Iron-Fragment-Substituted Heterosiloxanes of Gallium $[Cp(OC)_2Fe-SiR_2OGaR'_2]_2$ (R, R′ = Alkyl, Aryl) − Structures of $[Cp(OC)_2Fe-SiR_2OGaMe_2]_2$ (R = Me, Ph)[‡]

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Keywords: Gallium / Iron / Silanols / Silicon / Siloxanes

The trialkylgallanes GaR''_3 [R′ = Me, *i*Pr (**2a** and **2b**)] react with the ferrio-silanols $Cp(OC)_2Fe–Si(R)(R')OH$ [R = R′ = Me, *i*Pr, Ph (**1a**–**c**), R = Me, R′ = Ph (**1d**)] by alkane elimination to yield the iron-substituted siloxy-gallanes $[Cp(OC)_2Fe–Si(R)(R')OGaR''_2]_2$ (**3a**–**e**). According to molecular mass determination in benzene (**3a**, **3b**, **3d**), X-ray analyses (**3a**, **3d**) and NMR spectroscopy (**3e**), the novel hetero-siloxanes exist as dimers both in solution and in the solid state. The bonding situation and geometry of the ferrio-heterosiloxane $[Cp(OC)_2Fe–SiH_2OGaH_2]_2$ has been analyzed by density functional calculation.

Introduction

Heterosiloxanes, siloxanes containing Si−O−E moieties (E = heteroelement), represent a class of compounds in organometallic chemistry that has attracted widespread interest in material science and catalysis in recent decades. Due to the presence of the heteroelement, they may serve as models for heteroelement-doped silicates and silicones, which often exhibit special properties such as high thermal stability or catalytic activity. In this context, the preparation of group 13 heterosiloxanes (E = Al, Ga, In) has become a growing field of research concerning catalytically active zeolites, such as gallium-containing zeolites for the dehydrogenation and dehydrocyclization of alkanes.[3−8] Early studies by Schmidbaur[9−11] describe various heterosiloxanes represented by compounds such as $[R_3SiOEMe_2]_2$ (E = Ga, In; R = Me, Ph)[10] for group 13 elements. Recent work by Roesky has shown that the related reactions of organosilanetriols $RSi(OH)_3$ preferentially yield compounds such as $[RSiO_3E{\cdot}D]_4$ (E = Al, Ga, In; D = THF, dioxane), characterized by three-dimensional polyhedral cage structures.[3−5] The access to transition metal-substituted silanols $L_nM-SiMe_{3-x}(OH)_x$ (x = 1−3) now offers the possibility of obtaining a novel kind of heterosiloxane in which the silicon atom bears a transition metal fragment. Metallo-silanols show reduced H acidity of the Si−OH function and remarkable stability towards self-condensation, a behavior contrasting with that of organosilanols $R_{4-x}Si(OH)_x$ (x = 1−3), which usually convert into siloxanes. This high stability, caused by the electron-rich metal fragment, predisposes metallo-silanols to act as excellent precursors for selective reactions with chlorosilanes, yielding metallo-siloxanes and -polysiloxanes $L_nM-SiMe_{3-x}(OSiR'_3)_x$ [x = 1−3; R'_3Si = Me_3Si, $Me_2(H)Si$].[12−20] Moreover, these properties should allow the preparation of metal fragment-substituted heterosiloxanes of gallium and indium by alkane elimination. These species could represent attractive models for silica- or zeolite-based catalysts, in which L_nM represents an catalytically active metal fragment.

In this paper we present the first examples of successful coupling reactions between metallo-silanols $Cp(OC)_2Fe-Si(R)(R')OH$ (R = R′ = Me, *i*Pr, Ph; R = Me, R′ = Ph)[13,14,21] and diverse trialkylgallanes. Moreover, we describe investigations concerning the influence of the transition metal fragment on the aggregation mode.

[‡] Synthesis and Reactivity of Silicon Transition Metal Complexes, 60. Part 59: Ref.[1], Metallo-Silanols and Metallo-Siloxanes, 31. Part 30: Ref.[2]

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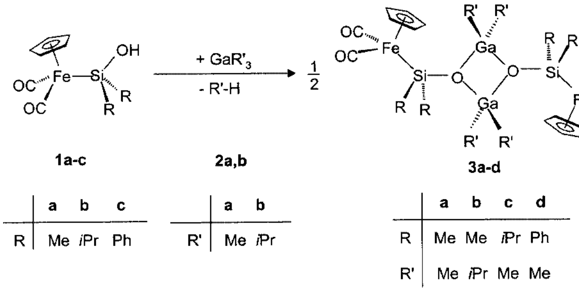
DOI: 10.1002/ejic.200200598

Results and Discussion

Synthesis of Iron Fragment-Substituted Heterosiloxanes of Gallium

Treatment of the trialkylgallanes **2a** and **2b** with stoichiometric amounts of the ferrio-silanols Cp(OC)$_2$Fe−SiR$_2$OH [R = Me (**1a**), *i*Pr (**1b**), Ph (**1c**)] in *n*-pentane at room temperature yielded, by the elimination of alkane, after 2 h (**3a**, **3c**, **3d**) or 16 h (**3b**) the metal fragment-substituted heterosiloxanes **3a**−**d**. The trimethylgallane **2a** was preferably employed as an Et$_2$O adduct, which proved to be much easier to handle (Scheme 1).



Scheme 1. Synthesis of iron fragment-substituted heterosiloxanes of gallium

Compounds **3a**−**d** are isolated after recrystallization from *n*-pentane at −78 °C as light yellow, microcrystalline powders in 73−86% yields. The compounds are slightly soluble in *n*-pentane or *n*-hexane and reasonably soluble in benzene or toluene. Unlike the starting materials, they may even be handled in air for short times without decomposition.

The ^{29}Si NMR resonances of **3a**−**d** show the typical downfield shifts of Cp(OC)$_2$Fe-substituted silicon atoms (**3a**: δ = 66.57 ppm, **3b**: δ = 64.10 ppm, **3c**: δ = 78.92 ppm, **3d**: 54.86 ppm). The observed range appears close to that for the corresponding ferrio-silanols (**2a**: δ = 66.05 ppm, **2b**: δ = 76.36 ppm, **2c**: 50.38 ppm).

Molecular mass determinations of **3a**, **3b**, and **3d** in benzene by freezing-point depression reveal the presence of dimers, originating from intermolecular interaction between the Lewis acidic group 13 element and the Lewis basic oxygen atoms of the Si−O units. This result is in good accordance with the findings for metal-free siloxy-gallanes.[9−11] The aggregation to dimers in the solid state was additionally confirmed by X-ray analyses of **3a** and **3d**. These results clearly indicate that the Cp(OC)$_2$Fe fragment at the silicon does not induce O−Ga π-interaction sufficient to prevent dimerization.

Treatment of the ferrio-silanol Cp(OC)$_2$FeSi(Me)(Ph)OH (**1d**), bearing a chiral silicon atom, with GaMe$_3$·Et$_2$O (**2a**) in *n*-pentane produces the heterosiloxane **3e** as a beige, microcrystalline solid in 82% yield.

The aggregation of **3e**, due to Ga−O interaction, results in the formation of *like* and *unlike* diastereomers (Figure 1), as can be directly confirmed in solution by ^{1}H NMR spectroscopy (C$_6$D$_6$, Figure 2). Since the two diastereomers differ in the topicities of their Ga-bonded methyl groups, the *like* diastereomer (*RR*/*SS*), which has a C_2 axis as symmetry element, provided free rotation around the O−Si axis, and has homotopic methyl groups, while the *unlike* diastereomer (*RS*/*SR*), characterized by a mirror plane, has diastereotopic methyl groups. This stereochemical situation gives rise to three signals for the Ga-bonded methyl groups in the ^{1}H NMR and the ^{13}C NMR spectra: two for the *unlike* form and one for the *like* form. The diastereomeric ratio can be determined as 50:50 by integration of these signals. Moreover, two signals, located very close to each other, are observed for all other NMR resonances, due to the existence of diastereomers.

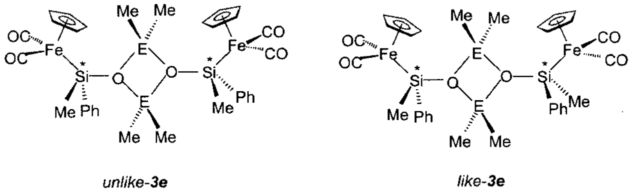

unlike-**3e** *like*-**3e**

Figure 1. *unlike*- and *like*-**3e**

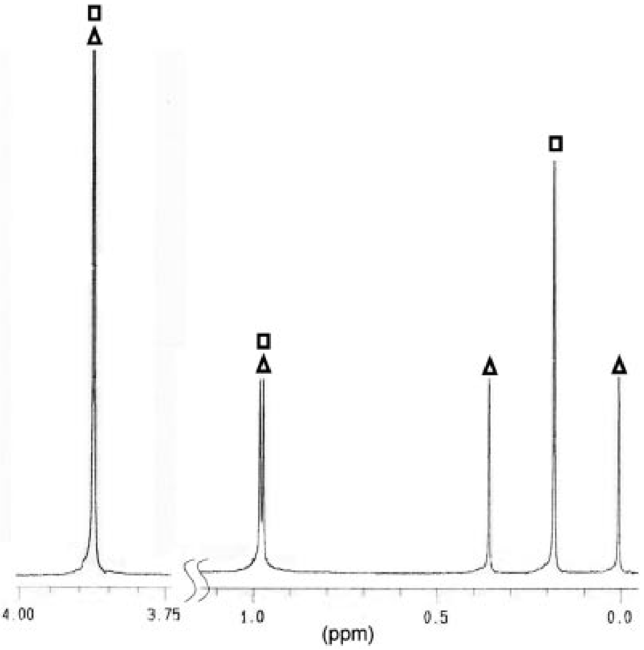


Figure 2. ^{1}H NMR([D$_6$]benzene, 300.4 MHz) of **3e** (aromatic region has been omitted for clarity); □ = *like*-**3e**, Δ = *unlike*-**3e**; *like*/*unlike* assignment of the SiMe and Cp signals is not possible

X-Ray Analyses of 3a and 3d

The results of the X-ray analyses of **3a** and **3d**, which to the best of our knowledge are the first structurally characterized siloxy-substituted diorgano compounds of gallium, are presented in Figure 3 and 4.

The structure-determining element is the rhombic, four-membered [Ga−O]$_2$ ring, a common feature of heteroatom-

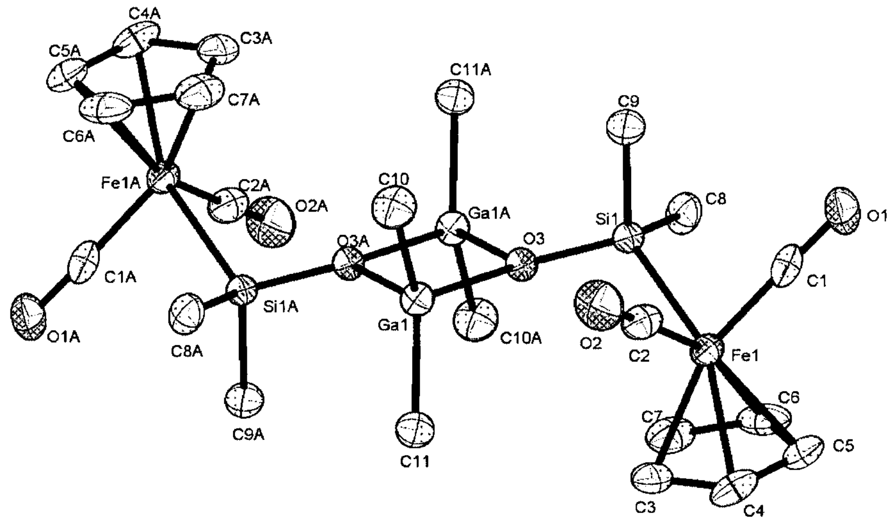


Figure 3. ORTEP plot of $[Cp(OC)_2FeSiMe_2{-}O{-}GaMe_2]_2$ (**3a**). Hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ga1−O3 1.957(3), Ga1−O3A 1.977(3), Ga1−C10 1.965(5), Ga1−C11 1.942(5), Si1−O3 1.667(3), Fe1−Si1 2.3229(16), Fe1−C1 1.730(6), Fe1−C2 1.756(5), O1−C1 1.164(6), O2−C2 1.143(6); Ga1−O3−Ga1A 96.61(13), O3−Ga1−O3A 83.39(13), C10−Ga1−C11 130.7(2), O3−Ga1−C10 110.25(19), O3−Ga1−C11 107.62(18), Si1−O3−Ga1 134.63(18), Si1−O3−Ga1A 125.98(17), O3−Si1−Fe1 113.56(12), O3−Si1−C8 106.4(2), O3−Si1−C9 106.8(2), C8−Si1−C9 106.2(3)

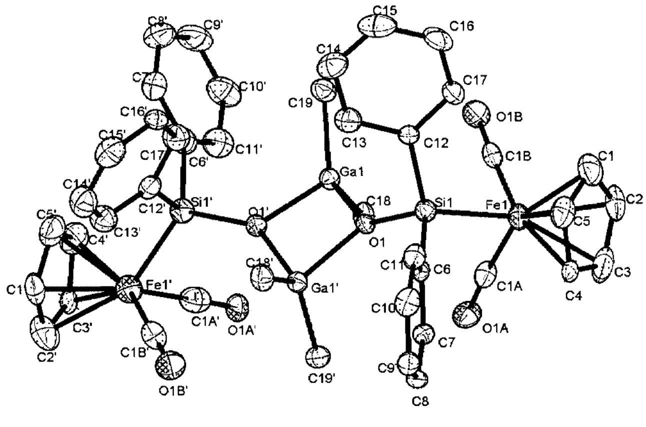


Figure 4. ORTEP plot of $[Cp(OC)_2FeSiPh_2{-}O{-}GaMe_2]_2$ (**3d**). Hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Fe1−C1a 1.7487(18), Fe1−C1b 1.7460(19), Fe1−Si1 2.3091(5), Si1−O1 1.6674(11), Si1′−O1′ 1.6703(11), O1−Ga1 1.9815(11), O1−Ga1′ 1.9754(11), O1′−Ga1′ 1.9792(19), O1′−Ga1 1.9748(11), Si1−C6 1.8914(17), Si1−C12 1.8909(16), Ga1−C19 1.9633(16), Ga1−C18 1.9615(16); C1a−Fe1−C1b 96.77(8), C1a−Fe1−Si1 86.86(6), C1b−Fe1−Si1 86.00(6), Fe1−Si1−C6 109.96(5), Fe1−Si1−C12 115.63, Fe1−Si1−O1 113.66(4), O1a−C1a−Fe1 175.59(16), O1b−C1b−Fe1 178.03(16), Ga1−O1−Ga1′ 96.78(5), Ga1−O1′−Ga1′ 96.87(5), O1−Ga1′−O1′ 82.10(4), O1−Ga1−O1′ 82.06(4), C18′−Ga1′−C19′ 127.04(7), C18−Ga1−C19 125.17(7); O1−Ga1−O1′−Ga1′ 11.24(4)

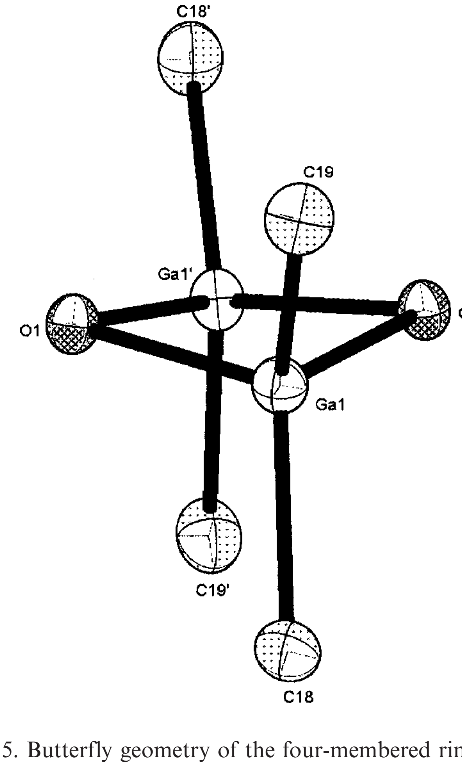


Figure 5. Butterfly geometry of the four-membered ring of **3d**

substituted group 13 dialkyl compounds, formed by the two oxygen atoms (O3/O3A in **3a**, O1/O1′ in **3d**) and the Lewis acidic gallium atoms (Ga1/Ga1A in **3a**, Ga1/Ga1′ in **3d**). In the case of **3a**, the four-membered ring, with a *trans* arrangement of the iron fragments, is planar (O3−Ga1A−O3A−Ga1 = 0°), while **3d**, with a *cis* position of the iron fragments, shows a butterfly geometry [O1−Ga1′−O1′−Ga1 = 11.24(4)°, Figure 5].

The group 13 element−oxygen bond lengths in **3a** [Ga1−O3 = 1.957(3) Å/Ga1−O3A = 1.977(3) Å] and **3d** [Ga1−O1 = 1.9815(11) Å/Ga1′−O1′ = 1.9792(19) Å] correspond to the bond lengths found for dimeric (alkoxy)-dialkylgallanes: $\{[(t\mathrm{Bu})_2\mathrm{Ga}\text{-}\mu\text{-}\mathrm{O}(t\mathrm{Bu})]_2$: 1.990 Å$\}$[22] and lie in the range between a coordinative interaction and a sigma bond.[23] A distorted tetrahedral geometry at the group 13 element is indicated by the angles formed by the ligands of

Ga1, with the smallest, endocyclic angle defined by the oxygen atoms [83.39(13)° (**3a**), 82.10(4)°/82.06(4)° (**3d**)] and the largest one formed by the two exocyclic methyl ligands [130.7(2)° (**3a**), 127.04.(7)°/125.17(7)° (**3d**)]. A nearly planar distorted trigonal coordination at the bridging oxygens is confirmed by the sum of angles, of 357°/358°, with individual angles between the ligands varying from 96.61(13)°/96.78(5)° to 134.63(18)°/132.47(6)° for **3a** and **3d**, respectively. The substituents at the silicon atoms in **3a** and **3d** show the expected tetrahedral arrangements, with small angles between the organic substituents and the oxygen [106.4(2)−106.8(2)° (**3a**); 103.37(6)°−108.72(7)° (**3d**)] and large angles including the metal fragment [110.05(16)°−113.56(12)° (**3a**); 109.96(5)°−115.63(6)° (**3d**)]. The iron-silicon distances of 2.3229(16) Å (**3a**) and 2.3091(5)/2.3086(5) Å (**3d**) and the silicon-oxygen distances of 1.667(3) (**3a**) and 1.6674(11)/1.6703(11) Å (**3d**) show no peculiarity compared to the Fe−Si distance in related complexes {[Cp(OC)$_2$Fe-Si(F)(Me)O]$_2$: 2.265(1) Å;[12] Cp(OC)$_2$Fe-SiH$_2$-SiH$_3$: 2.2980(9) Å,[24] {Cp(OC)$_2$Fe-Si-(OMe)(Me)[2-(Me$_2$HNCH$_2$)C$_6$H$_4$]}PF$_6$: 2.305(2) Å[25]} or the Si−O distance in silanols and siloxanes {(*t*Bu)(Me)$_2$SiOH: 1.663 Å;[26] [Cp(OC)$_2$Fe-Si(F)(Me)O]$_2$: 1.603(1) Å[12]}.

DFT Calculations

Quantum chemical calculations[27] at a density functional level (B3LYP[28,29] with the 6−31 g(d) basis set[30−32]) were performed on parent **3**, omitting the alkyl groups at the gallium center. A *cis* (C_2 symmetry) and a *trans* (C_i symmetry) equilibrium structure are predicted. (Figure 6). Both structures relate to energy minima on the corresponding electronic hypersurface, as substantiated by corresponding vibrational analysis.

The two conformations are similar in energy, ($\Delta E = 3.0$ kcal/mol, with ZPE correction), with the *trans* geometry being slightly more stable. The trigonal planar-coordinated oxygen atoms and the almost rectangular, planar arrangement of the four-membered gallium−oxygen ring are consistent with the experimentally obtained results. A fairly weak puckering effect is observed for the *cis* conformation ($< \mathrm{O{-}Ga{-}O'{-}Ga'} = 2.4°$). Because of this small puckering, no further analysis of its energy potential was attempted. The resulting iron-silicon distances are somewhat shorter (2.28 Å) and the silicon−oxygen distances longer (1.69 Å) than those found experimentally.

The bonding situation in the heterosiloxanes is best described in terms of donor-acceptor bonds (see Figure 1). This view is also lent support by an analysis of the electron density distributions with the electron localization function (ELF). The electron density is shifted predominantly to the electronegative oxygen atoms, and no through-space interactions between the Ga atoms or the oxygen atoms could be found. A further analysis was also performed for substrates methyl-substituted at the gallium atoms. Again, the energy difference between *cis* and *trans* conformations is fairly small ($\Delta E = 0.4$ kcal/mol, without ZPE correction).

Conclusion

This paper shows that the metallo-silanols Cp(OC)$_2$Fe−SiR$_2$OH (R = Me, *i*Pr, Ph), although characterized by lower acidity than triorganosilanols, react with trialkylgallanes to yield the first transition metal fragment-substituted heterosiloxanes. The observed dimeric structures correspond with findings obtained for triorganosiloxy derivatives, which means that no sufficient influence on the

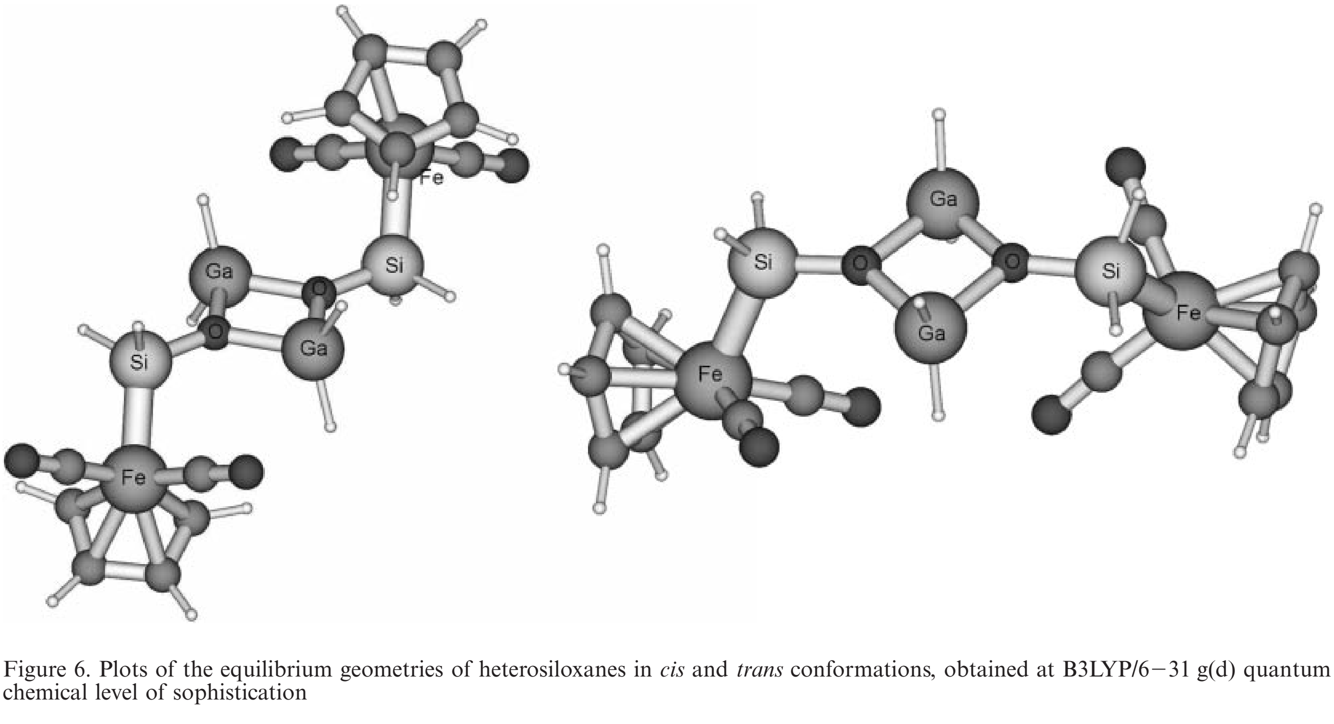


Figure 6. Plots of the equilibrium geometries of heterosiloxanes in *cis* and *trans* conformations, obtained at B3LYP/6−31 g(d) quantum chemical level of sophistication

structure and aggregation is exerted by the presence of an $Cp(OC)_2Fe$ fragment. Because of this result, forthcoming papers will deal with siloxygallanes containing metal fragments with higher steric demand and increased electron density, such as $C_5Me_5(Me_3P)_2Fe$.

Experimental Section

General: All manipulations were performed under purified and dried nitrogen by standard Schlenk-type techniques. Solvents were rigorously dried with an appropriate drying agent, distilled, and saturated with nitrogen prior to use. IR: Perkin−Elmer 283 grating spectrometer. NMR: Jeol Lambda 300 (300.4 MHz, 75.6 MHz and 59.6 MHz, for ^1H, ^{13}C and ^{29}Si, respectively). ^1H and ^{13}C spectra are referenced to the residual proton signal or natural abundance carbon signal of $[D_6]$benzene at $\delta = 7.15$ ppm (^1H) or $\delta = 128.0$ ppm (^{13}C), respectively. ^{29}Si chemical shifts are referenced to external TMS. Molecular mass determinations by freezing point depression were performed in benzene solution with a Knauer 24.00 cryoscopic unit. Melting points: Du Pont-9000 thermal analysis system. Elemental analyses were performed in the laboratories of our institute. Starting materials were prepared by literature procedures: $Cp(OC)_2Fe\text{-}SiMe_2OH$ (**1a**),[13] $Cp(OC)_2Fe{-}Si(iPr)_2OH$ (**1b**),[21] $Cp(OC)_2Fe{-}SiPh_2OH$ (**1c**),[13] $Cp(OC)_2Fe{-}Si(Me)(Ph)OH$ (**1d**),[35] $GaMe_3{\cdot}OEt_2$ (**2a**)[33] and $Ga(iPr)_3$ (**2b**).[34]

1. Bis{{[dicarbonyl(η^5-cyclopentadienyl)ferrio]dimethylsiloxy}dimethylgallane} (3a): A solution of $Cp(OC)_2Fe{-}SiMe_2OH$ (**1a**, 235 mg, 0.93 mmol) in *n*-pentane (20 mL) was added dropwise at 0 °C to a stirred solution of $GaMe_3{\cdot}OEt_2$ (**2a**, 394 mg, 1.12 mmol) in *n*-pentane (10 mL). The reaction mixture was warmed to 25 °C over 15 min and stirred for an additional 2 h, resulting in the precipitation of **3a**. Compound **3a** was separated by filtration, washed with two portions of cold (0 °C) *n*-pentane (3 mL) and dried in vacuo. Yield 261 mg (80%), light yellow, microcrystalline powder, m.p. 101 °C (dec.). ^1H NMR ($[D_6]$benzene): $\delta = 4.19$ (s, 5 H, C_5H_5), 0.69 [s, 6 H, $(H_3C)Si$], 0.19 ppm [s, 6 H, $(H_3C)Ga$]. $^{13}C\{^1H\}$ NMR ($[D_6]$benzene): $\delta = 215.7$ (s, CO), 83.9 (s, C_5H_5), 12.5 [s, $(CH_3)Si$], −1.6 ppm [s, $(CH_3)Ga$]. $^{29}Si\{^1H\}$ NMR ($[D_6]$benzene): $\delta = 66.57$ ppm (s). IR (*n*-pentane/toluene): $\tilde{\nu} = 1994$ (w)/1989 (vs), 1943 (vs)/1930 (s) cm^{-1} (CO). $C_{22}H_{34}Fe_2Ga_2O_6Si_2$ (701.82, found 729.89): calcd. C 37.65, H 4.88; found C 37.78, H 4.56.

2. Bis{{[dicarbonyl(η^5-cyclopentadienyl)ferrio]dimethylsiloxy}di(1-methylethyl)gallane} (3b): This compound was prepared as described for **3a**, from $Cp(OC)_2Fe{-}SiMe_2OH$ (**1a**, 185 mg, 0.73 mmol), dissolved in *n*-pentane (10 mL), and $Ga(iPr)_3$ (**2b**, 219 mg, 1.10 mmol), dissolved in *n*-pentane (5 mL), at −78 °C and with stirring for 16 h after warming up to room temperature, resulting in partial precipitation of **3b**. Additional **3b** was crystallized at −78 °C. Compound **3b** was separated, washed with two portions of cold (−78 °C) *n*-pentane (3 mL), and dried in vacuo. Yield 248 mg (83%), light yellow, microcrystalline powder, m.p. 79 °C (dec.). ^1H NMR ($[D_6]$benzene): $\delta = 4.25$ (s, 5 H, C_5H_5), 1.58 [d, $^3J_{HCCH} = 7.6$ Hz, 12 H, $(H_3C)_2CH$], 1.20 [sept, $^3J_{HCCH} = 7.6$ Hz, 2 H, $HC(CH_3)_2$], 0.84 ppm [s, 6 H, $(H_3C)Si$]. $^{13}C\{^1H\}$ NMR ($[D_6]$benzene): $\delta = 216.2$ (s, CO), 84.0 (s, C_5H_5), 22.3 [s, $(CH_3)_2CH$], 21.2 [s, $CH(CH_3)_2$], 14.4 ppm [s, $(CH_3)Si$]. $^{29}Si\{^1H\}$ NMR ($[D_6]$benzene): $\delta = 64.10$ ppm (s). IR (*n*-pentane/toluene): $\tilde{\nu} = 1998$ (w)/1990 (vs), 1946 (vs)/1931 (s) cm^{-1} (CO). $C_{30}H_{50}Fe_2Ga_2O_6Si_2$ (814.02, found 858.79): calcd. C 44.26, H 6.19; found C 44.17, H 5.95.

3. Bis{{[dicarbonyl(η^5-cyclopentadienyl)ferrio]di(1-methylethyl)siloxy}-dimethylgallane} (3c): This compound was prepared as described for **3a**, from $Cp(OC)_2Fe\text{-}Si(iPr)_2OH$ (**1b**, 163 mg, 0.53 mmol), dissolved in *n*-pentane (10 mL), and $Me_3Ga{\cdot}Et_2O$ (**2b**, 104 mg, 0.55 mmol), dissolved in *n*-pentane (5 mL), at −78 °C, with stirring for 2 h after warming up to room temperature, resulting in partial precipitation of **3c**. Additional **3c** was crystallized at −78 °C. Compound **3c** was separated, washed with two portions of cold (−78 °C) *n*-pentane (3 mL), and dried in vacuo. Yield 186 mg (86%), light beige, microcrystalline powder, m.p. 94 °C (dec.). ^1H NMR ($[D_6]$benzene, 300.4 MHz): $\delta = 4.36$ (s, 5 H, C_5H_5), 1.68 [sept, $^3J_{(HCCH)} = 7.1$ Hz, 2 H, $HC(CH_3)_2$], 1.24 [d, $^3J_{(HCCH)} = 7.1$ Hz, 6 H, $(H_3C)_2CH$], 1.24 [d, $^3J_{(HCCH)} = 7.1$ Hz, 6 H, $(H_3C)_2CH$], 0.37 ppm (s, 6 H, H_3CGa). $^{13}C\{^1H\}$ NMR ($[D_6]$benzene, 75.45 MHz): $\delta = 216.7$ (s, CO), 83.1 (s, C_5H_5), 24.8 [s, $CH(CH_3)_2$], 20.5 [s, $(CH_3)_2CH$], 19.6 [s, $(CH_3)_2CH$], 0.6 ppm (s, CH_3Ga). $^{29}Si\{^1H\}$ NMR ($[D_6]$benzene, 59.58 MHz): $\delta = 78.92$ ppm (s). IR (Et_2O): $\tilde{\nu} = 1994$ (vs), 1938 (vs) cm^{-1} (CO). $C_{30}H_{50}Fe_2Ga_2O_6Si_2$ (814.02, found 842.51): calcd. C 44.26, H 6.19; found C 43.98, H 6.01.

4. Bis{{[dicarbonyl(η^5-cyclopentadienyl)ferrio]diphenylsiloxy}-dimethylgallane} (3d): This compound was prepared as described for **3a**, from $Cp(OC)_2Fe\text{-}SiPh_2OH$ (**1c**, 180 mg, 0.48 mmol), dissolved in *n*-pentane (10 mL), and $Me_3Ga{\cdot}Et_2O$ (**2b**, 94 mg, 0.50 mmol), dissolved in *n*-pentane (5 mL), at −78 °C and with stirring for 2 h after warming up to room temperature, resulting in partial precipitation of **3d**. Additional **3d** was crystallized at −78 °C. Compound **3d** was separated, washed with two portions of cold (−78 °C) *n*-pentane (3 mL), and dried in vacuo. Yield 166 mg (73%), light beige, microcrystalline powder, m.p. 144 °C (dec.). ^1H NMR ($[D_6]$benzene, 300.4 MHz): $\delta = 7.80$ [d, $^3J_{HCCH} = 6.8$ Hz, 4 H, *o*-H], 7.30−7.18 (m, 6 H, *m*/*p*-H), 3.95 (s, 5 H, H_5C_5), −0.05 ppm (s, 6 H, H_3CGa). $^{13}C\{^1H\}$ NMR ($[D_6]$benzene, 75.45 MHz): $\delta = 215.8$ (s, CO), 145.1 (s, *i*-C, C_6H_5Si), 134.9 (s, *o*-C, C_6H_5Si), 129.1 (s, *p*-C, C_6H_5Si), 127.8 (s, *m*-C, C_6H_5Si), 84.8 (s, C_5H_5), −1.4 ppm (s, CH_3Ga). $^{29}Si\{^1H\}$ NMR ($[D_6]$benzene, 59.58 MHz): $\delta = 54.86$ ppm (s). IR (Et_2O): $\tilde{\nu} = 1999$ (vs), 1945 (vs) cm^{-1} (CO). $C_{21}H_{21}FeGaO_3Si$ (475.05): calcd. C 53.10, H 4.46; found C 52.72, H 4.29.

5. (*RR*)-(*RS*)-Bis{{[dicarbonyl(η^5-cyclopentadienyl)ferrio](methyl)-(phenyl)siloxy}-dimethylgallane} (3e): This compound was prepared as described for **3a**, from $Cp(OC)_2FeSi(Me)(Ph)OH$ (**1d**, 132 mg, 0.42 mmol), dissolved in *n*-pentane (25 mL), and $Me_3Ga{\cdot}Et_2O$ (**2b**, 85 mg, 0.45 mmol), dissolved in *n*-pentane (5 mL), at −78 °C and with stirring for 2 h after warming up to room temperature, resulting in partial precipitation of **3e**. Additional **3e** was crystallized at −78 °C. Compound **3e** was separated, washed with two portions of cold (−78 °C) *n*-pentane (3 mL) and dried in vacuo. Yield 142 mg (82%), light beige, microcrystalline powder, m.p. 92 °C (dec.). ^1H NMR ($[D_6]$benzene, 300.4 MHz): $\delta = 7.74{-}7.70$ (m, 4 H, *o*-H), 7.23−7.11 (m, 6 H, *m*/*p*-H), 3.89/3.88 (s, 10 H, H_5C_5), 0.98/0.97 (s, 6 H, H_3CSi), 0.36 (s, 3 H, H_3CGa, *ul*), 0.18 (s, 6 H, H_3CIn, *lk*), 0.01 ppm (s, 3 H, H_3CIn, *ul*). $^{13}C\{^1H\}$ NMR ($[D_6]$benzene, 75.45 MHz): $\delta = 216.1/215.6$ (s, CO), 146.8/146.6 (s, *i*-C, C_6H_5Si), 133.3/133.2 (s, *o*-C, C_6H_5Si), 128.9 (s, *p*-C, C_6H_5Si), 127.8/127.8 (s, *m*-C, C_6H_5Si), 84.3 (br. s, C_5H_5), 10.8/10.8 (s, CH_3Si), −0.7 (s, CH_3Ga, *ul*), −1.1 (s, CH_3Ga, *lk*), −1.5 ppm (CH_3Ga, *ul*). $^{29}Si\{^1H\}$ NMR ($[D_6]$benzene, 59.58 MHz): $\delta = 59.32/59.22$ ppm (s). IR (Et_2O): $\tilde{\nu} = 1992$ (vs), 1934 (vs) cm^{-1}. $C_{16}H_{19}FeGaO_3Si$ (412.98): calcd. C 46.53, H 4.64; found C 46.37, H 4.78.

6. X-ray Analyses of $[Cp(OC)_2Fe\text{-}SiMe_2O\text{-}GaMe_2]_2$ (3a) and $[Cp(OC)_2Fe\text{-}SiPh_2O\text{-}GaMe_2]_2$ (3d): Suitable crystals were obtained by slow evaporation of saturated solutions of **3a/3d** in *n*-pentane at room temperature. Data collection was performed on an Enraf−Nonius CAD4-diffractometer with use of graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 173(2) K. The positions of the hydrogen atoms were calculated by an idealized geometry.

Compound 3a: $C_{22}H_{34}Fe_2Ga_2O_6Si_2$, M = 701.82; triclinic; space group: $P\bar{1}$ (No. 2); a = 8.147(2) Å, b = 9.035(2) Å, c = 11.1026(19) Å; α = 80.259(19)°, β = 78.398(18)°, γ = 64.15(2)°; V = 717.3(3) Å^3; Z = 2; $D_{calcd.}$ = 1.625 g·cm^{-3}; crystal size: 0.55 × 0.50 × 0.50 mm^3; μ(Mo-K_α) = 2.965 mm^{-1}, semiempirical absorption correction ($T_{min.}/T_{max.}$: 0.9294/0.9993); scale range: 1.88° < θ < 22.92°; F(000): 356; total reflections: 2144; independent reflections: 1977; structure solution: SHELXS-96;[36] 1977 reflections used in structure refinement (158 parameters) with SHELXL-96;[37] GoF = 1.091, residual electron density: 0.414/−0.437 e·Å^{-3}, R_1 = 0.0319, wR_2 = 0.0810.

Compound 3d: $C_{42}H_{42}Fe_2Ga_2O_6Si_2$, M = 950.08; monoclinic; space group $P2_1/c$ (No. 14), a = 16.95554(3) Å, b = 13.5810(2) Å, c = 17.4890(3) Å, α = 90°, β = 91.691(1)°, γ = 90°, V = 4025.46(12) Å^3, Z = 4, $D_{calcd.}$ = 1.568 g·cm^{-3}; crystal size: 0.30 × 0.25 × 0.2 mm^3; μ(Mo-K_α) = 2.137 mm^{-1}; semi-empirical absorption correction ($T_{min.}/T_{max.}$: 0.7188/0.6165); scale range: 2.59° < θ < 28.30°; F(000): 1936, total reflections: 66887; independent reflections: 9935; structure solution: SHELXS-96;[36] 2059 reflections used in structure refinement (158 parameters) with SHELXL-96;[37] GoF = 1.056, residual electron density: 0.460/−0.480 e·Å^{-3}, R_1 = 0.0337, wR_2 = 0.0658.

CCDC-155725 (**3a**) and CCDC-184033 (**3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm "Spezifische Phänomene in der Siliciumchemie") as well as from the Fonds der Chemischen Industrie. M. N. wishes to thank the DAAD for financial support.

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Received October 29, 2002