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Synthesis and structures of some di- and triferrocenylmethane derivatives

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Dedicated to Professor Armin de Meijere on the occasion of his 65th birthday

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Abstract

Some triferrocenylmethane derivatives were prepared by reaction of triferrocenylmethanol (**5**) with triphenylcarbenium tetrafluoroborate followed by a nucleophile. Crystal structure analyses of triferrocenylmethane (**7**) and of 1,1,1-triferrocenyl-2,2-dimethylpropane (**11**) show that the conformation adopted by the triferrocenylmethyl group differs significantly with the steric bulk of the substituent at the central carbon atom. Treatment of 1,1′-bis(tributylstannyl)ferrocene (**13**) with 1 equiv. of butyllithium followed by chloroethylformiate affords complexes with one (**14**), two (**15**) or three ferrocenyl units (**16**) depending on the amount of chloroethylformiate used. Compound **16** is the first triferrocenylmethane derivative with substituents at the opposite cyclopentadienyl ring. Threefold lithiation of this compound is shown to work using butyllithium followed by dimethylformamide.

Keywords: Ferrocene; Triferrocenylmethane; Crystal structure analysis; Lithiation

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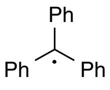
1. Introduction

The triphenylmethyl system has attracted the interest of organic chemists since the days of Gomberg, who investigated the triphenylmethyl radical (**1**) [1]. Later was found that it does not dimerize with formation of hexaphenylethane but to give the quinoid dimer **2** [2]. Now triphenylmethylcarbenium tetrafluoroborate or hexafluorophosphate are commercial reagents for hydride abstraction and other reactions [3].



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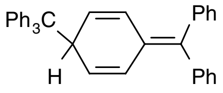

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The chemistry of ferrocene (**4**) has been investigated under a variety of aspects such as homogeneous catalysis, organic synthesis or materials science since its discovery more than 50 years ago [4]. Recently, Bunz and coworkers [5] reported evidence of ferrocene being more aromatic than benzene. A more fundamental difference between ferrocene and benzene is the three-dimensional structure of ferrocene making it less symmetric. In this context, a comparison of the triferrocenylmethyl system with **1** is of interest with respect to the chemistry at the quasi-benzylic carbon atom. If the cyclopentadienyl

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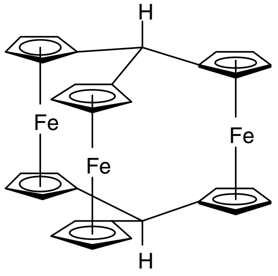
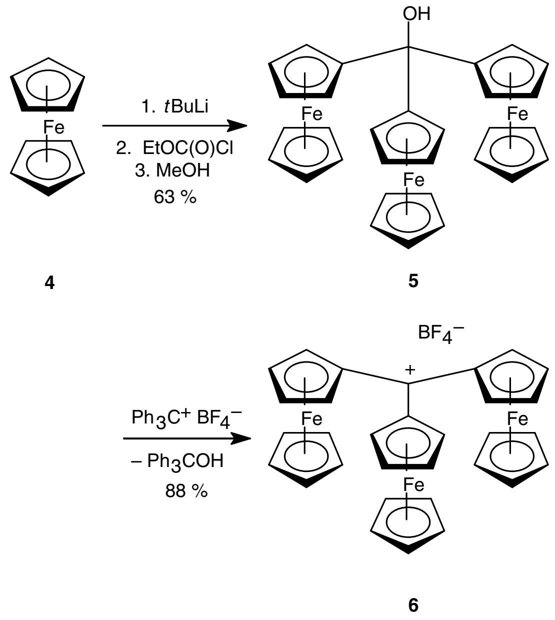
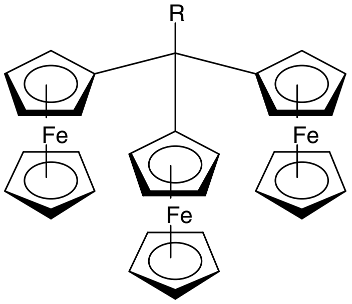
rings next to this carbon atom adopted a coplanar conformation, one would expect chemistry similar to other benzylic carbon atoms. However, due to the steric bulk of the ferrocene substituents this is not likely to be the case. Here, we report the synthesis of some known as well as of some new derivatives of triferrocenylmethane. Some derivatives were reported between 1962 and 1973; however, the analytical data published are restricted to elemental analyses and in some cases to ^{1}H NMR spectra [6–8]. Interesting derivatives are ferrocenylboranes published by Wrackmeyer and coworkers [9] and Wagner and coworkers [10–12]. In the context of multiply bridged ferrocenes with the ultimate goal of a synthesis of **3** and derivatives thereof we are particularly interested in derivatives, which are functionalized at the opposite cyclopentadienyl ligands. Here, we include syntheses of some di- and triferrocenylmethyl derivatives with substituents at this cyclopentadienyl ligand. We note that a gallium analogue of **3** has been published by Jutzi and coworkers [13].



3

Triferrocenylmethanol (**5**) was prepared in 63% yield by single deprotonation of ferrocene with *tert*-butyllithium in hexane/THF followed by treatment with ethyl chloroformate. From **5**, triferrocenylcarbenium tetrafluoroborate (**6**) was obtained in 88% yield by treatment with triphenylcarbenium tetrafluoroborate as a green-blue solid, which is stable under exclusion of air. Compound **6** has earlier been described [14], however, our new procedure has the advantage to avoid the presence of water. Compound **6** was treated with a number of nucleophiles. The reaction with lithium aluminum hydride gave the parent compound triferrocenylmethane (**7**) [7] in 35% yield. The reaction with methyllithium afforded 1,1,1-triferrocenylethane (**8**) [8] in 29% yield. Treating **6** with *sec*-butyllithium resulted in a 50% yield of *rac*-1,1,1-triferrocenyl-2-methylbutane (**9**), and the reaction with butyllithium gave 1,1,1-triferrocenylpentane (**10**) [7] in 63% yield. 1,1,1-Triferrocenyl-2,2-dimethylpropane (**11**) [7] was obtained in 37% yield by treatment of **6** with *tert*-butyllithium.





7: R = H (35 %)
8: R = Me (29 %)
9: R = CH(Me)Pr (50 %)
10 : R = Bu (63 %)
11 : R = *t*Bu (37 %)

It was possible to crystallize the parent compound **7** from petroleum ether. The crystals obtained were suitable for an X-ray structure analysis (Fig. 1).

The analysis shows that **7** adopts an almost trigonal structure with all three ferrocenyl substitutents having cyclopentadienyl ligands whose π systems are essentially perpendicular to the quasi benzylic C–H bond. Compound **7** is the least sterically hindered representative of this class of compounds, and the ferrocenyl substituents point away from one another thereby minimizing their steric interaction.

In addition, it was possible to crystallize the sterically most demanding compound in the series, *tert*-butyl derivative **11**, from benzene. The crystal structure analysis of **11** is shown in Fig. 2.

With respect to the central C31–C32 bond the molecule adopts a staggered conformation for obvious

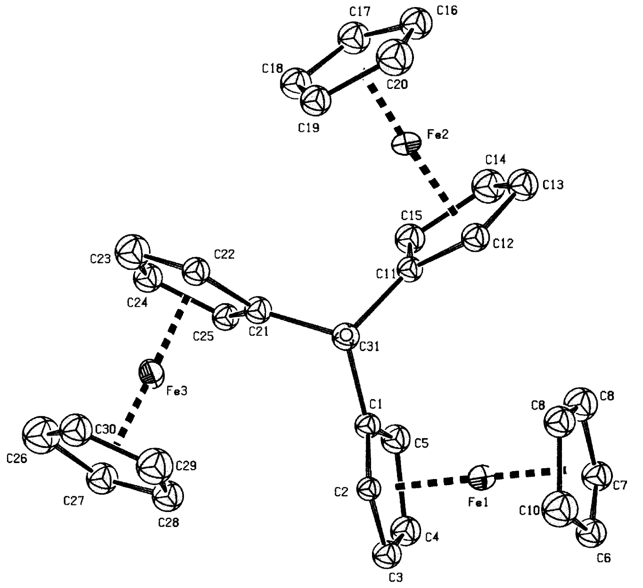
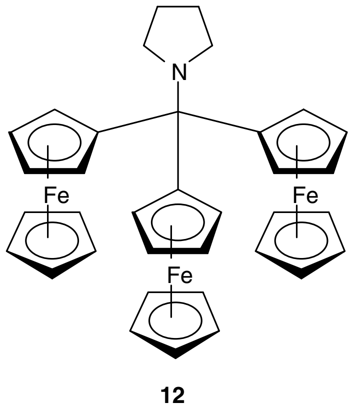


Fig. 1. Structure of **7** in the crystal. Selected bond lengths (Å), angles (°) and dihedral angles (°): C1–C31 1.521(13), C11–C31 1.580(13), C21–C31 1.52(2), C1–C2 1.442(13), C11–C12 1.422(12), C21–C22 1.447(13), C2–C3 1.379(13), C12–C13 1.408(14), C22–C23 1.45(2), C3–C4 1.35(2), C13–C14 1.36(2), C23–C24 1.36(2), C4–C5 1.48(2), C14–C15 1.456(13), C24–C25 1.406(14), C1–C5 1.395(13), C11–C15 1.366(13), C21–C25 1.439(14), Fe1–C1 2.070(10), Fe1–C2 2.034(10), Fe1–C3 1.979(12), Fe1–C4 1.974(12), Fe1–C5 2.054(12); C1–C31–C21 113.1(8), C1–C31–C11 112.9(8), C21–C31–C11 110.3(9); C2–C1–C31–C21–103(1), C2–C1–C31–C11 131(1), C12–C11–C31–C21 134(1), C15–C11–C31–C1 79(1), C22–C21–C31–C1 132(1), C25–C21–C31–C11 76(1).

steric reasons. More interestingly, the conformation of the triferrocenylmethyl unit differs from that in **7**. In **11**, the ferrocenyl (Fc) substituents show a more screwed conformation than in **7**. While one of the Fc–C31 bonds has an anti-conformation, the conformation of another is almost eclipsed, and that of the third one is more gauche.

It is possible to introduce a nitrogen nucleophile by reaction of **6** with pyrrolidine. the sterically crowded tertiary amine **12** is obtained in 91% yield.



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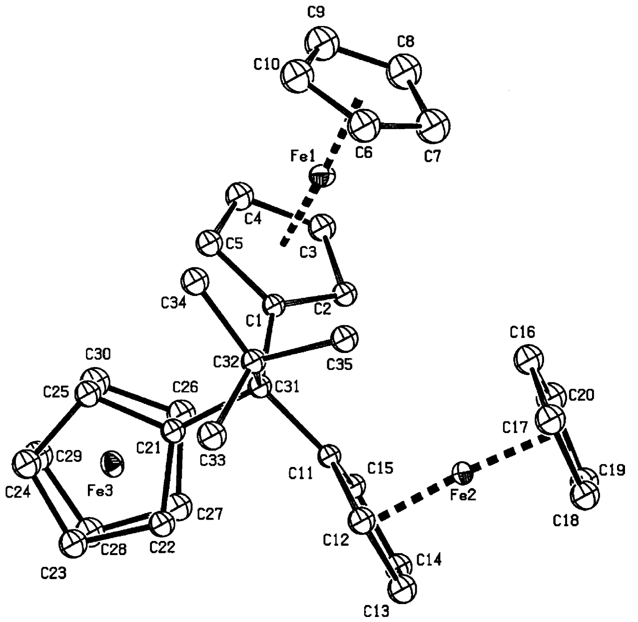
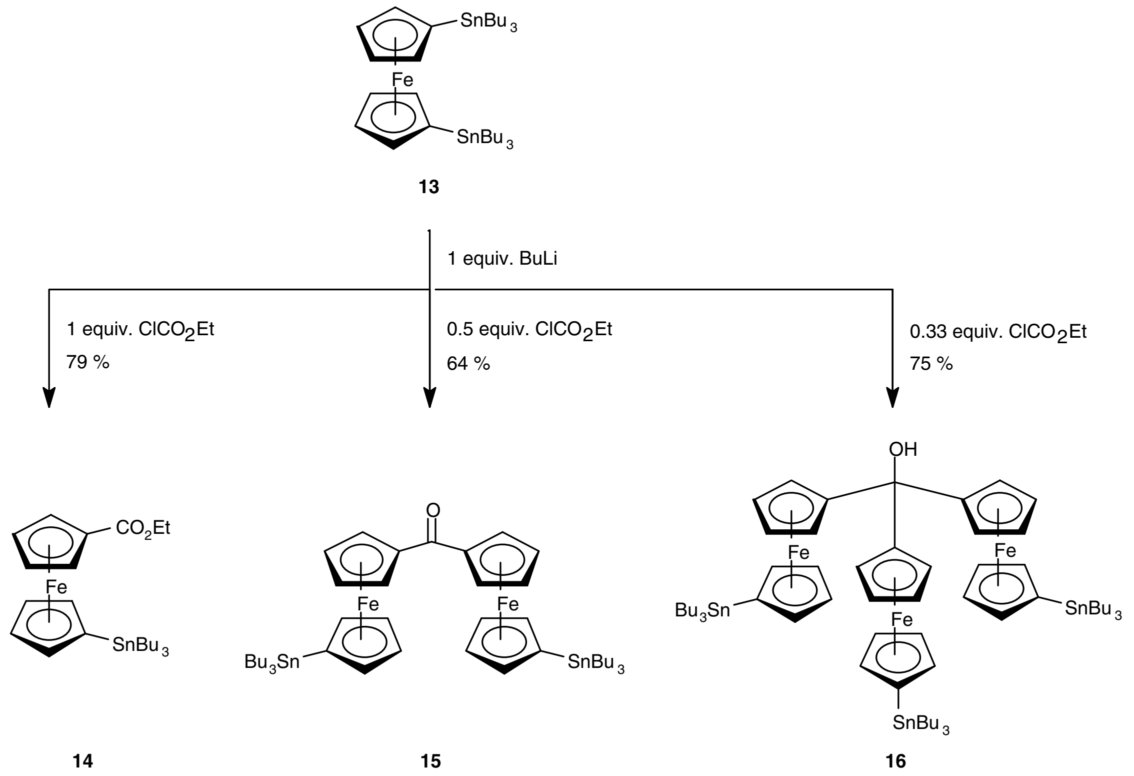


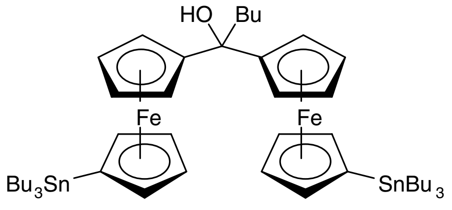
Fig. 2. Structure of **11** in the crystal. Selected bond lengths (Å) and angles (°): C1–C31 1.548(4), C1–C2 1.417(4), C2–C3 1.423(4), C3–C4 1.398(5), C4–C5 1.417(5), C1–C5 1.441(4), C1–Fe1 2.159(3), C2–Fe1 2.058(3), C3–Fe1 2.016(3), C4–Fe1 2.017(3), C5–Fe1 2.052(3), C11–C31 1.555(4), C21–C31 1.555(4), C31–C32 1.606(4); C1–C31–C11 110.9(2), C1–C31–C21 108.9(2), C11–C31–C21 103.3(2); C2–C1–C31–C21–118.6 (3), C2–C1–C31–C11–5.5(4), C12–C11–C31–C21 -89.9(3), C15–C11–C31–C1–47.1(4), C22–C21–C31–C1 136.7(3), C25–C21–C31–C11–173.0(3), C1–C31–C32–C33 162.2(3), C11–C31–C32–C34 171.1(3), C21–C31–C32–C35 164.9(3).

The differences in the crystal structures of **7** and **11** let us conclude that a sterically bulky substituent at the central quasi-benzylic carbon atom induces conformational changes, which bring the unsubstituted cyclopentadienyl ligands closer to one another. Therefore, it made sense to envisage coupling reactions between these ligands in order to approach the ultimate target molecule **3**. Such reactions require suitable functionality at the cyclopentadienyl ligands. Stannyl substituents are particularly promising in this context as they are easily replaced by lithium after treatment with butyllithium [15–17].

When 1,1′-bis(tributylstannyl)ferrocene (**13**) [18] was treated with 1 equiv. of butyllithium followed by 1 equiv. of ethyl chloroformate difunctionalized ferrocene **14** was obtained in 79% yield. When under otherwise identical reaction conditions 0.5 equiv. of ethyl chloroformiate was used, the diferrocenylketone **15** was isolated in 64% yield. Finally, use of 0.33 equiv. of ethyl chloroformiate resulted in a 75% yield of the tristannylated triferrocenylmethanol **16**. Attempts to protect the keto group in **15** as an acetal failed and resulted in destannylated products only.



In a brief assessment of the chemical properties of ketone **15** treatment with butyllithium resulted in the formation of alcohol **17** in 76% yield. However, attempts to form the ethylene acetal failed. Treatment of **15** with ethylene glycol and a catalytic amount of *para*-toluenesulfonic acid resulted in partial destannylation with formation of **18** in 28% yield.



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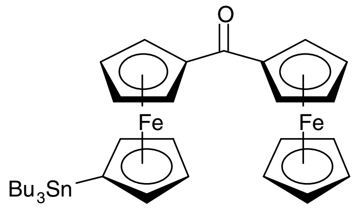
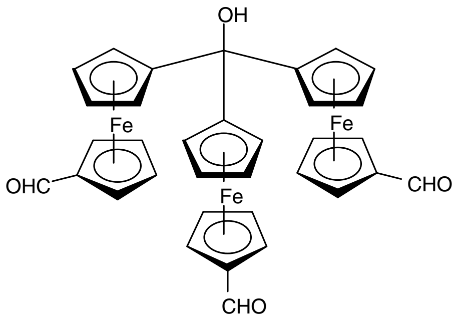


18

Compound **16** is the first triferrocenylmethane derivative with substituents at the cyclopentadienyl ligands opposite to the coupling ones. As a first test for the feasibility of a multiple transmetallation **16** was treated with 6 equiv. of butyllithium followed by an excess of dimethylfomamide (DMF). After aqueous work up the tris-aldehyde **19** was obtained as a red liquid in 26% yield, which corresponds to an average yield of 64% per formylation step. This clearly shows that a threefold transmetallation works. Next, the hydroxy functional group in **16** was replaced by a sterically more bulky *tert*-butyl substituent. This was done by treatment of **16** with triphenylcarbenium tetrafluoroborate followed by 1.2 equiv. of *tert*-butyllithium. Compound **20** was obtained in 36% yield as a red liquid after column chromatography. The compounds can be stored in the air for some time without any sign of decomposition. However, after some months a dark solid forms, which can easily be removed by filtration through silica gel.

In conclusion, we found that an increase in steric bulk of a substituent at the central carbon atom of triferrocenylmethane causes a conformation with the opposite cyclopentadienyl rings being closer to one another. We reported the first triferrocenylmethane derivatives with functionalized opposite cyclopentadienyl rings and showed that trimetallation of **16** is possible by treatment with butyllithium. Investigations directed towards the synthesis of **3** and related compounds using **16** and **20** as starting materials are under way in our laboratories.



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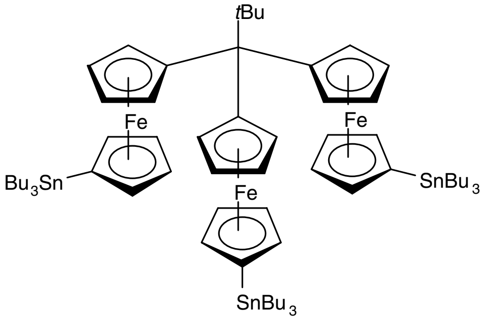

20

2. Experimental part

2.1. General

See [19]; melting points were determined with a Büchi apparatus according to Dr. Tottoli without any correction. *tert*-Butylmethyl ether (TBME), diethyl ether (DEE), petroleum ether (PE) and tetrahydrofuran (THF) were distilled from sodium–potassium alloy/benzophenone. Reagents were purchased and used without further purification.

2.2. Triferrocenylmethanol (**5**)

Ferrocene (**4**) (2.00 g, 10.0 mmol) in 5 mL of anhydrous hexane and 5 mL of THF was stirred for 30 min at 25 °C and then cooled to 0 °C. *t*-Butyllithium (6.00 mL, 1.7 M in pentane, 10.0 mmol) was slowly added over 10 min, and the mixture was stirred for 1 h at 0 °C. At this point, freshly distilled ethyl chloroformate (0.15 mL, 1.60 mmol) was added and the color of the mixture changed from yellow to black. After warming to 25 °C, the mixture was stirred at this temperature for 1 h. Protonation was performed with 20 mL MeOH. The ethereal layer was washed with 3 × 20 mL of water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography over silica gel (deactivated with Et_3N 5% in PE, 4 × 25 cm), elution with PE/$CHCl_3$ 1:1 gave pure triferrocenylmethanol (**5**) (0.59 g, 1.0 mmol, 63%) identical with an authentic sample (NMR) [20,21].

2.3. Triferrocenylmethyl tetrafluoroborate (**6**)

See [7,14]. To a well stirred solution of triferrocenylmethanol (**5**) (0.537 g, 1.0 mmol) in 20 mL of dry THF, Ph_3CBF_4 (370 mg, 1 mmol) was slowly added and the solution immediately turns blue-black. The reaction mixture was stirred at 25 °C for two hours until all starting material disappeared (TLC, silica CH_2Cl_2) and then the solvent was evaporated and the dark solid washed 3 × 20 mL with dry hexane to give pure tiferrocenylmethylenium tetrafluoroborate (**6**) as a green-blue solid (0.524 g, 88%), which does not melt until 250 °C. IR (ATR): $\tilde{\nu} = 3100\ \mathrm{cm}^{-1}$ (w, =CH), 1439 (s), 1023, 1023, 1002 (s, =CH), 853 (s, Cp–H). ^{1}H NMR (400 MHz, 297 K, [D_6]-acetone): $\delta =$ 4.69 (s, 15H, Cp), 5.68 (s, 6H, Cp–R), 5.70 (s, 6H, Cp–R). ^{13}C NMR (100 MHz, BB, 297 K, [D_6]-acetone): $\delta = 75.4$ (s, Cp–*C*H), 80.6 (s, Cp–*C*H), 81.8 (s, Cp–*C*H), 89.3 (s, Cp–*C*R), 209 (s, *C*–Cp^3). MS (ESI, ES+): *m/z* = 566 [M$^+$]. $C_{31}H_{27}BF_4Fe_3$: Calcd. C 56.94, H 4.16. Found C 56.98, H 4.16%.

2.4. General procedure for reactions of **6** with nucleophiles (GP)

To a well stirred solution of the nucleophil, at −78 °C in THF, triferrocenylmethylenium tetrafluoroborate (**6**) was added. The solution was let to warm to 25 °C and then stirred for 20 min. H_2O was added and the reaction crude dissolved in MTBE. The organic layer was washed three times with 20 mL of water each and dried over $MgSO_4$. The solvent was removed under reduced pressure, giving the pure compound after recrystalization.

2.5. Triferrocenylmethane (**7**)

See [7]. GP, **6** (500 mg, 0.77 mmol); $LiAlH_4$ (0.87 g, 23 mmol); Et_2O (150 mL); crystallization from petroleum ether gave 156 mg of **7** (0.27 mmol, 35%) as a yellow solid, which decomposed without melting above 200 °C. IR (ATR): $\tilde{\nu} = 3092\ \mathrm{cm}^{-1}$ (m, =CH), 1454, 1409 (m, CH_2), 1104, 1036, 1000 (s, =CH), 817, 807 (s, Cp–H). ^{1}H NMR (400 MHz, 297 K, $CDCl_3$): $\delta = 3.97$ (s, 15H, CpH), 4.10 (s, 12H, CpH), 4.16 (s, 1H, CH). ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, $CDCl_3$): $\delta = 38.7$ (s, Fc_3*C*H), 66.5 (s, Cp–*C*H), 68.4 (s, Cp–*C*H), 68.9 (s, Cp–*C*H), 95.7 (s, Cp–*C*R).

2.6. Crystal structure analysis of **7**

See [22]. $C_{31}H_{28}Fe_3$, molecular weight, 568.08: crystal system orthorhombic, space group *Pbca*, $a = 9.394(2)$, $b = 18.354(4)$, $c = 27.517(7)$ Å, $\alpha = 90°$, $\beta = 90°$,

$\gamma = 90°$. $V = 4744(2)$ Å^3, $Z = 8$, $\rho_{\text{calcd.}} = 1.591$ g cm^{-3}, $F(0\,0\,0) = 2336e$, $\mu = 1.829$ mm^{-1}, size $0.48 \times 0.22 \times 0.20$ mm, Stoe IPDS area detector diffractometer, $T = 300$ K, Mo K$\alpha = 0.71073$ A, $\theta_{\min} = 2.34°$, $\theta\text{max} = 24.19°$, 37,426 measured reflections (±10, ±20 and ±31), 3545 unique [$R_{\text{int}} = 0.2405$], 1229 observed ($I > 2\sigma(I)$) [$R_{\text{int}} = 0.074$], completeness of data: 93.8%, no absorption correction, no extinction correction, refinement method Full-matrix least-squares on F^2, goodness-of-fit on $F^2 = 1.157$, $R_1 = 0.0776$, $wR_2 = 0.0993$ ($I > 2\sigma(I)$), minimal and maximal residual electron density −0.5/0.6 e Å^{-3}.

*2.7. 1,1,1-Triferrocenylethane (**8**)*

See [7]. GP, **6** (100 mg, 0.15 mmol); MeLi (0.35 ml, 1.6 M in diethyl ether, 0.56 mmol); THF (10 mL); crystallization from petroleum ether gave 25 mg of **8** (0.04 mmol, 29%) as a yellow solid (m. p. 308–310 °C). IR (ATR): $\tilde{\nu} = 3079$ cm^{-1} (m, =CH), 2962 (m, CH), 1258, 1085, 1003 (s, =CH), 791 (s, Cp–H). ^{1}H NMR (400 MHz, 297 K, CDCl$_3$): $\delta = 2.10$ (s, 3H, CH_3), 4.00 (s, 6H, CpH), 4.04 (s, 15H, CpH), 4.10 (s, 6H, CpH). ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, CDCl$_3$): $\delta = 26.8$ (s, CH$_3$), 36.6 (s, Fc$_3$$C$Me), 66.4 (s, Cp–$C$H), 67.8 (s, Cp–$C$H), 68.7 (s, Cp–$C$H), 102.2 (s, Cp–$C$R).

*2.8. 1,1,1-Triferrocenyl-2-methylbutane (**9**)*

GP, **6** (114 mg, 0.18 mmol); *sec*-butyllithium (0.9 ml, 1.6 M in hexane, 0.15 mmol); THF (10 mL); crystallization from petroleum ether gave 55 mg of **9** (0.09 mmol, 50%) as a yellow solid (m.p. 177.5–178 °C). IR (ATR): $\tilde{\nu} = 3095$ cm^{-1} (w, =CH), 2955, 2870 (w, CH), 1104, 1052, 997 (s, =CH), 805 (s, Cp–H). ^{1}H NMR (400 MHz, 297 K, CDCl$_3$): $\delta = 0.63$ (m, 1H, *s*-Bu), 0.96 (t, 3H, $^3J = 7.34$ Hz, *s*-Bu), 1.25 (d, 3H, $^3J = 6.64$ Hz, *s*-Bu), 2.08 (m, 1H, *s*-Bu), 2.9 (m, 1H, *s*-Bu), 4.05 (s, 15H, CpH), 4.17 (s, 3H, CpH), 4.20 (s, 3H, CpH), 4.40 (s, 3H, CpH), 4.50 (s, 3H, CpH). ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, CDCl$_3$): $\delta = 13.4$ (s, CH$_3$), 16.2 (s, CH$_3$), 26.8 (s, CH$_2$), 46.0 (s, CH), 46.3 (s, Fc$_3$$C$R), 66.0 (s, Cp–$C$H), 66.4 (s, Cp–$C$H), 69.2 (s, Cp–$C$H), 69.4 (s, Cp–$C$H), 69.8 (s, Cp–$C$H), 98.2 (s, Cp–$C$R). MS (ESI, ES$^+$): $m/z = 624$ [M$^+$]. HRMS (ESI, C$_{35}$H$_{37}$Fe$_3$): Calcd. 625.0943. Found 625.0949. C$_{35}$H$_{36}$Fe$_3$: Calcd. C 67.35, H 5.81. Found C 66.61, H 5.743%.

*2.9. 1,1,1-Triferrocenylpentane (**10**)*

See [7]. **6** (99.0 mg, 1.5 mmol); butyllithium (0.94 mL, 1.6 M in hexane, 1.5 mmol); THF (10 mL); crystallization from petroleum ether gave 59.0 mg of **10** (0.1 mmol, 63%) as yellow crystals (m.p. 232 °C). IR (ATR): $\tilde{\nu} = 3086$ cm^{-1} (m, =CH), 2949, 2866 (m, CH), 1105, 1028, 1000 (s, =CH), 814, 757, 697 (s, Cp–H). ^{1}H NMR (400 MHz, 297 K, CDCl$_3$): $\delta = 0.98$ (t, 3H, $^3J = 7.3$, Bu), 1.34–1.40 (q, $^3J = 7.3$ Hz, 2H, Bu), 1.65–1.70 (m, 2H, Bu), 2.32–2.33 (m, 2H, Bu), 4.00 (s, 15H, CpH), 4.11 (broad s, 6H, CpH), 4.24 (broad s, 6H, CpH). ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, CDCl$_3$): $\delta = 14.4$ (s, CH$_3$), 23.9 (s, CH$_2$), 28.0 (s, CH$_2$), 40.8 (s, Fc$_3$$C$ Me), 43.7 (s, CH$_2$), 66.1 (s, Cp–CH), 68.0 (s, Cp–CH), 69.0 (s, Cp–CH), 99.3 (s, Cp–CR). identical with an authentic sample.

*2.10. 1,1,1-Triferrocenyl-2,2-dimethylpropane (**11**)*

See [7]. To a solution of **5** (587 mg, 1.00 mmol) in Et$_2$O (100 mL) was added dropwise Ph$_3$CBF$_4$ (366 mg, 1.10 mmol) at 25 °C, and the solution was let to react until no starting material remained (TLC). Then the green solid (**6**) was filtered and washed with three times with 50 mL of Et$_2$O each. The solid was dissolved in 50 ml of THF and cooled to −78 °C, then 1.3 mL of *t*-butyllithium (1.7 M in hexane, 2.20 mmol) was added. The reaction mixture was let to warm to 25 °C and after an additional hour 25 mL of H$_2$O was added. The ethereal layer was washed with three times with 20 mL of water each, dried over MgSO$_4$, and the solvent was removed under reduced pressure. Column chromatography over silica gel (4×5 cm, hexane) gave **11** (232 mg, 0.37 mmol, 37 %) as yellow crystals (m.p. 200–201 °C). Recrystallization from benzene gave pure crystals suitable for an X-ray structure analysis. IR (ATR): $\tilde{\nu} = 3091$ cm^{-1} (m, =CH), 2901 (m, CH), 1477, 1392 (m, CH$_2$), 1106, 1052, 1037, 1000 (s, =CH), 814 (s, Cp–H), 684, 660 (s). ^{1}H NMR (400 MHz, 297 K, CDCl$_3$): $\delta = 1.30$ (s, 9H, *t*-Bu), 4.05 (s, 15H, Cp), 4.17 (s, 6H, Cp–R), 4.49 (s, 6H, Cp–R); ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, CDCl$_3$): $\delta = 31.3$ (s, 3C, CH$_3$,*t*-Bu), 38.9 (s, 1C, *t*-Bu), 49.9 (s, 1C, C–*t*-Bu), 65.5 (s, 6C, Cp–R), 69.6 (s, 15C, Cp), 70.3 (s, 6C, Cp–R), 98.6 (s, 3C, Cp–R).

*2.11. Crystal structure analysis of **11***

See [22]. C$_{38}$H$_{39}$Fe$_3$ (C$_{35}$H$_{36}$Fe$_3$ · 0.5C$_6$H$_6$), molecular weight, 663.24 g/mol, red prissm II a, crystal system triclinic. Space group $P\bar{1}$, (No. 2), $a = 9.132(3)$, $b = 11.416(4)$, $c = 14.467(4)$ Å, $\alpha = 103.94(4)°$, $\beta = 90.80(4)°$, $\gamma = 93.14(4)°$. $V = 1461.0(8)$ Å^3, $Z = 2$, $\rho_{\text{calcd.}} = 1.508$ g/cm^3, $F(0\,0\,0) = 690e$, $\mu = 1.496$ mm^{-1}, size $0.67 \times 0.25 \times 0.06$ mm, Stoe IPDS diffractometer, $T = 300(2)$ K, Mo K$\alpha = 0.71073$ A, $2\theta_{\min} = 4.10°$, $2\theta_{\max} = 26.02°$, $-10 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 14$, $-17 \leqslant 1 \leqslant 17$, 17,364 measured, 5332 unique [$R_{\text{int}} = 0.0501$], and 3426 observed reflections, completeness of data: 92.7%, no absorption correction, no extinction correction, 370 refined parameters, $R_{\text{gt}}(F) = 0.0350$, $wRF^2 = 0.0681$, goodness-of-fit 1.042, minimal and maximal residual electron density −0.33, 0.49 e Å^{-3}.

2.12. *N-(Triferrocenylmethyl)pyrrolidine (**12**)*

GP, **6** (111 mg, 0,17 mmol); pyrrolidine (0.2 ml, 2.4 mmol); THF (10 mL); crystallization from petroleum ether gave 99 mg *N*-(triferrocenylmethyl)pyrrolidine (**12**) (0.15 mmol, 91%) as a yellow-red solid (m.p. 100 °C). IR (ATR): $\tilde{\nu} = 3089$ cm^{-1} (w, =CH), 2960, 2924, 2871, 2811 (w, CH), 1104, 1053, 1031, 1000 (s, =CH), 797 (s, Cp–H). ^{1}H NMR (400 MHz, 297 K, $\mathrm{CDCl_3}$): $\delta = 1.63$ (s, 4H, $\mathrm{N{-}CH_2C}\mathit{H}_2$), 3.05 (s, 4H, $\mathrm{N{-}C}\mathit{H}_2\mathrm{CH_2}$), 4.03 (s, 15H, CpH), 4.16 (s, 6H, CpH), 4.49 (s, 6H, CpH). ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, $\mathrm{CDCl_3}$): $\delta = 23.0$ (s, 2C, $\mathrm{N{-}CH_2}\mathit{C}\mathrm{H_2}$), 47.8 (s, 2C, $\mathrm{N{-}}\mathit{C}\mathrm{H_2CH_2}$), 66.1 (s, 6C, CpH), 69.4 (s, 15C, CpH); 69.5 (s, 6C, CpH), 94.9 (s, 3C, CpR). MS (ESI, ES$^+$): *m*/*z* = 566 [$\mathrm{Fc_3C^+}$].

2.13. *1-Ethoxycarbonyl-1′-tributylstannylferrocene (**14**)*

To a solution of 1,1′-bis(tributylstannyl)ferrocene (**13**) [16,18] (2.000 g, 2.6 mmol) in THF (20 mL) was added dropwise BuLi (1.50 mL, 1.6 M in pentane, 2.4 mmol) at −78 °C. The reaction mixture was stirred for an additional 1 h at −78 °C and then freshly distilled ethyl chloroformate was added (0.25 ml, 2.6 mmol) at this temperature. After stirring at −78 °C for 1 h more, 20 mL of water was added. The ethereal layer was washed with three times with 20 mL of water each, dried over $\mathrm{MgSO_4}$, and the solvent was removed under reduced pressure. Column chromatography over silica gel 4 × 25 cm, hexane/chloroform (1:1) gave pure (TLC, ^{1}H NMR) **14** (1.136 g, 2.1 mmol, 79%) as a red liquid. IR (ATR): $\tilde{\nu} = 2957$ cm^{-1}, 2929, 2871 (m, CH), 1714 (m, C=O), 1459 (w, $\mathrm{CH_3}$ or $\mathrm{CH_2}$), 1376 (w, $\mathrm{CH_3}$), 1274, 1259 (m, C–O), 1131 (m, C–O), 1009 (s, =CH), 791 (s, arC–H). ^{1}H NMR (400 MHz, 297 K, $\mathrm{CDCl_3}$): $\delta = 0.9$ (t, 9H, $^3J = 7.3$ Hz, $\mathrm{SnCH_2CH_2CH_2C}\mathit{H}_3$), 1.02–1.04 (m, 6H, $\mathrm{SnCH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.31–1.37 (m, 9H, $\mathrm{SnCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$, $\mathrm{CH_2C}\mathit{H}_3$), 1.51–1.55 (m, 6H, $\mathrm{SnC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 4.00 (t, 2H, $^3J = 1.6$ Hz, Cp), 4.25 (q, 2H, $^3J = 7.1$ Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 4.28 (t, 2H, $^3J = 1.9$ Hz, Cp), 4.35 (t, 2H, $^3J = 1.6$ Hz, Cp), 4.73 (t, 2H, $^3J = 1.9$ Hz, Cp). ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, $\mathrm{CDCl_3}$): $\delta = 10.2$ (s, $\mathrm{SnCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 13.7 (s, $\mathrm{SnCH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 14.6 (s, $\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 27.4 (s, $\mathrm{SnCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 29.1 (s, $\mathrm{Sn}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 60.0 (s, $\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 69.9 (s, Cp–H), 70.6 (s, Cp–R), 71.1 (s, Cp–H), 71.3 (s, Cp–R), 72.6 (s, Cp–H), 75.9 (s, Cp–H), 171.6 (s, CO); MS (ESI, ES+): *m*/*z*: 549 [M + H$^+$]; HRMS (ESI, $\mathrm{C_{25}H_{41}O_2FeSn}$): Calcd. 549.1478. Found: 549.1473 [M + H]. $\mathrm{C_{25}H_{40}FeO_2Sn}$: Calcd. C 54.88, H 7.37. Found C 54.96, H 7.27%.

2.14. *Di[1,1′-(tributylstannyl)ferrocenyl]methanone (**15**)*

To a solution of 1,1′-bis(tributylstannyl)ferrocene (**13**) [16,18] (1.7 g, 2.2 mmol) in THF (15 mL) was added dropwise BuLi (1.6 M in hexane, 1.5 mL, 2.4 mmol) at −78 °C. The reaction mixture was stirred for an additional 1 h at −78 °C and then freshly distilled ethyl chloroformate was added (0.1 mL, 1.1 mmol) at this temperature. After stirring at −78 °C for 1 h, 20 mL of water was added. The ethereal layer was washed three times with 20 mL of water, dried over $\mathrm{MgSO_4}$ and the solvent was removed under reduced pressure. Column chromatography over silica gel (4 × 25 cm, hexane/chloroform 1:1) gave pure **15** (0.56 g, 0.07 mmol, 64%) as a red liquid. IR (ATR): $\tilde{\nu} = 3086$ cm^{-1} (w, =CH), 2954, 2921, 2870, 2850 (s, CH), 1624 (s, C=O), 1456 (s, $\mathrm{CH_3}$ or $\mathrm{CH_2}$), 1375 (m, $\mathrm{CH_3}$), 1287 (s, C–O). ^{1}H NMR (400 MHz, 297 K, $\mathrm{CDCl_3}$): $\delta = 0.9$ (t, 9H, $^3J = 7.3$ Hz, $\mathrm{SnCH_2CH_2CH_2C}\mathit{H}_3$), 0.98–1.02 (m, 6H, $\mathrm{SnCH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.29–1.38 (m, 6H, $\mathrm{SnCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.49–1.55 (m, 6H, $\mathrm{SnC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 4.01 (t, 2H, $^3J = 1.6$ Hz, Cp), 4.33 (t, 2H, $^3J = 1.6$ Hz, Cp), 4.41 (t, 2H, $^3J = 1.9$ Hz, Cp), 4.91 (t, $J = 1.9$ Hz, 2H, Cp). ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, $\mathrm{CDCl_3}$): $\delta = 10.3$ (s, $\mathrm{SnCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 13.7 (s, $\mathrm{SnCH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 27.4 (s, $\mathrm{SnCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 29.2 (s, $\mathrm{Sn}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 70.4 (s, Cp–H), 70.6 (s, Cp–R), 71.5 (s, Cp–H), 73.1 (s, Cp–H), 76.0 (s, Cp–H), 80.3 (s, Cp–R), 199.1 (C=O). MS (ESI, ES$^+$): *m*/*z* = 979 [M$^+$+H]. HRMS [ESI,$\mathrm{C_{45}H_{71}OFe_2Sn_2}$ (M$^+$+H)]: Calcd. 979.2248. Found 979.2236. $\mathrm{C_{45}H_{70}Fe_2OSn_2}$: Calcd. C 55.37, H 7.23. Found C 54.78, H 7.113%.

2.15. *Tris[1′-(tributylstannyl)ferrocenyl]methanol (**16**)*

To a solution of 1,1′-bis(tributylstannyl)ferrocene (**13**) [16,18] (5 g, 6.5 mmol) in THF 20 mL was added dropwise *n*-BuLi (1.6 M in pentane, 4.0 mL, 6.4 mmol) at −78 °C. The reaction mixture was stirred for an additional 1 h at −78 °C and then freshly distilled ethyl chloroformate was added (0.1 mL, 1.3 mmol) at this temperature. After stirring at −78 °C for 24 h, 25 mL of $\mathrm{H_2O}$ was added. The ethereal layer was washed with three times with 20 mL of water each, dried over $\mathrm{MgSO_4}$, and the solvent was removed under reduced pressure. Column chromatography over silica gel (deactivated with $\mathrm{Et_3N}$ 5% in PE, 4 × 25 cm, hexane) gave 1410 mg (0.97 mmol, 75%) of pure **16** as a red liquid. IR (ATR): $\tilde{\nu} = 3400$ cm^{-1} (br, –OH), 3088 (w, =CH), 2954, 2922, 2870, 2851 (*s*, CH). ^{1}H NMR (400 MHz, 297 K, $\mathrm{CDCl_3}$): $\delta = 0.90$ (t, 27H, $^3J = 7.3$ Hz, $\mathrm{SnCH_2CH_2CH_2C}\mathit{H}_3$), 0.97–1.01 (m, 18H, $\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.31–1.37 (m, 18H, $\mathrm{SnCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.51–1.56 (m, 18H, $\mathrm{SnC}\mathit{H}_2\mathrm{CH_2CH_2\ CH_3}$), 2.72 (s, 1H, $\mathrm{O}\mathit{H}$), 3.92 (t, 6H, $^3J = 1.6$ Hz, Cp), 4.00 (t, 6H, $^3J = 1.8$ Hz, Cp), 4.03 (t, 6H, $^3J = 1.7$ Hz, Cp), 4.27 (t, 6H, $^3J = 1.6$ Hz, Cp). ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, $CDCl_3$): $\delta = 10.2$ (s, $\mathrm{SnCH_2CH_2}C\mathrm{H_2CH_3}$), 13.7 (s, $\mathrm{SnCH_2CH_2CH_2}C\ \mathrm{H_3}$), 27.4 (s, $\mathrm{SnCH_2}C\ \mathrm{H_2CH_2CH_3}$), 29.2 (s, $\mathrm{Sn}C\mathrm{H_2CH_2CH_2CH_3}$), 66.8 (s, *Cp*–COH), 67.2 (s, *Cp*–COH), 69.3 (s, *Cp* -COH), 71.7 (s, Cp–Sn), 99.4 (s, *C*–OH), 75.1 (s, Cp–Sn), 71.7 (s, Cp–Sn). $C_{67}H_{106}Fe_3OSn_3$: Calcd. C 55.45, H 7.36. Found C 56.89, H 7.819%.

2.16. 1,1-Bis[1′-(tributylstannyl)ferrocenyl]pentan-1-ol (**17**)

To a solution of **15** (411 mg, 0.4 mmol) in THF (30 mL) was added dropwise butyllithium (1.6 M in pentane, 0.3 mL, 0.5 mmol) at −78 °C. The reaction mixture was stirred for 1h at −78 °C. After stirring at −78 °C for 1 h, 20 mL of water was added. The ethereal layer was diluted with 20 mL MTB-ether and washed with three times with 20 mL of water each, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography over silica gel (4 × 25 cm, deactivated with Et_3N 5% in PE, hexane/chloroform (1:1)) gave **17** (0.395 g, 0.4 mmol, 76%) as a red liquid. IR (ATR): $\tilde{\nu} = 3100\ \mathrm{cm^{-1}}$ (w, =CH), 2956, 2923, 2871, 2853 (s, CH), 1462 (w, CH_3 or CH_2), 1259 (m, CH_3), 1025 (s, =CH), 808 (s, Cp–H). ^{1}H NMR (400 MHz, 297 K, $CDCl_3$): $\delta = 0.93$ (t, 21H, $^3J = 7.3$ Hz, $\mathrm{SnCH_2\text{-}CH_2CH_2C}H_3$, *Bu*), 1.05–1.09 (m, 12H, $\mathrm{SnCH_2CH_2\text{-}C}H_2\mathrm{CH_3}$), 1.32–1.41 (m, 16H, $\mathrm{SnCH_2C}H_2\mathrm{CH_2CH_3}$, *Bu*), 1.54–1.60 (m, 12H, $\mathrm{SnC}H_2\mathrm{CH_2CH_2CH_3}$), 2.06–2.10 (m, 2H, *Bu*), 2.35 (s, 1H, O*H*), 3.98 (t, 2H, $^3J = 1.6$ Hz, Cp), 4.02–4.04 (m, 8H, Cp–Sn, Cp-H), 4.06 (t, 2H, $^3J = 1.9$ Hz, Cp), 4.13 (t, 2H, $^3J = 1{,}5$ Hz, Cp), 4.34 (t, 4H, $^3J = 1.9$ Hz, Cp–Sn). ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, $CDCl_3$): $\delta = 10.2$ (s, $\mathrm{SnCH_2\text{-}CH_2}C\mathrm{H_2CH_3}$), 13.7 (s, $\mathrm{SnCH_2CH_2CH_2}C\mathrm{H_3}$), 14.1 (s, $\mathrm{CH_2CH_2CH_2}C\mathrm{H_3}$), 23.3 (s, *Bu*), 26.4 (s, *Bu*), 27.4 (s, $\mathrm{SnCH_2}C\mathrm{H_2CH_2CH_3}$), 29.2 (s, $\mathrm{Sn}C\mathrm{H_2CH_2\text{-}CH_2CH_3}$); 43.6 (s, *Bu*), 66.3 (s, Cp–H), 66.7 (s, $\mathrm{Cp_{sn}}$–H), 66.9 (s, Cp-H), 69.4 (s, Cp–R), 71.3 ($\mathrm{Cp_{sn}}$–H), 71.8 (s, Cp–$\mathrm{SnBu_3}$), 74.8 (s, Cp–H), 74.9 (s, Cp–H), 99.0 (s, *C*–OH). MS (ESI, $\mathrm{ES^+}$): *m/z* = 1034 [$\mathrm{M^+}$]. HRMS [ESI, $C_{49}H_{82}OFe_2Sn_2$ ($\mathrm{M^+ + 2H}$)]: Calcd. 1034.3097. Found 1034.3109.

2.17. (Ferrocenyl)(1′-tributylstannylferrocenyl)methanone (**18**)

A solution of **15** (500 mg, 0.51 mmol), ethylene glycol (21.0 mL, 20.0 mol), and *para*-toluenesulfonic acid in 30 mL of toluene was stirred for 12 h at reflux temperature. Hydrolysis was performed by addition of 20 mL sat. aqu. $NaHCO_3$, and the ethereal layer was washed with water until neutral pH, dried over $MgSO_4$ after which the solvent was removed under reduced pressure. Column chromatography (silica gel, 4 × 25 cm, hexane/$CHCl_3$ 8:2) gave pure **18** (96 mg, 0.14 mmol, 28%) as a red liquid. IR (ATR): $\tilde{\nu} = 3089\ \mathrm{cm^{-1}}$ (w, =CH), 2954, 2923, 2851 (s, CH), 1623 (s, C=O), 1459 (s, CH_3 or CH_2), 1377 (m, CH_3), 1288, 1260 (s, C–O). 1045, 1021 (s). ^{1}H NMR (400 MHz, 297 K, $CDCl_3$): $\delta = 0.92$ (t, 9H, $^3J = 7.28$ Hz, $\mathrm{SnCH_2CH_2CH_2C}H_3$), 1.01–1.04 (m, 6H, $\mathrm{SnCH_2CH_2C}H_2\mathrm{CH_3}$), 1.33–1.38 (m, 6H, $\mathrm{SnCH_2C}H\ _2\mathrm{CH_2CH_3}$), 1.53–1.58 (m, 6H, $\mathrm{SnC}H_2\mathrm{CH_2CH_2CH_3}$), 4.03 (t, 2H, $^3J = 1.62$ Hz, Cp), 4.99 (t, 2H, $^3J = 1.88$ Hz, Cp), 4.19 (s, 5H, Cp), 4.36 (t, 2H, $^3J = 1.64$ Hz, Cp), 4.43 (t, 2H, $^3J = 1.94$ Hz, Cp), 4.51 (t, 2H, $^3J = 1.88$ Hz,, Cp), 4.94 (t, 2H, $^3J = 1.52$ Hz, Cp); ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, $CDCl_3$): δ = 10.5 ($\mathrm{SnCH_2CH_2}C\mathrm{H_2CH_3}$), 13.9 ($\mathrm{SnCH_2CH_2CH_2}C\mathrm{H_3}$), 27.5 ($\mathrm{SnCH_2}C\mathrm{H_2CH_2CH_3}$), 29.3 ($\mathrm{Sn}C\mathrm{H_2CH_2CH_2CH_3}$), 70.0 (Cp–H), 70.4 (Cp–H), 70.6 (Cp–H), 71.4 (Cp–R), 71.5 (Cp–H), 73.2 (t, *J*(CSn) = 15 Hz, $\mathrm{Cp_{sn}}$–H), 74.4 (Cp–$\mathrm{SnBu_3}$), 76.1 (t, ^3J(CSn) = 19.5 Hz, $\mathrm{Cp_{sn}}$–H); 80.2 (Cp–CO), 80.6 (Cp–C=O), 199.2 (C=O). MS (ESI, $\mathrm{ES^+}$): *m/z* = 689.1761 [$\mathrm{M^+ + H}$]. HRMS [ESI, $C_{88}H_{46}OFe_2Sn$ ($\mathrm{M^+ + H}$)]: Calcd. 689.1191. Found 689.1218.

Subsequent elution with hexane/$CHCl_3$ 1:1 gave diferrocenylketone (0.111 g, 0.28 mmol) identical with an authentic sample [23].

2.18. Tris[1′-formylferrocenyl]methanol (**19**)

To a solution of **16** (523 mg, 0.4 mmol) in 2 mL of THF was added dropwise butyllithium (1.3 mL, 1.6 M in pentane, 2.1 mmol) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C and then an excess of DMF (8 mL) was added at this temperature. After stirring at −78 °C for 1 h more, 25 mL of water was added. The ethereal layer was washed three times with 20 mL of water each, dried over $MgSO_4$, and the solvent was removed at reduced pressure. Crystallization from chloroform/petroleum ether gave 62 mg (0.1 mmol, 26%) of pure **17**. IR (ATR): $\tilde{\nu} = 3401\ \mathrm{cm^{-1}}$ (b, –OH), 3099 (w, =CH), 2956, 2924, 2853, (s, CH), 1678 (s, C=O); ^{1}H NMR (400 MHz, 297 K, $CDCl_3$): = 2.78 (s, 1H, O*H*), 4.24 (s, 6H, Cp), 4.31 (s, 6H, Cp), 4.47 (s, 6H, Cp), 4.70 (s, 6H, Cp), 9.92 (s, 3H, CHO); ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, $CDCl_3$): $\delta = 68.3$ (Cp–H), 68.7 (Cp–R), 69.0 (Cp–COH), 70.8 (Cp–R), 74.3 (Cp–H), 79.3 (Cp–CHO); 100.8 (*C*–OH), 194.0 (*C*HO). MS (ESI, ES+): *m/z*: 690.9489 [100%, $\mathrm{M + Na^+}$]; HRMS (ESI) ($C_{34}H_{28}O_4Fe_3Na$): Calcd. 690.9933. Found: 690.9946 [$\mathrm{M + Na^+}$].

*2.19. 2,2,-Dimethyl-1,1,1-tris[tri(1′-tributylstannyl)ferrocenyl]propane (**20**)*

To a solution of **16** (0.149 g, 0.1 mmol) in 20 mL of anhydrous THF was added dropwise Ph_3CBF_4 (74 mg, 0.2 mmol) at 25 °C and the solution was let to react until no starting material remained (TLC). Then the solution was cooled to −78 °C, and 0.2 mL of *tert*-butyllithium (1.7 M in hexane, 0.12 mmol) was added. The reaction mixture was let to warm to 25 °C and after an additional hour 25 mL of water was added. The ethereal layer was diluted with 25 mL petroleum ether and washed three times with 25 mL of water each, dried over $MgSO_4$, and the solvent was removed at reduced pressure. Column chromatography over silica gel (4×25 cm, petroleum ether) gave pure **18** (54 mg, 0.04 mmol, 36%). IR (ATR): $\tilde{\nu} = 3089\ cm^{-1}$ (w, =CH), 2956, 2925, 2871, 2854 (s, CH). ^1H NMR (400 MHz, 297 K, $CDCl_3$): $\delta = 0.90$ (t, 27H, $^3J = 7.3$ Hz, $SnCH_2CH_2CH_2CH_3$), 0.97–1.01 (m, 18H, $SnCH_2CH_2CH_2CH_3$), 1.31–1.37 (m, 18H, $SnCH_2CH_2CH_2CH_3$), 1.51–1.56 (m, 18H, $CH_2CH_2CH_2CH_3$), 2.72 (s, 1H, OH), 3.92 (t, 6H, $^3J = 1.6$ Hz, Cp), 4.00 (t, 6H, $^3J = 1.8$ Hz, Cp), 4.03 (t, 6H, $^3J = 1.7$ Hz, Cp), 4.27 (t, 6H, $^3J = 1.6$ Hz, Cp). ^{13}C NMR (100 MHz, BB, HMQC, HMBC, 297 K, $CDCl_3$) = 10.2 ($SnCH_2CH_2CH_2CH_3$), 13.7 ($SnCH_2CH_2CH_2CH_3$), 27.4 ($SnCH_2CH_2CH_2CH_3$), 29.2 ($CH_2CH_2CH_2CH_3$), 66.8 (HCp–COH), 67.2 (HCp–COH), 69.3 (Cp–COH), 71.7 (Cp–Sn); 71.7 (HCp–Sn), 75.1 (s, HCp–Sn), 99.4 (s, C–OH). $C_{71}H_{114}Fe_3Sn_3$: Calcd. C 57.18, H 7.70. Found C 57.29, H 7.449%.

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