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Full Paper

[Tris(alkoxydimethylsilyl)methyl]alkylferrocenes as New Ferrocenyl Multifunctional Silyl Ethers

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[Tris(trimethylsilyl)methyl]alkylferrocenes and [tris(dimethylsilyl)methyl]alkylferrocenes were synthesized by treatment of tris(trimethylsilyl)methyllithium and tris(dimethylsilyl)methyllithium in THF with 3-bromopropylferrocene or 4-bromobutylferrocene at 0°C. [Tris(alkoxydimethylsilyl)methyl]alkylferrocenes were obtained by dehydrocoupling with various aliphatic and benzylic alcohols in the presence of the Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene) in good to excellent yields. 4-[Tris(benzyloxydimethylsilyl)methyl]butylferrocene was also prepared from the transetherification of 4-[tris(methoxydimethylsilyl)methyl]butylferrocene with benzyl alcohol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene as catalyst.

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Introduction

The discovery of bis(η^5-cyclopentadienyl)iron, ferrocene, in 1951,[1] and the subsequent characterization of its structure, greatly stimulated research in organometallic chemistry. Since then, metallocenes have attracted enormous interest from both fundamental and applied points of view. The chemistry of ferrocene-based structures has received attention because of their importance in fields such as redox electrochemistry, materials science, novel materials, organic synthesis,[2–5] catalysis for asymmetric synthesis,[6–9] biology,[10–12] and non-linear optical materials.[13–15] Recent discoveries of a broad range of applications in the biomedical and aerospace industries and as coating and catalysts greatly increased interest in the incorporation of transition metals into organic monomers and polymers.[16–20]

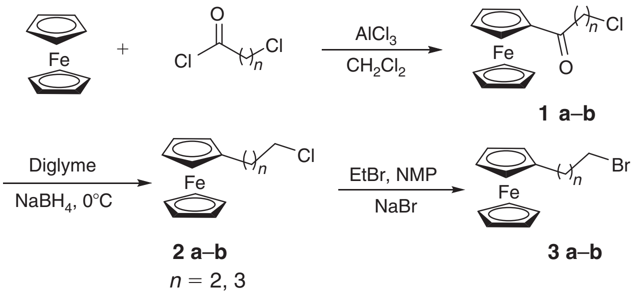
Since the synthesis of the first silyl metal complex (η^5-C_5H_5)Fe(CO)$_2$SiMe$_3$ by Wilkinson in 1956, research on transition metal silyl compounds has continued because these compounds are assumed to be key intermediates in several important stoichiometric and catalytic transformations.[21,22] Organosilicon reagents and compounds are also valuable in organic synthesis, e.g. for making silyl ethers and silyl ketals.[23] A special feature of hydrosilanes is their ability to undergo alcoholysis (dehydrocoupling), leading to alkoxysilanes and gaseous hydrogen. The rate of dehydrocoupling depends significantly on the extent of Si–H bond polarization in the silane, and the reaction occurs in the presence of either nucleophilic or electrophilic catalysts.[24,25] Over the years, there have been significant developments in the synthesis of silyl ethers and their applications in organic chemistry owing to their versatility, compatibility with a wide range of reaction conditions, safety, and the ease with which they can be handled. They are used to tether reactants for stereospecific intramolecular reactions,[26–28] as protecting agents for many functional groups,[29] and as anchoring reagents and substrates for solid-supported synthesis, organic synthesis,[30] and multistep synthesis.[31] They have important applications in inorganic synthesis as precursors in the preparation of sol gels and other condensed siloxane materials,[32] and prodrugs for drug delivery.[33] Here, we report the synthesis of [tris(alkoxydimethylsilyl)methyl] alkylferrocenes via dehydrocoupling reactions of some ferrocenyl organosilicon compounds with various aliphatic and benzylic alcohols and the Karstedt catalyst.

Results and Discussion

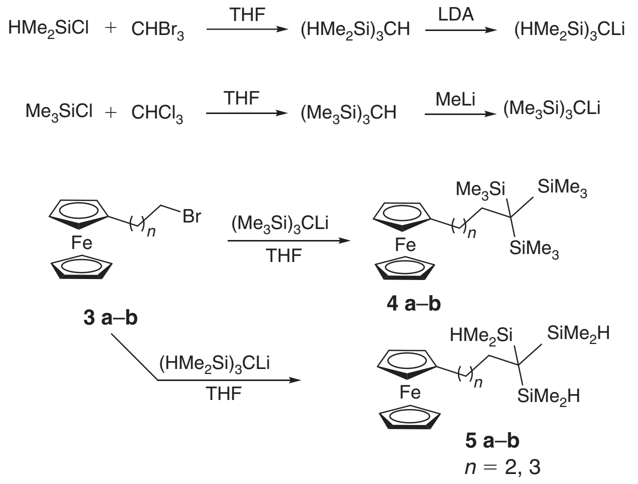
3-Chloropropyroylferrocene **1a** and 4-chlorobutanoylferrocene **1b** were prepared by Friedel–Crafts acylation of ferrocene with 3-chloropropanoyl chloride and 4-chlorobutanoyl chloride, respectively, in CH_2Cl_2 in the presence of $AlCl_3$ as catalyst.[34] 3-Chloropropanoylferrocene **2a** and 4-chlorobutanoyl ferrocene **2b** were obtained in high yields from the reduction of **1a** and **1b** respectively by $NaBH_4$ in diglyme.[35] 3-Bromopropylferrocene **3a** and 4-bromobutylferrocene **3b** were prepared from the reaction of compounds **2a**–**b** with ethyl bromide and sodium bromide in NMP (*N*-methyl-2-pyrrolidone) as solvent (Scheme 1).[36]

Tris(trimethylsilyl)methane was prepared by the reaction of chlorotrimethylsilane, chloroform, and Li in THF. A THF solution of tris(trimethylsilyl)methyllithium, $(Me_3Si)_3CLi$, was obtained by treatment of $(Me_3Si)_3CH$ with MeLi under reflux in THF (Scheme 2).[37] Various 4-halobutylferrocenes were converted into [tris(trimethylsilyl)methyl]alkylferrocenes **4a**–**b** and [tris(dimethylsilyl)methyl]alkylferrocenes **5a**–**b**.

Initially, compound **2b** was treated with $(Me_3Si)_3CLi$ at low temperatures (−78 and 0°C) but after 24 h, no product was obtained. CuI failed to catalyze this reaction (Table 1).[38]



Scheme 1. Synthesis of **3a** and **3b**.



Scheme 2. Synthesis of **4a**–**b** and **5a**–**b**.

Table 1. Reaction of 2a–c and 3a–b with $LiC_3(SiMe_3)$ in THF

Entry	Compound	Temperature [°C]	Yield [%]^A	Time [h]
1	**2a**	−70 and 0	0	24
2	**2b**	−70 and 0	0	24
3	**2c**	−70 and 0	0	24
4	**3a**	0	90	4
5	**3b**	0	93	4

^{A}Isolated yields.

Similarly, under the same conditions, 4-iodobutylferrocene **2c** was treated with $(Me_3Si)_3CLi$, but again none of the desired product was obtained. Finally, the reaction of 3-bromopropylferrocene **3a** and 4-bromobutylferrocene **3b** with tris(trimethylsilyl)methyllithium at 0°C in THF gave 3-[tris(trimethylsilyl)methyl]propylferrocene **4a** and 4-[tris(trimethylsilyl)methyl]butylferrocene **4b** in 90 and 93 % yields after 4 h (Scheme 2).

Similarly, 3-[tris(dimethylsilyl)methyl]propylferrocene **5a** and 4-[tris(dimethylsilyl)methyl]butylferrocene **5b** were synthesized in 87 and 90 % yields, respectively, from compounds **3a** and **3b** and $(HMe_2Si)_3CLi$ in THF at 0°C.

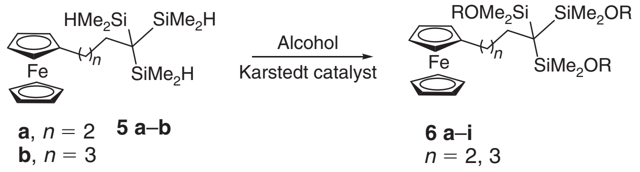
The precursor $(HMe_2Si)_3CH$ was made by the reaction of $CHBr_3$ and Mg with HMe_2SiCl in THF[39,40] and $(HMe_2Si)_3CLi$ was prepared by lithiation of $(HSiMe_2)_3CH$ with LDA (lithium diisopropylamide) at room temperature (Scheme 2).[40]

We recently used dehydrocoupling reactions for the preparation of tris(alkoxydimethylsilyl)methanes,[41] calix[4]arenes bearing silyl ether groups,[39] and functionalized poly(methylalkoxy)siloxanes[42] under mild conditions with Karstedt catalysis. We also applied this methodology in the synthesis of ferrocenyl silyl ethers and for the attachment of ferrocenyl groups to the cellulose acetate butyrate backbone.[43]

Table 2. Synthesis of [tris(alkoxydimethylsilyl)methyl]alkylferrocenes

Entry	Compounds	Alcohol	Products	Yield [%]^A
1	**5b**	CH_3OH	**6a**	94
2	**5b**	CH_3CH_2OH	**6b**	90
3	**5b**	$CH_3CH_2CH_2OH$	**6c**	88
4	**5b**	$CH_3(CH_2)_3OH$	**6d**	85
5	**5b**	$PhCH_2OH$	**6e**	91
6	**5a**	CH_3OH	**6f**	93
7	**5a**	CH_3CH_2OH	**6g**	90
8	**5a**	$CH_3CH_2CH_2OH$	**6h**	87
9	**5a**	$CH_3(CH_2)_3OH$	**6i**	82

^{A}Isolated yields.



Scheme 3. Synthesis of [tris(alkoxydimethylsilyl)methyl]alkylferrocenes.

In order to explore the synthesis of silyl ethers derivatives of [tris(dimethylsilyl)methyl]alkylferrocenes, compound **5b** in THF was first treated with methanol at room temperature and the Karstedt catalyst but after 12h, the reaction was not complete. The same result was obtained under reflux. With methanol as solvent, none of the desired product was obtained after 12 h at room temperature, but under reflux, the desired silyl ether **6a** was obtained after 4 h in excellent yield (entry 1, Table 2, 94 %) (Scheme 3).

For other alcohols, heating at 70–80°C gave the desired silyl ethers in good to excellent yields (Table 2).

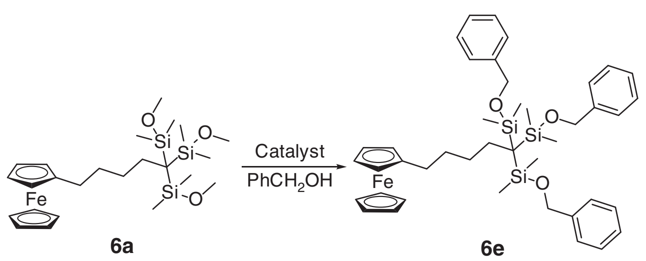
Primary aliphatic alcohols with long alkyl chains are less reactive than with short chains (Table 2). Alcohols with an aromatic ring such as benzyl alcohol gave the corresponding silyl ethers in high yield (entry 5, Table 1, 91 %), but phenols failed to give the desired phenolic silyl ethers.

Finally, from the transetherification[44] of **6a** with benzyl alcohol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst, 4-[tris(benzyloxydimethylsilyl)methyl]butyl ferrocene **6e** was obtained in 73 % yield (Scheme 4).

The ^1H NMR spectrum of compound **6e** (Fig. 1) shows the benzylic CH_2 at 4.6 ppm and aromatic protons at 7.2–7.3 ppm. The peak from ferrocenyl protons appears at 4–4.1 ppm and the singlet ascribed to $SiMe_2$ is at 0.3 ppm. Transetherification reactions of ferrocenyl silyl ethers with other alcohols and polymers bearing hydroxyl groups are under investigation.

Conclusion

In summary, we report the synthesis of [tris(trimethylsilyl)methyl]alkylferrocenes and [tris(dimethylsilyl)methyl]alkylferrocenes. [Tris(alkoxydimethylsilyl)methyl]alkylferrocenes were prepared by dehydrocoupling reactions of hydrosilane derivatives with various aliphatic and benzylic alcohols in the presence of the Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene). The results show that tris(alkoxydimethylsilyl)methyl-functionalized alkylferrocenes prepared from bromoalkylferrocenes are useful building blocks for the preparation of several kinds of ferrocenyl silyl ethers.



Scheme 4. Synthesis of **6e** via transetherification.

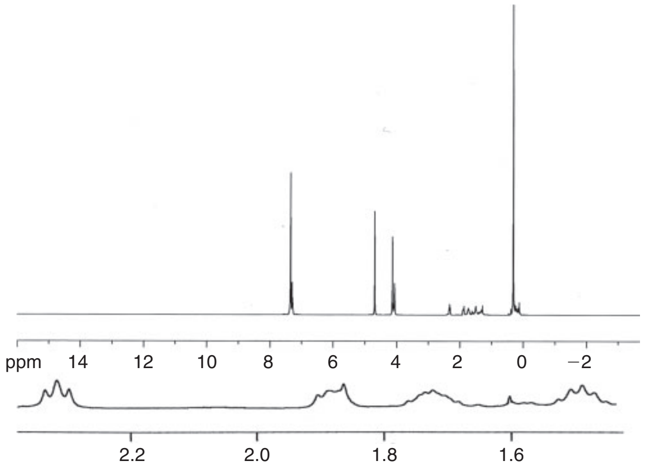


Fig. 1. ^{1}H NMR (ppm) spectra of 4-[tris(benzyloxydimethylsilyl)methyl]butylferrocene.

Some of them can be used in the synthesis of new organosilyl macromolecules and dendrimers. The transetherification of 4-[tris(methoxydimethylsilyl)methyl]butylferrocene with various alcohols in the presence of DBU as catalyst appears to be a simple but effective way to synthesize other ferrocene-substituted tris(alkoxydimethylsilyl)methanes.

Experimental

Chemicals were either prepared in our laboratory or purchased from Merck, Fluka, and Aldrich. Commercial products were used without purification. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at room temperature with CDCl$_3$ solvent. Fourier-transform (FT)IR spectra were recorded on a Bruker Tensor 270 spectrometer. Mass spectra were obtained with a GC-Mass Agilent quadrupole mode 5973N instrument, operating at 70 eV. Elemental analyses were carried out with an Elementar Vario EL III instrument.

*Preparation of Chloroalkylferrocenes **2a–b***

3-Chloropropyroylferrocene **1a**, 4-chlorobutyroylferrocene **1b**, 3-chloropropylferrocene **2a**, and 4-chlorobutylferrocene **2b** were prepared according to the procedures described by Graindorge et al.[34] and Fort et al.[35]

*General Procedure for Preparation of Bromoalkylferrocene **3a–b***

A mixture of 0.015 mol of chloroalkylferrocene derivatives, 15 mL of ethyl bromide, and 0.003 mol of sodium bromide (0.32 g) was heated at 65°C for 3 days. The mixture was allowed to cool and then poured into a mixture of ice, water, and brine in a separatory funnel. The lower layer was removed and washed with brine and distilled water. The solvent was removed and the product purified by column chromatography on silica. A brown band was eluted with a hexane/ethyl acetate (6 : 2) mixture to give the product.

*3-Bromopropylferrocene **3a***

From 3.94 g 3-chloropropylferrocene, 4.42 g of brown oil (96 % yield) was obtained. $\nu_{\max}$ (KBr)/cm^{-1} 3090 (Cp–H), 2929 (C–H), 1636, 1437 (C=C), 1103, 1000, (Cp), 816 (C–Br). δ_H (400 MHz, CDCl$_3$) 2.02–2.09 (m, 2H, Cp–CH$_2$–C*H*$_2$), 2.49–2.55 (t, 2H, Cp–C*H*$_2$), 3.41–3.44 (t, 2H, CH$_2$–Br), 4.08–4.13 (d, 9H, Cp). δ_C (100 MHz, CDCl$_3$) 26.8, 32.6, 32.87 (–CH$_2$–), 66.2, 67.0, 67.4 (Cp), 68.1 (C$_1$ Cp). *m/z* (electron ionization (EI)) 306 [M]$^+$, 308 [M + 2]$^+$, 199 [FcCH$_2$]$^+$ (Fc = ferrocene), 121 [CpFe]$^+$. Calc. for $C_{13}H_{15}BrFe$: C 50.8, H 4.9. Found: C 50.5, H 4.7 %.

*4-Bromobutylferrocene **3b***

From 4.15 g 4-chlorobutylferrocene, 4.72 g brown oil (98 % yield) was obtained. $\nu_{\max}$ (KBr)/cm^{-1} 3090 (Cp–H), 2928 (C–H), 1684, 1454 (C=C), 1103, 1000, (Cp), 815 (C–Br), 485 (Fc). δ_H (400 MHz, CDCl$_3$) 1.62–1.69 (m, 2H, Cp–CH$_2$–C*H*$_2$), 1.85–1.92 (m, 2H, C*H*$_2$–CH$_2$–Br), 2.34–2.38 (t, 2H, Cp–C*H*$_2$), 3.41–3.44 (t, 2H, CH$_2$–Br), 4.05 (s, 4H, Cp), 4.10 (s, 5H, Cp). δ_C (100 MHz, CDCl$_3$) 27.6, 28.4, 31.4, 32.8 (–CH$_2$–), 66.1, 66.9, 67.3, 67.4 (Cp), 87.4 (C$_1$ Cp). *m/z* (EI) 320 [M]$^+$, 322 [M + 2]$^+$, 199 [FcCH$_2$]$^+$, 121 [CpFe]$^+$. Anal. Calc. for $C_{14}H_{17}BrFe$: C 52.3, H 5.3. Found: C 52.0, H 5.5 %.

Preparation of Tris(trimethylsilyl)methyllithium, $(Me_3Si)_3CLi$

The reagent was prepared as described by Gröbel and Seebach.[37]

Preparation of Tris(dimethylsilyl)methyllithium, $(HSiMe_2)_3CLi$

A 50-mL round-bottom flask equipped with a stirrer, septum, and gas-inlet needle was charged with diisopropylamine (0.53 g, 5.3 mmol) and 15 mL of THF. The flask was placed in a water–ice bath and then *n*-BuLi (3.8 mL, 1.5 M solution in hexane) was added dropwise with stirring to form a clear yellow solution. The solution was stirred for an additional 30 min. The LDA solution was transferred into a dropping funnel after which it was added dropwise to a 50-mL round-bottom flask containing tris(dimethylsilyl)methane, (HSiMe$_2$)$_3$CH, (1.0 g, 5.3 mmol), in 10 mL THF under argon at room temperature. The orange-red solution was stirred at ambient temperature for 10h.

*General Procedure for Preparation of Compounds **4a–b** and **5a–b***

To a stirred solution of (Me$_3$Si)$_3$CLi or (HSiMe$_2$)$_3$CLi (5.3 mmol) in THF at 0°C was added 3-bromopropylferrocene **3a** or 4-bromobutylferrocene **3b** (5.0 mmol) in 10 mL THF, and the mixture was stirred for another 3 h at room temperature. It was then poured into saturated aqueous ammonium chloride solution (50 mL) and extracted with CH$_2$Cl$_2$ (2 × 50 mL). The organic phase was washed with water (100 mL) and dried (Na$_2$SO$_4$), and the solvent was removed to yield a viscous oil.

*3-[Tris(trimethylsilyl)methyl]propylferrocene **4a***

From 3 g 3-bromopropylferrocene, 4.04 g (96 % yield) of yellowish oil was obtained. $\nu_{\max}$ (KBr)/cm^{-1} 3093 (Cp–H), 2953 (C–H), 1412 (C=C), 1252, 841 (Si–C), 1104, 1020 (Cp), 484 (Fc). δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 0.13 (s, 27H, $\mathrm{SiMe_3}$), 1.66–1.75 (m, 4H, $\mathrm{-CH_2-}$), 2.25–2.29 (t, 2H, Cp–CH_2), 4.04 (s, 4H, Cp), 4.10 (s, 5H, Cp). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) 1.75 ($\mathrm{SiMe_3}$), 4.9 ($\mathrm{C(SiMe_3)_3}$), 29.8, 30.0, 30.3 ($\mathrm{-CH_2-}$), 65.1, 66.9, 67.3 (Cp), 87.8 ($\mathrm{C_1}$ Cp). *m/z* (EI) 458 $[\mathrm{M}]^+$, 199 $[\mathrm{FcCH_2}]^+$, 121 $[\mathrm{CpFe}]^+$, 73 $[\mathrm{SiMe_3}]^+$. Anal. Calc. for $\mathrm{C_{23}H_{42}FeSi_3}$: C 68.5, H 10.5. Found: C 68.2, H 10.3 %.

4-[Tris(trimethylsilyl)methyl]butylferrocene ***4b***

From 3 g 4-bromobutylferrocene, 4.11 g (93 % yield) of a yellowish oil was obtained. $\nu_{\max}$ (KBr)/$\mathrm{cm^{-1}}$ 3094 (Cp–H), 2952 (C–H), 2903 (C–H), 1630, 1409 (C=C), 1255, 840 (Si–C), 1105, 1000 (Cp), 490 (Fc). δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 0.11 (s, 27H, $\mathrm{SiMe_3}$), 1.41–1.54 (m, 4H, $\mathrm{-CH_2-}$), 1.60–1.64 (m, 2H, Cp–$\mathrm{CH_2}$–CH_2), 2.30–2.34 (t, 2H, Cp–CH_2), 4.03–4.04 (d, 4H, Cp), 4.09 (s, 5H). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) 1.7 ($\mathrm{SiMe_3}$), 5.1 ($\mathrm{C(SiMe_3)_3}$), 28.5, 29.2, 30.0, 31.7 ($\mathrm{-CH_2-}$), 66.0, 67.0, 67.4 (Cp), 88.2 ($\mathrm{C_1}$ Cp). *m/z* (EI) 472 [M]+, 199 $[\mathrm{FcCH_2}]^+$, 121 $[\mathrm{CpFe}]^+$, 73 $[\mathrm{SiMe_3}]^+$. Anal. Calc. for $\mathrm{C_{24}H_{44}FeSi_3}$: C 60.9, H 9.3. Found: C 60.4, H 9.1 %.

3-[Tris(dimethylsilyl)methyl]propylferrocene ***5a***

From 3 g 3-bromopropylferrocene, 3.54 g (87 % yield) of a yellowish oil was obtained. $\nu_{\max}$ (KBr)/$\mathrm{cm^{-1}}$ 3093 (Cp–H), 2955 (C–H), 2107 (Si–H), 1631, 1416 (C=C, Cp), 1253, 839 (Si–C), 1104, 973, 896 (C–H). δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 0.16–0.17 (d, 18H, $\mathrm{SiMe_2}$), 1.64–1.76 (m, 4H, $\mathrm{-CH_2-}$), 2.25–2.29 (t, 2H, Cp–CH_2), 4.01–4.02 (m, 3H, Si–H), 4.04 (s, 4H, Cp), 4.09 (s, 5H, Cp). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) −4.12 ($\mathrm{SiMe_2}$), 0.33 ($\mathrm{C(SiMe_2)_3}$), 29.1, 29.4, 29.5 ($\mathrm{-CH_2-}$), 66.0, 66.9, 67.4 (Cp), 87.8 ($\mathrm{C_1}$ Cp). *m/z* (EI) 416 $[\mathrm{M}]^+$, 199 $[\mathrm{FcCH_2}]^+$, 121 $[\mathrm{CpFe}]^+$. Anal. Calc. for $\mathrm{C_{20}H_{36}FeSi_3}$: C 57.6, H 8.7. Found: C 57.3, H 8.9 %.

4-[Tris(dimethylsilyl)methyl]butylferrocene ***5b***

From 3.94 g 4-bromobutylferrocene, 3.62 g (90 % yield) of a yellowish oil was obtained. $\nu_{\max}$ (KBr)/$\mathrm{cm^{-1}}$ 3093 (Cp–H), 2955, 2845, 2107 (Si–H), 1416, 1253, 1104, 873, 839, 689, 489. δ_{H} (400 MHz, $\mathrm{CDCl_3}$,) 0.15–0.16 (d, 18H, $\mathrm{SiMe_2}$), 1.44–1.55 (m, 4H, $\mathrm{-CH_2-}$), 1.61–1.65 (t, 2H, Cp–$\mathrm{CH_2}$–CH_2), 2.30–2.34 (t, 2H, Cp–CH_2), 3.99–4.02 (m, 3H, Si–H), 4.03–4.04 (d, 4H, Cp), 4.09 (s, 5H, Cp). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) −4.1 ($\mathrm{SiMe_2}$), 0.39 ($\mathrm{C(SiMe_2)_3}$), 28.2, 28.3, 29.0, 31.3 ($\mathrm{-CH_2-}$), 66.2, 67.1, 67.3 (Cp), 88.4 ($\mathrm{C_1}$ Cp). *m/z* (EI) 430 $[\mathrm{M}]^+$, 199 $[\mathrm{FcCH_2}]^+$. Anal. Calc. for $\mathrm{C_{21}H_{38}FeSi_3}$: C 58.5, H 8.8. Found: C 58.1, H 8.6 %.

General Procedure for the Synthesis of [Tris (alkoxydimethylsilyl)methyl]alkylferrocene ***6a–i***

A 50-mL round-bottom two-neck flask with a magnetic stirrer was charged with **5a** or **5b** (0.20 g, 0.48 mmol **5a**, or 0.46 mmol **5b**) and ROH (20 mL) under dry argon. Karstedt catalyst ($[\mathrm{Pt}]/[\mathrm{Si{-}H}] = 7.2 \times 10^{-3}$) was then added and the reaction progress was monitored; several samples were taken over time and were analysed by FTIR spectroscopy. The mixture was stirred at 60–80°C until complete disappearance of the Si–H bond in the FTIR spectra. After completion of the reaction, the mixture was allowed to cool to room temperature. Then the alcohol was evaporated under reduced pressure and the residue purified by flash column chromatography (silica gel, 10 : 1 *n*-hexane/ethyl acetate) to give a highly viscous oily product.

4-[Tris(methoxydimethylsilyl)methyl]butylferrocene ***6a***

Yellowish oil. $\nu_{\max}$ (KBr)/$\mathrm{cm^{-1}}$ 3093 (Cp–H), 2933 (C–H), 1628, 1461 (C=C), 1252, 855 (Si–C), 1088 (Cp), 999 (Si–O), 485. δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 0.18 (s, 18H, $\mathrm{SiMe_2}$), 1.42–1.48 (m, 2H, $\mathrm{-CH_2-}$), 1.52–1.57 (m, 2H, $\mathrm{-CH_2-}$), 1.69–1.73 (t, 2H, $\mathrm{-CH_2-}$), 2.29–2.33 (t, 2H, Cp–CH_2), 3.37 (s, 9H, $\mathrm{OCH_3}$), 4.02–4.04 (d, 4H, Cp), 4.09 (s, 5H, Cp). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) −0.9 ($\mathrm{SiMe_2}$), 16.1 ($\mathrm{-C(SiMe_2OCH_3)}$)), 27.4, 28.4, 29.3, 31.6 ($\mathrm{-CH_2-}$), 48.9 ($\mathrm{OCH_3}$), 65.9, 66.9, 67.3 (Cp), 88.4 ($\mathrm{C_1}$ Cp). *m/z* (EI) 520 $[\mathrm{M}]^+$, 400 $[\mathrm{M{-}FeCp}]^+$, 199 $[\mathrm{FcCH_2}]^+$, 121 $[\mathrm{CpFe}]^+$. Anal. Calc. for $\mathrm{C_{24}H_{44}FeO_3Si_3}$: C 55.3, H 8.5. Found: C 54.9, H 8.2 %.

4-[Tris(ethoxydimethylsilyl)methyl]butylferrocene ***6b***

Yellowish oil. $\nu_{\max}$ (KBr)/$\mathrm{cm^{-1}}$ 3094 (Cp–H), 2969 (C–H), 1632, 1388 (C=C), 1251, 849 (Si–C), 1107, 1079 (Cp), 1000 (Si–O), 485. δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 0.19 (s, 18H, $\mathrm{SiMe_2}$), 1.12–1.16 (t, 9H, $\mathrm{-CH_3}$), 1.42–1.46 (m, 2H, $\mathrm{-CH_2-}$), 1.58–1.62 (m, 2H, $\mathrm{-CH_2-}$), 1.71–1.75 (t, 2H, $\mathrm{-CH_2-}$), 2.29–2.33 (s, 2H, Cp–CH_2), 3.58, 3.63 (q, 6H, $\mathrm{OCH_2}$), 4.02–4.05 (d, 4H, Cp), 4.09 (s, 5H, Cp). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) −0.34 ($\mathrm{SiMe_2}$), 15.4 ($\mathrm{-CH_3}$), 17.5, 27.5, 28.5, 28.6, 29.2, 21.7, 56.6 ($\mathrm{OCH_2}$), 65.9, 66.9, 67.3 (Cp), 88.5 ($\mathrm{C_1}$ Cp). *m/z* (EI) 562 $[\mathrm{M}]^+$, 199 $[\mathrm{FcCH_2}]^+$, 121 $[\mathrm{CpFe}]^+$. Anal. Calc. for $\mathrm{C_{27}H_{50}FeO_3Si_3}$: C 57.6, H 8.9. Found: C 57.3, H 8.7 %.

4-[Tris(propoxydimethylsilyl)methyl]butylferrocene ***6c***

Yellowish oil. $\nu_{\max}$ (KBr)/$\mathrm{cm^{-1}}$ 3094 (Cp–H), 2958 (C–H), 1631, 1459 (C=C), 1252, 857 (Si–C), 1085, 1004, 486. δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 0.18 (s, 18H, $\mathrm{SiMe_2}$), 0.87–0.90 (t, 9H, $\mathrm{-CH_3}$), 1.41–1.45 (t, 2H, $\mathrm{-CH_2-}$), 1.51–1.55 (m, 6H, $\mathrm{-CH_2-}$), 1.54–1.64 (m, 2H, $\mathrm{-CH_2-}$), 1.71–1.75 (t, 2H, $\mathrm{-CH_2-}$), 2.28–2.32 (t, 2H, Cp–CH_2), 3.45–3.48 (t, 6H, $\mathrm{OCH_2}$), 4.02–4.04 (d, 4H, p), 4.09 (s, 5H, Cp). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) −0.4 ($\mathrm{SiMe_2}$), 9.6 ($\mathrm{-CH_3}$), 15.3, 24.8, 27.5, 28.6, 29.2, 31.7, 62.9 ($\mathrm{OCH_2}$), 65.9, 67.0, 67.4 (Cp), 88.4 ($\mathrm{C_1}$ Cp). *m/z* (EI) 604 $[\mathrm{M}]^+$, 199 $[\mathrm{FcCH_2}]^+$, 121 $[\mathrm{CpFe}]^+$. Calc. for $\mathrm{C_{30}H_{56}FeO_3Si_3}$: C 59.5, H 9.3. Found: C 59.1, H 9.4 %.

4-[Tris(butoxydimethylsilyl)methyl]butylferrocene ***6d***

Yellowish oil. $\nu_{\max}$ (KBr)/$\mathrm{cm^{-1}}$ 3094 (Cp–H), 2957 (C–H), 1647, 1540 (C=C), 1250, 847 (Si–C), 1090, 1035 (Cp), 977 (Si–O), 483. δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 0.18 (s, 18H, $\mathrm{SiMe_2}$), 0.89–0.92 (t, 9H, $\mathrm{-CH_3}$), 1.30–1.38 (m, 6H, $\mathrm{-CH_2-}$), 1.39–1.50 (m, 8H, $\mathrm{-CH_2-}$), 1.56–1.61 (t, 2H, $\mathrm{-CH_2-}$), 1.70–1.74 (t, 2H, $\mathrm{-CH_2-}$), 2.28–2.32 (t, 2H, Cp–CH_2), 3.49–3.52 (t, 6H, $\mathrm{OCH_2}$), 4.02–4.05 (d, 4H), 4.09 (s, 5H). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) −0.4 ($\mathrm{SiMe_2}$), 12.9, 15.2, 18.1, 27.5, 28.5, 28.6, 29.3, 31.7, 33.8, 60.8 ($\mathrm{OCH_2}$), 65.9, 66.9, 67.3 (Cp), 88.5 ($\mathrm{C_1}$ Cp). *m/z* (EI) 646 $[\mathrm{M}]^+$, 199 $[\mathrm{FcCH_2}]^+$, 121 $[\mathrm{CpFe}]^+$. Anal. Calc. for $\mathrm{C_{33}H_{62}FeO_3Si_3}$: C 61.2, H 9.6. Found: C 61.6, H 9.4 %.

4-[Tris(benzyloxydimethylsilyl)methyl]butylferrocene ***6e***

Yellowish oil. $\nu_{\max}$ (KBr)/$\mathrm{cm^{-1}}$ 3089 (Ar–H), 3029, 2924 (C–H), 1649, 1496 (C=C), 1254, 858 (Si–C), 1064, 728, 484. δ_{H} (400 MHz, $\mathrm{CDCl_3}$) 0.30 (s, 18H, $\mathrm{SiMe_2}$), 1.44–1.52 (m, 2H, $\mathrm{-CH_2-}$), 1.69–1.75 (m, 2H, $\mathrm{-CH_2-}$), 1.86–1.90 (t, 2H, $\mathrm{-CH_2-}$), 2.29–2.33 (t, 2H, Cp–CH_2–), 4.05 (s, 4H, Cp), 4.12 (s, 5H, Cp), 4.68 (s, 6H, $\mathrm{OCH_2}$), 7.26–7.29 (m, 3H, Ar–H), 7.34–7.35 (d, 12H, Ar–H). δ_{C} (100 MHz, $\mathrm{CDCl_3}$) −0.1 ($\mathrm{SiMe_2}$), 15.8, 27.5, 28.5, 28.6, 29.3, 31.8, 63.5 ($\mathrm{OCH_2}$), 65.9, 67.0, 67.4 (Cp), 88.3 ($\mathrm{C_1}$ Cp), 125.5, 125.7, 127.0, 140.3 (Ar). Anal. Calc. for $\mathrm{C_{42}H_{56}FeO_3Si_3}$: C 67.3, H 7.5. Found: C 67.1, H 7.4 %.

3-[Tris(methoxydimethylsilyl)methyl]propylferrocene ***6f***

Yellowish oil. ν_{max} (KBr)/cm^{-1} 3093 (Cp–H), 2953 (C–H), 1628, 1462 (C=C), 1252, 856 (C–Si), 1088 (Cp), 999 (Si–O), 483. δ_H (400 MHz, $CDCl_3$) 0.20 (s, 18H, $SiMe_2$), 1.78–1.81 (m, 4H, –CH_2–), 2.22–2.25 (t, 2H, Cp–C*H*$_2$), 3.38 (s, 9H, OCH_3), 4.03 (d, 4H, Cp), 4.1 (s, 5H, Cp). δ_C (100 MHz, $CDCl_3$) −0.9 ($SiMe_2$), 16.0, 27.5, 29.7, 30.2 (–CH_2–), 48.9 (OCH_3), 65.8, 66.8, 67.3 (Cp), 88.3 (C_1 Cp). *m*/*z* (EI) 506 $[M]^+$, 199 $[FcCH_2]^+$, 121 (14 %) $[CpFe]^+$. Anal. Calc. for $C_{23}H_{42}FeO_3Si_3$: C 54.5, H 8.3. Found: C 54.1, H 8.1 %.

3-[Tris(ethoxydimethylsilyl)methyl]propylferrocene ***6g***

Yellowish oil. ν_{max} (KBr)/cm^{-1} 3094 (Cp–H), 2970 (C–H), 1631, 1388 (C=C), 1252, 853 (Si–C), 1106, 1079 (Cp), 999 (Si–O), 483. δ_H (400 MHz, $CDCl_3$) 0.21 (s,18H, $SiMe_2$), 1.13–1.16 (t, 9H, –CH_3), 1.77–1.87 (m, 4H, –CH_2–), 2.22–2.26 (t, 2H, Cp–C*H*$_2$), 3.59–3.64 (q, 6H, OCH_2), 4.03 (d, 4H, Cp), 4.1 (s, 5H, Cp). δ_C (100 MHz, $CDCl_3$) −0.3 ($SiMe_2$), 15.3, 17.5 (–CH_3), 27.6, 29.7, 29.9 (–CH_2), 56.6 (OCH_2), 65.8, 66.8, 67.3 (Cp), 88.4 (C_1 Cp). *m*/*z* (EI) 548 $[M]^+$, 199 $[FcCH_2]^+$, 121 $[CpFe]^+$. Anal. Calc. for $C_{26}H_{53}FeO_3Si_3$: C 56.9, H 8.8. Found: C 56.7, H 8.6 %.

3-[Tris(propoxydimethylsilyl)methyl]propylferrocene ***6h***

Yellowish oil. ν_{max} (KBr)/cm^{-1} 3094 (Cp–H), 2959 (C–H), 1646, 1254, 849 (Si–C), 1083, 1002 (Cp), 882 (Si–O), 483. δ_H (400 MHz, $CDCl_3$) 0.22 (s, 18H, $SiMe_2$), 0.88–0.92 (t, 9H, –CH_3), 1.51–1.58 (m, 6H, –CH_2–), 1.76–1.87 (m, 4H), 2.25–2.29 (t, 2H, Cp–C*H*$_2$), 3.49–3.52 (t, 6H, OCH_2), 4.02 (s, 4H, Cp), 4.09 (5H, Cp). δ_C (100 MHz, $CDCl_3$) −0.3 ($SiMe_2$), 9.6 (–CH_3), 16.1, 24.7, 27.7, 29.8, 30.6 (–CH_2), 63.2 (OCH_2), 65.9, 66.9, 67.3 (Cp), 87.9 (C_1 Cp). *m*/*z* (EI) 590 $[M]^+$, 199 $[FcCH_2]^+$, 121 $[CpFe]^+$. Anal. Calc. for $C_{29}H_{54}FeO_3Si_3$: C 58.9, H 9.21. Found: C 58.6, H 8.9 %.

3-[Tris(butoxydimethylsilyl)methyl]propylferrocene ***6i***

Yellowish oil. ν_{max} (KBr)/cm^{-1} 3094 (Cp–H), 2953 (C–H), 1647, 1462 (C=C), 1252, 851 (Si–C), 1091, 1036 (Cp), 964 (Si–O), 887, 484. δ_H (400 MHz, $CDCl_3$) 0.20 (s, 18H, $SiMe_2$), 0.88–0.92 (t, 9H, –CH_3), 1.34–1.44 (m, 6H, –CH_2–), 1.46–1.51 (m, 6H, –CH_2–), 1.7–1.84 (m, 4H, –CH_2–), 2.23–2.26 (t, 2H, Cp–C*H*$_2$), 3.45–3.50 (t, 6H, OCH_2), 4.02–4.03 (d, 4H, Cp), 4.10 (s, 5H, Cp). δ_C (100 MHz, $CDCl_3$) −0.4 ($SiMe_2$), 12.9 (–CH_3), 15.2, 18.1, 27.7, 29.8, 30.1, 33.8 (CH_2), 60.9 (OCH_2), 65.8, 66.8, 67.3 (Cp), 88.4 (C_1 Cp). *m*/*z* (EI) 632 $[M]^+$, 199 $[FcCH_2]^+$, 121 $[CpFe]^+$. Anal. Calc. for $C_{32}H_{65}FeO_3Si_3$: C 60.7, H 9.5. Found: C 60.2, H 9.2 %.

Synthesis of 4-[Tris(benzyloxydimethylsilyl)methyl] butylferrocene ***6e*** *via Transetherification*

A mixture of 0.25 g (0.48 mmol) of 4-[tris(methoxydimethylsilyl)methyl]butylferrocene **6a**, 3 mL benzyl alcohol, and 0.001 g DBU as catalyst was stirred for 3 h at 50°C. The benzyl alcohol was then removed under reduced pressure and the residue purified by column chromatography (silica gel, 10 : 1 *n*-hexane/ethyl acetate) to give **6e** as yellowish oil in 73 % yield.

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