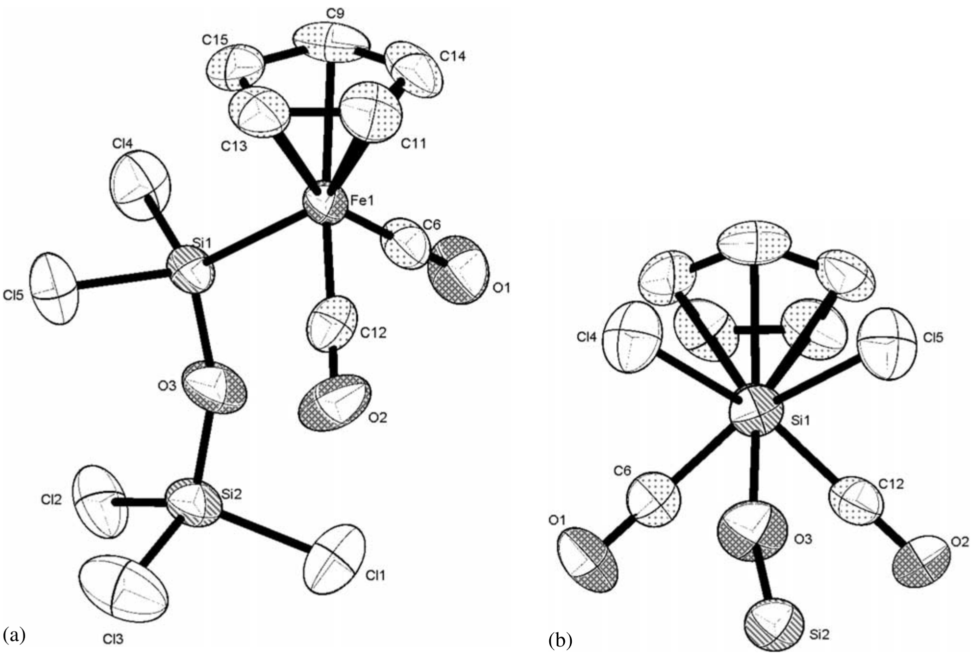
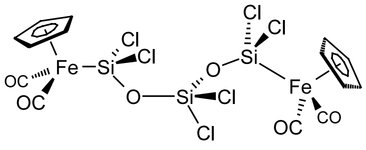


Fig. 1. (a) Molecular structure of $Cp(OC)_2Fe{-}SiCl_2OSiCl_3$ (**3a**). Ellipsoids are drawn at the 50% probability level for heavy atoms. Hydrogen atoms have been omitted for clarity. Only the major contributors to the disordered $SiCl_3$-group are shown. Selected bond lengths (Å) and angles (°): Fe(1)–Si(1) 2.2099(11), Si(1)–O(3) 1.641(3), Si(1)–Cl(4) 2.0638(14), Si(1)–Cl(5) 2.0723(14), Si(2)–O(3) 1.562(3), C(12)–Fe(1)–Si(1) 86.50(12), C(6)–Fe(1)–Si(1) 87.27(11), C(12)–Fe(1)–C(6) 94.35(15), Si(2)–O(3)–Si(1) 159.2(2), O(3)–Si(1)–Cl(4) 103.36(12), O(3)–Si(1)–Cl(5) 104.19(11), Cl(4)–Si(1)–Cl(5) 103.11(6), O(3)–Si(1)–Fe(1) 113.28(11), Cl(4)–Si(1)–Fe(1) 116.21(5), Cl(5)–Si(1)–Fe(1) 115.16(5). (b) *Newman* projection with respect to the Fe–Si-bond. Hydrogen atoms and chlorine atoms attached to Si2 have been omitted for clarity.



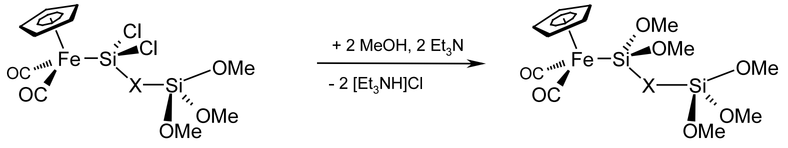
8

3.2. Methanolysis of polychlorinated metallo-siloxanes and metallo-silanes

One of the major advantages of the prepared polychlorinated metallo-siloxanes and -silanes is the number of functionalized positions within the Si–X–Si-skeleton which enable further substitution reactions.

In the case of **3a** and **5** the α-Si-atoms show decreased electrophilicity due to the electron-donating influence of the transition metal fragment. Thus, they can be used for regiospecific Cl/OMe-exchange reactions, involving preferentially the γ-silicon atom if treated with three equivalents of MeOH in Et_2O as solvent. The products **9a**,**b** can be converted into the fully methoxy-substituted derivatives **10a**,**b** within 1 h by using methanol as solvent or adding high excess of methanol to a etheral solution in the presence of NEt_3.

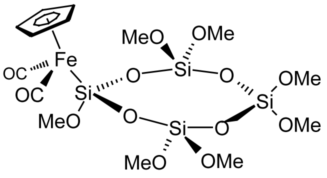
As it was indicated by the ^{29}Si-NMR data of the ferrio-cyclotetrasiloxane **7a**, the transition metal has no influence on the γ-silicon atom. Consequently, treatment of **7a** with two equivalents of MeOH does not result in regiospecific exchange at the ε-silicon atom. According to ^{1}H-NMR spectra a mixture of different products with the general formula presumably $Cp(OC)_2FeSi_4O_4(OMe)_xCl_{(7-x)}$ ($x = 1{-}7$) is formed, which cannot be separated. The use of an excess of



9	**a**	**b**
X	O	CH_2

10	**a**	**b**
X	O	CH_2

methanol in Et_2O as solvent after 2 h leads to the fully methoxy-substituted ferrio-cyclotetrasiloxane (**11**).



11

Forthcoming papers will present extended studies concerning the reactivities of metallo-perchlorosilanes, especially those involving chlorine/metalate or chlorine/hydroxyl exchange reactions leading to novel types of metallo-siloxanes [29] and metallo-siloxanols.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 185280 for compound **3a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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