# $[(\mu_2\text{-CO})Cp_2(OC)_2Fe_2][Cp(OC)_2Fe]SiH$: A SiH-Functionalized Tris(metallo)silane. Synthesis from $[Cp(OC)_2Fe]_2SiH_2$[1]

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*Summary: The first tris-metalated silane,* $[(\mu_2\text{-CO})Cp_2(OC)_2Fe_2][Cp(OC)_2Fe]SiH$*, was prepared via photoreaction of* $Cp(OC)_2Fe{-}CH_3$ *with the bis(ferrio)silane* $[Cp(OC)_2Fe]_2SiH_2$*.*

Hydrosilanes are attractive synthetic precursors for the preparation of a vast number of silicon-containing compounds, including metal silyl complexes, available via oxidative addition to electronically unsaturated metal complexes. This route gives access to diverse $SiR_2H$ and $SiRH_2$ metal complexes, but $SiH_3$ derivatives starting from $SiH_4$ have been realized only in a few cases.[2] A more effective access to $SiH_3$ and even $Si_2H_5$ metal complexes involves Cl/H exchange at the silicon of the corresponding metallo-chlorosilanes $L_nM{-}Si(R)Cl_2$ ($R = H, Cl, SiCl_3$; $L_nM = Cp(OC)(L)Fe, Cp(OC)_2Ru, Cp(OC)_2(Me_3P)W$; $L = CO, PR_3$),[3] a process which allows us to study the chemistry of these special silyl complexes in a broader range. In this context, it has been demonstrated that the metal-bound $SiH_3$ group is a valuable synthetic tool for the generation of metallo-silanetriols via oxygenation reactions,[4] or silylidyne metal clusters with the silicon surrounded by a maximum of four transition-metal groups.[2a,5] Application of a Cl/H exchange reaction for the generation of $SiH_2$-bridged dinuclear complexes $L_nM{-}SiH_2{-}ML_n$ is an attractive goal, since the known synthetic procedure for these species involves volatile silicon reagents requiring special synthetic procedures: e.g., the dihalosilanes $H_2SiX_2$ ($X = Cl, I$), the metalation of which yields the $(OC)_4Co$-,[6] $Cp(OC)_2Fe$-[7] and $(OC)_5Mn$-substituted[7,8] derivatives. Other preparations involve the reaction of $KSiH_3$ with $Cp_2TiCl_2$, leading to $(\mu_2\text{-}SiH_2)(TiCp_2)_2$,[9] or of $SiH_4$ with $(C_5Me_5)Mn(CO)_2(THF)$, yielding $[C_5Me_5(OC)_2Mn(H)]_2SiH_2$.[10] We here report the realization of $SiH_2$ formation at iron centers via the Cl/H exchange route and the use of the resulting bis(metallo)silane for generation of the first SiH-functionalized tris(metallo)silane.

When the sodium metalate $Na[Fe(CO)_2Cp]$, suspended in cyclohexane, was treated with the (ferrio)dichlorosilane **1**, the bis(ferrio)chlorosilane **3**[11] was obtained (Scheme 1), which on treatment with $LiAlH_4$ in diethyl ether produces the $SiH_2$ species **5** in moderate yield (57%). The ruthenium homologue **6** is obtained via analogous metalation of **2** and hydrogenation of the binuclear species **4** in 64% yield.[12]

The low values of $\tilde{\nu}_{SiH}$ (2037 and 2025 cm$^{-1}$) and $^1J_{SiH}$ (166 and 136 Hz) indicate electron rich Si−H bonds in **5** and **6**.[13] Slow condensation of *n*-pentane into a saturated solution of **5** in benzene resulted in the growth of pale yellow crystals. The molecular structure of **5** was verified by single-crystal X-ray diffraction,[14] showing the typical pseudotetrahedral coordination of the Fe ligands and a significant deviation from the ideal tetrahedral

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(11) (a) For $[Cp(OC)_2Fe]_2Si(Cl)H$ (**3**) see: Malisch, W.; Ries, W. *Chem. Ber.* **1979**, *112*, 1304−1315. (b) $[Cp(OC)_2Ru]_2Si(Cl)H$ (**4**): $^1H$ NMR ($C_6D_6$) $\delta$ 4.64 (s, 1H, SiH), 4.50 (s, 10 H, $C_5H_5$); $^{29}Si\{^1H\}$ NMR ($C_6D_6$) $\delta$ 98.75; IR (benzene) $\tilde{\nu}_{SiH}$ 2050 (br), $\tilde{\nu}_{CO}$ 2019 (s), 1993 (s), 1973 (vs), 1959 (vs), 1933 (vs) cm$^{-1}$. Anal. Calcd for $C_{14}H_{11}ClO_4Ru_2Si$: C, 33.04; H, 2.18. Found: C, 32.68; H, 2.06. Mp: 86 °C dec.

(12) $[Cp(OC)_2Fe]_2SiH_2$ (**5**): $^1H$ NMR ($C_6D_6$) $\delta$ 5.07 (s, $^1J_{HSi} = 166$ Hz, 2 H, SiH), 4.28 (s, 10 H, $C_5H_5$); $^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ 216.13 (CO), 84.33 ($C_5H_5$); $^{29}Si$ NMR ($C_6D_6$) $\delta$ 23.1 (t, $^1J_{SiH} = 166$ Hz); IR (cyclohexane) $\tilde{\nu}_{SiH}$ 2037 (w), $\tilde{\nu}_{CO}$ 1992 (vs), 1954 (s), 1944 (vs) cm$^{-1}$. Anal. Calcd for $C_{14}H_{12}Fe_2O_4Si$: C, 43.79; H, 3.15. Found: C, 43.62; H, 3.23. $[Cp(OC)_2Ru]_2SiH_2$ (**6**): $^1H$ NMR ($C_6D_6$) $\delta$ 4.77 (s, 2H, $^1J_{HSi} = 136$ Hz, SiH), 4.50 (s, 10 H, $C_5H_5$); IR (*n*-pentane) $\tilde{\nu}_{SiH}$ 2025 (w), $\tilde{\nu}_{CO}$ 2000 (s), 1983 (vs), 1972 (s), 1943 (vs) cm$^{-1}$. Anal. Calcd for $C_{14}H_{12}O_4Ru_2Si$: C, 35.44; H, 2.55. Found: C, 35.31; H, 2.43.

(13) (a) Mitchell, T. N.; Marsmann, H. *J. Organomet. Chem.* **1978**, *150*, 171. (b) Brinckmann, F. E.; Coyle, T. D. *J. Phys. Chem.* **1968**, *72*, 660.

(14) Crystal data of **5**: $C_{14}H_{12}Fe_2O_4Si$, $M_r = 382.02$, triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$, $a = 6.318(3)$ Å, $b = 10.652(4)$ Å, $c = 12.453(7)$ Å, $\alpha = 67.8845(6)°$, $\beta = 75.3508(6)°$, $\gamma = 72.7943(6)°$, $V = 732.1(7)$ Å$^3$, $d_{calcd} = 1.742$ g/cm$^3$, $\mu$(Mo K$\alpha$) = 20.7 cm$^{-1}$, $2\theta_{max} = 54°$, $T = 293$ K, $R1(I > 2\sigma(I)) = 0.028$, $wR2 = 0.032$, GooF = 1.002 for 3011 reflections and 238 parameters.

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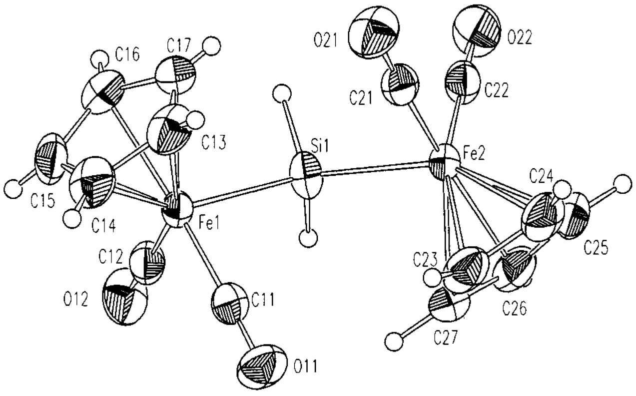


**Figure 1.** Molecular structure of $[Cp(OC)_2Fe]_2SiH_2$ (**5**).

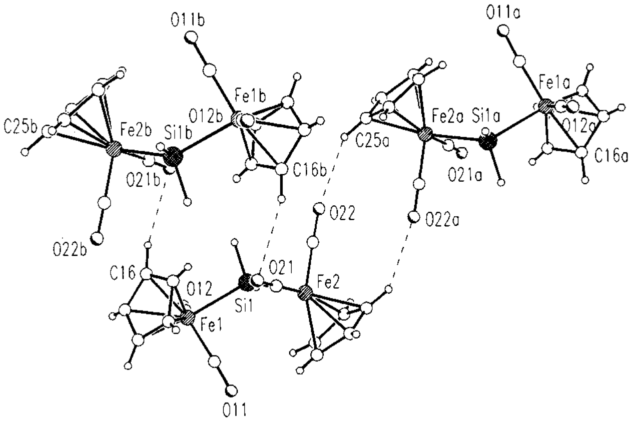
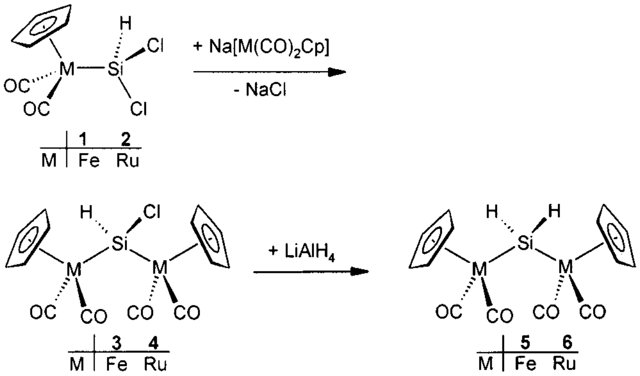


**Figure 2.** Hydrogen-bonded chain structure of **5**.

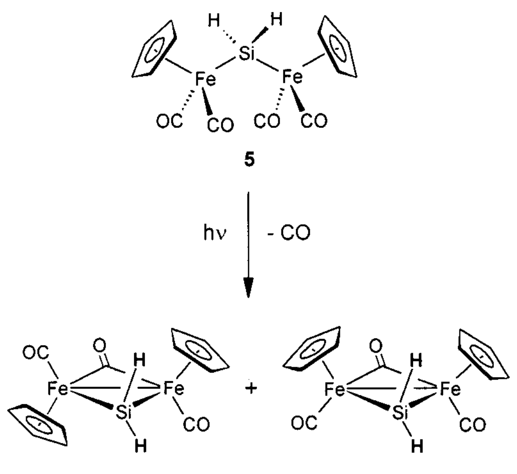
**Scheme 1**



substitution geometry at silicon (Fe1–Si–Fe2 = 123.48(6)°) due to the bulkiness of the iron fragment (Figure 1). A view along the Fe1-Si axis reveals a distorted staggered conformation with the following pairs of substituents in trans positions: CO/Fe2, CO/H1, and Cp/H2. The Fe–Si bond distances (2.3435(12) and 2.3393(12) Å) correspond to the sum of covalence radii of iron and silicon.[15]

Hydrogen bonds between Cp protons and carbonyl groups of neighboring molecules are linking the individual monomers to a chain structure (Figure 2). One of the metal fragments (Fe2) is involved in three H(Cp)···CO interactions using both carbonyl groups and one Cp hydrogen; the other (Fe1) has a single hydrogen bond with a Cp proton.[16]

**Scheme 2**



Selected bond lengths (Å) and angles (deg) for **5** are as follows: Fe1–C11, 1.744(3); Fe1–C12, 1.747(3); O11–C11, 1.151(4); O12–C12, 1.138(4); O21···H16, 2.714; O22···H25, 2.626; Fe1–Si–Fe2, 123.48(6); Si1–Fe–C11, 88.77(10); Si–Fe1–C12, 83.39(10); C11–Fe1–C12, 93.85(14).

Highly light sensitive **5** is rapidly converted upon UV irradiation into the bis(ferrio)silane $[Cp(OC)Fe]_2(\mu_2\text{-}CO)(\mu_2\text{-}SiH_2)$ (**7**) with elimination of CO. **7** is obtained as a dark red crystalline solid and is characterized by an additional $\mu_2$-CO bridge and an Fe–Fe bond (Scheme 2).[17,18]

Moreover, **7** forms a mixture of a trans (**7a**) and cis isomers (**7b**). As a consequence, the $^1H$ NMR spectrum of **7** shows two sets of signal patterns for the SiH protons, with an AB coupling ($^2J_{HSiH}$ = 22 Hz) for the dominating cis isomer **7b** (74%) having the hydrogen atoms in different chemical environments, while the two equivalent $SiH_2$ protons of the trans isomer **7a** (26%) give rise to a singlet signal.

A dynamic isomerization process—found between the different diastereomers of silylene complexes $[Cp(OC)Fe]_2(\mu_2\text{-}CO)(\mu_2\text{-}SiR_2)$ (R = alkyl, aryl) using temperature-dependent NMR spectra[19]—could not be observed in the case of **7a**,**b** due to insufficient thermal stability.[20]

The SiH functionality of the silicon iron compound **5** offers excellent possibilities for further metalation of the Si atom, which has been realized via the oxidative additon of an SiH unit of **5** to the methyl iron complex $Cp(OC)_2Fe–CH_3$. When a solution of **5** in benzene was

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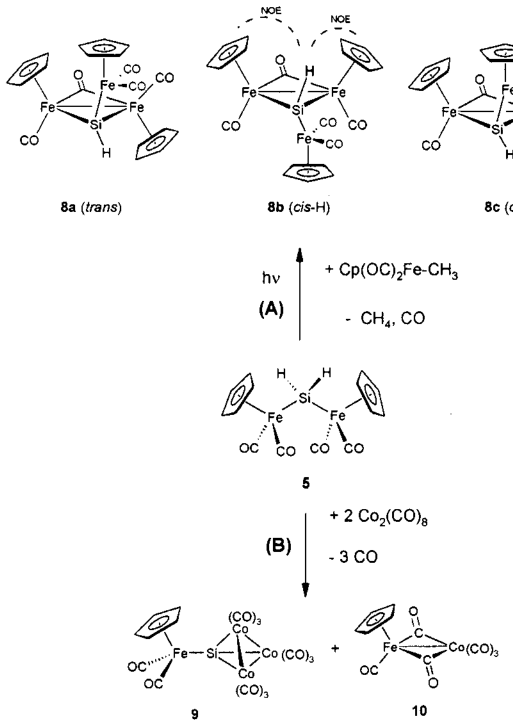
(15) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989.

(16) A detailed survey of hydrogen bonding in structurally related dinuclear transition-metal complexes has been provided by Braga et al. (see: Braga, D.; Grepioni, F.; Biradha, K.; Pedireddi, V. R.; Desiraju, G. R. *J. Am. Chem. Soc.* **1995**, *117*, 3156–3166). However, $[Cp(OC)_2Fe]_2SiH_2$ (**5**) is, to our knowledge, the first bis-metalated silane for which intermolecular bonding is described.

(17) $^1H$ NMR ($C_6D_6$): **7a** (trans), $\delta$ 6.83 (s, 2H, SiH), 4.30 (s, 10H, $C_5H_5$); **7b** (cis), $\delta$ 7.04, 6.43 (AB, $^2J_{HSiH}$ = 22 Hz, 2 H, SiH), 4.10 (s, 10H, $C_5H_5$). $^{13}C\{^1H\}$ NMR ($C_6D_6$): **7a** (trans), $\delta$ 286.21, 218.46 (CO), 84.90 ($C_5H_5$); **7b** (cis), $\delta$ 272.32, 212.32 (CO), 83.83 ($C_5H_5$). $^{29}Si\{^1H\}$ NMR ($C_6D_6$): $\delta$ 185.30 (trans); 180.93 (cis). IR (cyclohexane): $\tilde{\nu}_{SiH}$ 2015 (w), $\tilde{\nu}_{CO}$ 1994 (m), 1973 (vs), 1955 (s), 1940 (m), 1792 (s) $cm^{-1}$. Anal. Calcd for $C_{13}H_{12}Fe_2O_3Si$: C, 43.86; H, 3.40. Found: C, 43.42; H, 3.31.

(18) In contrast, the ruthenio derivative **6** is photochemically stable under the same conditions. This is a remarkable difference from the $\mu_2$-$CH_2$ homologue, which can be photochemically converted into $[Cp(OC)Ru]_2(\mu_2\text{-}CO)(\mu_2\text{-}CH_2)$. See: (a) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679–1680. (b) Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Morris, M. J. *J. Organomet. Chem.* **1981**, *215*, C30.

**Scheme 3**



irradiated for 9 h with UV light in the presence of $Cp(OC)_2Fe-CH_3$, the dark red tris(metallo)silane **8** is formed (Scheme 3, path A).[21] The $\mu_2$-silylene species **7** is likely to be an intermediate in this process.

All three possible isomers were observed in the $^1H$ NMR spectrum of **8**. The trans isomer **8a** was formed in marginal amounts only (4%) and could be easily identified from its three separate Cp signals of identical intensity (4.25, 4.53, and 4.54 ppm). In context with the favored cis arrangement of the endocyclic Fe ligands, the cis(H) form **8b**, with minimal steric repulsion of the ring ligands, is the main isomer (76%), in comparison to the cis(Fe) form **8c**. The identity of **8b** could be verified by a $^1H/^1H$ NOE spectrum, which shows a coupling between the SiH moiety (8.53 ppm) and the two endocyclic Cp ligands (4.28 ppm).

The $^{29}Si$ resonances of **8b**,**c** were detected at remarkably low field (293.67 and 276.31 ppm), a consequence of the paramagnetic contribution of the three transition-metal fragments to the chemical shift.[13] The strong electron release of the three iron substituents with respect to the silicon is particularly evident in the SiH stretching mode (2012 $cm^{-1}$), which is shifted to even lower frequencies by 25 $cm^{-1}$ compared to the SiH mode in the bis-metalated system **5**. The same effect can be observed in the $^1J_{SiH}$ coupling constant of **8b** (143 Hz), which is 23 Hz smaller than that of **5**.

Attempts to perform the well-established $H/Co(CO)_4$ exchange[3a] on **5** using $Co_2(CO)_8$ yields—probably via the originally expected spirocyclic compound $\mu_2$-$\{[Cp(OC)_2Fe]_2Si\}$-$Co_2(CO)_6(\mu_2\text{-}CO)$—the silylidyne tricobalt cluster **9**, which is isolated in 34% yield (Scheme 3, path B).[3a] Additional formation of the heterobinuclear complex **10**[22] indicates cleavage of the Fe−Si bond in the proposed intermediate by $HCo(CO)_4$, which is generated during the metalation process.

The first metalation experiments of the bis(ferrio)silane **5** indicate a high reactivity of the electron-rich SiH moiety, which in our experience should offer further interesting exchange reactions, including e.g. the insertion of oxygen to give hydroxy-functionalized derivatives.[23] For this process not only the bis(metallo)silanes **5** and **7** but especially the tris-metalated species **8** appear to be attractive precursors.

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**Supporting Information Available:** Text giving full experimental procedures and characterization data for the bis- and tris(metallo)silanes **5**−**8** and tables giving data from the X-ray crystallographic analysis of **5**. This material is available free of charge via the Internet at http://pubs.ac.org.

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[20] DFT calculations at the B3PW91/6-311+G(d) level of theory (geometries of **7a**,**b** and the transition state calculated with B3PW91/6-31G(d)) predict an activation barrier of $E_a(\text{cis/trans}) = 89.9$ kJ $mol^{-1}$ and $E_a(\text{trans/cis}) = 88.6$ kJ $mol^{-1}$. These values are in good agreement with the experimental results obtained by Ogino for the isomerization of the complexes $[Cp(OC)Fe]_2(\mu_2\text{-}CO)(\mu_2\text{-}SiHR)$ (R = *t*Bu, CHPh).[19]

[21] $^1H$ NMR ($C_6D_6$): **8a** (trans), $\delta$ 8.15 (1H, SiH), 4.54, 4.53, 4.25 (5 H, $C_5H_5$); **8b** (cis-H), $\delta$ 8.53 (1H, $^1J_{SiH} = 143$ Hz, SiH), 4.48 (5H, $C_5H_5$), 4.28 (10H, $C_5H_5$); **8c** (cis-Fe), $\delta$ 7.49 (1H, SiH), 4.40 (10H, $C_5H_5$), 4.24 (5H, $C_5H_5$). $^{13}C\{^1H\}$ NMR ($C_6D_6$) for three isomers: $\delta$ 214.57, 215.25, 222.60 (CO); 84.38, 84.65, 85.11, 85.48, 85.63, 86.84, 88.48 ($C_5H_5$). $^{29}Si\{^1H\}$ NMR ($C_6D_6$): $\delta$ 293.67 (*cis*-H), 276.31 (*cis*-Fe). IR (cyclohexane): $\tilde{\nu}_{SiH}$ 2012 (w, br); $\tilde{\nu}_{CO}$ 1987 (s), 1956 (s), 1945 (s), 1781 (vs) $cm^{-1}$. Anal. Calcd for $C_{20}H_{16}Fe_3O_5Si$ (531.97): C, 45.16; H, 3.03. Found: C, 44.48; H, 3.16.

[22] (a) Manning, A. R. *J. Chem. Soc. A* **1971**, 2321−2325. (b) Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 2675−2685.

[23] Malisch, W.; Vögler, M.; Schumacher, D.; Nieger, M. *Organometallics*, submitted for publication.