Synthesis and Reactivity of Silicon Transition Metal Complexes, 43[≠]

Iron and Ruthenium Fragment Substituted Disilanes $C_5R_5(OC)_2M–Si_2X_5$ (R = H, Me; M = Fe, Ru; X = Cl, H): Synthesis, Structural and Raman Spectroscopic Characterisation, DFT Calculation

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Dedicated to Professor Helmut Werner on occasion of his 65th birthday

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Reaction of the sodium metalates $Na[M(CO)_2C_5R_5]$ [M = Fe, R = H (**1a**), Me (**1b**); M = Ru, R = H (**1c**), Me (**1d**)] with an equimolar amount of hexachlorodisilane yields the metallo-pentachlorodisilanes $C_5R_5(OC)_2M–SiCl_2–SiCl_3$ (**2a–d**), which can be converted into the pentahydrido analogues $C_5R_5(OC)_2M–SiH_2–SiH_3$ (**3a–c**) via Cl/H exchange with $LiAlH_4$. Due to the activating effect of the transition metal fragment chlorination of **3a–c** with CCl_4 or $HCCl_3$ occurs at the α-silicon to give $C_5R_5(OC)_2M–SiCl_2–SiH_3$ (**4a–c**). The metallo-disilanes were characterised by ^1H-, ^{13}C-, ^{29}Si-NMR, IR and especially Raman spectroscopy. The structures of $C_5H_5(OC)_2Fe–Si_2Cl_5$ (**2a**) and$C_5Me_5(OC)_2Fe–Si_2H_5$ (**3b**) have been determined by X-ray analysis; **2a,b**, **3a,b** were theoretically described by DFT calculations.

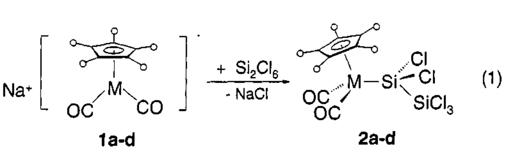
Introduction

Iron-substituted disilanes $Cp(OC)_2Fe{-}SiR_2{-}SiR_3$[1][2] have preferentially been the subject of studies concerning the photoinduced rearrangement to silyl(silylene) complexes $Cp(OC)Fe({=}SiR_2)SiR_3$.[3] If organic substituents are attached to the silicon atoms this species represent a short-lived intermediate which is confirmed only by IR matrix studies[4] or by the isolated photolysis product $Cp(OC)_2Fe{-}SiR_3$.[3a−d] However, introduction of alkoxy groups at the β-silicon leads to oxygen stabilised cyclic (bis)silylene complexes $R_2Si^a{-}Cp(OC)Fe{-}SiR_2{\cdots}O^aR'$(*Si^a−O^a*).[3e,f]

A limited number of investigations have been reported concerning complexes containing "inorganic" substituents at the silicon atoms, for instance hydrogen or halogen.[5][6] Therefore, we have undertaken efforts to establish efficient routes for the synthesis of metallo-pentachloro- and -pentahydridodisilanes.[6] These ligands offer the possibility to study the influence of the transition metal fragment on the exchange reactivities of the silicon atoms in α- or β-position as well as on the stability of the M−Si−Si bonding arrangement with respect to fragmentation. Support for the interpretation of the findings is expected from a detailed vibrational analysis using especially Raman spectroscopy combined with DFT calculations.

I. Preparative Results

In accordance with former experiments[6] a suspension of the sodium metalates **1a−d** in cyclohexane is combined with hexachlorodisilane in a molar ratio of 1:1 and the reaction mixture stirred at room temperature under exclusion of light for 3 to 48 hours to give the metallo-pentachlorodisilanes **2a−d** (Equation 1).



(1)

	a	b	c	d
M	Fe	Fe	Ru	Ru
—○	H	Me	H	Me

2a−d are isolated as pale yellow microcrystalline solids in good yields, which show considerable solubility in *n*-pentane and aromatic solvents. **2a−d** can be stored as solids under an atmosphere of nitrogen for months without decomposition.

Heterogeneous "salt elimination" according to Equation (1) is the only way to guarantee controlled mono-metallation of Si_2Cl_6 as analogous experiments with

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[≠] Part 42: S. Möller, H. Jehle, W. Malisch, W. Seelbach in *Organosilicon Chemistry: From Molecules to Materials, Vol. 3,* (Eds.: N. Auner, J. Weis) VCH, Weinheim **1998**, 267−270.

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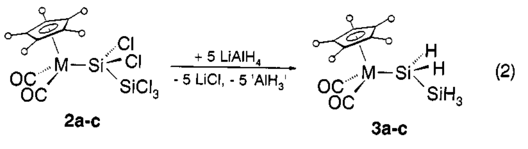
Na[Fe(CO)$_2$Cp] (**1a**) performed by Hengge et al. proved using THF as a solvent.[5] In this case homogeneous reaction yields a mixture of **2a** and the bis(iron)disilane [Cp(OC)$_2$Fe−SiCl$_2$]$_2$ which makes separation necessary giving rise to a reduced yield of **2a** (41%).

The stability of the iron−silicon or ruthenium−silicon bonds of **2a−c** allows exchange reactions at the silicon atoms without Fe−Si bond cleavage. An attractive example in this context is the Cl/H exchange of the silicon bound chlorine atoms which is achieved by treatment of a solution of **2a−c** at −78 °C in diethyl ether with LiAlH$_4$. For a molar ratio of 1:5 after 2 h of stirring at room temperature both silicons were fully hydrogen substituted (Equation 2).



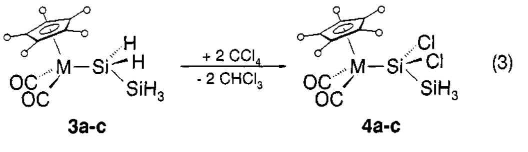
2a-c **3a-c** (2)

	a	b	c
M	Fe	Fe	Ru
R	H	Me	H

The metallo-disilanes **3a−c** are obtained after crystallisation from pentane at −78 °C (**3b**) or sublimation in high vacuum (**3a,c**), respectively, as light yellow (**3a,b**) to colorless (**3c**) waxy solids, which show a good solubility in *n*-pentane and benzene.[7]

The pronounced electron releasing capacity of the transition metal fragment induces a highly hydridic character of the hydrogens at the α-silicon compared with that at the β-position, a fact that is clearly deduced from IR- and ^{29}Si-NMR data (see below).

As a consequence, the hydrogens of the metallo-pentahydridodisilanes **3a−c** next to the metal are selectively substituted by chlorine at room temperature after 3 hours using CCl$_4$ to give exclusively the metallo-dichlorodisilanes **4a−c** (Equation 3).



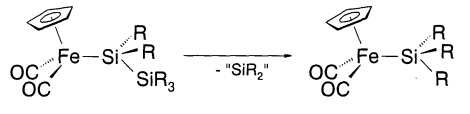
3a-c **4a-c** (3)

	a	b	c
M	Fe	Fe	Ru
—○	H	Me	H

The same procedure can be realised with HCCl$_3$, but more severe reaction conditions are necessary (40 °C, 12 h). **4a−c**, which represent the first complexes bearing a dichloro-disilanyl ligand, are obtained as yellow solids in good yields, which are purified by crystallisation from pentane at −78 °C. Solubility is comparable to that of **3a−c**.

A characteristic of ferrio-disilanes Cp(OC)$_2$Fe−SiR$_2$−SiR$_3$ (R = alykl) is the photoinduced rearrangement with elimination of the SiR$_2$ group to give the monosilyl complex Cp(OC)$_2$Fe−SiR$_3$ via oxidative addition of the Si−Si bond to the metal atom.[3] A comparable reaction, at least concerning the final product, is observed for the pentachloro- and pentahydridodisilanyl complexes **2a,c** and **3**.

In accordance with these results photolysis of **2a/3a** in benzene/cyclohexane at room temperature leads to the silyl iron complexes **5**[8] or **6**,[9] respectively, after 120 h. **2a** additionally shows this behaviour in the solid state (Equation 4).



2a, 3a **5, 6** (4)

The thermal stability of the metallo-disilanes **2, 3** decreases on going from the pentachloro- to the pentahydrido derivatives. Heating **2a** in cyclohexane to 65 °C for 32 h does not result in any decomposition, while in the case of **3a** under these conditions Cp(OC)$_2$Fe−SiH$_3$ (**6**) is isolated quantitatively. A detailed examination of the silylene elimination involved in the photodegradation as well as trapping experiments concerning the silylenes SiH$_2$[10] and SiCl$_2$[11] are currently under way.

II. Spectroscopic Data

NMR Spectroscopy

Substantial information concerning the electronic character of the silicon atoms of **3a−c** is given by the ^1J(SiH) coupling. It is generally accepted that this parameter can be correlated with the s-electron density in the Si−H bond.[12] The SiH$_2$ units next to the transition metal give rise to a low value of the ^1J(SiH) coupling constants [179.5 Hz (**3a**), 172.4 Hz (**3b**), 181.0 Hz (**3c**)] compared to Si$_2$H$_6$[13] characterising the transition metal ligand as an efficient electron releasing group. The ^1J(SiH) value of the SiH$_3$ moiety is higher (184−186 Hz), but still below that of Si$_2$H$_6$ indicating a reduced "transition metal effect" on the β-silicon.

The difficulties of correlating the ^{29}Si-NMR shifts of organosilicon compounds on the basis of purely inductive effects have been pointed out in the literature.[14] Due to this fact only some empirical regularities of the ^{29}Si-NMR data will be discussed.

1.) The signals for **2** at low field (δ = −2 to +76) and **3** at high field (δ = −45 to −95) appear in the range characteristic of the corresponding disilanes Si$_2$R$_6$ [R = Cl (δ = −6.14);[15a] H (δ = −104.1)[15b]]. The metallo-dichlorodisilane **4a** with differing substituents at the silicon atoms follows these trends (**4a**: δ = +93 and −83). In each case the resonance of the metal-substituted silicon is characterised by an enormous low-field shift with the maximum for **4a** compared to the silicon in the β-position.

2.) The δ-value of the SiX$_3$ moiety is approximately identical for all species [δ = +1 to −2 (**2**, X = Cl), δ = −93 to −95 (**3**, X = H)]. In comparison to Si$_2$R$_6$ (R = Cl, H) the small low-field shift of this resonance of ca. 5−10 ppm indicates a minor influence of the transition metal fragment on the β-silicon of **2** and **3**. The largest difference (21 ppm) is obtained for the SiH_3 resonance of the ferrio-dichlorodisilane **4a** ($\delta = -83$).

3.) Exchange of the iron against the ruthenium group causes a high-field shift of approximately 20 ppm for the α-silicon resonance. The chemical shift of the SiX_3 moieties remains unaffected.

Vibrational Spectroscopy and Density Functional Theory Calculations

Among the methods that can be used for the simulation of vibrational spectra, density functional methods are known to give very good results for vibrational wavenumbers compared to *ab initio* methods.[16]

a) Comparison of measured and calculated Raman bands of **2a**, **3a,b**:

The former assignments of the complex **3a** were based on normal coordinate analysis (NCA).[17] They agree with the results of DFT calculations. The simulation of vibrational spectra with NCA is based on a purely mechanical model, where an initial force constant matrix is chosen with a limited number of force constants [$(3N - 6)(3N - 5)/2$ in nonredundant internal coordinates for a nonlinear molecule], and then a force constant refinement is carried out.

Table 1. Comparison of measured (Raman spectra) and calculated wavenumbers of **3a** and **3b**

3a Measured [cm^{-1}]	**3a** Calculated [cm^{-1}]	**3b** Measured [cm^{-1}]	**3b** Calculated [cm^{-1}]	Mode description
2141	2177	/	2174	$\nu_{asym}(SiH_3)$
2132	2163	2135	2161	$\nu_{asym}(SiH_3)$
	2141		2141	$\nu_{sym}(SiH_3)$
2098	2126	2063	2108	$\nu_{asym}(SiH_2)$
2087	2098	2076	2082	$\nu_{sym}(SiH_2)$
2008	1906	2008	1887	$\nu_{sym}(CO)$
1959	1865	1959	1846	$\nu_{asym}(CO)$
1114	1102	594	575	Cp-ring breathing
606	611	606	617	$\nu_{asym}(FeC)$
441	425	449	425	$\nu(SiSi)$
373	359	412	401	$\nu_{sym}(Fe\text{-}Cp)$[a]

[a] Also partly a $C-CH_3$ out-of-plane bending vibration in Cp* compound.

Quantum mechanical calculations like DFT use another approach to obtain a force field: here, all necessary force constants are calculated by the second derivative of the energy with respect to the coordinates ($\partial^2E/\partial q_i \partial q_j$). This method is more satisfying because of the avoidance of the empirical force constant refinement. Compared to conventional *ab initio*-methods, DFT has the advantage that an empirical scaling of force constants giving a *Scaled Quantum Mechanical* (SQM) force field of Pulay *et al.*[18] is not necessary to account for the lack of correlation energy. However, a scaling is often introduced to account for the anharmonicity. But we favoured to compare measured anharmonic wavenumbers with calculated *un*scaled harmonic wavenumbers rather than to introduce an empirical scaling procedure, because scaling does not change the fact we can get from the second derivatives only harmonic wavenumbers.

In comparison to NCA, the wavenumbers for the CH stretching vibrations obtained from DFT calculation and partly the SiH stretching vibrations were calculated to be too high.

Significant is the lowering of the ring breathing vibration to 575 cm^{-1}, according to the higher mass of the ring substituents.

Difficulties in the assignment of the pentamethylcyclopentadienyl complex **3b** arise from the great number of additional bands especially in the $\nu(C-C)$ and $\delta(CH)$ region due to the five methyl groups. Most of these vibrations are not summarized in Table 1.

Further complications originate from coupling of different internal coordinates: some formerly "pure" vibrations are coupled with vibrations of the substituent, e.g. the ν_{sym}(Fe−Cp) is in the case of the pentamethylcyclopentadienyl complex also partly a $C-CH_3$ out-of-plane bending vibration. This gives the explanation for the unexpected shift in the calculations and in the spectra (because of the higher mass of the Cp*) towards higher wavenumbers [from 359 to 401 cm^{-1} (calc.), from 373 to 412 cm^{-1} (exp.)]. Consequently, the wavenumber shift in this case *cannot* be taken as a direct measure of bond strength. However, for the ν(CO) value, such an interpretation is possible, because this vibration is only coupled with the other CO stretching vibration. Both vibrations ν_{sym}(CO) and ν_{asym}(CO) are shifted by 35 cm^{-1} to lower wavenumbers switching from a cyclopentadienyl (Cp) to a pentamethylcyclopentadienyl (Cp*) ligand in the iron compounds **2a,b** and **3a,b**, respectively, which is in accordance with the higher electronic density in the case of **3b** causing a stronger back bonding from the metal to the carbonyl carbon and, consequently, a weaker CO bond. This shift is confirmed by the DF calculation, although the absolute value of ν_s(CO) and ν_{as}(CO) differ by nearly 100 cm^{-1} from the experimental data. In addition, the change of substituents at the silicon from H (**3a,b**) to Cl (**2a**) causes a shift of the ν(CO) band to higher wavenumbers. The identical spectral position of the carbonyl modes in **2b** and **3a** shows, that the difference in the −I-effect between the Cl atoms of **2b** and the H atoms of **3a** is compensated by the different electronic donor capacities of the Cp* and Cp ligands. Characterisation of the SiH stretching modes is an effective way to get information about the electronic structure of the Si atom and how it is influenced by the metal fragment. The IR spectra of **3a** show two weak bands at 2071 and 2133 cm^{-1}, which are assigned to the SiH stretching modes of the silylene and the silyl fragment.[19] In this case the signal at 2133 cm^{-1} can be assigned to an overlap of the symmetric and antisymmetric stretching modes of the silyl group.[20] Compound **3b**, with the better electron donating ligand C_5Me_5, shows the stretching modes of the silylene group at 2063 cm^{-1} [$\nu_{as}(SiH_2)$] and at 2076 cm^{-1} [$\nu_s(SiH_2)$]. The symmetric and the antisymmetric stretching modes of the silyl group overlap in their spectral position and appear at 2135 cm^{-1}.

The SiSi stretching mode is found in a narrow spectral range around 445 cm^{-1} and its position is primarily independent from all the other ligands. The DFT calculations show that this vibration is indeed a pure SiSi stretching, and no other internal coordinates are involved. So, we can conclude that changes in the electronic density of the metal atom have no influence on this bond.

Table 2. Comparison of measured (FT Raman spectrum) and calculated wavenumbers of **2a**

Measured [cm^{-1}]	Calculated [cm^{-1}]	Mode description
2022	1937	ν_{sym}(CO)
1991	1901	ν_{asym}(CO)
1120	1102	Cp ring breathing
607	600	ν_{asym}(FeC)
528	523	ν(SiSi) + ν(SiCl)
493	496	ν(SiCl) + ν(SiSi) +
386	345	ν_{asym}(Fe-Cp)
290	321	ν_{asym}(Fe-Cp)
233	249	ν(FeSi) + δ(SiCl)
213	200	($SiCl_3$) in phase def. + ($SiCl_2$) bending
202	182	($SiCl_3$) in phase def.

The measured spectrum in Table 2 is a Fourier transform Raman spectrum with excitation in the NIR (1064 nm), because in the visible region decomposition in the laser focus occurred. The CO stretching vibrations appear at 2022 and 1991 cm^{-1}, indicating a higher CO stretching force constant than in the case of $Cp(OC)_2Fe-SiH_2SiH_3$ (2008 and 1959 cm^{-1}) which is in accordance with the higher electronegativity of the chlorine atom. The CC stretching vibrations of the coordinated cyclopentadienyl anion as well as the significant Cp ring breathing vibration do not change compared to $Cp(OC)_2Fe-SiH_2SiH_3$. For many other vibrations, the internal coordinates are more coupled than in $Cp(OC)_2Fe-SiH_2SiH_3$. This is an effect of the higher mass of chlorine, which is much closer to the mass of the other atoms compared to hydrogen. In contrast, for **3a,b** no band exists that can be assigned to be a pure Si−Si stretching vibration.

III. X-ray Analysis of $C_5H_5(OC)_2Fe-SiCl_2SiCl_3$ (2a), $C_5Me_5(OC)_2Fe-SiH_2SiH_3$ (3b) and Comparison to DFT Calculations

Final verification of the structures of **2a** and **3b** came from X-ray crystallographic studies (Figures 1−3). **3b** is to our knowledge the first structurally characterized metallo-derivative of Si_2H_6.

The octahedral coordination sphere at the iron centre is in both cases indicated by the ligand-metal-ligand angles close to 90°. Larger angles are found between the carbonyl carbon atoms [94.2(11)° (**2a**); 96.0 (11)° (**3b**)] while the angles between the silicon atom and the CO ligands [88.4(8)°/88.3(8)° (**2a**); 85.5(8)°/88.5(8)° (**3b**)] are smaller. The Fe−Si bond length with a value of 2.224(7) Å (**2a**), 2.298(9) Å (**3b**) lies within the range of known iron silicon compounds[21a−h] with the usual trend of a bond shortage due to electronegative substituents like chlorine.[21c] The Si1−Si2 distance of 2.333(9) Å (**2a**), 2.335(11) Å (**3b**) is close to that of known disilanes (e. g. Me_6Si_2: 2.340 Å[22])

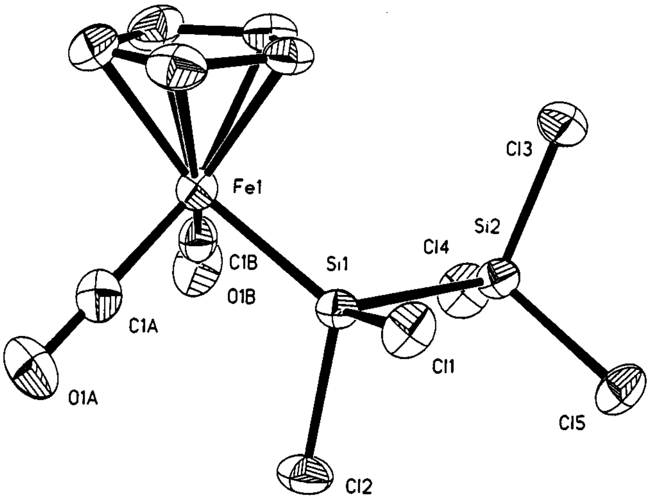


Figure 1. ORTEP view of $C_5H_5(OC)_2Fe-SiCl_2-SiCl_3$ (**2a**). Selected bond lenghts [Å], angles [°] and torsion angles [°]: Fe−Si1 2.2239(7), Si1−Si2 2.3333(9), Si1−Cl1 2.0859(8), Si1−Cl2 2.0811(9), Si2−Cl3 2.0410(9), Si2−Cl4 2.0421(9), Si2−Cl5 2.0358(9), Fe−C1a−O1a 178.9(3), Fe−C1b−O1b 178.8(9), Cl1−Si1−Si2 99.53(3), Cl3−Si2−Si1 111.60(4), Fe−Si1−Si2 119.20(3), C1a−Fe1−Si1 88.27(8), Fe1−Si1−Si2−Cl5 175.05(3), Fe1−Si1−Si2−Cl4 −63.76(5), Fe1−Si1−Si2−Cl3 55.53(4), Cl1−Si1−Si2−Cl5 46.59(5), C1a−Fe1−Si1−Cl1 −80.11(8), C1b−Fe1−Si1−Cl1 −174.37(8), Cp(Z)−Fe1−Si1−Si2 68.2, Cp(Z)−Fe1−Si1−Cl1 51.7, Cp(Z)−Fe1−Si1−Cl2 6.2.

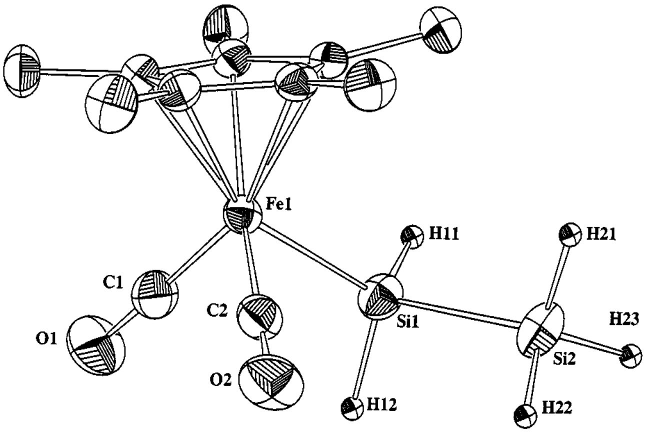


Figure 2. ORTEP view of $C_5Me_5(OC)_2Fe-SiH_2-SiH_3$ (**3b**). Selected bond lenghts [Å], angles [°] and torsion angles [°]: Fe−Si1 2.2980(9), Si1−Si2 2.3355(11), Si1−H11 1.43(2), Si1−H12 1.47(2), Si2−H21 1.41(3), Si2−H22 1.37(3), Si2−H23 1.42(3); C1−Fe1−Si1 85.46(8), C2−Fe1−Si1 88.52(8), H11−Si1−H12 102.7(12),H11−Si1−Fe 114.7(9), H12−Si1−Fe 113.4(9), H11−Si1−Si2 106.6(9), Si2−Si1−Fe 115.15(5), H21−Si2−H22 106.0(16), H21−Si2−Si1 111.4(12), H23−Si2−Si1 113.2(12), C1−Fe−C2 95.96(11), Fe−C1−O1 178.6(2), Fe−C2−O2 177.9(2); C2−Fe−Si1−Si2 −50.50(8), C1−Fe−Si1−Si2 −146.60(8), H11−Si1−Si2−H21 83.0(16), H11−Si1−Si2−H22 −159.3(14), H11−Si1−Si2−H23 −38.3(15), H12−Si1−Si2−H21 −169.3(16), H12−Si1−Si2−H22 −51.6(15), H12−Si1−Si2−H23 69.4(16), Fe −Si1−Si2−H21 −45.4(13), Fe−Si1−Si2−H22 −72.3(11), Fe−Si 1−Si2−H23 −166.7(13), Cp(Z)−Fe1−Si1−Si2 82.56, Cp(Z)−Fe-1−Si1−H11 41.72, Cp(Z)−Fe1−Si1−H12 159.25.

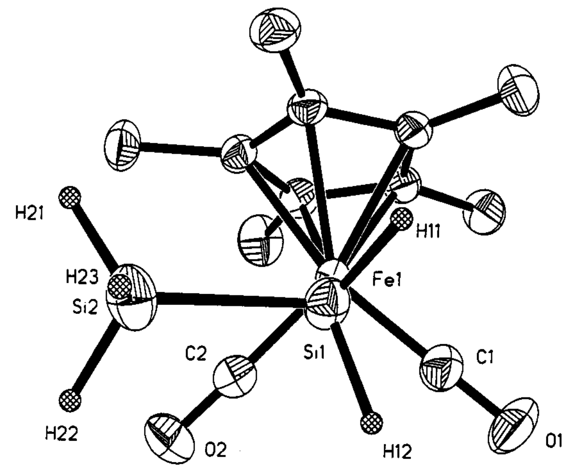


Figure 3. Newman like projection along the Fe−Si bond of **3b**

as well as to other disilanyl-metal-complexes[21f] including the tungsten derivative $C_5Me_5(OC)_2(Me_3P)W-SiCl_2-SiCl_3$ (Si1−Si2: 2.350 Å).[6] While Si−Cl distances of **2a** at Si2 (Si2−Cl3 2.0410(9), Si2−Cl4 2.0421(9), Si2−Cl5 2.0358(9) Å) are in the range of chlorosilanes,[21i] the analogous distances at the metal bound silicon exhibit a significant elongation (Si1−Cl1 [2.086(8) Å], Si1−Cl2 [2.081(9) Å]) due to the electron releasing capacity of the transition metal fragment. The Newman projection along the Fe−Si bond (Figure 3) reveals a staggered pseudo-ethane conformation with the following pairs of "*trans*"-arranged substituents: Cp*/X, CO/X, CO/SiX_3 (X = Cl, H).The gauche position of the SiX_3 group (X = H, Cl) with respect to the cyclopentadienyl unit found for **2a**, **3b** is typical for pseudo-tetrahedral halfsandwich iron complexes of the type $C_5R_5(OC)_2$-Fe−Si_2X_5 (X = H, Cl, alkyl);[21h] at the metal centre more crowded complexes like the pseudo tetragonal monopyramidal tungsten compound$C_5Me_5(OC)_2(Me_3P)W-SiCl_2-SiCl_3$ prefer the trans arrangement.[6] Distorsion with respect to the ideal conformation of about 20° (**3b**)/ 8° (**2a**) for all the substituents at Si1 deduced from the dehedral angles Cp(Z)−Fe1−Si1−Si2 (82.6°)/(68.2°), Cp(Z)−Fe1−Si1−H11 (41.7°)/ Cp(Z)−Fe1−Si1−Cl1 (51.7°) and Cp(Z)−Fe1−Si1−H12 (159.3°)/ Cp(Z)−Fe1−Si1−Cl2 (6.2°) indicates the higher sterical demand of the SiX_3 group compared to the hydrogen or chlorine atoms.

The octahedral coordination sphere is also found in the calculation, and the corresponding bond angles show a very good agreement between the measured and calculated structures. In our calculations, the Si−Cl bond lengths of **2a** are somewhat overestimated, but they show the same behaviour concerning the effect of the iron fragment close to Si1, where the Si−Cl bonds are longer than those at Si2. Comparison of X-ray data of **3b** and the calculated structural data obtained by DFT method reveals a slightly different conformation, which is deduced from bond and torsion angles. The Si_2H_5 moiety is turned clockwise about 10° around the Fe−Si bond. However, the structural parameters reproduce reasonably the experimental values. An interesting aspect of the calculation are the Si−H bond lengths, which cannot be determined by X-ray structure analysis with satisfying accuracy. In the DFT calculation, the bond lengths at Si1 (next to the iron fragment) are elongated compared to the SiH_3-group, a result that parallels

Table 3. Comparison of selected structural parameters from X-ray data and DFT calculations for $C_5H_5(OC)_2FeSiCl_2-SiCl_3$ (**2a**), C_5Me_5-$(OC)_2Fe-SiH_2-SiH_3$ (**3b**)

	X-ray data **2a**	calculated		X−ray data **3b**	calculated
Fe1−Si1	2.224	2.275	Fe1−Si1	2.298	2.362
Si1−Si2	2.333	2.397	Si1−Si2	2.336	2.364
Si1−Cl1	2.086	2.220	Si1−H11	1.43	1.507
Si1−Cl2	2.081	2.210	Si1−H12	1.47	1.512
Si2−Cl3	2.041	2.198	Si2−H21	1.41	1.501
Si2−Cl4	2.042	2.189	Si2−H22	1.37	1.497
Si2−Cl5	2.036	2.169	Si2−H23	1.42	1.501
Fe1−C1a	1.770	1.752	Fe1−C1		1.736
Fe1C1b	1.765	1.754	Fe1−C2		1.737
C1a−O1a	1.137	1.189	C1−O1		1.199
C1b−O1b	1.143	1.189	C1−O2		1.120
C1a−Fe1−Si1	88.3	88.9	C1−Fe1−Si1	85.5	84.7
C1b−Fe1−Si1	88.4	91.4	C2−Fe1−Si1	88.5	87.1
Cl1−Si1−Cl2	103.6	104.9	H11−Si1−H12	102.7	104.4
Cl1−Si1−Fe1	115.2	113.3	H11−Si1−Fe1	114.7	111.2
Cl2−Si1−Fe1	117.0	114.4	H12−Si1−Fe1	113.4	112.6
Cl1−Si1−Si2	99.5	102.4	H11−Si1−Si2	106.6	106.4
Cl3−Si2−Cl4	111.6	105.8	H21−Si2−H22	106.0	107.1
C1−Fe1−C2	94.2	94.1	C1−Fe1−C2	96.0	94.6
Fe1−C1a−O1a	178.9	177.0	Fe1−C1−O1	178.6	177.8
Fe1−C1b−O1b	178.8	176.5	Fe1−C2−O2	177.9	178.1
C1a−Fe1−Si1−Si2	160.0	169.0	C2−Fe1−Si1−Si2	−50.5	−59.0
C1b−Fe1−Si1−Si2	65.7	75.0	C1−Fe1−Si1−Si2	−146.6	−153.9
Cl1−Si1−Si2−Cl4	−178.4	−173.8	H11−Si1−Si2−H22	−159.3	−172.0
Fe1−Si1−Si2−Cl3	55.5	67.8	Fe1−Si1−Si2−H21	−45.4	−57.9
Cl1−Si1−Fe1−C1a	−80.1	−71.0	H11−Si1−Fe1−C1		82.9
Cl1−Si1−Fe1−C1b	−174.4	−165.0	H11−Si1−Fe1−C2		177.8

the finding for the Si_2Cl_5 derivative (*vide supra*) and offers a reasonable explanation for the higher reactivity of the SiH_2-group compared to the SiH_3 moiety. This difference is in addition established in the measured as well as in the calculated vibrational spectrum of **3b**.

Experimental Section

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 (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: Varian MAT 112 S (70 eV). 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. − DTA: Du Pont 9000. − Starting Materials: Na[Fe(CO)$_2$C$_5$R$_5$] (R = H,[23a] Me[23b]), Na[Ru(CO)$_2$C$_5$R$_5$] (R = H,[24a] Me[24]).

1. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1,2,2,2-pentachlorodisilane (2a): A suspension of 2150 mg (10.8 mmol) of Na[Fe(CO)$_2$Cp] (**1a**) in 50 mL of cyclohexane is treated with 3190 mg (12.0 mmol) of hexachlorodisilane and the mixture is stirred for 3 d at room temperature in the absence of light. After filtration of insoluble material (unreacted **1a** and formed NaCl), removal of the solvent and excess of hexachlorodisilane in vacuo the dark red residue is treated 6 times with 30 mL of pentane. The combined extracts are evaporated in vacuo to 15 mL and cooled to −78°C. Crystallised **2a** is filtered off, washed with 10 mL of cold pentane and dried in vacuo. − Yield 3800 mg (86%). − Pale yellow microcrystalline powder. − M.p. 63−64°C. − ^{1}H NMR: δ = 4.16 (s, H$_5$C$_5$). − ^{29}Si NMR (CDCl$_3$): δ = 76.81 (s, α-Si), −2.37 (s, β-Si). − IR (pentane): $\tilde{\nu}$ = 2035 cm^{-1} (vs), 1998 (vs) [ν(CO)]. − MS (rel. to ^{28}Si, ^{35}Cl and ^{56}Fe, 70 eV, 30°C): *m/z* (%) = 408 (3, [M]$^+$), 380 (8, [M − CO]$^+$), 352 (30, [M − 2CO]$^+$), 275 (55, [M − SiCl$_3$]$^+$), 254 (77, [M − 2CO, − SiCl$_2$]$^+$), 247 (11, [M − CO, − SiCl$_3$]$^+$), 156 (87, [CpFeCl]$^+$), 121 (44, [CpFe]$^+$), 93 (100, [CpSi]$^+$), 91 (22, [FeCl]$^+$). − $C_7H_5Cl_5FeO_2Si_2$ (410.40): calcd. C 20.48, H 1.23, Cl 43.19; found C 20.10, H 1.51, Cl 43.50.

2. 1-[Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio]-1,1,2,2,2-pentachlorodisilane (2b): According to **1.** from 1880 mg (6.96 mmol) of Na[Fe(CO)$_2$C$_5$Me$_5$] (**1b**) and 2058 mg (7.65 mmol) of hexachlorodisilane in 60 mL of cyclohexane after 18 h. The obtained residue is stirred for 1 h with 35 mL of benzene, insoluble material filtered off and the clear filtrate evaporated in vacuo to 10 mL. After addition of 40 mL of *n*-pentane **2b** precipitates, is filtered off, washed with 20 mL of cold pentane and dried in vacuo. − Yield 2100 mg (63%). − Pale yellow microcrystalline powder. − M.p. 165°C. − ^{1}H NMR: δ = 1.50 [s, (H$_3$C)$_5$C$_5$]. − ^{13}C NMR: δ = 212.7 (s, CO), 97.76 [s, C$_5$(CH$_3$)$_5$], 9.16 [s, (CH$_3$)$_5$C$_5$]. − ^{29}Si NMR: δ = 75.65 (s, α-Si), −0.20 (s, β-Si). − IR (pentane): $\tilde{\nu}$ = 2013 cm^{-1} (s), 1981 (sh), 1975 (vs) [ν(CO)]. − MS (rel. to ^{28}Si, ^{35}Cl and ^{56}Fe, 70 eV, 80°C): *m/z* (%) = 478 (2, [M]$^+$), 450 (3, [M − CO]$^+$), 422 (15, [M − 2CO]$^+$), 345 (58, [M − SiCl$_3$]$^+$), 324 (12, [M − 2CO, − SiCl$_2$]$^+$), 289 (26, [M − 2CO, − SiCl$_3$]$^+$), 226 (100, [C$_5$Me$_5$FeCl]$^+$), 191 (83, [C$_5$Me$_5$ − Fe]$^+$), 163 (80, [C$_5$Me$_5$Si]$^+$). − $C_{12}H_{15}Cl_5FeO_2Si_2$ (480.55): calcd. C 29.99, H 3.15, Cl 36.89; found C 30.46, H 3.20, Cl 37.10.

3. 1-[Dicarbonyl(η^5-cyclopentadienyl)ruthenio]-1,1,2,2,2-pentachlorodisilane (2c): According to **1.** from 520 mg (2.12 mmol) of Na[Ru(CO)$_2$Cp] (**1c**) and 720 mg (2.90 mmol) of hexachlordisilane in 20 mL of cyclohexane after 14 h. − Yield 561 mg (58%). − Yellow microcrystalline powder. − M.p. 72°C (DTA). − ^{1}H NMR: δ = 4.44 (s, H$_5$C$_5$). − ^{13}C NMR: δ = 196.8 (s, CO), 87.84 (s, C$_5$H$_5$). − ^{29}Si NMR: δ = 58.31 (s, α-Si), −1.19 (s, β-Si). − IR (pentane): $\tilde{\nu}$ = 2043 cm^{-1} (vs), 1997 (vs) [ν(CO)]. − $C_7H_5Cl_5O_2RuSi_2$ (455.62): calcd. C 18.45, H 1.11, Cl 38.91; found C 19.14, H 1.23, Cl 38.46.

4. 1-[Dicarbonyl(η^5-pentamethylcyclopentadienyl)ruthenio]-1,1,2,2,2-pentachlorodisilane (2d): According to **1.** from 780 mg (2.35 mmol) of K[Ru(CO)$_2$C$_5$Me$_5$] (**1d**) and 760 mg (2.82 mmol) of hexachlorodisilane in 60 mL of cyclohexane after 18 h. − Yield 1005 mg (85%). − Yellow microcrystalline powder. − M.p. 62°C (decomp., DTA). − ^{1}H NMR: δ = 1.45 [s, (H$_3$C)$_5$C$_5$]. − ^{13}C NMR: δ = 199.5 (s, CO), 101.4 [s, C$_5$(CH$_3$)$_5$], 9.5 [s, (CH$_3$)$_5$C$_5$]. − ^{29}Si NMR: δ = 56.69 (s, α-Si), 1.29 (s, β-Si). − IR (pentane): $\tilde{\nu}$ = 2024 cm^{-1} (vs), 1980 (vs) [ν(CO)]. − $C_{12}H_{15}Cl_5RuO_2Si_2$ (525.76): calcd. C 27.41, H 2.88; found C 28.46, H 3.20.

5. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]disilane (3a): A suspension of 347 mg (9.14 mmol) LiAlH$_4$ in 40 mL of diethyl ether is cooled to −78°C and 750 mg (1.83 mmol) of Cp(OC)$_2$Fe−SiCl$_2$−SiCl$_3$ (**2a**), dissolved in 30 mL of diethyl ether, are added within 15 min. After 30 min of stirring the reaction mixture is warmed up to room temperature and stirred for another 2 h. Insoluble materials are filtered off, the solvent removed in vacuo and the oily residue extracted with 35 mL of petroleum ether (boiling range 50−70°C). After reducing the volume of the extract in vacuo to 6 mL and cooling to −78°C **3a** precipitates, is separated, washed with 5 mL of cold pentane and dried in vacuo. Further purification is achieved by sublimation at 80−85°C/10^{-2} Torr. − Yield 310 mg (71%). − Yellow, microcrystalline powder. − M.p. 16−17°C. − ^{1}H NMR: δ = 4.10 (s, 5 H, H$_5$C$_5$), 3.95 [q, ^{1}*J*(HSi) = 179.5 Hz, ^{2}*J*(HSiSi) = 4.6 Hz, ^{3}*J*(HSiSiH) = 3.2 Hz, 2 H, H$_2$Si], 3.66/3.30 [t, ^{1}*J*(HSi) = 186.1 Hz, ^{2}J(HSiSi) = 7.7 Hz, ^{3}*J*(HSiSiH) = 3.2 Hz, 3 H, H$_3$Si]. − ^{29}Si NMR: δ = −53.92 (SiH$_2$), −93.81 [^{1}*J*(SiSi) = 67.3 Hz, SiH$_3$]. − IR (pentane): $\tilde{\nu}$ = 2133 cm^{-1} (w, SiH$_3$), 2087 (w, SiH$_2$) [ν(SiH)]; 2007 (s), 1968 (vs) [ν(CO)]. − MS (rel. to ^{28}Si and ^{56}Fe, 70 eV, 35°C): *m/z* (%) = 238 (22, [M]$^+$), 210 (11, [M − CO]$^+$), 182 (19, [M − 2CO]$^+$), 179 (39, [M − CO, − SiH$_3$]$^+$), 151 (31, [M − 2CO, − SiH$_3$]$^+$), 149 (68, [CpFe−Si]$^+$), 121 (100, [CpFe]$^+$), 93 (71, [CpSi]$^+$). − $C_7H_{10}FeO_2Si_2$ (238.20): calcd. C 35.29, H 4.24; found C 35.84, H 4.51.

6. 1-[Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio]disilane (3b): According to **5.** from 1010 mg (2.10 mmol) of C$_5$Me$_5$(OC)$_2$Fe−SiCl$_2$−SiCl$_3$ (**2b**) and 395 mg (10.5 mmol) of LiAlH$_4$ in 80 mL of diethyl ether after stirring for 4 h. **3b** is purified by recrystallisation from 15 mL of *n*-pentane. − Yield 630 mg (97%). − Deep yellow crystals. − M. p. 64°C. − ^{1}H NMR: δ = 3.75 [m, 5 H, ^{1}*J*(HSi) = 172.4 Hz (SiH$_2$), ^{1}*J*(HSi) = 184.4 Hz (SiH$_3$), H$_5$Si$_2$], 1.40 [s, 15 H, (H$_3$C)$_5$C$_5$]. − ^{13}C NMR: δ = 215.68 (s, CO), 95.12 [s, C$_5$(CH$_3$)$_5$], 9.42 [s, (CH$_3$)$_5$C$_5$]. − ^{29}Si NMR: δ = −45.19 (SiH$_2$), −95.61 (SiH$_3$). − IR (petroleum ether): $\tilde{\nu}$ = 2127 cm^{-1} (w, SiH$_3$), 2071 (w, SiH$_2$) [ν(SiH)]; 1994 (vs), 1947 (vs) [ν(CO)]. − MS (rel. to ^{28}Si and ^{56}Fe, 70 eV, 35°C): *m/z* (%) = 308 (15, [M]$^+$), 280 (60, [M − CO]$^+$), 252 (7, [M − 2CO]$^+$), 250 (55, [M − CO, − SiH$_2$]$^+$), 249 (23, [M − CO, − SiH$_3$]$^+$), 248 (100, [M − Si$_2$H$_5$]$^+$), 247 (24, [M − Si$_2$H$_6$]$^+$), 219 (87, [C$_5$Me$_5$FeSi]$^+$), 191 (48, [C$_5$Me$_5$Fe]$^+$), 163 (83, [C$_5$Me$_5$Si]$^+$). − $C_{12}H_{20}FeO_2Si_2$ (308.35): calcd. C 46.74, H 6.55; found C 47.05, H 6.68.

7. 1-[Dicarbonyl(η^5-cyclopentadienyl)ruthenio]disilane (3c): According to **5.** from 91 mg (2.39 mmol) of LiAlH$_4$ and 210 mg (0.47 mmol) of Cp(OC)$_2$Ru−SiCl$_2$−SiCl$_3$ (**2c**) in 30 mL of diethyl ether after stirring for 2 h at room temperature, extraction of the residue with 10 mL of petroleum ether (40−60) and sublimation at 40°C/10^{-5} Torr. − Yield 112 mg (82%). − Colorless waxy solid. −

M.p. −12 to −14)°C. − ^{1}H NMR: δ = 4.41 (s, 5 H, H_5C_5), 3.73 [q, ^3J(HSiSiH) = 3.36 Hz, 2 H, H_2Si], 3.66 [t, ^3J(HSiSiH) = 3.36 Hz, 3 H, H_3Si]. − ^{29}Si NMR: δ = −76.6 [dq, ^1J(SiH) = 181.0 Hz, ^2J(SiSiH) = 5.0 Hz, SiH_2], −94.0 [dt, ^1J(SiH) = 186.1 Hz, ^2J(SiSiH) = 6.6 Hz, SiH_3]. − IR (pentane): ṽ = 2129 cm^{-1} (w, SiH_3), 2084 (w, SiH_2) [ν(SiH)]; 2022 (vs), 1978 (vs) [ν(CO)]. − $C_7H_{10}O_2RuSi_2$ (283.39): calcd. C 29.67, H 3.56; found C 29.54, H 3.51.

8. 1-[Dicarbonyl(η^5-cyclopentadienyl)ferrio]-1,1-dichlorodisilane (4a): A solution of 175 mg (0.73 mmol) of $Cp(OC)_2Fe-SiH_2-SiH_3$ (**3a**) in 5 mL of cyclohexane is combined with 566 mg (3.68 mmol) of CCl_4 and the reaction mixture stirred for 3 h at room temperature and monitored by ^{1}H NMR. After removing volatile components (solvent, formed chloroform and excess of CCl_4) in vacuo the orange residue is extracted twice with 7 mL each of petroleum ether (50−70) and the volume of the extract is reduced in vacuo to 5 mL. **4a** crystallises after cooling for 3 h to −78 °C, is filtered off and dried in vacuo at 10 °C. − Yield 205 mg (91%). − Yellow microcrystalline powder. − M.p. 23−24 °C. − ^{1}H NMR: δ = 4.07 (s, 5 H, H_5C_5), 3.83 (s, 3 H, HSi). − ^{13}C NMR: δ = 211.5 (s, CO), 85.07 (s, C_5H_5). − ^{29}Si NMR: δ = 93.6 (s, α-Si), −83.23 (s, β-Si). − IR (pentane): ṽ = 2150 cm^{-1} [w, ν(SiH)]; 2028 (s), 2021 (m), 1989 (vs), 1981 (s) [ν(CO)]. − MS (rel. to ^{28}Si, $^{35-}$Cl and ^{56}Fe, 70 eV, 35 °C): *m*/*z* (%) = 306 (8, [M]$^+$), 278 (41, [M − CO]$^+$), 250 (7, [M − 2CO]$^+$), 247 (49, [M − CO, − SiH_3]$^+$), 219 (86, [M − 2CO, − SiH_3]$^+$), 149 (18, [CpFeSi]$^+$), 121 (37, [CpFe]$^+$), 93 (100, [CpSi]$^+$). − $C_7H_8Cl_2FeO_2Si_2$ (307.08): calcd. C 27.32, H 2.49, Cl 22.81; found C 27.38, H 2.63, Cl 23.00.

9. 1-[Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio]-1,1-dichlorodisilane (4b): According to **8.** from 210 mg (0.68 mmol)/90 mg (0.29 mmol) of $C_5Me_5(OC)_2Fe-SiH_2-SiH_3$ (**3b**) and 7 mL of CCl_4/ 2 mL of $CHCl_3$ after 80 min at room temperature/12 h at 40 °C. The brown residue obtained is extracted with 10 mL of a 1:1 mixture of petroleum ether (50−70)/methylcyclohexane, the extract evaporated in vacuo to dryness and the residue dissolved in 4 mL of pentane. **4b** crystallises on cooling to −78 °C. − Yield 200 mg (77%)/ 98 mg (89%). − Yellow microcrystalline powder. − M.p. 119−120 °C. − ^{1}H NMR: δ = 3.97 (s, 3 H, H_3Si), 1.49 [s, 15 H, $(H_3C)_5C_5$]. − ^{13}C NMR: δ = 215.6 (s, CO), 94.9 [s, $C_5(CH_3)_5$], 9.41 [s, $(CH_3)_5C_5$]. − IR (pentane): ṽ = 2141 cm^{-1} [w, ν(SiH)]; 2008 (s), 2001 (m), 1970 (vs), 1961 (s) [ν(CO)]. − MS (rel. to ^{28}Si, ^{35}Cl and ^{56}Fe, 70 eV, 60 °C): *m*/*z* (%) = 376 (4, [M]$^+$), 348 (14, [M − CO]$^+$), 320 (8, [M − 2CO]$^+$), 289 (8, [M − 2CO, − SiH_3]$^+$), 226 (4, [C_5Me_5FeCl]$^+$), 191 (13, [C_5Me_5Fe]$^+$), 163 (100, [C_5Me_5Si]$^+$), 135 (19, [C_5Me_5]$^+$). − $C_{12}H_{18}Cl_2FeO_2Si_2$ (377.23): calcd. C 38.21, H 4.82, Cl 18.80; found C 38.33, H 4.92, Cl 18.55.

10. 1-[Dicarbonyl(η^5-cyclopentadienyl)ruthenio]-1,1-dichlorodisilane (4c): According to **8.** from 105 mg (0.37 mmol) of $Cp(OC)_2Ru-SiH_2-SiH_3$ (**3c**) in 15 mL of benzene and 550 mg (3.60 mmol) of CCl_4 after 15 h. After dissolving the beige residue in 1 mL of benzene and addition of 10 mL of pentane **4c** precipitates, is filtered off and dried in vacuo. − Yield 85 mg (65%). − Light beige powder. − M.p. 68 °C (decomp.). − ^{1}H NMR: δ = 4.48 (s, 5 H, H_5C_5), 3.71 (s, 3 H, H_3Si). − IR (benzene): ṽ = 2151 cm^{-1} [w, ν(SiH)]; 2025 (s), 2017 (m), 1979 (vs), 1970 (s) [ν(CO)]. − $C_7H_8Cl_2O_2RuSi_2$ (352.29): calcd. C 23.87, H 2.29, Cl 20.13; found C 24.79, H 1.49, Cl 19.87.

11. Photolysis of $Cp(OC)_2Fe-SiCl_2-SiCl_3$ (2a): A solution of 100 mg (0.24 mmol) of $Cp(OC)_2Fe-SiCl_2-SiCl_3$ (**2a**) in 5 mL of benzene is irradiated for 120 h with UV-light (quartz lamp TQ 718, 700 W, Hanau). Insoluble materials are filtered off and the yellow filtrate is evaporated in vacuo to dryness. The residue is extracted with 10 mL of pentane, and the volume of the extract is reduced to 3 mL. After cooling to −78 °C $Cp(OC)_2Fe-SiCl_3$ (**5**)[9a] precipitates. − Yield 43 mg (59%). − Light beige, microcrystalline powder.

12. Photolysis of $Cp(OC)_2Fe-SiH_2-SiH_3$ (3a): A solution of 93 mg (0.39 mmol) of $Cp(OC)_2Fe-SiH_2-SiH_3$ (**3a**) in 5 mL of cyclohexane is irridiated for 120 h with UV light (quartz lamp TQ 718, 700 W, Hanau). A white unidentified precipitate is separated and the filtrate evaporated in vacuo to dryness, yielding $Cp(OC)_2Fe-SiH_3$ (**6**).[8][21] − Yield 43 mg (53%).

13. Thermolysis of $Cp(OC)_2Fe-SiH_2-SiH_3$ (3a): A solution of 146 mg (0.61 mmol) of $Cp(OC)_2Fe-SiH_2-SiH_3$ (**3a**) in 8 mL of cyclohexane is heated to 65 °C for 32 h. Workup according to **12.** yields $Cp(OC)_2Fe-SiH_3$ (**6**).[8][21] − Yield 93 mg (73%).

14. X-ray Crystal Structure Determination of 2a: Suitable single crystals of $Cp(OC)_2FeSi_2Cl_5$ were obtained from a saturated *n*-pentane solution at −20 °C. Crystal data for $Cp(OC)_2FeSi_2Cl_5$: $C_7H_5Cl_5FeO_2Si_2$, $M = 410.39$, triclinic, space group *P*-1 (No. 2), yellow crystals, dimensions $0.20 \times 0.20 \times 0.30$ mm^3, $a = 12.1711(4)$, $b = 8.7557(4)$, $c = 13.9851(6)$ Å, $\alpha = 90°$, $\beta = 100.589(2)°$, $\gamma = 90°$, $V = 1465.0(2)$ Å^3, $D_c = 1.861$ Mg m^{-3}, $Z = 4$, μ (Mo-*K*α) = 2.088 mm^{-1}, $T = 123(2)$ K, $F(000) = 808$; 17118 reflections were collected on a Nonius Kappa CCD diffractometer ($2\theta_{max.} = 56.6°$, $-16 \le h \le 16$, $-11 \le k \le 11$, $-17 \le l \le 16$), 3292 symmetry independent reflections ($R_{int} = 0.1011$) were used for the structure solution (Patterson methods)[1] and refinement (full-matrix least-squares on F^2,[2] 155 parameters, 0 restraints), non-hydrogen atoms were refined anisotropically, $wR2 = 0.0572$ [$R_1 = 0.037$ for 3292 $I > 2\,\sigma(I)$].Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114922. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambrigde CB2 1EZ, UK (Fax: int. code +(1223)336−033; E-mail: teched@ccdc.cam.ac.uk).

15. X-ray Crystal Structure Determination of 3b: Yellow crystals of **3b**, suitable for X-ray diffraction were grown by slow diffusion of pentane into a saturated toluene solution of **3b** at −30 °C. Crystal data: $C_{12}H_{20}FeO_2Si_2$, $M = 308.31$, triclinic, space group: *P*-1 (No. 2), $a = 7.739(3)$ Å, $b = 8.233(5)$ Å, $c = 13.875(6)$ Å, $\alpha = 77.795(8)°$, $\beta = 84.945(8)°$, $\gamma = 63.262(9)°$, $V = 771.7(6)$ Å^3, $Z = 2$, $d_{calcd.}$: 1.327 gcm^{-3}, CAD4-diffractometer (Enraf−Nonius), radiation type: Mo-K_α, wavelength: λ = 0.71073 Å, graphite monochromator, crystal size: $0.55 \times 0.50 \times 0.50$ mm, temperature: 173(2) K, ω/Θ-scan, scale range: 1.50° < Θ < 24.92°, F(000): 324, total reflections: 5300, independant reflections: 2691, observed reflections: 2310 with $I > 2\sigma(I)$, absorption coefficient: μ = 1.121 mm^{-1}, semi-empirical absorption correction (T_{min}/T_{max}: 0.9716/ 0.9983), structure solution: SHELXS-96[25a] with patterson methods, structure refinement: SHELXL-96[25b] (234 parameters), $R_1 = 0.0249$, $wR_2 = 0.0614$. The absorption correction was conducted semi-empirically with the help of of the SDP-program.[26] All atoms were determined by Fourier-transformation, the non-hydrogens refined anisotropically by the method of the smallest mean-square-errors (full-matrix least-squares) while the hydrogen atoms were refined isotropically.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101420. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. Code + 44(1223)336−033; E-mail: deposit@ccdc.cam.ac.uk].

16. Matrix Isolation Raman Spectra of $Cp(OC)_2Fe-SiH_2-SiH_3$ (3a): For the Raman spectroscopic investigations of **3a** the sample was isolated in a krypton matrix at 20 K by using the "slow-spray-on" technique.[27] The matrix isolation apparatus consisted of a cryocooler (CTI Cryogenics, model 22C) and a turbo-pumping unit (Pfeiffer/Balzers, TPH 170).[28] The sample material was sublimated in a Knudsen cell at 308 K and a pressure of 10^{-7} – 10^{-8} mbar. Afterwards the gas was directly mixed with the matrix gas (krypton) in a heated nozzle, from where it was deposited on a highly polished gold plated copper cold head at 20 K. For excitation of the Raman spectra we used the 647 nm line of a krypton ion laser (Spectra Physics, model 2025). The laser beam was focussed on the matrix layer in a 30° angle to the target. The scattered light was dispersed by means of a double monochromator (Spex, model 1404) and the signal was detected by a CCD camera system (Photometrics, Spectra 9000). For the spectrum a resolution of 3 cm^{-1} was chosen. Data acquisition and spectra analyses were performed by a commercial software package (MAPS, Photometrics).

17. Density Functional Calculations of 2a, 3a: The quantum mechanical calculations were performed using Gaussian94.[29] For the best combination of exchange and correlation functionals concerning vibrational frequencies[30] we used Becke's 1988 exchange functional[31] in combination with the Perdew-Wang 91 gradient-corrected correlation functional[32] (BPW91). As basis sets we tested the Los Alamos effective core potential (ECP) plus double zeta[33] on iron, silicon and chlorine, whereas for the rest of the atoms (all first-row elements) the Dunning/Huzinaga full double zeta basis set[34] was applied. All calculations were performed on DEC alphastations 500 [400 MHz]). Wavenumber calculations are only valid at a stationary point,so in every calculation a full geometry optimization had to be done first.

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[1] [1a] W. Malisch, *J. Organomet. Chem*. **1972**, *39*, C28–C30. – [1b] W. Malisch, *ibid.* **1974**, *82*, 185–199.

[2] [2a] R. B. King, K. H. Pannell, *Z. Naturforsch* **1969**, *24b*, 262. – [2b] B. K. Nicholson, J. Simpson, *J. Organomet. Chem.* **1974**, *72*, 211–220. – [2c] L. Parkanyi, K. H. Pannell, C. Hernandez, *J. Organomet. Chem*. **1983**, *252*, 127–132.

[3] [3a] K. H. Pannell, J. Cervantes, C. Hernandez, J. Cassias, S. Vincenti, *Organometallics* **1986**, *5*, 1056–1057. – [3b] K. H. Pannell, J. M. Rodzell Jr., C. Hernandez, *J. Am. Chem. Soc.* **1989**, *111*, 4482–4485. – [3c] H. Tobita, K. Ueno, H. Ogino, *Chem. Lett.* **1986**, 1777–1780. – [3d] K. H. Pannell, S.-H. Lin, R. N. Kapoor, F. Cervantes-Lee, M. Pinon, L. Parkanyi, *Organometallics* **1990**, *9*, 2454–2462. – [3e] H. Tobita, K. Ueno, M. Shimoi, H. Ogino, *J. Am. Chem. Soc.* **1990**, *112*, 3415–3420. – [3f] T. Takeuchi, H. Tobita, H. Ogino, *Organometallics* **1991**, *10*, 835–836.

[4] A. Haynes, M. W. George, M. T. Haward, M. Poliakoff, J. J. Turner, N. M. Boag, M. Green, *J. Am. Chem. Soc.* **1991**, *113*, 2011–2020.

[5] [5a] B. Stadelmann, P. Lassacher, H. Stüger, E. Hengge, *J. Organomet. Chem.* **1994**, *482*, 201–206. – [5b] M. J. Michalczyk, C. A. Recatto, J. C. Calabrese, M. J. Fink, *J. Am. Chem. Soc.* **1992**, *114*, 7955–7957.

[6] W. Malisch, R. Lankat, W. Seelbach, J. Reising, M. Noltemeyer, R. Pikl, U. Posset, W. Kiefer, *Chem. Ber.* **1995**, *128*, 1109–1115.

[7] **3a** has already been mentioned in ref.[5] but yields are considerable lower (41%) in those experiments.

[8] H.-U. Wekel, W. Malisch, *J. Organomet. Chem.* **1984**, *264*, C10–C13.

[9] [9a] W. Jetz, W. A. G. Graham, *J. Am. Chem. Soc.* **1967**, *89*, 2773–2775. – [9b] U. Schubert, G. Kraft, E. Walther, *Z. Anorg. Allg. Chem.* **1984**, *519*, 96–106.

[10] [10a] M. Schmeisser, P. Voss, *Z. Anorg. Allg. Chem.* **1964**, *334*, 50–56. – [10b] P. W. Schenk, H. Bloching, *ibid.* **1964**, *334*, 57–65. – [10c] K. Hassler, E. Hengge, W. Raml, *Monatshefte Chem.* **1980**, *111*, 581–590. – [10d] H. E. O'Neal, M. A. Ring, W. H. Richardson, G. F. Licciardi, *Organometallics* **1989**, *8*, 1968–1973. – [10e] R. Becerra, H. M. Frey, B. P. Mason, R. Walsh, M. S. Gordon, *J. Am. Chem. Soc.* **1992**, *114*, 2751–2752. – [10f] R. Becerra, H. M. Frey, B. P. Mason, R. Walsh, *J. Organomet. Chem.* **1996**, *521*, 343–349.

[11] [11a] A. Y. Vanderwielen, M. A. Ring, H. E. O'Neal, *J. Am. Chem. Soc.* **1975**, *97*, 993–998. – [11b] H. Bock, B. Solouki, G. Maier, *Angew. Chem.* **1985**, *97*, 205–206; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 205–206. – [11c] J. M. Coffin, T. P. Hamilton, P. Pulay, I. Hargittai, *Inorg. Chem.* **1989**, *28*, 4092–4094. – [11d] M. S. Gordon, W. Nelson, *Organometallics* **1995**, *14*, 1067–1069.

[12] H. Marsmann, ^{29}Si-NMR-Spectroscopic Results in *NMR-Basic Principles and Progress*, Springer, Berlin-Heidelberg-New York, **1981**, Bd. 7, S. 65.

[13] R. L. Scholl, G. E. Maciel, W. K. Musker, *J. Am. Chem. Soc.* **1972**, *94*, 6376–6385.

[14] R. Loewer, M. Vongehr, H. C. Marsmann, *Chem.-Ztg.* **1975**, *99*, 33.

[15] H. C. Marsmann, H. G. Horn, *Z. Naturforsch.* **1972**, *27b*, 1448–1451.

[16] [16a] X. Zhou, C .J. M. Wheeless, R. Liu, *Vibrational Spectroscopy* **1996**, *12*, 53–63. – [16b] X. Zhou, R. Liu, *Vibrational Spectroscopy* **1996**, *12*, 65–71. – [16c] X. Zhou, S. J. Mole, R. Liu, *Vibrational Spectroscopy* **1996**, *12*, 73–79.

[17] C. Fickert, PhD thesis, Würzburg, **1998**.

[18] P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, A. Vargha, *J. Am. Chem. Soc.* **1983**, *105*, 7037–7047.

[19] The infrared data concerning the ν(Si–H) values of **3a** differ considerably from those given by Hengge et al.[5]. These authors report only one band at 2030 cm^{-1} which is in accordance to that of $Cp(OC)_2Fe-SiH_3$, the decomposition product of **3a**.

[20] S. Schmitzer, U. Weis, H. Käb, W. Buchner, W. Malisch, T. Polzer, U. Posset, W. Kiefer, *Inorg. Chem.* **1993**, *32*, 303–306.

[21] [21a] W. Malisch, S. Möller, O. Fey, H.-U. Wekel, R. Pikl, U. Posset, W. Kiefer, *J. Organomet. Chem.* **1996**, *507*, 117–124. – [21b] W. Palitzsch, U. Bohme, G. Roewer, *J. Organomet. Chem.* **1997**, *540*, 83–88. – [21c] U. Schubert, G. Kraft, E. Walther, *Z. Anorg. Allg. Chem.* **1984**, *519*, 86. – [21d] R. West, E. K. Pham, *J. Organomet. Chem.* **1991**, *402*, 215. – [21e] L. Parkanyi, K. H. Pannell, C. Hernandez, *J. Organomet. Chem.* **1983**, *252*, 127. – [21f] T. J. Drahnak, R. West, J. C. Calabrese, *J. Organomet. Chem.* **1980**, *198*, 55. – [21g] W. Höhnle, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **1980**, *464*, 139. – [21h] K. H. Pannell, S.-H. Lin, R. N. Kapoor, F. Cervantes-Lee, M. Pinon, L. Parkanyi, *Organometallics* **1990**, *9*, 2454–2462. – [21i] W. S. Sheldrick, in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), John Wiley & Sons Ltd, New York, **1989,** 227.
[22] B. Beagly, J. J. Monaghan, *J. Molec. Struct.* **1971**, *8*, 401. – W. S. Sheldrick, in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), John Wiley & Sons Ltd, New York, **1989**.

[23] [23a] T. S. Piper, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1956**, *3*, 104–124. – [23b] T. Blackmore, M. I. Bruce, F. G. A. Stone, *J. Chem. Soc. (A)* **1968**, 2158–2162.

[24] [24a] D. H. Gibson, W.-L. Hsu, F. U. Ahmed, *J. Organomet. Chem.* **1981**, *215*, 379–401. – [24b] A. Stasunik, D. Wilson, W. Malisch, *J. Organomet. Chem.* **1984**, *270*, C18–C22.

[25] [25a] G. M. Sheldrick, SHELXS-96, *Program for Structure Solution*, Göttingen **1996**. – [25b] G. M. Sheldrick, SHELXL-96, *Program for Structure Determination*, Göttingen **1996**.

[26] Enraf.Nonius, *Structure-Determination-Package*, Enraf–Nonius, Delft, The Netherlands **1984**.

[27] M. J. Almond, A. J. Downs, in *Spectroscopy of Matrix Isolated Species, Advances in Spectroscopy*, (Eds.: R. J. H. Clark, R. E. Hester), Vol. 17, Wiley, Chichester, UK, **1989**, p.15.

[28] D. Gernet, W. Kiefer, *Fresenius J. Anal. Chem.* **1998**, *362*, in press.

[29] Gaussian94, Revision D.5, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Chee-

seman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomberts, R. L. Martin, D. J. Fox, J. S.Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Heat-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**.

[30] A. Gbureck, R. Pikl, W. Kiefer, *Asian J. Phys.*, submitted.

[31] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.

[32] J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244.

[33] [33a] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270−283. – [33b] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284−298. – [33c] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299−310.

[34] T. H. Dunning, Jr., P. J. Hay, in *Modern Theoretical Chemistry*, (Ed.: H. F. Schaefer), III, Plenum: New York, **1976**, 1−28.

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