New Cyclohexasilanyl Derivatives with Cobalt and Iron Substituents

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The first cobalt–cyclosilanyl derivatives $Si_6Me_{11}Co(CO)_3PPh_3$, 1,4-$[Co(CO)_3PPh_3]_2Si_6Me_{10}$, and 1-$[Co(CO)_3PPh_3]$-4-$[Fe(CO)_2Cp]Si_6Me_{10}$ were synthesized from $Na[Co(CO)_3PPh_3]$ with cyclohexasilanyl halides. 1-$[Co(CO)_3PPh_3]$-4-$[Fe(CO)_2Cp]Si_6Me_{10}$ was prepared from 1-H-4-$[Fe(CO)_2Cp]Si_6Me_{10}$ and 1-Cl-4-$[Fe(CO)_2Cp]Si_6Me_{10}$. These compounds are the first examples of cyclohexasilanes bearing two different substituents, other than methyl. In contrast to the $Co(CO)_3PPh_3$ group, which does not show a significant influence on the Si–Si bonds compared to non-metal substituents, NMR studies (especially the measurement of the Si–Si coupling constants) reveal a strong influence between the $Fe(CO)_2Cp$ group and the Si–Si bonds within the cyclohexasilane cycle.

Introduction

The properties of Si–transition metal bonds recently attracted attention because of the possible applicability of silicon–transition metal compounds as catalysts and for chemical vapor deposition (CVD) experiments leading to Si/C/M phases (M = transition metal). However, only a limited number of transition metal polycyclosilanes, in particular compounds containing Si–Co bonds,[1-3] are known.

In recent studies, cyclosilanyl derivatives $Si_6Me_{11}X$ (X = F, Cl, Br, I, OH, $Mo(CO)_3Cp$, $Fe(CO)_2Cp$, etc.) and 1,4-$Si_6Me_{10}X_2$ (X = Cl, Br, $Fe(CO)_2Cp$, etc.)[3] turned out to be rather thermally stable, making them particularly interesting for CVD experiments.

We have now succeeded in the preparation of the first cyclosilanylcobalt compounds [tricarbonyl(triphenylphosphino)cobalt]undecamethylcyclohexasilane ($Si_6Me_{11}Co(CO)_3PPh_3$), 1,4-bis[tricarbonyl(triphenylphosphino)cobalt]decamethylcyclohexasilane (1,4-$[Co(CO)_3PPh_3]_2Si_6Me_{10}$), and 1-[tricarbonyl(triphenylphosphino)cobalt]-4-(dicarbonylcyclopentadienyliron)decamethylcyclohexasilane (1-$[Co(CO)_3PPh_3]$-4-$[Fe(CO)_2Cp]Si_6Me_{10}$), the first cyclohexasilane bearing two different transition-metal substituents.

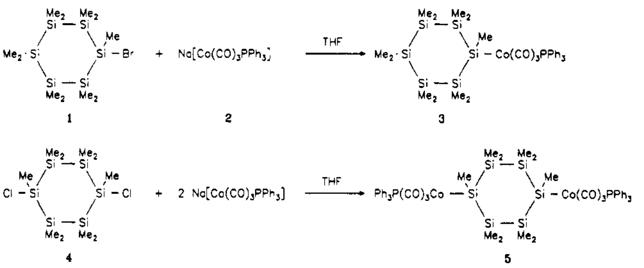
In this paper we report their synthesis and investigation by ^{29}Si, ^{13}C, ^{1}H, and ^{31}P NMR. NMR spectroscopic results are compared to results recently obtained for 1,4-$[Fe(CO)_2Cp]_2Si_6Me_{10}$, because NMR studies of $Si_6Me_{11}Fe(CO)_2Cp$[4] revealed a strong influence of the transition-metal substituents on the Si–Si bond system within the Si_6Me_{11} ring.

Results and Discussion

Synthesis. Si–Co bonds usually are synthesized from $Co_2(CO)_8$ and silicon hydrides. Only a few organosilicon halides react with the $[Co(CO)_4]^-$ anion because of its poor nucleophilicity.[5] Attempts to use undecamethylcyclohexasilane derivatives $Si_6Me_{11}X$ (X = Cl, Br, I) or $Si_6Me_{11}H$ as a Si educt have been unsuccessful.

Only when $Si_6Me_{11}I$ is reacted with $Na[Co(CO)_4]$ in diethyl ether could slow reaction be observed. However, in a side reaction siloxanes are formed by cleavage of the diethyl ether.

Scheme I



Substitution of carbonyl ligands by the triphenylphosphine group increases the nucleophilicity of the corresponding transition-metal anions.[6-8] Therefore, $Na[Co(CO)_3PPh_3]$ in THF smoothly reacts with $Si_6Me_{11}Br$ or 1,4-$Cl_2Si_6Me_{10}$ to $Si_6Me_{11}Co(CO)_3PPh_3$ (**3**) and 1,4-$Cl_2Si_6Me_{10}$-1,4-$[Co(CO)_3PPh_3]_2Si_6Me_{10}$ (**5**), respectively (Scheme I).

3 and **5** are obtained as fine, yellow crystals, which are somewhat thermally stable and only little sensitive to oxygen and water. Unfortunately, the quality and size of the crystals did not allow an X-ray structure determination to be made so far. Despite the rather poor solubility in benzene, especially of compound **5**, the Si–Si coupling constants could be determined with use of the INEPT–INADEQUATE–NMR technique. Application of ^{59}Co NMR was unsuccessful because of the asymmetric environment of the Co atom causing very broad signals ($\Delta\nu >$ 5000 Hz). **5** showed rather different behavior in the ^{29}Si NMR compared to 1,4-$[Fe(CO)_2Cp]_2Si_6Me_{10}$. Therefore, we attempted the synthesis of 1-$[Co(CO)_3PPh_3]$-4-$[Fe(CO)_2Cp]Si_6Me_{10}$ (**13**), the first disubstituted cyclohexasilane bearing different transition-metal substituents, by the reaction sequence in Scheme II.

1,4-$Cl_2Si_6Me_{10}$[9] reacts with $LiAlH_4$ in diethyl ether to yield 1,4-$H_2Si_6Me_{10}$ (**6**). Silicon hydrides can be converted into the corresponding silicon halides by alkyl halides.[10] When **6** is reacted with 1 equiv of $CHBr_3$, the resulting reaction mixture contains three products: **6** (10%), 1-Br-4-H-Si_6Me_{10} (**7**) (70%), and 1,4-$BrSi_6Me_{10}$ (**8**) (20%). These products can be separated either by preparative gas chromatography or by utilizing the different solubilities of the $Fe(CO)_2Cp$ derivatives of **7** and **8**, 1-[Fe-

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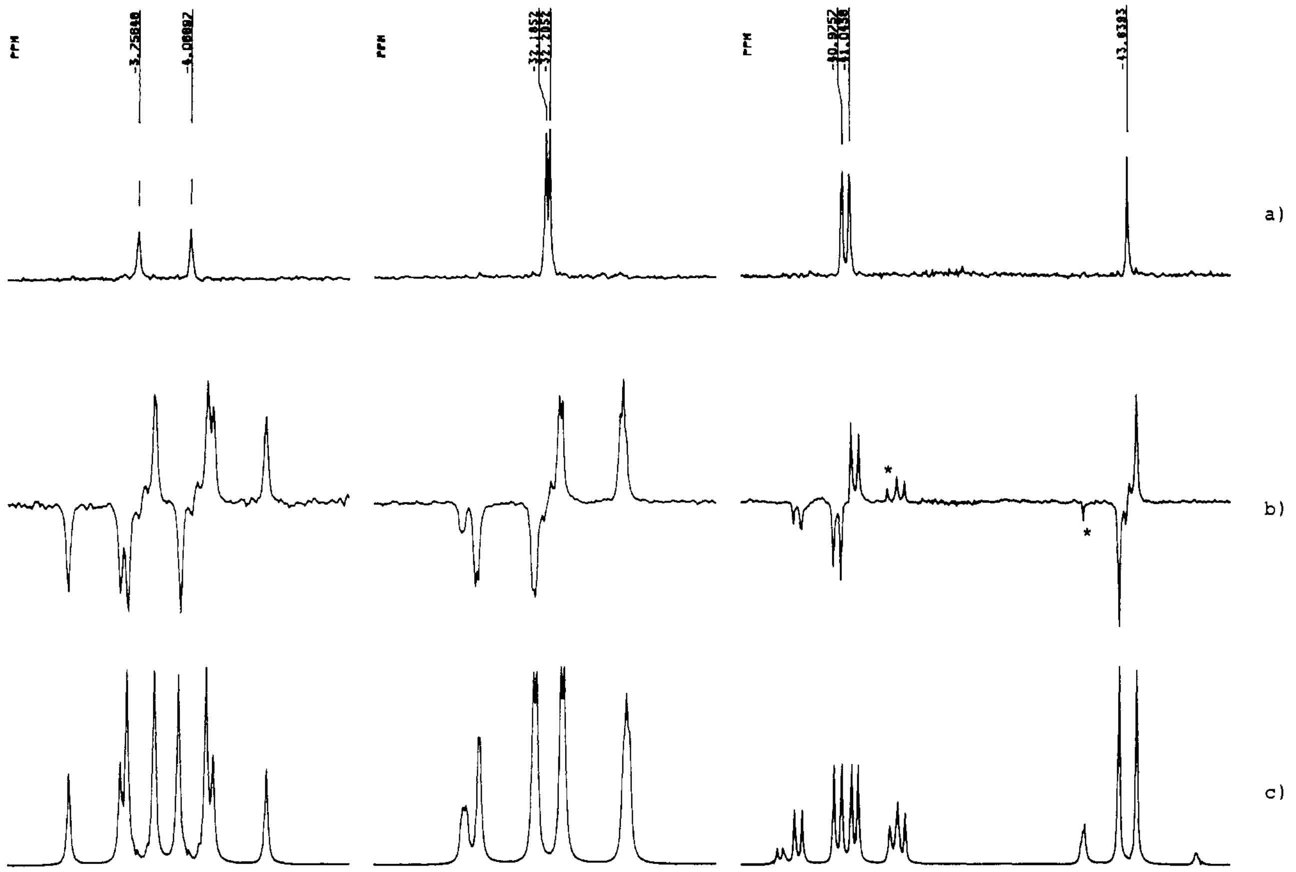

Figure 1. (a) INEPT-^{29}Si NMR spectrum of $Si_6Me_{11}[Co(CO)_3PPh_3]$. (b) INEPT-INADEQUATE-^{29}Si NMR spectrum of $Si_6Me_{11}[Co(CO)_3PPh_3]$ with J_{opt} = 10 Hz. The asterisk indicates the two inner lines of the AB quartet of Si(3) and Si(4). (c) Simulation of the ^{29}Si-INEPT-INADEQUATE spectrum of $Si_6Me_{11}[Co(CO)_3PPh_3]$. Because of the nature of the simulation program, the peaks of the simulated spectrum do not reflect the real intensities shown in b.

$(CO)_2Cp]$-4-HSi_6Me_{10} (**10**) and 1,4-$[Fe(CO)_2Cp]_2Si_6Me_{10}$ (**4**), which are easily obtained after the mixture of **6**–**8** is treated with $Na[Fe(CO)_2Cp]$ in THF. The solubilities of the final reaction products in alkanes markedly increase in the order **6** > **10** > **11**, allowing their separation by simple recrystallization from hexane.

10 reacts with CCl_4 to 1-$[Fe(CO)_2Cp]$-4-$ClSi_6Me_{10}$ (**12**) and $CHCl_3$. This reaction, however, only occurs at room temperature when a slow nitrogen stream is passed through the solution to remove the $CHCl_3$.[11] **12** finally reacts with $Na[Co(CO)_3PPh_3]$ to yield the yellow crystalline 1-[Co-$(CO)_3PPh_3]$-4-$[Fe(CO)_2Cp]Si_6Me_{10}$ (**13**). **13** is slightly soluble in alkanes and, like **11** and **5**, is rather stable at higher temperatures.

NMR. In the ^{29}Si NMR spectra of **3**, **5**, and **13** the signals are split into doublets because of the Si–P coupling. Remarkably, the absolute values of the coupling over three bonds is smaller than that over four bonds (compare Figure 1a). That probably results from the different signs of the $^2J_{Si-P}$, $^3J_{Si-P}$, and $^4J_{Si-P}$.[12] Therefore, correct assignment of the signals can only be achieved by INEPT-INADEQUATE-^{29}Si NMR (Figure 1b).

The first-order coupling over one bond between Si(1)/Si(2) and Si(2)/Si(3) can easily be determined because it is first order. Si(3) and Si(4), however, exhibit an AB system because the chemical shift difference is similar to the coupling constant in magnitude. Since they are coupled to P, strictly speaking it is an ABX system. The X part, however, does not affect the magnitude of the $^1J_{Si(3)-Si(4)}$. Fortunately, the inner two lines of the AB quartet unambiguously can be assigned in the spectra. So calculation of the coupling constants is possible with use of the formula

$$|J| = \left| \frac{1}{2}\left(\frac{\Delta\nu^2}{|f_2 - f_3|} + f_2 + f_3 \right) - f_2 \right|$$

where f_2 and f_3 are frequencies of the inner two lines (Hz) and $\Delta\nu$ is the chemical shift difference (Hz). When the spectra are simulated employing the laacoon algorithm and the coupling constants are either derived directly from the spectra or calculated by the above formula, excellent agreement between simulated and experimental spectra is obtained (compare Figure 1c). Stereoisomers of 1,4-disubstituted cyclohexasilanes exhibit different chemical shifts in ^{29}Si NMR (compare Figure 2a). The magnitude of this chemical shift difference depends on the nature of the groups attached to the cyclohexasilane ring (compare Table I) because different substituents show different anisotropic contributions to the shielding constant of the measured nuclei in the axial and equitorial positions.

Table I. Absolute Values of the Shift Difference |Δδ| for the Cis and Trans Stereoisomers of 1,4-Disubstituted Decamethylcyclohexasilane Derivatives (Uncertainty of the Values Is Better than ±0.002 ppm)

$XSi_6Me_{10}Y$		|Δδ| (ppm)			
X	Y	Si(1)	Si(2)	Si(3)	Si(4)
H	H	0.66	0.27	0.27	0.66
Br	Br	1.68	0.16	0.16	1.68
Cl	Cl	0.56	0.24	0.24	0.56
$Fe(CO)_2Cp$	H	0.22	0.04	1.51	3.13
$Fe(CO)_2Cp$	Cl	0.0	1.13	1.63	1.57
$Fe(CO)_2Cp$	$Fe(CO)_2Cp$	0.0	0.0	0.0	0.0
$Co(CO)_3PPh_3$	$Fe(CO)_2Cp$	0.0	0.0	0.0	0.0
$Co(CO)_3PPh_3$	$Co(CO)_3PPh_3$	0.44	1.19	1.19	0.44

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Scheme II

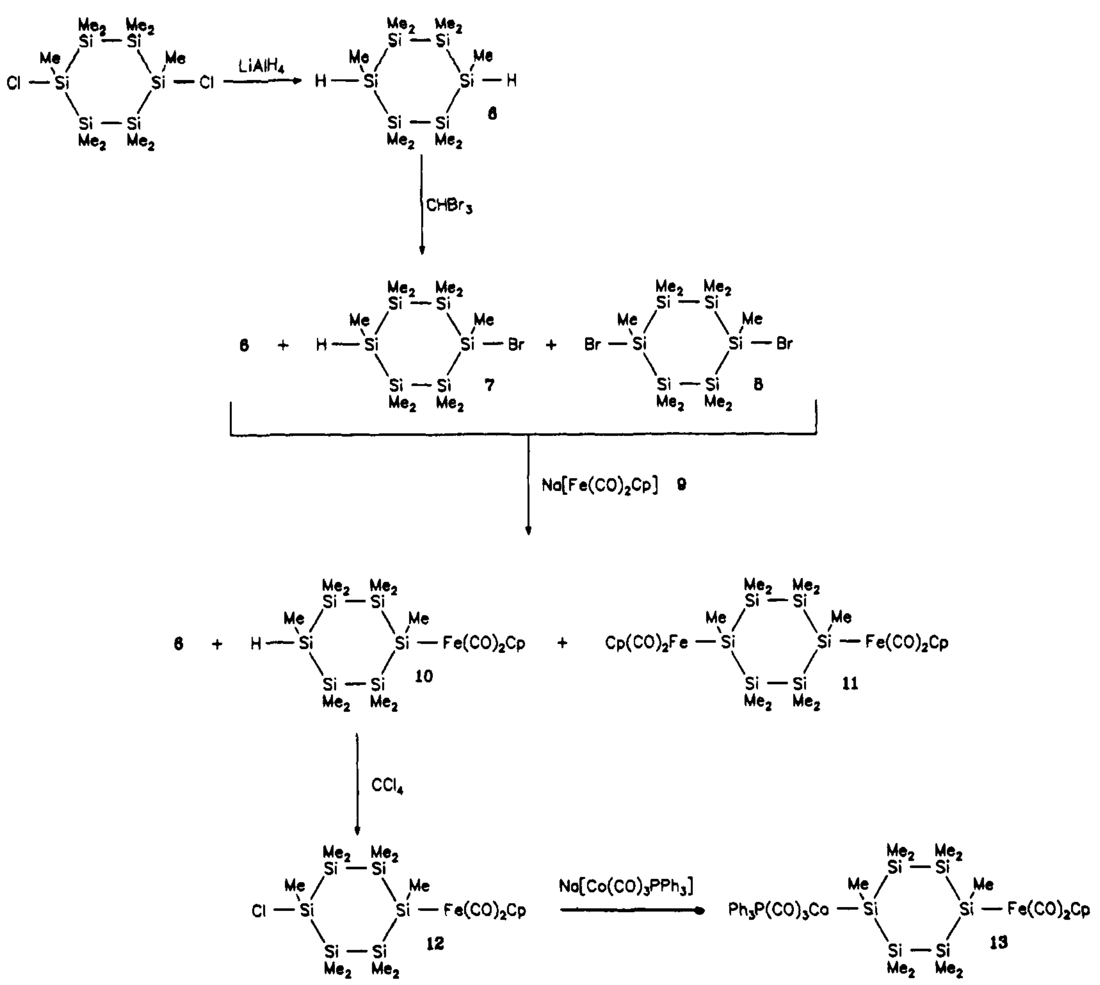

Table II. Si-Si Coupling Constants over One and Two Bonds (Uncertainty of the Values Is Better than ±0.13 Hz)[a]

SXi_6-$Me_{10}Y$		Si-Si coupling constants (|Hz|)				
X	Y	$^1J_{1-2}$	$^1J_{2-3}$	$^1J_{3-4}$	$^2J_{1-3}$	$^2J_{2-4}$
H	H	59.3		59.3	10.8	10.8
Br	Br	58.1/58.6		58.1/58.6	13.8/13.1	13.8/13.1
Cl	Cl	61.2		61.2	12.8/12.9	12.8/12.9
Fp	H	50.3/50.0	57.4/56.9	58.6/59.0	6.9/6.8	10.0/10.1
Fp	Fp	50.2		50.2	6.9	6.9
Co	Fp	49.5	50.2	49.6	9.4	6.6
Co	Co	51.9/51.0		51.9/51.0	10.0/10.0	10.0/10.0
Co	CH_3	51.6	57.7	63.0	9.6	9.4

[a] Fp = $Fe(CO)_2Cp$.

For $Fe(CO)_2Cp$ this difference for ^{29}Si is rather small. Therefore, the cis/trans stereoisomers of compounds 11 and 13 can only be observed by ^1H NMR, but not in the ^{29}Si NMR spectra where the chemical shifts differ by less than 0.1 Hz (compare Figure 2b). This observation could possibly be explained by conformational changes of the cyclohexasilane ring.

In Table II the absolute values for the Si-Si coupling constants over one or two bonds are given. 1,4-Disubstituted cyclohexasilanes exhibit coupling constants similar to those of the monosubstituted derivatives.[4]

Values between 6.6 and 6.9 Hz for $^2J_{Si(Fe)-Si}$ in the $Fe(CO)_2Cp$ derivatives are rather small compared to other decamethylcyclohexasilanes. The corresponding $Co(CO)_3PPh_3$ derivatives, on the contrary, exhibit quite normal values for $^2J_{Si(Co)-Si}$ between 9.4 and 10.1 Hz. This observation once more indicates the strong influence of the $Fe(CO)_2Cp$ group on the Si-Si bonds within the cyclohexasilane ring. It is particularly apparent in compound 13 with coupling constants $^2J_{Si(Fe)-Si}$ = 6.6 Hz and $^2J_{Si(Co)-Si}$ = 9.4 Hz.

Experimental Section

General Data. All manipulations involving air-sensitive materials were performed under nitrogen with use of standard Schlenk techniques. All solvents were dried with Na/K alloy under nitrogen and distilled prior to use. Tetrachloromethane and tribromomethane were dried with molecular sieves (4 Å) and distilled.

Bromoundecamethylcyclohexasilane,[3,4] 1,4-dichlorodecamethylcyclohexasilane,[9] sodium dicarbonylcyclopentadienylferrate,[13] and sodium tricarbonyl(triphenylphosphino)cobaltate[8] were prepared according to published procedures.

All NMR spectra were recorded with a Bruker MSL 300 spectrometer (^1H, 300.13 MHz; ^{29}Si, 59.627 MHz; ^{13}C, 75,47 MHz; ^{31}P, 121.49 MHz). For ^{13}C and ^{31}P spectra, a simple CYCLOPS pulse sequence with quatrature detection and BB decoupling was used. ^{29}Si spectra were recorded with use of an INEPT pulse sequence with BB decoupling during data acquisition only (gated decoupling). The Si-Si coupling constants over one and two bonds were measured with use of an one-dimensional INEPT-INADEQUATE pulse sequence with gated decoupling.[14] All samples were dissolved in C_6D_6. TMS was used as external standard for ^{29}Si, ^{13}C, and ^1H. All ^{31}P shifts are relative to external 85% H_3PO_4. All shifts are reported (ppm) relative to the standards, and all coupling constants are given as absolute values (Hz). All ^{29}Si NMR spectra were measured with a sweep width of 4000 Hz and an FID size of 32K data points. Simulation of the INADEQUATE spectra

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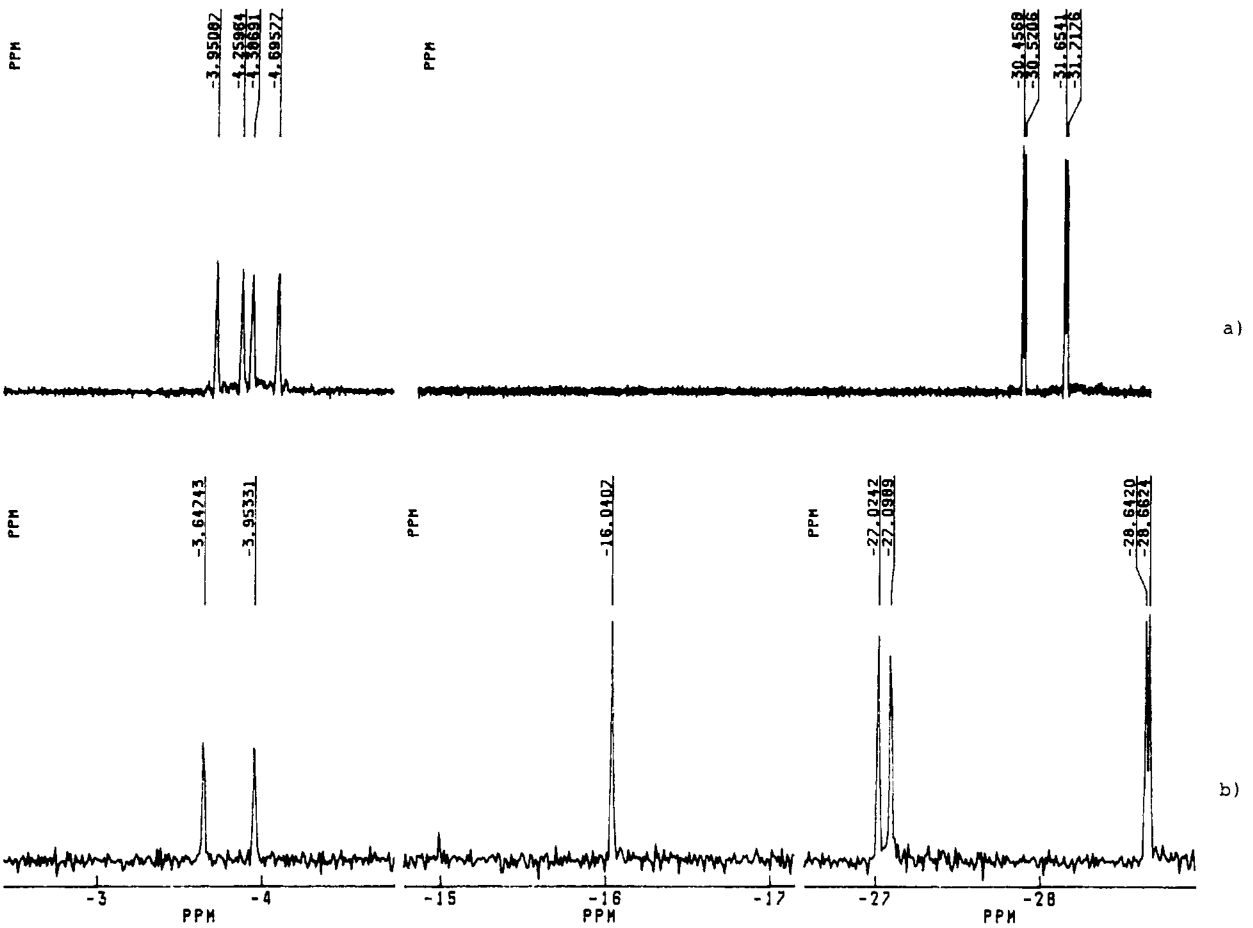

Figure 2. (a) INEPT-^{29}Si NMR spectrum of both stereoisomers (cis/trans) of 1,4-[Co(CO)$_3$PPh$_3$]$_2$Si$_6$Me$_{10}$. (b) INEPT-^{29}Si NMR spectrum of 1-[Co(CO)$_3$PPh$_3$]-4-[Fe(CO)$_2$Cp]Si$_6$Me$_{10}$. No splitting of the ^{29}Si resonanzes for the two stereoisomers can be observed.

was performed with the PANIC software from Bruker with an Aspect 3000 computer. Assignment of NMR signals to of cis/trans stereoisomers was achieved via the relative intensities and the use of Si–Si coupling constants.

IR spectra were recorded in pentane with a Perkin-Elmer 883 IR spectrometer. Mass spectra were recorded with a Finnigan Mat-212 spectrometer. C, H analyses were performed on a Heraeus-Mikro-K1 apparature. Co, Fe analyses were obtained from ASA, Graz, Austria, by AAS spectroscopy.

1,4-Dihydrodecamethylcyclohexasilane. A 6.4-mmol portion of LiAlH$_4$ in 20 mL of diethyl ether was added dropwise to 5 g of 1,4-Si$_6$Me$_{10}$Cl$_2$ (12.8 mmol) dissolved in 50 mL of diethyl ether at 0 °C. The reaction mixture was allowed to warm to room temperature and subsequently was stirred for 1 h. At this moment, no more starting material could be detected by GC analysis. The solution was poured into 100 mL of ice-cooled 1 N H$_2$SO$_4$. After separation of the organic layer, the aqueous layer was extracted three times with about 10 mL of pentane. The combined organic layers were neutralized with NaHCO$_3$ and dried with Na$_2$SO$_4$. After filtration and evaporation of the solvents, the product was destilled at 85 °C (10^{-3} bar), yielding 3.8 g (92%) of 1,4-Si$_6$Me$_{10}$H$_2$ as an oily product. ^{29}Si NMR (ppm): -67.49/-68.45; -40.45/-40.72; ^{1}H NMR (ppm): 3.64 (q)/3.75 (q) (2 H); 0.22–0.24 (m) (30 H); IR (cm^{-1}): 2120 ($\nu_{\text{Si-H}}$); MS: 321 (M$^+$). Anal. Calcd/Found: C, 37.43/37.2; H, 10.05/9.8.

Reaction of Si$_6$Me$_{10}$H$_2$ with CHBr$_3$. 1,4-Si$_6$Me$_{10}$H$_2$ (3 g, 9.3 mmol) and CHBr$_3$ (2.36 g, 9.3 mmol) were refluxed in 30 mL of heptane for about 3 h. Then, GC analysis showed three products: 1,4-Si$_6$Me$_{10}$H$_2$ (10%), 1,4-Si$_6$Me$_{10}$BrH (70%), and 1,4-Si$_6$Me$_{10}$Br$_2$ (20%). The peaks were assigned by GC–MS analysis. After evaporation of the solvent, this reaction mixture was used without further purification for the subsequent reaction. Data for 1-Br-4-H-Si$_6$Me$_{10}$ follow. ^{29}Si NMR (ppm): 10.64/9.49; -39.22/-39.01; -41.16/-41.42; -67.22/-69.05. ^{1}H NMR (ppm): 3.57 (q)/4.06 (q) (1 H); 0.9–0.1 (m) (30 H). MS: 399 (M$^+$).

1-(Dicarbonylcyclopentadienyliron)-4-hydrodecamethylcyclohexasilane. To the mixture of 1,4-Si$_6$Me$_{10}$H$_2$, 1,4-Si$_6$Me$_{10}$BrH, and 1,4-Si$_6$Me$_{10}$Br$_2$, obtained by the reaction of 1,4-Si$_6$Me$_{10}$H$_2$ and CBr$_3$H described above, dissolved in about 100 mL of THF was added dropwise 9.3 mmol of Na[Fe(CO)$_2$Cp] in 50 mL of THF at -50 °C. After addition was complete, the mixture was allowed to warm to room temperature and stirred, until no more Na[Fe(CO)$_2$Cp] could be detected in the IR spectra. After evaporation of the solvent, the oily residue was dissolved in 100 mL of toluene and filtered. Toluene was then removed under reduced pressure and replaced by 20 mL of pentane to allow separation of the reaction products. Si$_6$Me$_{10}$[Fe(CO)$_2$Cp]$_2$ and [Fe(CO)$_2$Cp]$_2$, insoluble in pentane, were removed by filtration through a Celite pad. The filtrate was cooled to -70 °C, causing precipitation of HSi$_6$Me$_{10}$Fe(CO)$_2$Cp as a yellow oil, yield 1.1 g, 34%. Si$_6$Me$_{10}$H$_2$ remains in solution. ^{29}Si NMR (ppm): -14.72/-14.95; -28.48/-29.44; -38.53/-40.04; -69.65/-69.05. ^{1}H NMR (ppm): 4.33 (s)/4.32 (s) (5 H); 3.72 (q); 3.56 (q) (1 H); 0.56–0.16 (m) (30 H). MS: 496 (M$^+$). IR (cm^{-1}): 2103 ($\nu_{\text{Si-H}}$); 1995, 1946 ($\nu_{\text{C-O}}$). Anal. Calcd/Found: C, 41.12/40.8; H, 7.25/7.4.

1-(Dicarbonylcyclopentadienyliron)-4-chlorodecamethylcyclohexasilane. A slow nitrogen stream was passed through a solution of 1.0 g (2.0 mmol) of HSi$_6$Me$_{10}$Fe(CO)$_2$Cp in 30 mL of CCl$_4$ at room temperature until the $\nu_{\text{Si-H}}$ at 2103 cm^{-1} in the IR spectra disappeared. After evaporation of the solvent, the yellow residue was recrystallized from 20 mL of pentane at -70 °C, yielding 0.81 g (76%) of yellow ClSi$_6$Me$_{10}$Fe(CO)$_2$Cp. ^{29}Si NMR (ppm): -14.98; -30.71/-29.58; -38.87/-36.74; 17.75/16.18. IR (cm^{-1}): 1995, 1951 ($\nu_{\text{C-O}}$). MS: 531 (M$^+$).

1-[Tricarbonyl(triphenylphosphino)cobalt]-4-(dicarbonylcyclopentadienyliron)decamethylcyclohexasilane. Na[Co(CO)$_3$PPh$_3$] (0.64 g, 1.5 mmol) and ClSi$_6$Me$_{10}$Fe(CO)$_2$Cp (0.8 g, 1.5 mmol) were dissolved in 200 mL of THF, and the resultant mixture was stirred for 8 h at room temperature. After evaporation of the solvent, the residue was suspended in 50 mL of benzene and filtered. Benzene was removed in vacuum, and the resulting brown solid residue was extracted with 60 mL of hexane. The solution was concentrated to 15 mL and filtered at -10 °C to give 0.53 g (39%) of dark yellow crystals of [Co-

(CO)$_3$PPh$_3$]Si$_6$Me$_{10}$[Fe(CO)$_2$Cp]. ^{29}Si NMR (ppm): −3.80 (d); −28.65 (d); −27.06 (d); −16.04 (s). ^{13}C NMR (ppm): 216.14; 201.50 (d); 135.79; 133.89; 133.74; 131.00; 129.36; 129.26; 82.81; 2.79; 2.47; −0.38; −0.49; −0.82. ^{1}H NMR (ppm): 7.61 (m), 6.99 (m) (15 H); 4.29 (s) (5 H); 0.70, 0.49, 0.35 (s) (30 H). ^{31}P NMR (ppm): 58.67 ($^2J_{\text{Si-P}}$ = 18.24 Hz, $^3J_{\text{Si-P}}$ = 1.21 Hz, $^4J_{\text{Si-P}}$ = 4.45 Hz). IR (cm^{-1}): 1992, 1973, 1941 ($\nu_{\text{C-O}}$). Mp: 151–155 °C dec. Anal. Calcd/Found: C, 50.67/50.1; H, 5.55/5.7; Fe, 6.20/6.1; Co, 6.54/6.7.

1,4-Dibromodecamethylcyclohexasilane. CHBr$_3$ (10 g, 40 mmol) and Si$_6$Me$_{10}$H$_2$ (5 g, 15.5 mmol) were refluxed in 20 mL of toluene until no more Si$_6$Me$_{10}$H$_2$ could be detected by GC analysis. Toluene and excess CHBr$_3$ were removed under vacuum. Sublimation of the white solid residue at 100 °C (10^{-3} bar) yielded 7 g (95%) of white crystalline Si$_6$Me$_{10}$Br$_2$. ^{29}Si NMR (ppm): 9.61/7.93; −39.88/−39.73.

1,4-Bis[tricarbonyl(triphenylphosphino)cobalt]decamethylcyclohexasilane. Na[Co(CO)$_3$PPh$_3$] (1.32 g, 3.0 mmol) and Si$_6$Me$_{10}$Cl$_2$ (0.6 g, 1.5 mmol) were stirred in 250 mL of THF for about 12 h at room temperature until the $\nu_{\text{C-O}}$ at 1932, 1856, and 1810 cm^{-1} disappeared in the IR spectra. The solvent was removed under vacuum, and the dark yellow residue was suspended in 50 mL of benzene. After filtration through a Celite pad and concentration of the solution to 15 mL, yellow crystals precipitated. Those were filtered off, rinsed with 30 mL of hexane, and dried under vacuum. Yield: 0.6 g, 35%. ^{29}Si NMR (ppm): −4.10/−4.54 (d); −30.49/−31.83 (d). ^{1}H NMR (ppm): 7.61 (m), 6.98 (m) (30 H); 1.12, 0.75, 0.66 (30 H). ^{13}C NMR (ppm): 201.61 (d); 135.898; 133.877; 133.717; 130.951; 129.313; 129.189; −1.180; −1.69; −2.76; −3.04. ^{31}P NMR (ppm): 58.761 ($^2J_{\text{Si-P}}$ = 18.43/18.58 Hz; $^3J_{\text{Si-P}}$ < 0.8 Hz; $^4J_{\text{Si-P}}$ = 3.62/3.61 Hz). IR (cm^{-1}): 1947 ($\nu_{\text{C-O}}$). Mp: 187–192 °C dec. Anal. Calcd/Found: C, 55.30/54.9; H, 5.59/5.4.

[Tricarbonyl(triphenylphosphino)cobalt]undecamethylcyclohexasilane. A 1.5-g (3.6-mmol) portion of Si$_6$Me$_{11}$Br was dissolved in 40 mL of THF and the resultant mixture added at −50 °C to 1.6 g (3.6 mmol) of Na[Co(CO)$_3$PPh$_3$] in 200 mL of THF. The reaction mixture was allowed to warm to room temperature and then stirred for 2 h. After evaporation of the solvent, the residue was extracted with 100 mL of pentane. The solution was concentrated until yellow crystals precipitated. Filtration at −30 °C gave 1.92 g (72%) of pure Si$_6$Me$_{11}$Co(CO)$_3$PPh$_3$. ^{29}Si NMR (ppm): −3.91 (d); −32.19 (d); −41.01 (d); −43.64 (s). ^{13}C NMR (ppm): 201.5 (d); 135.75; 135.186; 133.849; 133.71; 131.00; −1.745; −3.4; −4.34; −5.28; −5.527. ^{1}H NMR (ppm): 7.61 (m), 6.97 (m); 1.05 (d); 0.65; 0.61; 0.26. ^{31}P NMR (ppm): 58.57 ($^2J_{\text{Si-P}}$ = 18.51 Hz; $^3J_{\text{Si-P}}$ = 1.08 Hz; $^4J_{\text{Si-P}}$ = 4.06 Hz). Mp: 174–183 °C dec. Anal. Calcd/Found: C, 52.00/51.8; H, 6.55/6.4.

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Solution and Solid-State Conformations of 5,5′-Bis(trimethylsilyl)-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepins

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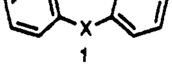
Three new 10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepins have been synthesized. The structures of two of the silepins, 5,5′-bis(trimethylsilyl)-4,6-dimethyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepin (**2**) and 5,5′-bis(trimethylsilyl)-10,11-5*H*-dibenzo[*b*,*f*]silepin (**3**), have been solved by X-ray crystallography. Compound **2** crystallizes in the orthorhombic space group *Pccn* with Z = 8, a = 14.888 (10) Å, b = 15.98 (2) Å, and c = 20.12 (3) Å. Compound **3** crystallizes in space group $C2/c$ (monoclinic) with Z = 4, a = 15.606 (5) Å, b = 16.061 (5) Å, c = 8.896 (3) Å, and β = 102.26 (2)°. The structures were refined to $R(F)$ = 0.0540 and 0.0553 and $R_w(F)$ = 0.0638 and 0.0586 for 719 and 617 reflections for **2** and **3**, respectively. The ^{1}H NMR spectra indicate that **2** exhibits a unique conformational rigidity at room temperature, while the remaining two silepins are fully fluxional to temperatures of −90 °C (183 K). The ethano bridge region for **2** exhibits an AA′BB′ pattern at room temperature and coalescence to A$_4$ occurs at 80 °C (353 K). The dynamic process associated with **2** was analyzed by DNMR4 techniques and the free energy of activation (ΔG^*) is found to be 16 kcal/mol for the inversion of the central seven-membered ring. A comparison of the solid-state and solution structures of **2** and related molecules is also given.

Dibenzoheteroepins (**1**) with appropriate aminoalkyl side chains exhibit diverse biological activities in the central nervous system. Attempts have been made to develop structure–activity relationships by using X-ray crystallography (solid state), nuclear magnetic resonance (solution studies), and computer-assisted molecular modeling.[1] Common functionalities such as an aromatic ring and an amine group appear to be important in the biological function of these compounds and the relationship of their relative positions have been analyzed.[2]



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Frequently, structural studies have been simplified by consideration of only the parent tricycle in order to separate the conformational properties of the framework from those of the side chain. The tricyclic framework can exist in varied conformations as a result of the twist of the C(10)–C(11) bond (the ethano bridge) and changes in bend angles (e.g., dihedral angles between benzo group planes).

Since the solid-state conformation may not be the biologically active conformer, solution studies could provide models for molecules in a more physiologically relevant environment. The dibenzoheteroepin framework most frequently studied in solution is the azepine system (**1**, X

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[1] (a) Bandolini, G.; Nicolini, M.; Tollenaere, J. P. *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 401. (b) Andrews, P. R.; Lloyd, E. J.; Martin, J. L.; Munro, S. L.; Sadek, M.; Wong, M. G. In *Molecular Graphics and Drug Design*; Burgen, A. S. V., Roberts, G. C. K., Tute, M. S., Eds.; Elsevier Science Publishers, B. V.: Amsterdam, 1986; Chapter 9.

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