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Synthesis and characterization of π cyclopentadienyl complexes of manganese and iron with one to five fluorosilyl substituents. Crystal and molecular structures of $[\text{Mn}(\text{C}_5\text{Br}\{\text{SiMe}_2\text{F}\}_4)(\text{CO})_3]$ and $[\text{Mn}(\text{C}_5\{\text{SiMe}_2\text{F}\}_5)(\text{CO})_3]$

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The reaction of AgSbF_6 with the cymantrenyl hydrosilanes $[\text{Mn}(\text{C}_5\text{Br}_{5-n}(\text{SiMe}_2\text{H})_n)(\text{CO})_3]$ ($n = 1-5$) gives the corresponding fluorosilanes. With the ferrocenylhydrosilanes $[\text{Fe}(\text{C}_5\text{Br}_{5-n}(\text{SiMe}_2\text{H})_n)(\text{C}_5\text{H}_5)]$ fluorination and oxidation to give the ferricenium salts $[\text{Fe}(\text{C}_5\text{Br}_{5-n}(\text{SiMe}_2\text{F})_n)(\text{C}_5\text{H}_5)]^+\text{SbF}_6^-$ ($n = 1-5$) occurs. Reaction of the latter with cobaltocene gives the corresponding neutral fluorosilanes. All compounds were characterized by a combination of NMR methods (^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{19}F ; sometimes also ^{29}Si) and in part as well by IR and HR mass spectrometry. The reactivity of the cymantrenyl fluorosilanes towards carbanions and MeOH was studied. X-ray diffraction analysis of $[\text{Mn}(\text{C}_5\text{Br}_{5-n}(\text{SiMe}_2\text{F})_n)(\text{CO})_3]$ ($n = 4-5$) shows paddle-wheel orientations of the SiMe_2F groups.

Introduction

Among the halosilanes, the fluorosilanes are particularly interesting because of their usefulness for the preparation of highly coordinated silicon compounds.^{1,2} This property allowed for their use as fluorescent fluoride sensors,³⁻⁵ but also as catalysts for C–F activation.⁶ However, they are also used for such different applications like the ^{18}F fluorination for cancer diagnostics,^{7,8} electrolyte additives for lithium secondary batteries,⁹ or “organic electroluminescent materials and devices”.¹⁰ For their synthesis, several methods are available, starting either from alkoxy-,¹¹ chloro-,¹²⁻¹⁵ or hydrosilanes.¹⁶⁻²² Most known fluorosilyl-cyclopentadienyl complexes are derivatives of ferrocene. They have been prepared from the corresponding hydrosilanes *via* fluorination with $\text{BF}_3\cdot\text{Et}_2\text{O}$,²³ from silaferrocenophanes *via* ring opening reactions,²⁴⁻²⁶ from dinuclear doubly SiMe_2 bridged ferrocenes *via* protonolysis with HBF_4 ,²⁷ or from ferrocenylchlorosilanes with CuF_2 .²⁸ Methods for functional group transformations including Si–X groups on group 4 metallocenes were summarized in 1999²⁹ and 2015.³⁰ Cyclopentadienyl complexes with more than two fluorosilyl substituents could not be obtained by any of these methods. As our group is interested in the per-functionalization of the cymantrenyl- and ferrocenyl systems, we decided to study the possibility of obtaining cyclopentadienyl com-

plexes with five fluorosilyl substituents. The results of these studies are reported in the following.

Results and discussion

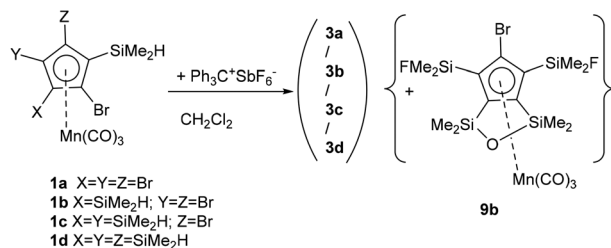
Synthesis

We decided to examine only the hydrosilane complexes $[\text{C}_5\text{Br}_{5-n}(\text{SiMe}_2\text{H})_n]\text{ML}$ ($\text{ML} = \text{Mn}(\text{CO})_3$, **1a–e**, FeCp , **2a–e**, $n = 1-5$).^{31,32} First of all, we tried the reaction of the Monosilyl-tetrabromocymantrene $[\text{Mn}(\text{C}_5\text{Br}_4\text{SiMe}_2\text{H})(\text{CO})_3]$ (**1a**) with $\text{CuF}_2\cdot 2\text{H}_2\text{O}$ in refluxing CCl_4 . After 15 hours, only traces of the desired fluorosilane $[\text{Mn}(\text{C}_5\text{Br}_4\text{SiMe}_2\text{F})(\text{CO})_3]$ (**3a**) besides unreacted **1a** could be isolated.

While the reaction of the salts $\text{Ph}_3\text{C}^+(\text{WCA})^-$ ($\text{WCA} =$ weakly coordinating anion) with hydrosilanes can lead to the formation of silylium ions, when no easily accessible fluorides are part of the WCA ,³³ trityl salts with anions like BF_4^- or SbF_6^- give only the corresponding fluorosilanes. The reaction of **1a–d** with Ph_3CSbF_6 yielded the desired fluorosilanes **3a–3d** always contaminated with Ph_3CH (in case of the reaction with **1d**, also the partial hydrolysis product **9b** was observed, *vide infra*). All attempts to separate the compounds met with failure (Scheme 1).

Although the use of AgBF_4 as a fluorination reagent for an optically active hydrosilane was noted already in 1969,²² and the use of AgSbF_6 for the fluorination of a triorganotin hydride was mentioned in 1984,³⁴ both silver salts apparently have

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Scheme 1 Reaction of the cymentrenyl-hydrosilanes **1a–1d** with Ph_3CSbF_6 . For the structures of the fluorosilanes see Scheme 2.

never been used for this purpose again. Still, as both are available commercially, we decided to look into their reactivity towards metallocenyl-hydrosilanes. First, we studied the cheaper AgBF_4 . However, we found, that this reaction took a very long time, at least at room temperature, and after several days, still unreacted hydrosilanes could be found in the product. Particularly, in the reaction of pentakis(dimethylsilyl) ferrocene, **2e**, with 5.5 equivalents of AgBF_4 for 24 h, and standard work-up (see Experimental part) single crystals could be obtained, that contained according to its mass spectra all members of the series $[\text{CpFe}\{\text{C}_5(\text{SiMe}_2\text{H})_n(\text{SiMe}_2\text{F})_{5-n}\}]$ ($n = 0–5$).

Thus, we turned to AgSbF_6 as a fluorination reagent. With **1a** in CH_2Cl_2 , we could observe rapid formation of elementary silver. After work-up, a mixture of **3a** and the dinuclear disiloxane $[(\text{OC})_3\text{Mn}(\text{C}_5\text{Br}_3\text{SiMe}_2)_2\text{O}]$ (**9e**) was obtained.

When the other silylated bromocymantrenes $[\text{Mn}\{\text{C}_5\text{Br}_{5-n}(\text{SiMe}_2\text{H})_n\}(\text{CO})_3]$ (**1b–e**, $n = 2–5$) were treated with an excess (with respect to the number of hydrosilyl groups) of AgSbF_6 in CH_2Cl_2 , the corresponding fluorosilylcymantrenes **3b–e** could be obtained in medium to excellent yields (for structural drawings, see Scheme 2). For comparison, we treated also $[\text{Mn}\{\text{C}_5\text{H}(\text{SiMe}_2)_4\}(\text{CO})_3]$ (**1f**) with AgSbF_6 and obtained the expected product of fluorination $[\text{Mn}\{\text{C}_5\text{H}(\text{SiMe}_2\text{F})_4\}(\text{CO})_3]$ (**5d**) in 51% yield. Careful examination of the NMR spectra showed, that sometimes the products of partial desilylation were also formed (e.g. **5b** in the reaction of **1c**, or **5d** in the reaction of **1e**) (Scheme 3).

Next, we looked at the ferrocene system. Here some complications might be expected, due to the known ability of AgSbF_6 to act as a strong oxidant towards substituted ferrocenes to give ferricenium salts.³⁵ In a first experiment, we treated $[\text{Fe}\{\text{C}_5(\text{SiMe}_2\text{H})_5\}(\text{C}_5\text{H}_5)]$ (**2e**) in CH_2Cl_2 with 5.5 equivalents AgSbF_6 . A bluish green solid was obtained, insoluble in hexane, nearly insoluble in CH_2Cl_2 and soluble in water with blue colour, which gradually disappeared. Extraction of the aqueous phase with hexane yielded, after evaporation *in vacuo*, only ferrocene. We concluded that the silver ion had oxidized the ferrocene to a ferricenium species, which was unstable in water. Therefore, we decided to reduce the primary oxidation product with cobaltocene. This time, we examined $[\text{Fe}\{\text{C}_5\text{Br}_3(\text{SiMe}_2\text{H})_2\}(\text{C}_5\text{H}_5)]$ (**2b**). After reaction with 2.5 eq. AgSbF_6 in CH_2Cl_2 a dark green oil was obtained, which was re-

dissolved in CH_2Cl_2 and treated with a hexane solution of cobaltocene, which yielded nearly immediately a yellow solution. Evaporation of solvent gave $[\text{Fe}\{\text{C}_5\text{Br}_3(\text{SiMe}_2\text{F})_2\}(\text{C}_5\text{H}_5)]$ (**4b**) in approximately 40% yield as a yellow oil (Scheme 4). The observed contamination with **6a** and **6b** (and very small amounts of **IIIb**) was due both to impurities in the starting material **2b** and partial desilylation reactions.

Since this approach was successful, we repeated it for all members of the series $[\text{Fe}\{\text{C}_5\text{Br}_{5-n}(\text{SiMe}_2\text{H})_n\}(\text{C}_5\text{H}_5)]$ ($n = 1–5$, **2a–2e**) and obtained the corresponding fluorosilanes $[\text{Fe}\{\text{C}_5\text{Br}_{5-n}(\text{SiMe}_2\text{F})_n\}(\text{C}_5\text{H}_5)]$ ($n = 1–5$, **4a–e**) (for structural formulae, see Scheme 2).

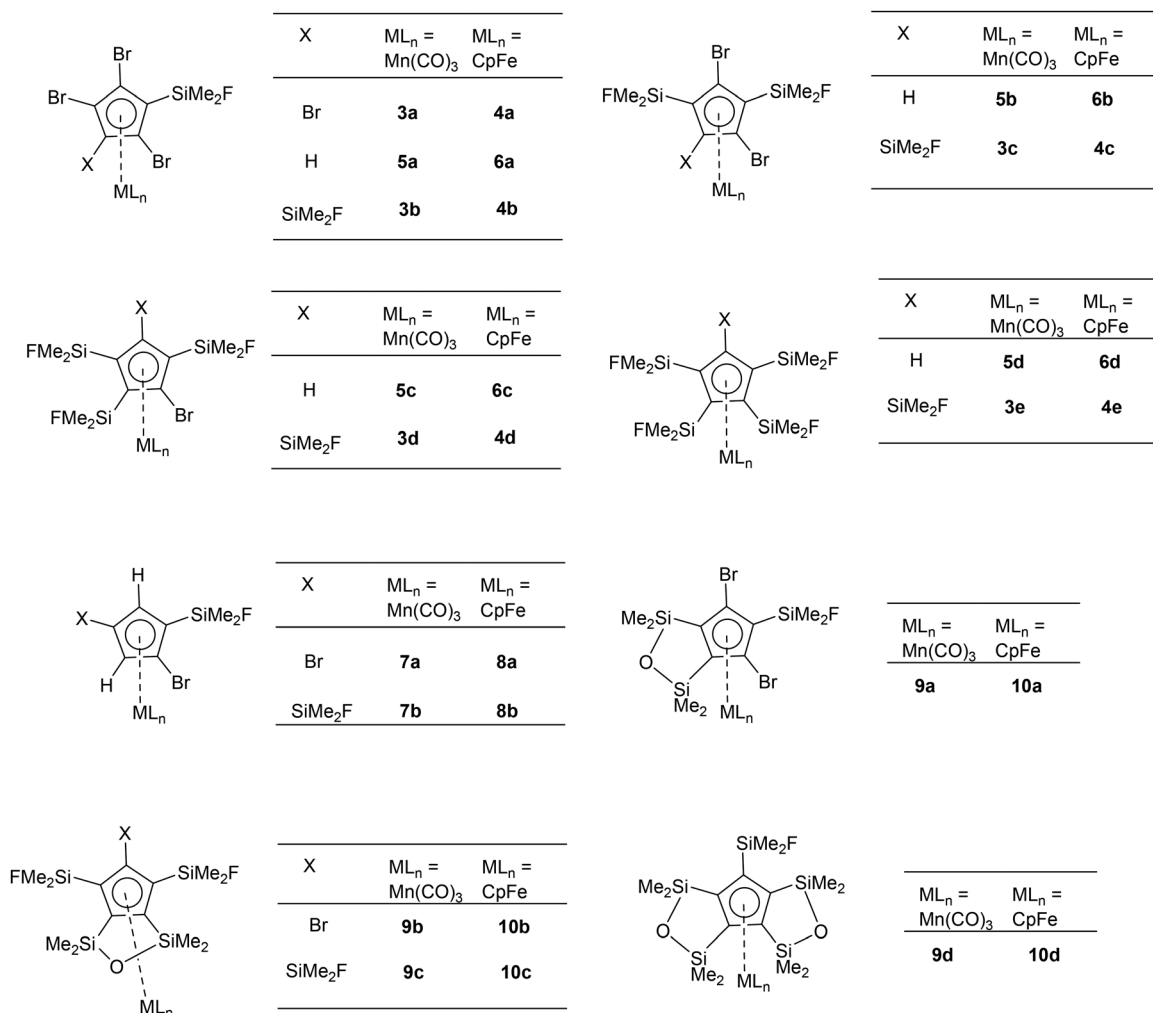
The desired fluorosilanes were always contaminated by products of partial desilylation. These desilylation reactions were most likely due to a reaction of the generated SbF_5 with adventitious moisture present in the solvent, which led to formation of HF, or, in part, to corresponding reactions on the silicagel chromatographic columns. Unfortunately, due to unknown reasons, all products of the reduction step with cobaltocene, were also contaminated with small amounts of phthalate esters (mostly bis(isooctyl)phthalate). Attempts to separate these compounds by chromatography met with failure.

Reactivity

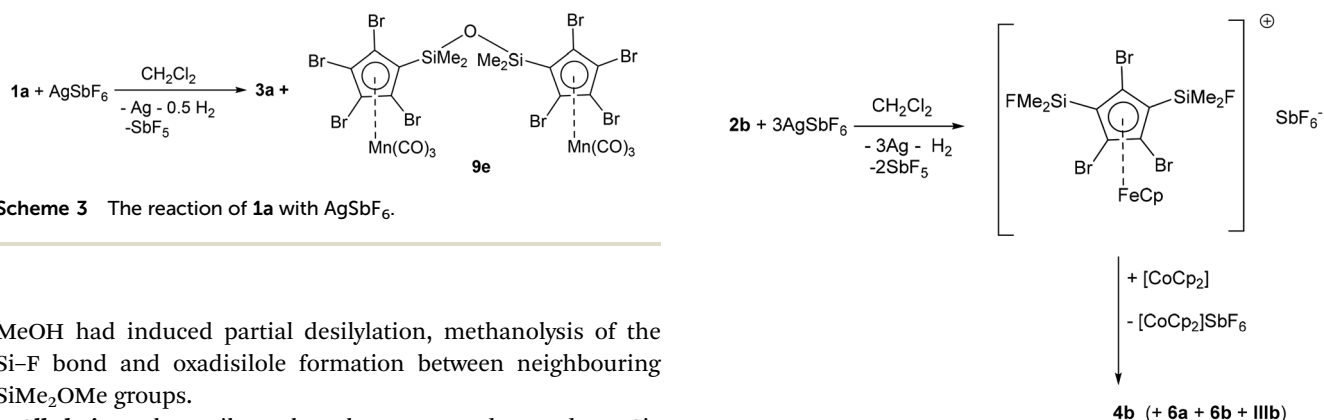
Hydrolysis and alcoholysis. The Si–F bond is one of the strongest known (*ca.* 638–697 kJ mol^{-1} , compared to a value of 512–570 kJ mol^{-1} for the Si–O and 400–490 kJ mol^{-1} for the Si–Cl bond).³⁶ From a thermodynamic view, the hydrolysis of fluorosilanes should be endothermic. However, one should keep in mind, that kinetically the Si–F bond is quite labile, mostly due to bond polarization, but also to the high tendency for formation of HF and/or its water adducts.³⁷ All the metallocenyl fluorosilanes prepared by us could be handled in air without apparent decomposition, which is in sharp contrast with our observations with the corresponding chlorosilanes.³⁸ Still, the mass spectra of the ferricenium ions **4c**⁺, **4d**⁺ and **4e**⁺, which were the primary products of the reactions of the corresponding hydrosilanes with AgSbF_6 , showed the presence of the disiloxanes **10a–d** (for structural formulae, see Scheme 2). These are structural analogs of the hydrolysis products, which we observed in the alcoholysis reactions of the chlorosilanes $[\text{Mn}\{\text{C}_5(\text{SiMe}_2\text{Cl})_n\text{Br}_{5-n}\}(\text{CO})_3]$, $n = 3–5$.³⁸ As NMR spectra of the isolated fluorosilanes **3a–e** and **4a–e** in C_6D_6 did not change during the course of one day, it can be assumed, that the hydrolysis occurred during the fluorination step, possibly induced by the presence of SbF_5 . When compound **3a** was treated with LiOH in Et_2O for 15 h, only the desilylation product **IIIb** and the disiloxane **9e** could be isolated.

A quite unusual reaction was observed for compound **3e**. Some of the single crystals, that had been obtained by recrystallization from hexane/MeOH solution and apparently contained some liquid MeOH in a specimen, were left standing in air for a couple of weeks. A ¹H-NMR spectrum, taken of the meanwhile “weathered” crystals, showed besides the original **3e** also the presence of $[\text{Mn}\{\text{C}_5\text{H}(\text{SiMe}_2\text{OMe})_4\}(\text{CO})_3]$ (**11a**) and $[\text{Mn}\{\text{C}_5\text{H}(\text{SiMe}_2\text{OMe})_2(\text{SiMe}_2\text{O})\}(\text{CO})_3]$ (**11b**). Apparently, the





Scheme 2 Structural drawings of all compounds described in this publication.



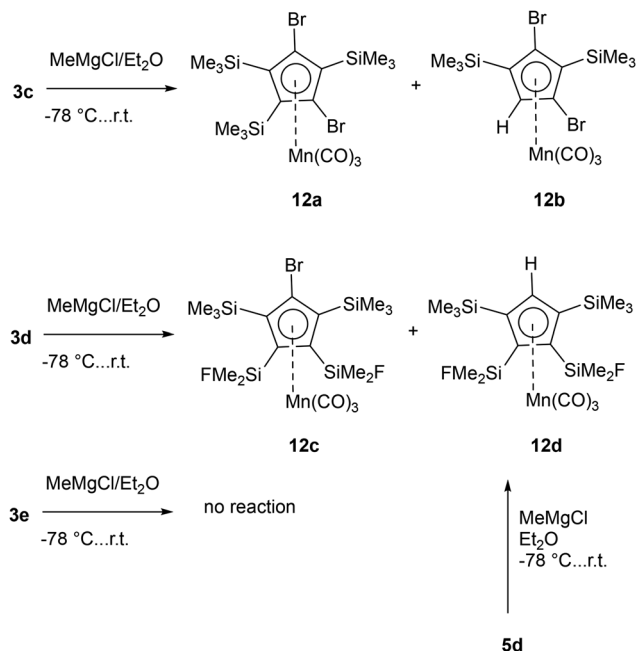
MeOH had induced partial desilylation, methanolysis of the Si–F bond and oxadisilole formation between neighbouring SiMe₂OMe groups.

Alkylation. Fluorosilanes have been reported to undergo Si–C bond formation reactions *via* treatment with lithium organyls and Grignard reagents.^{14,23,39–41} However, these reactions are rather slow in the absence of catalysts. In a first experiment, we treated **3c** with MeMgCl, and obtained a mixture of [Mn{C₅Br₂(SiMe₃)₃}(CO)₃] (**12a**) and [Mn{C₅HBr₂(SiMe₃)₂}(CO)₃] (**12b**). Next, we treated **3d** with MeMgCl, and obtained a mixture of [Mn{C₅Br(SiMe₂F)₂(SiMe₃)₂}(CO)₃] (**12c**) and [Mn

Scheme 4 Synthesis of **4b** from **2b**.

{C₅H(SiMe₂F)₂(SiMe₃)₂}(CO)₃] (**12d**), while with compound **5d** only **12d** could be isolated. However, when **3e** was treated with MeMgCl, the unchanged fluorosilane was recovered even after prolonged reaction time (Scheme 5).





Scheme 5 The reaction of the fluorosilanes **3c**–**e** with MeMgCl .

We studied also the reactivity of **3c** and **3d** towards LiMe and of **3e** towards AlMe_3 . The reaction of **3c** with LiMe yielded a mixture of **12a**, **12b** and $[\text{Mn}\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\}(\text{CO})_3]$ **12e**, while the reaction of **3d** with LiMe gave a mixture of several compounds, with $[\text{Mn}\{\text{C}_5\text{H}_3(\text{SiMe}_3)_4\}(\text{CO})_3]$ (**12f**) and **12d** as major components. Compounds **12a**, **b** and **12f** had been prepared by us earlier on a different route.^{42,43} But the pentasubstituted **3e** did not even react with AlMe_3 to give any SiMe_3 compounds, and **3e** could be recovered unchanged in 60% yield.

NMR spectroscopy

All compounds were characterized by ^1H , ^{19}F and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, some also by ^{29}Si NMR spectroscopy. As the NMR resonances of the substituted cyclopentadienyl rings in the series of cymantrenyl- and ferrocenyl-fluorosilanes appeared quite similar, the corresponding compound pairs **3a/4a**, **3b/4b**, **3c/4c** and so on, are discussed together.

The mono(fluorosilanes) 3a/4a. If the solution structure of these compounds were static, the methyl groups were not equivalent (proximal and distal position with respect to the metal), and two signals each in the ^1H NMR and ^{13}C NMR spectra should be expected. However, for both compounds only one signal was observed in all NMR spectra, and therefore, a fast exchange of the proximal and distal methyl groups at room temperature can be assumed. Sharp doublets in the ^1H spectra (A part of A_6X spin system, $J_{\text{H-F}} = 7.3$ Hz (**3a**); 7.4 Hz (**4a**)), and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (AX spin system, $J_{\text{C-F}} = 18.3$ Hz (**3a**); 14.9 Hz (**4a**)) characterize the SiMe_2F groups. The ^{19}F NMR spectrum of **3a** shows only a broad signal with two satellites due to fluorine–silicon coupling ($J_{\text{F-Si}} = 282$ Hz), while the corresponding spectrum of **4a** shows a well-resolved septet (X part of A_6X spin system, $J_{\text{H-F}} = 7.8$ Hz) also with two satellite

signal groups ($J_{\text{F-Si}} = 279$ Hz). The ^{29}Si NMR spectra of both compounds show a doublet each, due to Si-F coupling ($J_{\text{Si-F}} = 282$ Hz for **3a** and 280 Hz for **4a**). It should be noted in this context, that the known ferrocene derivative $[\text{Fe}(\text{C}_5\text{H}_4\text{SiMe}_2\text{F})(\text{C}_5\text{H}_5)]$ (**5**) was also fully characterized by NMR spectroscopy: ^1H NMR: doublet with $J_{\text{H-F}}$ of 6.9 Hz; $^{13}\text{C}\{^1\text{H}\}$ NMR: doublet with $J_{\text{C-F}}$ of 17 Hz; ^{19}F NMR: septet with $J_{\text{F-H}}$ of 6.8 Hz; ^{29}Si NMR: doublet with $J_{\text{Si-F}}$ of 272 Hz.²⁴

The bis(fluorosilanes) 3b/4b. In these compounds the methyl groups on silicon are diastereotopic. This was also noticed in the known compound $[\text{Fe}\{\text{C}_5\text{H}_3(\text{SiMe}_2\text{F})_2\}(\text{C}_5\text{H}_5)]$, which has the silyl substituents in relative 1,2 position, however.²⁷ In this compound, the ^1H NMR spectrum (at 270 MHz) showed a triplet for the methyl groups ($J_{\text{H-F}} = 7.8$ Hz), and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed two doublets of doublets, with $J_{\text{C-F}} \approx 17$ Hz and $J_{\text{C-F}} \approx 1.0$ Hz. No ^{19}F or ^{29}Si NMR data were given. The ^1H NMR spectrum (at 400 MHz) of **3b** shows two close ($\Delta\delta = 4.9$ Hz) doublets with $J_{\text{H-F}} = 7.3$ and 7.3 Hz, while its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (at 101 MHz) shows two doublets with $J_{\text{C-F}} = 13.8$ and 15.3 Hz. For compound **4b**, the ^1H NMR spectrum (at 270 MHz) shows an apparent doublet of doublets, with $J_{\text{H-F}} = 7.4$ Hz and 1.7 Hz, respectively, and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (at 68 MHz) two close ($\Delta\delta = 10.6$ Hz) doublets with $J_{\text{C-F}}$ of 15.1 and 15.0 Hz. The C_5H_5 ligand in **4b** is observed as a singlet in both ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, with peak widths of 0.49 and 2.52 Hz, respectively. The ^{19}F NMR spectra of both compounds appear as septets with ^{29}Si satellites ($J_{\text{F-H}} = 7.3$ Hz (**3b**) and 7.8 Hz (**4b**), respectively; $J_{\text{F-Si}} = 281$ Hz (**3b**) and 279 Hz (**4b**)).

The tris(fluorosilanes) 3c/4c. Although the ^1H NMR spectra of **3b** and **4b** are in principle higher order spectra (in a “static” model $\text{A}_3\text{A}'_3\text{B}_3\text{B}'_3\text{XX}'$ spin systems), they can be treated as first order spectra. However, a first look at the methyl regions of the ^1H NMR spectra of compounds **3c** and **4c** shows, that first order treatment is no longer possible (Fig. 1 and S3).

The two diastereotopic pairs of methyl groups at the SiMe_2F groups in 1,2 positions appear as two broad “triplets”, which

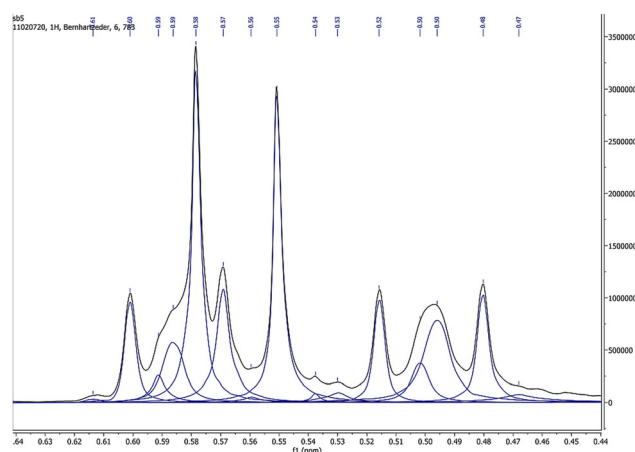


Fig. 1 ^1H NMR spectrum (SiCH_3 region; measured at 270 MHz) for compound **4c**.



overlap with the doublet of the two enantiotopic methyl groups at the “isolated” SiMe₂F group at 4-position. The overlap can be removed by measuring the spectrum at 500 MHz (see Fig. S9), but not the “strange” appearance of the triplets. A first-order analysis (as indicated in the left half of Fig. 1) would yield an interpretation of the “triplet” as a “doublet of doublets” with $^3J_{\text{H-F}} \approx ^6J_{\text{H-F}} = 3.7$ Hz, which does not make sense in comparison with the coupling constants found in compounds **3a,b** and **4a,b**. Unfortunately, we neither have access to NMR simulation programs capable of simulating such an A₃A'₃B₃B'₃C₃C'₃XX'Y spin system nor computational capabilities to perform these calculations. Also, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compounds **3c** and **4c** have to be treated as higher order spectra (Fig. 2 and S23). There are two apparent “triplets” for the two diastereotopic methyl carbons of the SiMe₂F groups in 1,2 position and one doublet for the enantiotopic methyl carbons of the SiMe₂F group in position 4.

First order analysis, as indicated in the (left) spectrum of **3c**, would yield apparent coupling constants $^2J_{\text{C-F}} \approx ^5J_{\text{C-F}}$ for the diastereotopic methyl groups of *ca.* 8.5 and 10.0 Hz, respectively, and $^2J_{\text{C-F}} = 15.1$ Hz for the isolated SiMe₂F group. Analogous interpretation of the spectrum of compound **4c** would yield identical values. Comparison with the $J_{\text{C-F}}$ values found for compounds **3a,b** and **4a,b** shows, that at least a first order interpretation of the “triplet” signals is not appropriate. Therefore, the observed spectra have to be interpreted as overlap of AXYZ, BXYZ and CXYZ spectra (due to the fact, that for statistical reasons only one of the methyl carbons can be a ^{13}C isotope, the totally ^{13}C enriched AA'BB'CXX'Y changes to three different isotopomers, and the XX'Y fluorine part changes to XYZ⁴⁴). Careful inspection of the spectrum of **4c** shows also the presence of “satellites” due to $^1J_{\text{C-Si}}$ couplings of *ca.* 50 Hz for the “triplets” and 60 Hz for the “doublet”. The C₅H₅ ligand in **4c** is observed in both ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra as a singlet, with peak widths of 0.84 and 3.25 Hz, respectively. The ^{19}F NMR spectra of both compounds show

two signals with relative intensities of 2 : 1. Both signals are broad with no resolvable fine structure for compound **3c**. However, for compound **4c**, the stronger signal is partially resolved, and the weaker signal appears as a well-resolved septet with $^3J_{\text{F-H}} = 7.6$ Hz (Fig. S14 and S19).

The tetrakis(fluorosilanes) 3d/4d/5d. As might be expected from the preceding section, the ^1H NMR spectra of the tetrakis (fluorosilanes) **3d** and **4d** look even more complicated and cannot be treated as first order (Fig. 3 and S4).

In addition to the complications by the higher order spin system (A₃A'₃B₃B'₃C₃C'₃XX')(C₃C'₃D₃D'₃YY'), further complications arise by dynamic effects due to hindered rotations of the individual SiMe₂F groups, as can be seen in the VT NMR spectra of **3d** (*vide infra*).

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3d** shows 16 lines in the SiCH₃ region (Fig. S24; unfortunately, no expanded view is available), while for compound **4d** twelve peaks can be resolved (Fig. 4). From theory, the spectrum in the SiCH₃ region should be an overlap of (AXYZW), (BXYZW), (CXYZW) and (DXYZW) spin systems. The C₅H₅ signal for compound **4d** appears in both ^1H and $^{13}\text{C}\{^1\text{H}\}$ as a singlet, with peak widths of 1.90 Hz and 3.06 Hz, respectively. In comparison with the ^1H NMR spectra of **4b** and **4c**, this is a significant line broadening, which hints to a reduction of the free rotation of the C₅H₅ ring around the Fe-centroid axis.

The ^{19}F NMR spectra of **3d** and **4d** show two well separated ($\Delta\delta = 9.1$ and 6.5 ppm, respectively) broad singlets (for compound **4d** peak widths of 30 and 24 Hz, respectively) with relative intensity 1 : 1 (Fig. S15 and S20).

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR room temperature spectra of the bromine-free compound **5d** show similar broad signals as the bromo compound **3d** (Fig. 5). Particularly, the ^1H NMR spectra look very similar, with just the relative positions of the “doublets” and “triplets” exchanged.

A formal first-order analysis might extract eight doublets each from both spectra, however, complications arise here again from dynamic line broadening effects, as can be seen in the VT NMR spectra (*vide infra*). The room temperature ^{19}F

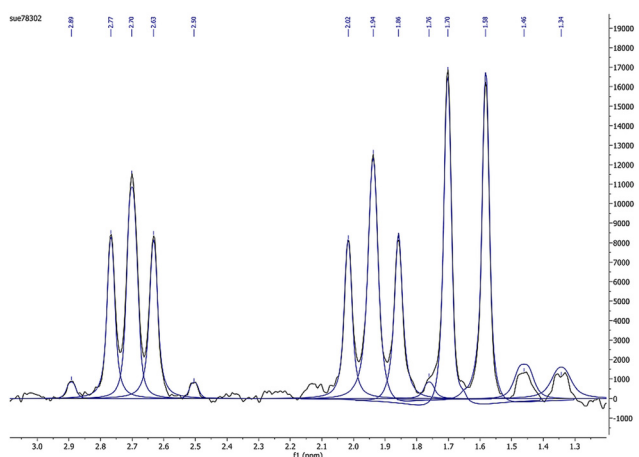


Fig. 2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (SiCH₃ region, measured at 126 MHz) of compound **4c**.

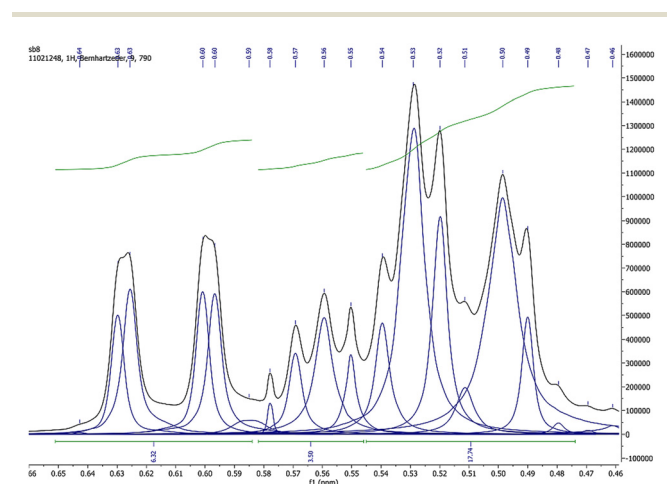


Fig. 3 ^1H NMR spectrum (SiCH₃ region, at 270 MHz) of compound **4d**.



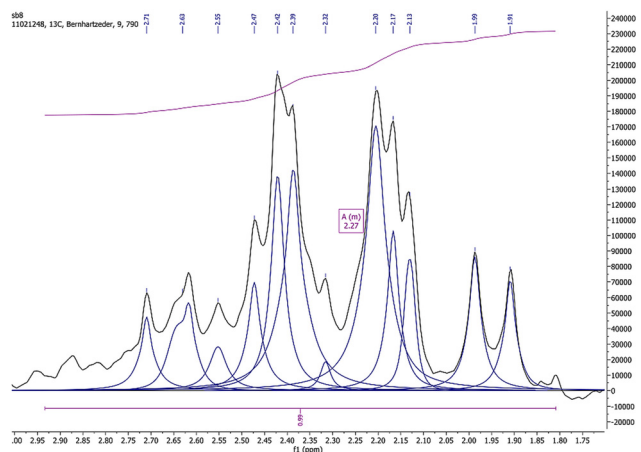


Fig. 4 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (SiCH_3 region, measured at 68 MHz) of compound **4d**.

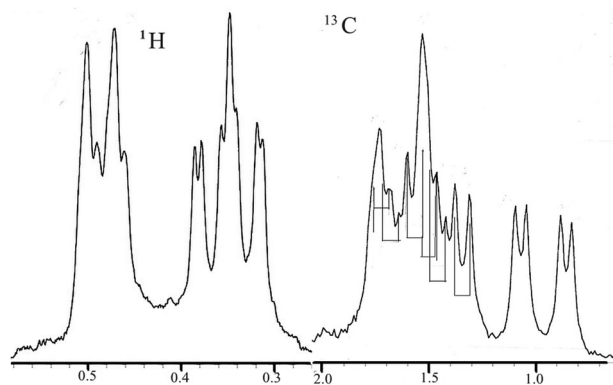


Fig. 5 Room temperature ^1H (left) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (SiCH_3 region, at 270 and 67.9 MHz, respectively) of compound **5d**.

NMR spectrum at 376 MHz shows one broad singlet (half width *ca.* 300 Hz) and a partially resolved multiplet with relative intensities 1 : 1 (Fig. S16).

The pentakis(fluorosilanes) 3e/4e. As soon as all five substituents are SiMe_2F , the molecules become part of the group of “multi-5-rotor molecular propellers”.⁴⁵ So far, the majority of these compounds contains the pentaaryl cyclopentadienyl, the $[\text{C}_5(^i\text{Pr})_5]$, and the $[\text{C}_5(\text{CH}_2\text{Ph})_5]$ ligands. A few examples with $[\text{C}_5(\text{SiMe}_2\text{H})_5]$ ligands exist also. In the context of the present study, most relevant are $[\text{CoCp}(\text{C}_5^i\text{Pr}_5)]^+\text{PF}_6^-$,⁴⁶ $[\text{FeCp}(\text{C}_5^i\text{Pr}_5)]$,⁴⁷ $[\text{Fe}(\text{C}_5^i\text{Pr}_5)(\text{CO})_2\text{Br}]$,⁴⁸ $[\text{Mo}(\text{C}_5^i\text{Pr}_5)(\text{CO})_3\text{Me}]$,⁴⁹ as well as $[\text{Mn}\{\text{C}_5(\text{SiMe}_2\text{H})_5\}(\text{CO})_3]$,³¹ $[\text{Fe}\{\text{C}_5(\text{SiMe}_2\text{H})_5\}\text{Cp}]$,³² and $[\text{Fe}\{\text{C}_5(\text{SiMe}_2\text{H})_5\}_2]$.⁵⁰ All of these compounds have in common, that the substituents ^iPr or SiMe_2H are “gear-meshed” creating a metallocenic chirality. The most stable form has the C–H or Si–H bond in or close to the cyclopentadienyl ring plane and five methyl groups each on both sides of this plane. Therefore, the ^1H NMR spectra of all $[\text{C}_5^i\text{Pr}_5]$ complexes show one septet for the C–H protons and two doublets for the diastereotopic methyl protons, while the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show one

singlet each for the diastereotopic methyl carbons. The same observation is made for the dekakis(dimethylsilyl)ferrocene,⁵⁰ while for the two other complexes with the $[\text{C}_5(\text{SiMe}_2\text{H})_5]$ ligand only one doublet is observed in the ^1H NMR and one singlet in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra.^{31,32} Similar “simplified” spectra can be observed in some of the $[\text{C}_5^i\text{Pr}_5]$ complexes at higher temperatures.^{46,48,49}

At r.t., both ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3e** show two broad unresolved multiplets for the SiMe_2F groups, besides a singlet for the $\text{Mn}(\text{CO})_3$ carbon atoms and a poorly resolved multiplet for the cyclopentadienyl carbon atoms (Fig. S5 and S25). The expected spin systems $(\text{A}_3\text{B}_3\text{X})$ $(\text{A}'_3\text{B}'_3\text{X}')_2(\text{A}''_3\text{B}''_3\text{X}'')_2$ for the SiMe_2F protons, overlap of a $(\text{AXX}'_2\text{X}''_2)$ with a $(\text{BXX}'_2\text{X}''_2)$ system for the SiMe_2F carbon atoms and a $(\text{MXX}'_2\text{X}''_2)$ for the cyclopentadienyl ring carbon atoms together with the effects of possibly hindered rotations make a detailed analysis of these spectra impossible. However, on cooling to $-10\text{ }^\circ\text{C}$ the ^1H NMR spectrum changes to a triplet ($J = 7.3\text{ Hz}$) and a doublet-of-doublets ($J = 7.0$ and 6.9 Hz)-structure (Fig. 6, further discussion in the VT section).

Unfortunately, the NMR samples studied for compound **4e** were contaminated by **4d** and **6d**, and therefore a reliable exact analysis of its NMR spectra is not possible. However, some general features can be discussed. In the room temperature ^1H NMR spectrum (in C_6D_6 , 270 MHz), the SiMe_2F methyl protons appear as a broad unresolved “singlet” (half width *ca.* 17 Hz) and the C_5H_5 protons as an extremely broad (half with 58 Hz) signal (Fig. S11). When the same compound is measured at $-70\text{ }^\circ\text{C}$ (in toluene- d_8 , 400 MHz), the methyl protons appear as two doublets of doublets. Measurement of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at $-70\text{ }^\circ\text{C}$ (in toluene- d_8 , 101 MHz), gives for the methyl carbon atoms 8 lines, which can also be interpreted as two doublets of doublets (Fig. 7).

The obvious similarity of the LT ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in the SiMe_2F region is on first sight not compatible

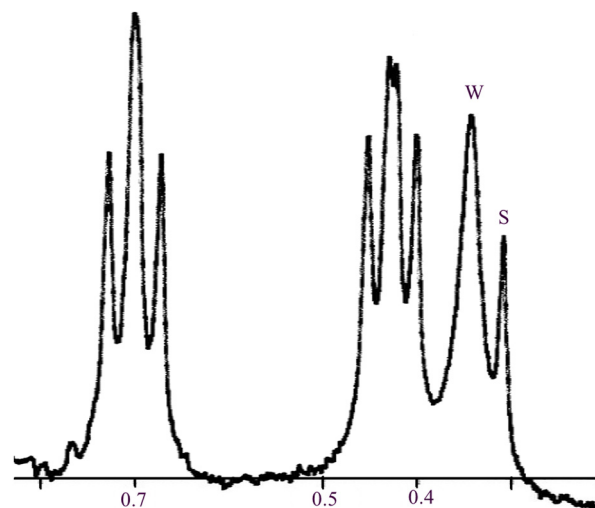


Fig. 6 ^1H spectrum of compound **3e** (SiCH_3 region, at 270 MHz, $-20\text{ }^\circ\text{C}$; S and W are the impurities silicon grease and water).



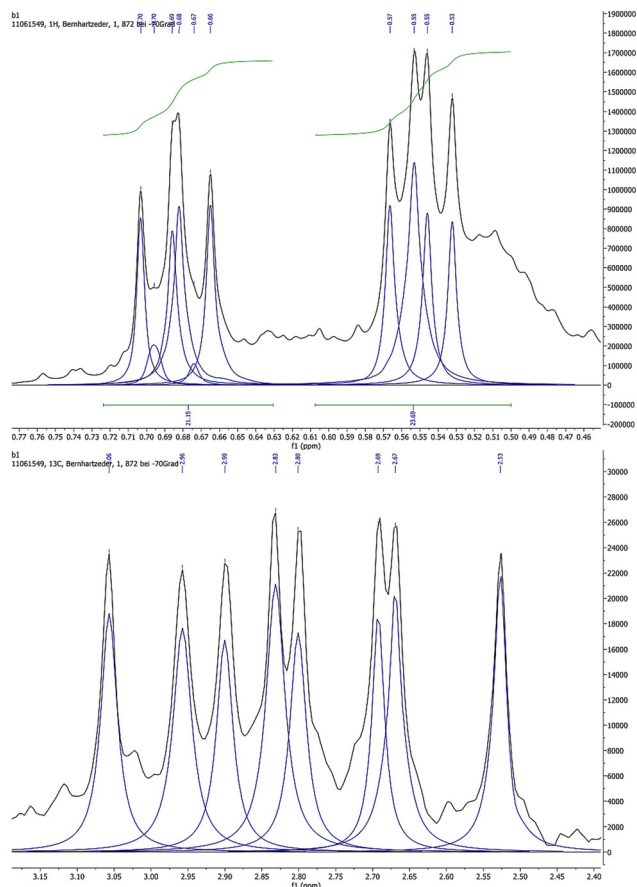


Fig. 7 Low temperature ($-70\text{ }^{\circ}\text{C}$) ^1H (top) and $^{13}\text{C}(^1\text{H})$ (bottom) NMR spectra of compound **4e** (SiCH_3 region, at 400 and 101 MHz, respectively).

with the expected spin systems, as explained above for the spectra of compound **3e**. The appearance of “doublets of doublets” with similar couplings (^1H : $\delta = 0.68$ (dd, $J_{\text{H-F}} = 8.4$ and 6.9 Hz), 0.55 (dd, $J_{\text{H-F}} = 8.3$ and 5.4 Hz); $^{13}\text{C}\{^1\text{H}\}$: $\delta = 2.93$ (dd, $J_{\text{C-F}} = 16.0$ and 10.0 Hz), 2.68 (dd, $J_{\text{C-F}} = 16.5$ and 14.2 Hz)) suggests, that each methyl group “sees” two fluorine atoms, and coupling occurs “through space”. Further long-range couplings are apparently too small to be resolved. This is reminiscent of the spectra obtained for $[\text{Mo}\{\text{C}_6(\text{SiMe}_2\text{F})_6\}(\text{CO})_3]$, described by Sakurai *et al.* some 30 years ago.⁵¹ However, in that complex only triplets (^1H) or unresolved multiplets (^{13}C) were obtained for the methyl groups at r.t., while for the free ligand at r.t. septets were observed. This difference was explained by the assumption, that a “merry-go-round” of the F atoms around the periphery of the free ligand, which makes all F atoms equivalent, was no longer possible in the coordinated ligand. It should be noted, however, that a “gear-meshed” rotation of the SiMe_2F groups is possible for six-membered rings, but not for five-membered ones (parity rule for gear trains⁴⁵).

VT NMR studies. The ^1H NMR spectra of the monosilyl compounds **3a** and **4a** showed at r.t. only one singlet, which is an

indication of rapid rotation of the SiMe_2F group around the $\text{C}_{\text{cp}}\text{-Si}$ bond, as no difference between distal and proximal methyl groups is observed. The ^1H NMR spectra of the disilyl compounds **3b** and **4b** show two doublets, which might be interpreted either as arising from the two diastereotopic methyl groups with no sign of long-distance couplings $^7J_{\text{H-F}}$, indicating a frozen or slow rotation, or as a doublet of doublets, arising from time-averaged methyl group signals, showing both $^3J_{\text{H-F}}$ and $^7J_{\text{H-F}}$ couplings. The general appearance of the spectra corresponds to the ones seen for $[\text{Fe}(\text{C}_5\text{H}_3^1\text{Pr}_2)_2]$ and $[\text{Mo}(\text{C}_5\text{H}_3^1\text{Pr}_2)(\text{CO})_3\text{Me}]$,⁴⁹ and also $[\text{Co}(\text{C}_5\text{H}_3^1\text{Pr}_2)(\text{PMe}_3)_2]$,⁵² but in contrast to $[\text{Co}(\text{C}_5\text{H}_3^1\text{Pr}_2)(\text{CO})_2]$,⁵³ which shows only one doublet for the isopropyl methyl groups. As the ^{19}F NMR spectra taken at the same temperature show only septets, the former interpretation of hindered rotation is preferred. As the room temperature ^1H and ^{13}C NMR spectra of the remaining compounds gave mostly only broad and badly resolved spectra, we decided to examine the VT-NMR spectra of compounds **3d**, **e** and **5d** as well as of compounds **4d,e** and **6d**.

When a toluene solution of **4d** is gradually cooled down, the “triplet” feature broadens first and loses its multiplet appearance, then both signals become broader and unresolved, and finally only a broad singlet with an extremely broad shoulder can be observed at $-70\text{ }^{\circ}\text{C}$ (Fig. S32). On the other hand, if the solution is heated to $+70\text{ }^{\circ}\text{C}$, both signals get better resolved. Unfortunately, instrument limitations did not allow for extension to both higher and lower temperatures. The observed behaviour is very unusual-opposite to what would be expected, and at present we have no explanation for it.

However, when a toluene solution of **3e** is gradually cooled down from r.t. to $-20\text{ }^{\circ}\text{C}$ and the heated to $+45\text{ }^{\circ}\text{C}$, a behaviour like expected can be observed (Fig. S33): on cooling the broad doublet feature observed at r.t. gets better resolved and a triplet (which actually might be a poorly resolved doublet of doublets) and a doublet of doublets appear at $-20\text{ }^{\circ}\text{C}$. On heating the broad “doublet” coalesces to a singlet at $45\text{ }^{\circ}\text{C}$. Further heating to $70\text{ }^{\circ}\text{C}$ or cooling to $-78\text{ }^{\circ}\text{C}$ does not change the appearance of the spectra (only slight “sharpening” of the “singlet” is observed at $+70\text{ }^{\circ}\text{C}$). Again, due to instrumental limitations, it is not possible to say, if and towards which multiplicity the broad singlet might change at higher temperatures. We also had a look at the Cp region of the $^{13}\text{C}\{^1\text{H}\}$ spectra at three temperatures (Fig. S34): quite unexpected, the appearance of the quaternary Cp signal did not change significantly both when going to high or to low temperature: two poorly resolved multiplets were observed at all temperatures, with the signals at high temperature showed less resolution than the ones at low temperature, as might be expected.

Cooling a toluene solution of **5d** from r.t. to $-20\text{ }^{\circ}\text{C}$ resulted in the appearance of three broad doublets, which broadened even more on going to $-70\text{ }^{\circ}\text{C}$ yielding finally three broad singlets (Fig. S35). On the other hand, heating this solution to $60\text{ }^{\circ}\text{C}$ resulted also in broadening, but the appearance as “doublet” and “triplet” remained. When looking at the ^{19}F NMR spectra at r.t. and $-80\text{ }^{\circ}\text{C}$, the appearance as two unre-



solved singlets did not change. However, the difference in chemical shifts between these singlets slightly increased on cooling down.

A VT ^{19}F NMR study of the ferrocene derivative **4d** (contaminated with **6d**) showed two broad singlets at r.t. (half widths *ca.* 33 Hz), that collapsed at $-70\text{ }^{\circ}\text{C}$ to two extremely broad (half widths 777 and 300 Hz, respectively) signals with no fine structure, that nearly disappeared in the noise (Fig. S36).

Similarly, when a toluene solution of a 2 : 1 mixture of **4d** and **4e** was cooled from r.t. to $-70\text{ }^{\circ}\text{C}$, the broad singlet for the C_5H_5 protons (half width 9.3 Hz) split up into two sharper singlets (half widths *ca.* 3.9 Hz). While the appearance of the SiMe_2F multiplets also changed upon cooling, due to the severe overlap of the multiplet signals no further discussion is possible (Fig. S37). It should be noted, that the assignment of the Cp signals to compounds **4d** and **4e** is based on comparison with purer samples of both species, and also to the corresponding ^{13}C and mass spectra. Still, it is hard to imagine, why the signals are broadened at r.t. An exchange between compounds **4d** and **4e** seems chemically impossible, and a slowed rotation of a C_5H_5 ligand has never been observed at such temperatures even in the case of extremely sterically demanding C_5R_5 ligands in ferrocenes of the type $[\text{Fe}(\text{C}_5\text{R}_5)(\text{C}_5\text{H}_5)]$. However, for the sterically related compound $[\text{Mo}(\text{C}_5^{\text{iPr}}\text{Pr}_5)(\text{CO})_3\text{Me}]$ it was reported, that a broad isopropyl resonance at r.t. split into two sets of signals at low temperature, and this was explained to the presence of two conformational isomers with respect to the relative orientation of the isopropyl groups.⁴⁹ A broad singlet for the cyclopentadienyl carbons in $[\text{Fe}(\text{C}_5^{\text{iPr}}\text{Pr}_5)(\text{CO})_2\text{Br}]$ was reported for the r.t. ^{13}C NMR spectrum, however, no low temperature data and also no ^1H data were given.⁴⁸ Although this is no “proof”, an interpretation of the broad Cp resonance at r.t. as a sign of the presence of two or more conformational isomers cannot be excluded. A ^{19}F VT NMR study of the same sample showed a very broad resonance (half width 182 Hz) at r.t. and a significantly sharper (half width 33 Hz) singlet with no fine structure at $-70\text{ }^{\circ}\text{C}$ (Fig. S38). This behaviour is quite interesting in light of the complete opposite observation in the ^{19}F NMR spectra of **4d** (*vide supra*), however, it parallels the observations made for the ^1H NMR spectrum. Unfortunately, again instrumental limitations prevented measurements at lower or higher temperatures.

Crystallographic studies

One common feature of metal complexes of the general type $\{\text{C}_n(\text{EXMe}_2)_n\}\text{ML}$ ($n = 5$ or 6 , $\text{E} = \text{C}$ or Si , $\text{X} = \text{H}$ or F), which all show a “gear-meshed” arrangement of the ring substituents, is that they all suffer from disorder problems. This is true for the already-mentioned pentakis(isopropyl)cyclopentadienyl complexes $[\text{FeL}(\text{CO})_2]_2$,⁴⁸ $[\text{FeL}(\text{C}_5\text{H}_5)]$ ⁴⁷ as well as $[\text{FeLBr}]_2$,⁵⁴ $[\text{CrL}(\text{C}_5\text{H}_5)]$,⁵⁵ $[\text{SnL}_2]$ ⁵⁶ and $[\text{SiL}(\text{C}_5\text{H}_5)]$ ⁵⁷ ($\text{L} = \text{C}_5^{\text{iPr}}\text{Pr}_5$) and also the pentakis(dimethylsilyl)cyclopentadienyl complexes $[\text{MnL}'(\text{CO})_3]$,³¹ $[\text{FeL}'_2]$ ⁵⁰ and $[\text{FeL}'(\text{C}_5\text{H}_5)]$ ³² ($\text{L}' = \text{C}_5\{\text{SiMe}_2\text{H}\}_5$). Although this disorder was not always discussed at all in the original papers, it can be found in the cif-files available at the

Cambridge Crystallographic Data Base. In all cases two positions were found for the methine carbon or silicon positions (mostly with uneven site occupation factors), and attached H atoms were added geometrically. In most cases splitting of the corresponding Cp carbon atoms was neither observed nor refined. For the already mentioned cobalt complex $[\text{CoL}(\text{C}_5\text{H}_5)]^+\text{PF}_6^-$,^{46,58} no disorder was reported. However, a closer look at the cif file shows some strange features, and an overlooked disorder seems probable here, too. The “Disorder in the Crystal Structures of Hexakis(dimethylsilyl)benzene and its Tricarbonyl Chromium, Molybdenum and Tungsten Complexes” was even the title of a paper by Kahr *et al.* from 1992.⁵⁹ Although the crystal structure of $\text{C}_6(\text{SiMe}_2\text{F})_6$ was reported,⁵¹ no mention was made of the occurrence of disorder, which, however, is present according to the cif file available at the CCDC. In all these hexasilylbenzene structures (except for one crystalline modification) two positions for the Si atoms could be found, however, due to poor data quality, no further splitting of atom positions could be found. This led to the appearance of non-radial $\text{C}_{\text{ar}}\text{-Si}$ bonds. When comparing these structures, one should keep two geometrical restrictions in mind: (1) exchanging silicon for carbon in the EXMe_2 substituents “increases the interatomic distances in the side chains” with the consequence, that “dimethyl silyl groups... should be less tightly geared than the isopropyl groups”.⁶⁰ (2) Increasing the ring size in C_nR_n ligands from $n = 5$ to $n = 6$, increases on one hand the distance of the R group from the center of the molecule, which is, however, more than compensated by the decrease of the angle between neighbouring ring centroid–substituent vectors from 72 to 60° , which leads to increased crowding of the substituents.⁴⁵ For example, the distance between the Si atoms in the $\text{C}_6(\text{SiMe}_2\text{H})_6$ complexes lie between 3.33 and $3.41\text{ \AA}$, while in the $\text{C}_5(\text{SiMe}_2\text{H})_5$ complexes they are between 3.58 and $3.67\text{ \AA}$ and between the methine carbon atoms in the $\text{C}_5^{\text{iPr}}\text{Pr}_5$ complexes between 3.18 and $3.25\text{ \AA}$.

Crystal and molecular structure of $[\text{Mn}\{\text{C}_5(\text{SiMe}_2\text{F})_5\}(\text{CO})_3]$, **3e.** Compound **3e** crystallizes in the orthorhombic space group $\text{Pna}2_1$ with one molecule on a general position in the asymmetric unit. As was expected, the molecule is disordered between two enantiomers, in an approximate 3 : 1 ratio. Fig. 8 shows an ORTEP3 representation of the molecular structure, with a superposition of both isomers.

Due to the application of numerous restraints on refinement of the structure, which used restrictions on many bond distances, a deeper discussion of the bond parameters is obsolete. However, some structural features shall be presented here. The Cp ring is planar (the σ_{pln} parameter, as defined by the program **PLATON**, is only $0.021\text{ \AA}$). The distance from manganese to the Cp centroid is $1.802(4)\text{ \AA}$ for the major isomer, which is slightly longer than the $1.784\text{ \AA}$ observed for the starting compound **1e**³¹ and the $1.775\text{ \AA}$ found in the only other known cymantrene derivative with five silyl substituents, $[\text{Mn}\{\text{C}_5(\text{Si}_2\text{Me}_4\text{O})_2\text{SiMe}_2\text{OMe}\}(\text{CO})_3]$.³⁸ The $\text{C}_{\text{cp}}\text{-Si}$ and Si-C_{Me} distances average at $1.893(7)$ and $1.847(4)\text{ \AA}$, respectively. For the two literature examples, the $\text{C}_{\text{cp}}\text{-Si}$ distances average both



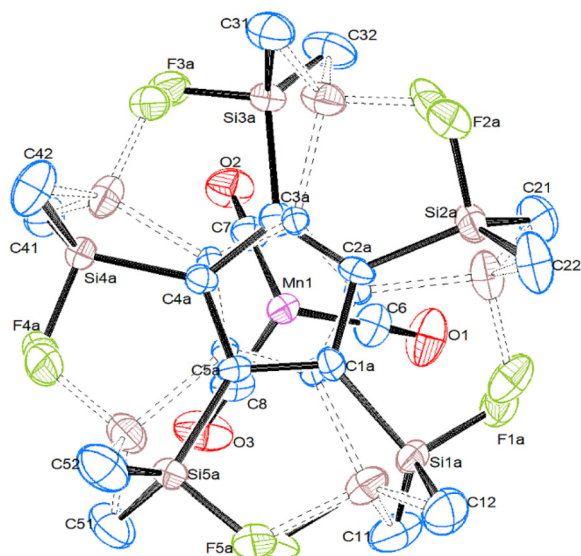


Fig. 8 Molecular structure of compound **3e**, superposition of both isomers.

at 1.87(1) Å, while the Si–C_{Me} average at 1.88(1) and 1.83(1) Å, respectively. A comparison with the C_{aryl}–Si bond lengths of [C₆(SiMe₂H)₆] and its M(CO)₃ complexes as well in [C₆(SiMe₂F)₆] does not make sense due to the fact, that in these compounds only the splitting of the Si positions was calculated, while only an averaged position of the attached benzene carbon atom was used. However, comparison of the Si–C_{Me} distances is possible. In free [C₆(SiMe₂H)₆] this parameter averages at 1.87(1) Å, in its W(CO)₃ and Mo(CO)₃ complexes at 1.874(7) and 1.88(1) Å, respectively, and in [C₆(SiMe₂F)₆] at 1.86(1) Å. All these values are slightly longer than the one found in **3e**. The Si–F bonds in **3e** average at 1.637(7) Å for the major “isomer” (1.63(2) Å for the minor), while in [C₆(SiMe₂F)₆] the average value is 1.68(1) Å. It should be mentioned, however, that in the latter no split of fluorine positions was found, while in our calculations, the related fluorine positions were 0.32(3)–0.54(3) Å apart.

Two Si atoms (Si3 and Si4) are approximately in the plane of the Cp ring ($\Delta = -0.07(1)$ and $-0.03(1)$ Å, respectively), two (Si2 and Si5) are significantly shifted to the distal ring side ($\Delta = -0.30(1)$ and $-0.39(1)$ Å), while the remaining Si atom is shifted by 0.15(1) Å to the proximal ring side. One F atom (F4) resides in the Cp ring plane ($\Delta = 0.02(2)$ Å), two (F1 and F3) are on the proximal side ($\Delta = 0.60(2)$ and $0.33(2)$ Å, respectively) and the remaining two on the distal ring side ($-0.81(2)$ and $-0.63(2)$ Å). Despite these differences, all the C_{cp}–Si–F angles are very similar, averaging at 100.1(4)°.

The parameter h , as introduced by Sakurai *et al.*,⁵¹ describes the distance of the Si atom from the plane defined by the three attached carbon atoms, measures between 0.407 and 0.424(3) Å for the major “isomer” of **3e** (0.36–0.44(1) Å for the minor). According to Sakurai, $h = 0$ Å for truly *thp* and $h = 0.6$ Å for truly tetrahedral environments of the Si atom. Thus,

the situation found in **3e** corresponds to a slightly distorted tetrahedral geometry.

The crystal structure shows weak intra- and intermolecular “non-classical” hydrogen bonds between methyl hydrogen atoms and fluorine as well as oxygen atoms. No other interactions (as F...O or π – π) are found. A packing diagram is shown in Fig. S48.

Crystal and molecular structure of [Mn{C₅(SiMe₂F)₄Br}(CO)₃], **3d.** Compound **3d** crystallizes in the orthorhombic space group *Pnma*, with half a molecule in the asymmetric unit, and shows the same kind of disorder as **3e**. It should be mentioned here, that apparently the ferrocene derivative [Fe{C₅(SiMe₂H)₄Br}₂] shows no sign of disorder.⁵⁰ Due to the fact, that the molecule resides on a mirror plane, the disorder is forced to be of a 1 : 1 type. Fig. 9 shows an ORTEP3 representation of the molecule.

Due to the fact, that numerous restraints were necessary for a convergent refinement, a thorough discussion of bond parameters is not possible. However, as in the case of the structure of **3e**, still several geometrical features deserve mentioning. The distance between manganese and the Cp ring centroid is 1.774(5) Å, and the C_{cp}–Si bonds and Si–C_{Me} bonds average at 1.875(5) Å and 1.79(2) Å, respectively, which are all shorter than in **3e**. The Cp ring is planar (rms = 0.0184, $\sigma_{\text{pln}} = 0.031$), with Br1 being 0.160(1) Å on the distal side. Three of the Si atoms are also on the distal side (Si2, Si3 and Si4 by 0.333(3), 0.106(3) and 0.250(3) Å, respectively), while Si1 resides on the proximal side by 0.162(2) Å. Two F atoms reside on the proximal side (F1 and F3 by 0.61(1) and 0.35(1) Å), while F2 and F4 are far on the distal side (0.865(5) and 0.598(6)). Despite the large deviations of the F atoms from the ring plane, the C_{cp}–

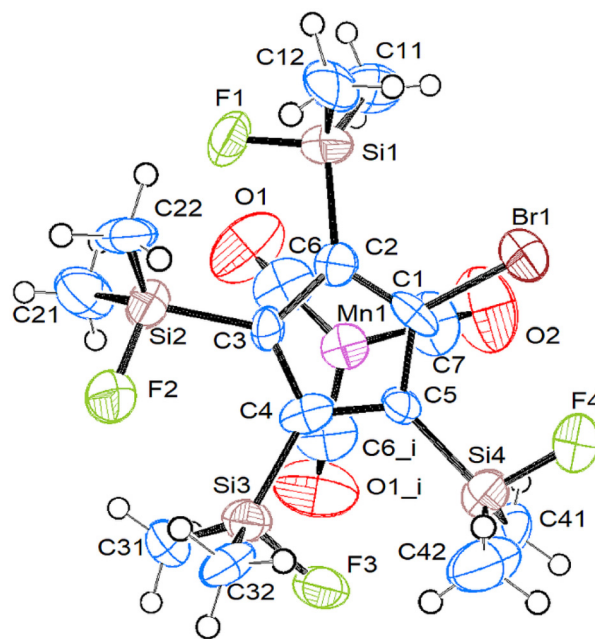


Fig. 9 Molecular structure of compound **3d** (ORTEP3 representation, 50% probability ellipsoids, only one enantiomer shown).



Si–F angles vary only between 100.5(7) and 104.8(4)°. The h parameter, defined as above, varies between 0.32 and 0.33(2) Å, and is thus significantly smaller than in **3e**, but still far from indicating a *tbp* geometry around silicon.

The crystal structure shows several weak intra- and inter-molecular hydrogen bonds between methyl hydrogen and F, Br and O atoms. A packing diagram is shown in Fig. S51.

Experimental

Materials and methods

The starting compounds **1a–f** and **2a–e** were prepared as described by us earlier.^{31,32} Reagents Ph_3CSbF_6 , AgSbF_6 and AgBF_4 as well as cobaltocene were obtained commercially and used as such. Solvents used for the reactions (CH_2Cl_2 and hexane) were purchased in the highest available purity and saturated either with N_2 or Ar, while solvents for chromatography were of analytical grade and were used as obtained. All reactions were performed under dry N_2 or Ar, using standard Schlenk techniques (Schlenk flasks/tubes were stored in a hot oven at 160 °C for at least 24 h and were assembled under a purge of inert gas while being still hot. The assembled flasks were then evacuated using standard oil pump vacuum (*ca.* 0.01 Torr), and then flushed with inert gas).

For standard column chromatography silica gel 100 C18 Reversed Phase (Fluka) was used, or standard silica gel (0.035–0.070 mm, 60A, Merck) was pre-treated with sufficient dry Et_2O and SiMe_3Cl with stirring for several days; then solvents were evaporated and the residue was kept in high vacuum for 8 h, and finally flashed with dry argon.

NMR spectra were measured on JEOL ECP-270 or EX-400 or Eclipse 500 instrument, using C_6D_6 as solvent. The chemical shifts were obtained relative to the residual solvent signals, as defined by the MestReNova software (version 14.1.1–24751) ($\delta_{\text{CHD}_5} = 7.160$ and 128.06 ppm, respectively). Mass spectra were obtained on Finnigan MAT 90 and JEOL Mstation 700 instruments, in DEI or FAB mode.

Synthetic procedures

General remark: ^1H , ^{19}F and ^{13}C NMR data are also given in the SI, Tables S2–S4.

Synthesis of $[\text{Mn}(\text{C}_5\text{Br}_4\{\text{SiMe}_2\text{F}\})(\text{CO})_3]$ (3a**).** A solution of **1a** (135 mg, 0.23 mmol) in CH_2Cl_2 (6 mL) was treated at r.t. with AgSbF_6 (121 mg, 0.35 mmol) with stirring for 3 h. After complete evaporation of the solvent *in vacuo* the residue was suspended in hexane (20 mL), filtered through silanized silica gel and brought to dryness *in vacuo*. A yellow solid (135 mg) was obtained, which consisted according to its ^1H NMR spectrum of a 2 : 1 mixture of the desired **3a** with the bimolecular disiloxane $[\text{Mn}_2(\text{C}_{10}\text{Br}_8\{\text{Si}_2\text{Me}_4\text{O}\})(\text{CO})_6]$ (**9e**) together with traces of $[\text{Mn}(\text{C}_5\text{Br}_4\text{H})(\text{CO})_3]$ (**IIa**). All attempts to separate these compounds met with failure.

^1H NMR (270 MHz): $\delta = 0.340$ (d, $J_{\text{HF}} = 7$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz): $\delta = 221.9$ (CO), 94.0s, 90.8s, 78.7 (d, $J_{\text{CF}} = 17$ Hz, $\text{C}_5\text{Br}_4\text{Si}$), 0.96 (d, $J_{\text{CF}} = 18$ Hz, SiCH_3). ^{19}F NMR (84.3 MHz): $\delta =$

-151.4 (“s”, br, $J_{\text{FSi}} = 282$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (22 MHz) $\delta = 21.8$ (d, $J_{\text{Si-F}} = 282$ Hz). IR (Nujol) $\nu_{\text{CO}} = 2040$ vs., 1971 vs.

Synthesis of $[\text{Mn}(\text{C}_5\text{Br}_3\{\text{SiMe}_2\text{F}\}_2)(\text{CO})_3]$ (3b**).** A solution of **1b** (200 mg, 0.36 mmol) in CH_2Cl_2 (5 mL) was treated with AgSbF_6 (469 mg, 1.37 mmol) with stirring for 5 h at r.t. After complete evaporation of the solvent *in vacuo* the residue was suspended in hexane (20 mL), filtered through silanized silica gel and brought to dryness *in vacuo*. A yellow crystalline solid (150 mg, 0.25 mmol, 69%) was obtained.

^1H NMR (400 MHz): $\delta = 0.414$ “d”, 0.401 “d”. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz): $\delta = 221.8$ (CO), 100.0s, 96.3s, 85.1 (d, $J_{\text{CF}} = 15$ Hz, $\text{C}_5\text{Br}_3\text{Si}_2$), 1.3 and 0.8 (2 d, $J_{\text{CF}} = 14$ and 15 Hz, SiCH_3). ^{19}F NMR (84.3 MHz): $\delta = -152.1$ (“h”, $J_{\text{FSi}} = 281$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (22 MHz) $\delta = 21.5$ (d, $J_{\text{Si-F}} = 279$ Hz). IR (Nujol) $\nu_{\text{CO}} = 2039$ vs., 1964 vs. EA (calc./found, %): C 24.29/23.67; H 2.04/2.28π.

Synthesis of $[\text{Mn}(\text{C}_5\text{Br}_2\{\text{SiMe}_2\text{F}\}_3)(\text{CO})_3]$ (3c**).** A solution of **1c** (325 mg, 0.61 mmol) in CH_2Cl_2 (6 mL) was treated with AgSbF_6 (720 mg, 2.10 mmol) with stirring for 15 h at r.t. After complete evaporation of the solvent *in vacuo* the residue was suspended in hexane (20 mL), filtered through silanized silica gel and brought to dryness *in vacuo*. A yellow oil (315 mg) was obtained, which consisted according to its ^1H NMR spectrum of a 17 : 1 mixture of the desired **3c** with $[\text{Mn}(\text{C}_5\text{Br}_2\text{H}\{\text{SiMe}_2\text{F}\}_2)(\text{CO})_3]$ (**5b**). All attempts to separate these compounds met with failure.

^1H NMR (400 MHz): $\delta = 0.53$ –0.45 m, 0.43–0.38 m. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz): $\delta = 222.7$ (CO), 102.3s, 94.6 “dd”, 88.5 (d, $J_{\text{CF}} = 15$ Hz, $\text{C}_5\text{Br}_2\text{Si}_3$), 2.3 “dd”, 1.4 “d”, 1.3 “dd” (SiCH_3). ^{19}F NMR (84.3 MHz): $\delta = -149.5$ (“s”, br, 2F, $J_{\text{FSi}} = 280$ Hz), -151.7 (m, 1F, $J_{\text{FSi}} = 281$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (22 MHz) $\delta = 23.2$ (d, $J_{\text{Si-F}} = 280$ Hz), 21.4 (d, $J_{\text{Si-F}} = 281$ Hz). IR (Nujol) $\nu_{\text{CO}} = 2032$ vs., 1955 vs.

Synthesis of $[\text{Mn}(\text{C}_5\text{Br}\{\text{SiMe}_2\text{F}\}_4)(\text{CO})_3]$ (3d**).** A solution of **1d** (500 mg, 0.97 mmol) in CH_2Cl_2 (10 mL) was treated with AgSbF_6 (1500 mg, 4.37 mmol) with stirring for 15 h at r.t. After complete evaporation of the solvent *in vacuo* the residue was suspended in hexane (20 mL), filtered through silanized silica gel and brought to dryness *in vacuo*. A yellow crystalline solid (343 mg, 0.58 mmol, 60%) was obtained. Recrystallization from hexane at -20 °C gave some crystals suitable for X-ray diffraction.

^1H NMR (270 MHz): $\delta = 0.571$ “td”, 0.455 “dt”. $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz): $\delta = 223.2$ (CO), 106.6s, 105.9 (d, $J_{\text{CF}} = 18$ Hz), 96.7 (d, $J_{\text{CF}} = 20$ Hz, C_5BrSi_4), 2.4 and 2.1 (2 × “ddd”, SiCH_3). ^{19}F NMR (377 MHz): $\delta = -139.6$ and -148.7 (2 × “s”, br, $J_{\text{FSi}} = 268$ and 278 Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (22 MHz, C_6D_6) $\delta = 23.2$ (d, $J_{\text{Si-F}} = 280$ Hz), 21.4 (d, $J_{\text{Si-F}} = 281$ Hz). IR (Nujol) $\nu_{\text{CO}} = 2029$ vs., 1968 vs., 1952 vs. m.p. 108–111 °C. EA: (calc./found, %) C 32.69/33.05; H 4.12/4.19.

Synthesis of $[\text{Mn}(\text{C}_5\text{H}\{\text{SiMe}_2\text{F}\}_4)(\text{CO})_3]$ (5d**).** A solution of **1f** (350 mg, 0.80 mmol) in CH_2Cl_2 (10 mL) was treated with AgSbF_6 (1240 mg, 3.61 mmol) with stirring for 15 h at r.t. After complete evaporation of the solvent *in vacuo* the residue was suspended in hexane (20 mL), filtered through silanized silica gel and brought to dryness *in vacuo*. A yellow solid (210 mg, 0.41 mmol, 51%) was obtained.



^1H NMR (270 MHz): δ = 5.578 (s, C_5H_5), 0.488 "d", 0.477 "d", 0.360 "dd", 0.327 "dd". $^{13}\text{C}\{^1\text{H}\}$ NMR (68 MHz): δ = 223.9 (CO), 106.8 "t", 106.0 ("d"), 95.2 ("dd", C_5HSi_4), 1.5 and 1.0 ($2 \times \text{m}$, SiCH_3). ^{19}F NMR (377 MHz): δ = -144.1 ("s", br, J_{FSi} = 266 Hz), -151.2 ("q", br, J_{FSi} = 275 Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (53 MHz) δ = 26.0 ("d", $J_{\text{Si-F}}$ = 266 Hz), 22.5 ("dd" AXX'YY' , $J_{\text{Si-F}}$ = 275 Hz and 4 Hz). IR (Nujol) ν_{CO} = 2021 vs., 1952 vs., 1938 vs. m.p. 43–45 °C. EA: (calc./found, %) C 37.76/37.89; H 4.96/5.13.

Synthesis of $[\text{Mn}(\text{C}_5\{\text{SiMe}_2\text{F}\}_5)(\text{CO})_3]$ (3e). A solution of **1e** (500 mg, 1.01 mmol) in CH_2Cl_2 (10 mL) was treated with AgSbF_6 (1909 mg, 5.56 mmol) with stirring for 15 h at r.t. After complete evaporation of the solvent *in vacuo* the residue was suspended in hexane (20 mL), filtered through silanized silica gel and brought to dryness *in vacuo*. A yellow crystalline solid (252 mg, 0.43 mmol, 43%) was obtained. Recrystallization from hexane/methanol at -20 °C gave some crystals suitable for X-ray diffraction.

^1H NMR (270 MHz): δ = 0.80–0.45 m. $^{13}\text{C}\{^1\text{H}\}$ NMR (68 MHz): δ = 223.8 (CO), 108.3 "d", (C_5Si_5), 2.2 and 1.9 ($2 \times$ "t", SiCH_3). ^{19}F NMR (84.3 MHz): δ = -135.3 ("s", br, J_{FSi} = 266 Hz). $^{29}\text{Si}\{^1\text{H}\}$ NMR (22 MHz) δ = 24.1 ("dd", $J_{\text{Si-F}}$ = 258 Hz and 12 Hz). IR (Nujol) ν_{CO} = 2024 vs., 1948 vs., 1910 sh. m.p. 133 °C. EA: (calc./found, %) C 36.95/36.79; H 5.17/5.10.

Synthesis of $[\text{Fe}(\text{C}_5\text{Br}_4\{\text{SiMe}_2\text{F}\})(\text{C}_5\text{H}_5)]$ (4a). A solution of **2a** (100 mg, 0.18 mmol) in CH_2Cl_2 (10 mL) was treated with AgSbF_6 (93 mg, 0.27 mmol) with stirring for 21 h. The suspension was filtered through glass wool, and the obtained greenish filtrate was treated with a solution of cobaltocene (25 mg, 0.13 mmol) in hexane (10 mL) with stirring for 30 min. The solvents were evaporated *in vacuo* and the residue extracted with hexane (10 mL). The extract was filtered through glass wool. Evaporation of the filtrate to dryness yielded a yellow oil (70 mg), which contained the desired product **4a** as main organometallic component (79% purity; contamination with *ca.* 15% $[\text{Fe}(\text{C}_5\text{Br}_{5-n}\text{H}_n)(\text{C}_5\text{H}_5)]$ (n = 0–2, **1b**, **1Ib**, **1IIb**), 3% apparently unreacted **2a** and 3% $[\text{Fe}(\text{C}_5\text{Br}_3\text{H}\{\text{SiMe}_2\text{F}\})(\text{C}_5\text{H}_5)]$ (**6a**) together with an unspecified molar amount of phthalate esters.

^1H NMR (400 MHz): δ = 4.05 (s, C_5H_5), 0.440 (d, J_{HF} = 7 Hz, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz): δ = 78.6 (C_5H_5), 85.2s, 83.6s, 66.1 (d, J_{CF} = 15 Hz, C_5SiBr_4), 1.19 (d, J_{CF} = 15 Hz, SiCH_3). ^{19}F NMR (254 MHz): δ = -151.3 ("h", J_{FSi} = 279 Hz). ^{29}Si INEPT NMR (54 MHz): δ = 24.6 (d, $J_{\text{Si-F}}$ = 280 Hz). HRMS (DEI^+): m/z = 577.6660, calc. for $\text{C}_{12}\text{H}_{11}^{79}\text{Br}_2^{81}\text{Br}_2\text{FSiFe}$ 577.6658.

Synthesis of $[\text{Fe}(\text{C}_5\text{Br}_3\{\text{SiMe}_2\text{F}\}_2)(\text{C}_5\text{H}_5)]$ (4b). A solution of **2b** (240 mg, 0.38 mmol) in CH_2Cl_2 (10 mL) was treated with AgSbF_6 (384 mg, 1.12 mmol) with stirring for 20 h. The suspension was filtered through glass wool, and the obtained greenish filtrate was evaporated to dryness. The remaining dark green oil was washed with hexane and re-dissolved in CH_2Cl_2 (10 mL). A solution of cobaltocene (60 mg, 0.32 mmol) in hexane (10 mL) was added with stirring for 30 min. The resulting yellow solution was evaporated to dryness *in vacuo*. Extraction of the residue with two 10 mL portions of hexane, followed by evaporation *in vacuo*, left a yellow oil (90 mg), which contained the desired product **4b** as main organo-

metallic component (84% purity; contamination with *ca.* 12% $[\text{Fe}(\text{C}_5\text{Br}_3\text{H}\{\text{SiMe}_2\text{F}\})(\text{C}_5\text{H}_5)]$ (**6a**) and 4% $[\text{Fe}(\text{C}_5\text{Br}_2\text{H}\{\text{SiMe}_2\text{F}\}_2)(\text{C}_5\text{H}_5)]$ (**6b**) and traces of **1IIb**, together with a small amount of phthalate esters.

^1H NMR (270 MHz): δ = 4.227 (s, C_5H_5), 0.508 and 0.502 ("dd", SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (68 MHz): δ = 76.5 (C_5H_5), 87.8s, 87.3s, 70.9 (d, J_{CF} = 14 Hz, $\text{C}_5\text{Br}_3\text{Si}_2$), 1.38 ("dd", SiCH_3). ^{19}F NMR (254 MHz): δ = -151.5 ("h", br, J_{FSi} = 279 Hz). HRMS (DEI^+): m/z = 573.7704, calc. for $\text{C}_{14}\text{H}_{17}^{79}\text{Br}_2^{81}\text{Br}_1\text{F}_2\text{Si}_2\text{Fe}$ 573.7718.

Synthesis of $[\text{Fe}(\text{C}_5\text{Br}_2\{\text{SiMe}_2\text{F}\}_3)(\text{C}_5\text{H}_5)]$ (4c). A solution of **2c** (190 mg, 0.37 mmol) in CH_2Cl_2 (10 mL) was treated with AgSbF_6 (447 mg, 1.30 mmol) with stirring for 20 h. The suspension was filtered through glass wool, and the obtained greenish filtrate was evaporated to dryness (350 mg). The remaining dark green oil was re-dissolved in CH_2Cl_2 (10 mL), and a solution of cobaltocene (66 mg, 0.35 mmol) in hexane (10 mL) was added with stirring for 30 min. The resulting yellow solution was evaporated to dryness *in vacuo*. Extraction of the residue with two 10 mL portions of hexane, followed by evaporation *in vacuo*, left a yellow oil (130 mg), which contained the desired product **4c** as main organometallic component (88% purity; contamination with *ca.* 12% $[\text{Fe}(\text{C}_5\text{Br}_2\text{H}\{\text{SiMe}_2\text{F}\}_2)(\text{C}_5\text{H}_5)]$ (**6b**) and traces of **1IIb**, together with a small amount of phthalate esters).

^1H NMR (400 MHz): δ = 4.295 (s, C_5H_5), 0.59–0.56 m, 0.553 "d", 0.50–0.47 m (SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz): δ = 74.5 (C_5H_5), 90.0s, 77.7 "dd", 74.3 (d, J_{CF} = 21 Hz, $\text{C}_5\text{Si}_3\text{Br}_2$), 2.70 m, 1.94 "t", 1.64 "d" (SiCH_3). ^{19}F NMR (254 MHz): δ = -151.3 and -149.0 ($2 \times$ "s", br). HRMS (DEI^+): m/z = 571.8765, calc. for $\text{C}_{16}\text{H}_{23}^{79}\text{Br}_1^{81}\text{Br}_1\text{F}_3\text{Si}_3\text{Fe}$ 571.8757.

Synthesis of $[\text{Fe}(\text{C}_5\text{Br}\{\text{SiMe}_2\text{F}\}_4)(\text{C}_5\text{H}_5)]$ (4d). A solution of **2d** (210 mg, 0.42 mmol) in CH_2Cl_2 (10 mL) was treated with AgSbF_6 (649 mg, 1.89 mmol) with stirring for 18 h. The suspension was filtered through glass wool, and the obtained greenish filtrate was evaporated to dryness. The remaining dark green oil was washed with hexane and re-dissolved in CH_2Cl_2 (10 mL). A solution of cobaltocene (75 mg, 0.40 mmol) in hexane (10 mL) was added with stirring for 30 min. The resulting yellow suspension was evaporated to dryness *in vacuo*. The residue was washed with hexane (10 mL). Extraction of the residue with two 10 mL portions of toluene, followed by evaporation *in vacuo*, left a dark solid together with an orange-coloured oil (160 mg), which contained the desired product **4d** as main organometallic component (84% purity; contamination with *ca.* 12% $[\text{Fe}(\text{C}_5\text{Br}_3\text{H}\{\text{SiMe}_2\text{F}\})(\text{C}_5\text{H}_5)]$ (**6a**) and 4% $[\text{Fe}(\text{C}_5\text{Br}_2\text{H}\{\text{SiMe}_2\text{F}\}_2)(\text{C}_5\text{H}_5)]$ (**6b**) and traces of **1IIb**, together with a small amount of phthalate esters).

^1H NMR (270 MHz): δ = 4.297 (s, C_5H_5), 0.64–0.47 (m, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (68 MHz): δ = 72.9 (C_5H_5), 93.1s, 84.0 (d, J_{CF} = 19 Hz), 81.4 (d, J_{CF} = 17 Hz, C_5BrSi_4), 2.93–1.81 m (SiCH_3). ^{19}F NMR (254 MHz): δ = -141.5 and -148.0 ($2 \times$ "s", br, J_{FSi} = 269 and 272 Hz). HRMS (DEI^+): m/z = 569.9794, calc. for $\text{C}_{18}\text{H}_{29}^{81}\text{BrF}_4\text{Si}_4\text{Fe}$ 569.9798.

Synthesis of $[\text{Fe}(\text{C}_5\{\text{SiMe}_2\text{F}\}_5)(\text{C}_5\text{H}_5)]$ (4e). (a) A solution of impure **2e** (200 mg, <0.42 mmol, contains *ca.* 15% **2d**) in



CH_2Cl_2 (12 mL) was treated with AgSbF_6 (793 mg, 2.31 mmol) with stirring for 21 h. The suspension was filtered through glass wool, and the obtained greenish filtrate was evaporated to dryness. The remaining dark green oil was washed with hexane and re-dissolved in CH_2Cl_2 (10 mL). A solution of cobaltocene (80 mg, 0.42 mmol) in hexane (10 mL) was added with stirring for 30 min. The resulting yellow suspension was evaporated to dryness *in vacuo*. The residue was washed with hexane (10 mL). Extraction of the residue with two 10 mL portions of toluene, followed by evaporation *in vacuo*, left a greenish solid together with an orange-coloured oil (20 mg), which contained the desired product **4e** besides **4d**, $[\text{Fe}(\text{C}_5\text{H}(\text{SiMe}_2\text{F})_4)(\text{C}_5\text{H}_5)]$ (**6d**) and other unidentified substances.

^1H NMR (270 MHz): δ = 4.47 (s, br, C_5H_5), 0.47 (m, br, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz): δ = 70.8 (C_5H_5), 108.3 “d” (C_5Si_5), 3.85 and 3.69 ($2 \times$ “d”, SiCH_3). ^{19}F NMR (377 MHz; -70°C): δ = -135.7 (“s”, br, J_{FSi} = 288 Hz). HRMS (DEI^+): m/z = 566.0867, calc. for $\text{C}_{20}\text{H}_{35}\text{F}_{15}\text{Fe}$ 566.0855.

(b) A similar procedure was performed, using 150 mg of impure **2e** (<0.30 mmol) and 330 mg AgBF_4 (1.65 mmol). After reduction with cobaltocene and standard work-up an orange-coloured oil was obtained (*ca.* 10 mg). Recrystallization from hexane at -25°C gave a few yellow crystals. NMR spectroscopic examination of these crystals showed that they consisted of a mixture of all members of the series $[\text{Fe}\{\text{C}_5(\text{SiMe}_2\text{H})_{5-n}(\text{SiMe}_2\text{F})_n\}(\text{C}_5\text{H}_5)]$, $n = 0-5$, in an approximate 1 : 0.8 : 0.7 : 0.25 : 0.5 : 2 ratios. Although the crystals could be measured on a diffractometer and an apparently reasonable solution could be found, it was not possible to resolve the different components. The general appearance was, however, similar to the picture of **3e** (Fig. S52), showing the same kind of disorder between enantiomers.

Crystallography

Crystals were measured on a Bruker Kappa CCD (**3e**) or a SYNTeX P3 (**3d**) diffractometer. The obtained data sets were solved using SHELXT⁶¹ and refined using SHELXL 2018/3.⁶² Examination of the structure solutions was performed with the program PLATON as part of the WINGX program suite.⁶³ Graphics were prepared using either ORTEP3 for windows or MERCURY, both being part of the WINGX program suite.⁶⁴ For further general details of the crystal structure determinations see Table S1 of the SI.

Crystals of **3e** were obtained from a hexane/MeOH mixture at -20°C and mounted on a KappaCCD diffractometer. Structure solution by SHELXT yielded the complete molecule (Fig. S47, left), which showed some “strange” non-radial $\text{C}_{\text{cp}}\text{-Si}$ bonds. A first difference Fourier analysis yielded five electron density maxima in the plane of the Cp ring close to the positions of the Si atoms (X1–X5 in Fig. S47, right). Atoms X1–X5 were interpreted as alternative Si positions, representing the enantiomer of the original solution. As the “strange” C–Si angles were present for both Si positions, it was decided, to set up also two series of Cp carbon atom positions with the necessary restraints to produce two C_5Si_5 systems with “proper” radial C–Si bonds. While this procedure turned out

successful, there was still a great asymmetry in the Si–F and Si–CMe bonds left. It was therefore decided, to set up two sets of complete $\text{C}_5(\text{SiMe}_2\text{F})_5$ ligands with two enantiomeric conformations and refining both the site occupation factors and several restraints (23 SADI restraints; SIMU and DELU for all C atoms), which lead satisfyingly to the final molecule. All non-hydrogen atoms could be refined anisotropically, except for the five Cp carbon atoms of the minor “isomer”.

Crystals of **3d** were obtained from hexane solutions at -20°C and mounted on a SYNTeX P3 four-circle diffractometer in omega-scan mode. Due to the instrumental limitations of a four-circle diffractometer, only a relatively small dataset could be obtained. Structure solution by SHELXT indicated, that the molecule resided on a mirror plane, with only half a molecule representing the asymmetric unit (Fig. S49a). Automatic application of the mirror operation generated the whole molecule; however, the occurrence of severe disorder problems became obvious (Fig. S49b). There were two positions for each substituent (leading to eight Si atoms and 2 Br atoms). As it was chemically not possible, that the Br atoms could bond to fluorine, a careful inspection of the situation allowed to select the atoms that were part of each “isomer” (Fig. S49c). Selecting one set of atoms (marked green in Fig. S49c) automatically generates the other set by application of the mirror operation. This necessitates a relative 1 : 1 occupation of both isomers. Starting from that point also a set of ring carbon positions was calculated to provide radial C–Si and C–Br bonds. Of course, many restraints (36 SADI restraints, +ISOR for all carbon atoms) were necessary to generate a stable “reasonable” refinement.

Conclusions

The synthesis and spectroscopic characterization of the complete series of fluorosilanes $[\text{M}\{\text{C}_5\text{Br}_{5-n}(\text{SiMe}_2\text{F})_n\}\text{L}]$ ($\text{ML} = \text{Mn}(\text{CO})_3$; $\text{Fe}(\text{C}_5\text{H}_5)$, $n = 1-5$) could be achieved. While the preparation of the cymantrene derivatives occurred without significant side reactions, the ferrocene derivatives were contaminated by several side products, derived from desilylation reactions. It might be advisable to isolate the ferrocenium intermediates as salts with other fluorine-free anions and purify them by recrystallization instead of chromatography. After such a purification, the following reduction might hopefully yield cleaner products.

Author contributions

S. S. and S. B. designed and performed the experiments and the analytical characterization by IR, MS and NMR spectroscopy. K. S. supervised the experiments, performed the X-ray data solutions and refinements and wrote the final manuscripts.



Conflicts of interest

There are no conflicts to declare.

Data availability

Copies of NMR, IR and mass spectra. See DOI: <https://doi.org/10.1039/d5dt01746g>.

CCDC 2475453 and 2475454 contains the supplementary crystallographic data for this paper.^{65a,b}

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References

- J. Gnidovec, E. Gruden, M. Tramšek, J. Iskr, J. Kvičala and G. Tavčar, *Dalton Trans.*, 2023, **52**, 5085–5094.
- M. Trojan, K. Kučňirová, Š. Bouzková, J. Cvačka, T. Čejka, G. Tavčar, M. Rybáčková and J. Kvičala, *Org. Biomol. Chem.*, 2024, **22**, 1047–1056.
- H. Ruppert and L. Greb, *Organometallics*, 2020, **39**, 4340–4349.
- P. Chen, W. Bai and Y. Bao, *J. Mater. Chem.*, 2019, **7**, 11731–11746.
- S. Yamaguchi, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2000, **122**, 6793–6794.
- R. Panisch, M. Bolte and T. Müller, *J. Am. Chem. Soc.*, 2006, **128**, 9676–9682.
- Y.-A. Heo, *Mol. Diagn. Ther.*, 2023, **27**, 631–636.
- M. Steffann, G. Bluet, S. Roy, C. Aubert, E. Fouquet and P. Hermange, *J. Labelled Compd. Radiopharm.*, 2024, **67**, 104–110.
- B. Roy, M. Kun, D. Kim and E. Park, *Europ. Pat. Applic* EP3355390A1, 2018.
- C. Lin, P.-L. T. Boudreault, C. Xia, Universal Display Corp, US2016/0190486A1, 2016.
- Y. R. Jorapur and T. Shimada, *Synlett*, 2012, 1064–1068.
- R. J. P. Corriu, J. M. Fernandez and E. Guerin, *J. Organomet. Chem.*, 1980, **192**, 347–352.
- R. Damrauer, R. A. Simon and B. Kanner, *Organometallics*, 1988, **7**, 1161–1164.
- A. Naka, Y. Matsumotu, T. Itano, K. Hasegawa, T. Shimamura, J. Ohshita, A. Kunai, T. Takeuchi and M. Ishikawa, *J. Organomet. Chem.*, 2009, **694**, 346–352.
- Y. Apeloig and O. Marin-Aharoni, *Croat. Chem. Acta*, 1992, **65**, 757–761.
- A. Kunai, T. Sakurai, E. Toyoda and M. Ishikawa, *Organometallics*, 1996, **15**, 2478, and references, cited therein.
- J. Yoshida, H. Tsujishima, K. Nakano and S. Isoe, *Inorg. Chim. Acta*, 1994, **220**, 129–135.
- J. Yoshida, H. Tsujishima, K. Nakano, T. Teramoto, K. Nishiwaki and S. Isoe, *Organometallics*, 1995, **14**, 567–569.
- A. Kunai and J. Ohshita, *J. Organomet. Chem.*, 2003, **686**, 3.
- J. E. Bulkowski, R. Stacy and C. H. Van Dyke, *J. Organomet. Chem.*, 1975, **87**, 137–143.
- J. Chojnowski, W. Fortuniak and W. Stanczyk, *J. Am. Chem. Soc.*, 1987, **109**, 7776–7781.
- L. H. Sommer and D. L. Bauman, *J. Am. Chem. Soc.*, 1969, **91**, 7076–7078.
- C. Breliere, R. J. P. Corriu and G. Royo, *J. Organomet. Chem.*, 1978, **148**, 107–118.
- S. C. Bourke, M. J. MacLachlan, A. J. Lough and I. Manners, *Chem. – Eur. J.*, 2005, **11**, 1989–2000.
- G. Masson, D. E. Herbert, G. R. Whittell, J. P. Holland, A. J. Lough, J. C. Green and I. Manners, *Angew. Chem., Int. Ed.*, 2009, **48**, 4961–4964.
- N. P. Reddy, T. Hayashi and M. Tanaka, *Chem. Commun.*, 1996, 1865–1866.
- H. Atzkern, J. Hiermeier, F. H. Köhler and A. Steck, *J. Organomet. Chem.*, 1991, **408**, 281–296.
- M. J. Kelly, A. E. J. Broomsgrove, I. R. Morgan, I. Siewert, P. Fitzpatrick, J. Smart, D. Vidovic and S. Aldridge, *Organometallics*, 2013, **32**, 2674–2684.
- T. Cuenca and P. Royo, *Coord. Chem. Rev.*, 1999, **193–195**, 447–498.
- J. Pinkas and M. Lamač, *Coord. Chem. Rev.*, 2015, **296**, 45–90.
- K. Sünkel and J. Hofmann, *Organometallics*, 1992, **11**, 3923–3925.
- S. Bernhartzeder, T. Blockhaus, M. Lang and K. Sünkel, *Inorganics*, 2025, **13**(2), 42.
- H. F. T. Klare, L. Albers, L. Süsse, S. Keess, T. Müller and M. Oestreich, *Chem. Rev.*, 2021, **121**, 5889–5985.
- W. A. Nugent, R. J. McKinney and R. L. Harlow, *Organometallics*, 1984, **3**, 1315–1317.
- F. S. T. Khan, A. L. Waldbusser, M. C. Carrasco, H. Pourhadi and S. Hematian, *Dalton Trans.*, 2021, **50**, 7433–7455.
- M. Cypriak, *J. Phys. Chem. A*, 2005, **109**, 12020–12026.
- C. Wängler, A. Kostikov, J. Zhu, B. Wängler and R. Schirmacher, *Appl. Sci.*, 2012, **2**, 277–302.
- K. Sünkel, J. Hofmann and S. Schubert, *Z. Naturforsch., B: J. Chem. Sci.*, 2014, **69**, 1221–1228.
- R. J. P. Corriu, C. Guerin, B. J. L. Henner and W. W. C. Wong Chi Man, *Organometallics*, 1988, **7**, 237–238.
- C. Breliere, R. J. P. Corriu, A. deSaxe and G. Royo, *J. Organomet. Chem.*, 1979, **166**, 153–168.
- A. Kawachi, H. Maeda, K. Mitsudo and K. Tamao, *Organometallics*, 1999, **18**, 4530–4533.
- K. Sünkel and J. Hofmann, *Chem. Ber.*, 1993, **126**, 1791–1795.
- K. Sünkel and J. Hofmann, *J. Coord. Chem.*, 1993, **30**, 261–264.
- M. Edgar, F. Zeinali, M. Mojally, C. Hughes, S. Riaz and G. W. Weaver, *J. Fluor. Chem.*, 2019, **224**, 35–44.



- 45 S. Brydges, L. E. Harrington and M. J. McGlinchey, *Coord. Chem. Rev.*, 2002, **233–234**, 75–105.
- 46 B. Gloaguen and D. Astruc, *J. Am. Chem. Soc.*, 1990, **112**, 4607–4609.
- 47 L. Burkhardt, C. Mueller, O. A. Groß, Y. Sun, H. Sitzmann and M. Bauer, *Inorg. Chem.*, 2019, **58**, 6609–6618.
- 48 H. Sitzmann, T. Dezember, W. Kaim, F. Baumann, D. Stalke, J. Kärcher, E. Dormann, H. Winter, C. Wachter and M. Kelemen, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2872–2875.
- 49 H. Sitzmann, *Chem. Ber.*, 1990, **123**, 2311–2315.
- 50 S. M. Rupf, R. Sievers, P. S. Riemann, M. Reimann, M. Kaupp, C. Fasting and M. Malischewski, *Dalton Trans.*, 2023, **52**, 6870–6875.
- 51 K. Ebata, T. Inada, C. Kabuto and H. Sakurai, *J. Am. Chem. Soc.*, 1994, **116**, 3595–3596.
- 52 W. Hofmann, W. Buchner and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 795–797.
- 53 J. J. Schneider, M. Nolte, C. Krüger and R. Boese, *J. Organomet. Chem.*, 1994, **468**, 239–247.
- 54 H. Bauer, D. Weismann, G. Wolmershäuser, Y. Sun and H. Sitzmann, *Eur. J. Inorg. Chem.*, 2014, 3072–3084.
- 55 I. Smytschkow, W. Gidt, Y. Sun, J. Langer, T. Böttcher, L. Kubíčková, O. Kaman and H. Sitzmann, *Organometallics*, 2021, **40**, 2951–2969.
- 56 H. Sitzmann, R. Boese and P. Stellberg, *Z. Anorg. Allg. Chem.*, 1996, **622**, 751–755.
- 57 P. Jutzi, A. Mix, B. Neumann, B. Rummel and H.-G. Stammer, *Chem. Commun.*, 2006, 3519–3521.
- 58 D. Buchholz, B. Gloaguen, J.-L. Fillaut, M. Cotrait and D. Astruc, *Chem. – Eur. J.*, 1995, **1**, 374–381.
- 59 B. Kahr, J. M. Chance and K. Mislow, *Mol. Cryst. Liq. Cryst.*, 1992, **210**, 195–214.
- 60 I. I. Schuster, W. Weissensteiner and K. Mislow, *J. Am. Chem. Soc.*, 1986, **108**, 6661–6663.
- 61 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8.
- 62 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.
- 63 L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849–854.
- 64 C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Crystallogr.*, 2020, **53**, 226–235.
- 65 (a) K. Sünkel, S. Bernhartzeder and S. Schubert, CCDC 2475453: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2p2xb1](https://doi.org/10.5517/ccdc.csd.cc2p2xb1); (b) K. Sünkel, S. Bernhartzeder and S. Schubert, CCDC 2475454: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2p2xc2](https://doi.org/10.5517/ccdc.csd.cc2p2xc2).

