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Synthesis of a tin-functionalized cyclopentadiene derivative

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Abstract

A 3-*tert*-butyl-1-(stannylpropyl)-functionalized cyclopentadienyl ligand precursor **6** is readily available in 64% overall yield from allylic alcohol **1** by a three-step reaction sequence including Pd-catalyzed hydrostannylation with Ph_3SnH. Treatment with $FeCl_2$ and $ZrCl_4 \cdot 2THF$ afforded corresponding ferrocene and zirconocene derivatives. Transmetallation of Sn–Ph with Li–Bu was observed under these reaction conditions by using BuLi as a base.

Keywords: Cyclopentadienyl ligand; Ferrocenes; Zirconocene; Pendant alkyl groups; Tin compounds; Hydrostannylation

1. Introduction

Cyclopentadienyl ligands are ubiquitous in organometallic chemistry. In the recent years functionalized cyclopentadienyl ligands with pendant donor atoms and metal complexes derived thereof have been synthesized in order to obtain chelate metal complexes [1–5] or to prepare heterobi- or polymetallic compounds by intermolecular coordination of the additional donor function [6]. Group 15 and group 16 elements are most common donor atoms in this field: oxygen [2] and nitrogen [3] as σ- and π-donors, sulfur [4] and phosphorus [4b,5] as σ-donors and π-acceptors. We envisioned pendant alkyl groups as pure σ-donor functions in a coordinating cyclopentadienyl side chain in order to form metal–carbon σ-bonds without additional lone pairs at the donor atom. In contrast to the above mentioned donor atoms (N, O, P, S) alkyl donors do not show Lewis basic character. Thus, they are not capable of interacting with strong Lewis acids such as boron or aluminium compounds, commonly employed to activate metal–chloro bonds in precatalysts for olefin polymerisation [7]. Furthermore, our concept focussed on the application of tin–alkyl moieties in the side chain of cyclopentadienyl ligands, allowing subsequent transmetallation reactions to form C,C-chelates [8] as well as heteropolymetallic compounds.

In this note, we would like to report on a straightforward synthesis of a new alkyl- and tin–alkyl-functionalized cyclopentadienyl derivative which does further implicate the generation of a plane of chirality when coordinating to a metal center. Our report includes the access to ferrocenes and a zirconocene bearing this 1,3-disubstituted cyclopentadienyl ligand.

2. Results and discussion

The synthetic route to target cyclopentadienyl ligand precursor **6** is shown in Scheme 1. Allylic alcohol **1** was considered as the building block for the C3-side chain. First, the tin function was introduced into **1** by hydrostannylation with Ph_3SnH. Following a literature procedure without any catalyst or radical promoter [9], the yield of product **2** was less than 20%, whereas attempts completely failed to react **1** in the presence of AIBN as a radical initiator at a temperature of 50 °C.

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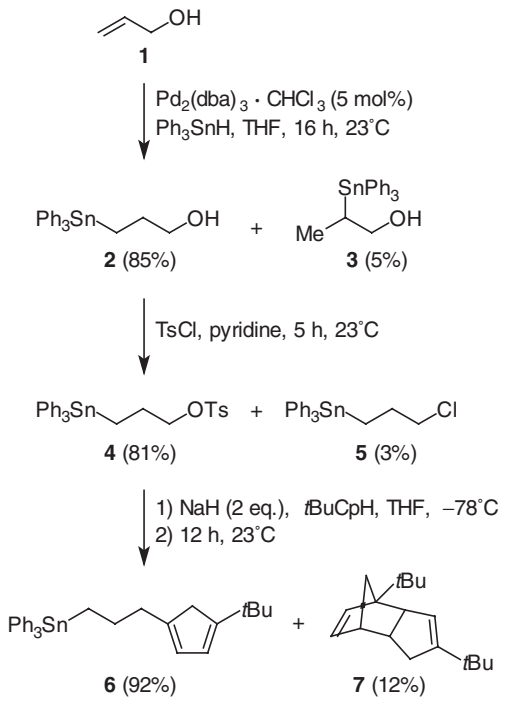


Scheme 1.

Therefore, we finally investigated three different Pd catalysts for the formation of **2** [10]. Applying the Pearlman-catalyst [$Pd(OH)_2/C$] and $Pd(PPh_3)_4$ alcohol **2** was obtained in 40% and 61% yield, respectively. The system of $Pd_2(dba)_3 \cdot CHCl_3$ without any additional ligating additives in THF as the solvent at ambient temperature, however, turned out to be optimal. Apart from major product **2** (85%), the regioisomeric hydrostannylation product **3** was isolated in 5% yield after chromatographic separation.

The primary alcohol function in **2** was activated as *p*-toluenesulfonic ester by using standard conditions [11] to give tosylate **4** in 81% yield and the chloro compound **5** as a byproduct in 3% yield, which is presumably formed from **4** and pyridinium chloride by Finkelstein reaction and could be separated by column chromatography. The synthesis was accomplished by conversion of tosylate **4** with the sodium salt of *tert*-butylcyclopentadiene (*t*BuCpH) [12] affording the 1,3-disubstituted cyclopentadienyl derivative **6** in high yields (92% reg. **4**) when a fourfold excess of *t*BuCpH was employed. In this case, however, dimer **7** (12% reg. *t*BuCpH) was formed as a byproduct by Diels–Alder reaction. The constitution of the tricyclic hydrocarbon **7** was elucidated by H,H-COSY, HMQC and HMBC NMR experiments. The NMR spectra of target compound **6** exhibit a threefold signal set which is caused by three C–C double bond isomers.

Conversion of ligand precursor **6** to give the corresponding ferrocene derivative was realized by deprotonation with BuLi at 0 °C and subsequent treatment of the reaction mixture with $FeCl_2$. Along the chromatographic purification, a red zone was eluted whose NMR spectra indicate a nonuniform species. Mass spectrometric investigations of this material exhibit seven signals at m/z = 1080, 1060, 1040, 1020, 1000, 980, and 960, all showing the typical $FeSn_2$ isotope pattern, and thus, were interpreted as the M^+ signals of seven species of the general formula **8** shown in Scheme 2. The m/z peaks at 1080 (M^+) and 960 (M^+) correspond to the species with two triphenylstannyl moieties ($n,m = 0$) and to the species with two tributylstannyl groups ($n,m = 3$), respectively. Exchange of a phenyl by a butyl residue results in a lowering of the molecular mass by $\Delta m/z = 20$. From this result we therefore concluded transmetallation of Sn–Ph with Li–Bu under the reaction conditions used, giving a mixture of ferrocenes with the general formula **8**. Interestingly, this transmetallation could be accomplished quantitatively by treatment of **8** with an excess of BuLi at 0 °C, finally yielding the unique material **9**. Derivative **9** gave both sufficient mass spectrometric data [$m/z = 960$ (M^+)] and elemental analysis. The NMR spectra, however, reveal a doubled signal set obviously caused by the two diastereomers (*rac* and *meso*) of this product.

Deprotonation of cyclopentadienyl derivative **6** with PhLi at 0 °C followed by reaction with $FeCl_2$ resulted in formation of ferrocene **10** bearing the two Ph_3Sn substituents [m/z = 1080 (M^+)]. Derivative **10** was obtained as an analytically pure material in 47% yield. Again a doubled signal set in the NMR spectra evidenced the existence of two diastereomers (*rac* and *meso*).

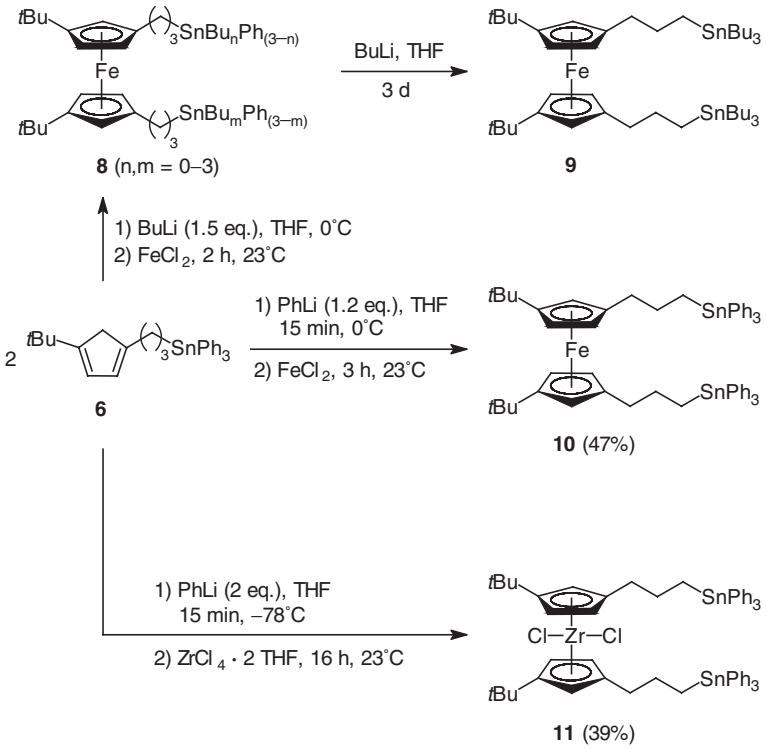
Finally, we succeeded in preparing the zirconocene dichloride **11** from derivative **6** by deprotonation with PhLi at −78 °C and subsequent treatment with $ZrCl_4 \cdot 2THF$. Compound **11** was isolated as a colorless oil, which shows the typical Cl_2Sn_2Zr isotope pattern in the mass spectra and, not surprising, exists as an inseparable mixture of a *rac*- and a *meso*-diastereomer.

In conclusion, the tin-functionalized 1,3-disubstituted cyclopentadienyl ligand precursor **6** is accessible in good yields by a convenient synthesis starting from allylic alcohol **1**. Pd-catalyzed hydrostannylation introduced the triphenylstannyl moiety. Compound **6** was successfully reacted with $FeCl_2$ and $ZrCl_4 \cdot 2THF$ to give two ferrocene derivatives **9**, **10** and one zirconocene **11**, respectively. A tin–lithium exchange with BuLi in the coordination sphere of ferrocene **8** allow for transformation of Sn–Ph into Sn–Bu groups.

3. Experimental

3.1. General

The commercial chemicals *n*-BuLi (Merck), NaH (Merck), iron(II) chloride (Aldrich), phenyllithium



Scheme 2.

(Fluka), triphenyltin hydride (Arcos), tris(dibenzylideneacetone)dipalladium chloroform adduct [$Pd_2dba_3 \cdot CHCl_3$] (Arcos), $ZrCl_4 \cdot 2THF$ (Aldrich), and THF [absolute ($H_2O \leqslant 0.005\%$), Fluka] were used as purchased without further purification. Ethyl acetate (EA) and hexanes (PE, bp 30–75 °C) were distilled prior to use for chromatography.

IR: attenuated total reflection (ATR).

3.2. 3-(Triphenylstannyl)-1-propanol (2)

Under exclusion of moisture and air Ph_3SnH (5.04 g, 14.4 mmol), THF (10 cm^3) and at −78 °C $Pd_2(dba)_3 \cdot CHCl_3$ (160 mg, 0.155 mmol) were added to **1** (1.67 g, 28.8 mmol), and the stirred reaction mixture was allowed to warm up to room temperature (16 h). After removal of all volatile materials, the residue was chromatographed (SiO_2, gradient PE/EA from 5:1 to 1:1, followed by EA). In a first fraction [R_f(PE/EA = 5:1) = 0.27] byproduct **3** (298 mg, 0.728 mmol, 5%) was obtained as a colorless solid. In a second fraction [R_f(PE/EA = 5:1) = 0.16] product **2** (4.97 g, 12.2 mol, 85%) was isolated as a colorless solid, mp 103 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.42$ (s, br, 1H, OH), 1.48–1.56 (m, 2H, 3-CH_2), 1.91–2.06 (m, 2H, 2-CH_2), 3.65 (t, $J = 6.3$ Hz, 2H, 1-CH_2), 7.37–7.41 (m, 9H, ArH), 7.55–7.72 (m, 6H, ArH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz): $\delta = 6.52$ (s, 3-CH_2), 29.14 [s, d, $^2J(^{13}C,^{117,119}Sn) = 21.4$ Hz, 2-CH_2], 65.28 [s, d, $^3J(^{13}C,^{117,119}Sn) = 33.0$ Hz, 1-CH_2], 128.38 [s, d, $^2J(^{13}C,^{117,119}Sn) = 47.8$ Hz, *o*-CH], 128.73 [s, d, $^4J(^{13}C,^{117,119}Sn) = 11.7$ Hz, *p*-CH], 136.88 [s, d, $^3J(^{13}C,^{117,119}Sn) = 35.3$ Hz, *m*-CH], 138.87 [s, d, d, $^1J(^{13}C,^{117}Sn) = 463.0$ Hz, $^1J(^{13}C,^{119}Sn) = 488.0$ Hz, *i*-C] ppm. IR (ATR): $\tilde{\nu} = 3331$ (m), 3061 (m), 3039 (m), 2935 (m), 2862 (m), 1480 (s), 1427 (s), 1074 (m), 730 (s), 699 (s), 659 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 410 (1) [M^+], 351 (100) [Ph_3Sn^+], 333 (54) [$M^+ - Ph$], 291 (8), 197 (32) [$PhSn^+$]. HRMS Calcd. 333.0301 (for $C_{15}H_{17}O^{120}Sn$). Found: 333.0300 ($M^+ - Ph$). Anal. Calcd. for $C_{21}H_{22}OSn$ (409.12): C 61.66, H 5.42. Found: C 61.65, H 5.48%. *Byproduct* ***3***: m.p. 96–97 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 1.41$ [d, dd, dd, $^3J(H,H) = 7.4$ Hz, $^3J(H,^{117}Sn) = 73.4$ Hz, $^3J(H,^{119}Sn) = 76.5$ Hz, 3H, 3-CH_3], 1.64 (t, $^3J = 4.9$ Hz, 1H, OH), 2.23–2.39 (m, 1H, 2-CH), 3.84–4.13 (m, 2H, 1-CH_2), 7.35–7.39 (m, 9H, ArH), 7.53–7.63 (m, 6H, ArH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): $\delta = 15.69$ [s, d, $^2J(^{13}C,^{117,119}Sn) = 16.8$ Hz, 3-CH_3], 27.62 [s, d, d, $^1J(^{13}C,^{117}Sn) = 396.2$ Hz, $^1J(^{13}C,^{119}Sn) = 414.2$ Hz, 2-CH], 67.28 [s, d, $^2J(^{13}C,2^{117,119}Sn) = 18.1$ Hz, 1-CH_2], 128.41 [s, d, $^2J(^{13}C,^{117,119}Sn) = 47.2$ Hz, *o*-CH], 128.74 [s, d, $^4J(^{13}C,^{117,119}Sn) = 10.7$ Hz, *p*-CH], 137.27 [s, d, $^3J(^{13}C,^{117,119}Sn) = 34.7$ Hz, *m*-CH], 136.69 (s, *i*-C) ppm. IR (KBr): $\tilde{\nu} = 3365$ (s), 3060 (m), 3016 (m), 2985 (m), 2893 (m), 2857 (m), 1479 (m), 1427 (vs), 1380 (m), 1072 (s), 1022 (m), 984 (s), 730 (vs), 699 (vs), 656 (m)

cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 410 (2) [M^+], 351 (95) [Ph_3Sn^+], 290 (100), 333 (54) [$M^+ - Ph$], 291 (100), 197 (49) [$PhSn^+$], 120 (33). Anal. Calcd. for $C_{21}H_{22}OSn$ (409.12): C 61.66, H 5.42. Found: C 61.87, H 5.41%.

3.3. 3-Triphenylstannylpropyl p-toluenesulfonate (4)

A solution of *p*-TsCl (2.32 g, 12.2 mmol) in pyridine (3.60 g, 45.5 mmol, 3.7 cm^3) was slowly added to **2** (4.97 g, 12.2 mmol), and the reaction mixture stirred at room temperature for 4 h. Then water (15 cm^3) was added, and the reaction mixture was acidified with 50% H_2SO_4–H_2O. The aqueous layer was extracted with CH_2Cl_2 (4×20 cm^3) and the combined organic layers were dried ($MgSO_4$). The solvent was distilled off, and the remaining volatile materials were removed under high vacuum. The residue was chromatographed (SiO_2, gradient PE/EA from 10:1 via 5:1 to 1:1, followed by EA). In a first fraction a mixture of **4** and byproduct **5** in a molar ratio of 5.6:1.0 was obtained (total 1.45 g, containing 178 mg, 0.401 mmol, 3% of **5**, and 1.27 g, 2.25 mmol, 18% of **4**). In a second fraction [R_f(PE/EA = 5:1) = 0.29] product **4** (4.34 g, 7.70 mmol, 63%) was isolated as a colorless solid, giving 81% overall yield of **4**, m.p. 75–76 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.37–1.60 (m, 2H, 3-CH_2), 1.95–2.10 (m, 2H, 2-CH_2), 2.45 (s, 3H, CH_3), 4.00–4.06 (t, J = 6.5 Hz, 2H, 1-CH_2), 7.27–7.35 (m, 2H, tosyl), 7.35–7.44 (m, 10H, Ph_3Sn), 7.44–7.66 (m, 5H, Ph_3Sn), 7.71–7.79 (m, 2H, tosyl) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz): δ = 5.80 (s, 3-CH_2), 21.57 (s, CH_3), 26.03 (s, 2-CH_2), 72.95 (s, 1-CH_2), 127.81 (s, tosyl-*o*-CH), 128.56 [s, d, $^2J(^{13}C,^{117,119}Sn)$ = 50.0 Hz, *o*-CH], 129.02 [s, d, $^4J(^{13}C,^{117,119}Sn)$ = 11.1 Hz, *p*-CH], 129.74 (s, tosyl-*m*-CH), 133.14 (s, tosyl-*i*-C), 136.88 [s, d, $^3J(^{13}C,^{117,119}Sn)$ = 35.7 Hz, *m*-CH], 137.89 (s, *i*-C), 144.56 (s, tosyl-*p*-CH) ppm. IR (ATR): $\tilde{\nu}$ = 3063 (m), 3046 (m), 1428 (s), 1359 (s), 1188 (s), 1176 (vs), 1096 (m), 1074 (m), 1021 (m), 997 (m), 955 (s), 895 (m), 815 (m), 772 (m), 728 (s), 699 (vs), 665 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 487 (24) [$M^+ - Ph$], 445 (42) [M^+–Bn – C_2H_4], 351 (100) [Ph_3Sn^+], 197 (24) [$SnPh^+$], 132 (90). HRMS Calcd. 487.0389 (for $C_{22}H_{23}O_3S^{120}Sn$). Found: 487.0389 ($M^+ - Ph$). Anal. Calcd. for $C_{28}H_{28}O_3SSn$ (563.30): C 59.70, H 5.01. Found: C 59.70, H 5.16%. *Byproduct* **5**: m.p. 106 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.42–1.94 (m, 2H, 1-CH_2), 2.10–2.49 (m, 2H, 2-CH_2), 3.66 (t, J = 6.7 Hz, 2H, 3-CH_2), 7.44–7.63 (m, 9H, ArH), 7.66–7.88 (m, 6H, ArH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz): δ = 7.88 [s, d, d, $^1J(^{13}C,^{117}Sn)$ = 364.6 Hz, $^1J(^{13}C,^{119}Sn)$ = 381.5 Hz, 1-CH_2], 29.80 [s, d, $^2J(^{13}C,^{117,119}Sn)$ = 16.1 Hz, 2-CH_2], 47.98 [s, d, $^3J(^{13}C,^{117,119}Sn)$ = 83.9 Hz, 3-CH_2], 128.55 [s, d, $^2J(^{13}C,^{117,119}Sn)$ = 46.4 Hz, *o*-CH], 128.99 [s, d, $^4J(^{13}C,^{117,119}Sn)$ = 11.1 Hz, *p*-CH], 136.91 [s, d, $^3J(^{13}C,^{117,119}Sn)$ = 35.6 Hz, *m*-CH], 138.12 [s, d, d, $^1J(^{13}C,^{117}Sn)$ = 476.5 Hz, $^1J(^{13}C,^{119}Sn)$ = 498.6 Hz, *i*-C] ppm. IR (ATR): $\tilde{\nu}$ = 3062 (m), 1480 (s), 1428 (vs), 1306 (m), 1258 (m), 1074 (s), 1023 (m), 997 (m), 729 (vs), 699 (vs), 676 (s), 658 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 351 (100) [$M^+ - Ph$], 309 (13), 197 (32) [$PhSn^+$], 154 (8), 120 (12). HRMS Calcd. 350.9962 (for $C_{15}H_{16}Cl^{120}Sn$). Found: 350.9962 ($M^+ - Ph$). Anal. Calcd. for $C_{21}H_{21}ClSn$ (427.54): C 59.00, H 4.95. Found: C 59.02, H 4.99%.

3.4. 4-(tert-Butyl)-1-(3-triphenylstannylpropyl)-1,3-cyclopentadiene (6)

Under exclusion of moisture and air *t*BuCpH (4.86 g, 39.8 mmol) was slowly added dropwise to NaH (2.38 g, 59.5 mmol, 60% suspension in paraffin) at −78 °C, and the stirred reaction mixture warmed to room temperature. After cooling to −78 °C, a solution of **4** (5.60 g, 9.95 mmol) in THF (12 cm^3) was added dropwise, and the reaction mixture allowed to warm up to room temperature (12 h). All volatile materials were removed, and the residue was chromatographed (SiO_2, PE/EA = 5:1). In a first fraction [R_f(PE/EA = 1:1) = 0.68] byproduct **7** (1.16 g, 4.75 mmol, 12% reg. *t*BuCpH) was obtained as a colorless solid. In a second fraction [R_f(PE) = 0.10] product **6** (4.68 g, 9.12 mmol, 92% reg. **4**) was isolated as a redbrown oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.92–1.35 (m, 9H, *t*-Bu), 1.53–1.67 (m, 2H, CH_2), 1.84–2.15 (m, 2H, CH_2), 2.21–2.59 (m, 2H, CH_2), 2.71–2.96 (m, 2H, CH_2), 5.71–6.53 (m, 2H, CH), 7.24–7.40 (m, 9H, ArH), 7.49–7.58 (m, 6H, ArH) ppm. IR (ATR): $\tilde{\nu}$ = 3063 (m), 3047 (m), 2959 (s), 2905 (m), 2867 (m), 1711 (m), 1480 (m), 1429 (vs), 1364 (m), 1075 (s), 1022 (m), 997 (m), 728 (vs), 699 (vs), 659 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 514 (2) [M^+], 437 (4) [$M^+ - Ph$], 351 (100) [Ph_3Sn^+], 309 (45), 273 (4) [Ph_2Sn^+], 197 (37) [$SnPh^+$], 154 (58), 120 (18) [t-$BuC_5H_3^+$], 77 (27) [Ph^+], 57 (39) [t-Bu^+]. HRMS Calcd. 514.1682 (for $C_{30}H_{34}{}^{120}Sn$). Found: 514.1679 (M^+).

3.5. 1,4-Di-tert-butyltricyclo[5.2.1.0^{1,7}]deca-3,8-diene (7)

Melting point 55–58 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.95 (s, 9H, *t*-Bu), 0.98 (s, 9H, *t*-Bu), 1.18 [ddt, ^2J(10-H$_{anti}$, 10-H$_{syn}$) = 7.9 Hz, ^3J(10-H$_{anti}$, 7-H) = 1.4 Hz, ^4J(10-H$_{anti}$, 8,9-H) = 0.8 Hz, 1H, 10-H$_{anti}$], 1.34 [dd, ^2J(10-H$_{syn}$, 10-H$_{anti}$) = 7.9 Hz, ^3J(10-H$_{syn}$, 7-H) = 1.8 Hz, 1H, 10-H$_{syn}$], 1.70 [dddd, ^2J(5-H$_{endo}$, 5-H$_{exo}$) = 16.7 Hz, ^3J(5-H$_{endo}$, 6-H) = 3.3 Hz, ^4J(5-H$_{endo}$, 2-H) = 3.6 Hz, ^4J(5-H$_{endo}$, 3-H) = 2.0 Hz, 1H, 5-H$_{endo}$], 2.15 [dddd, ^2J(5-H$_{exo}$, 5-H$_{endo}$) = 16.7 Hz, ^3J(5-H$_{exo}$, 6-H) = 10.1 Hz, ^4J(5-H$_{exo}$, 3-H) = 2.1 Hz, ^4J(5-H$_{exo}$, 2-H) = 1.8 Hz, 1 H, 5-H$_{exo}$], 2.74–2.79 (m, 2H, 6,7-H), 3.17 [dddd, ^3J(2-H,6-H) = 8.2 Hz, ^4J(2-H,5-H$_{endo}$) = 3.6 Hz, ^3J(2-H,3-H) = 2.0 Hz, ^4J(2-H,5-H$_{exo}$) = 1.8 Hz, 1H,

2-H], 5.15–5.16 [ddd, ^4J(3-H,5-H$_{endo}$) = 2.2 Hz, ^3J(3-H,2-H) = 2.0 Hz, ^4J(3-H,5-H$_{exo}$) = 2.0 Hz, 1H, 3-H], 5.88 (s, 2H, 8,9-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 27.83 (CH_3), 29.39 (CH_3), 31.41 (C), 32.77 (C), 33.38 (C-5), 44.35 (CH), 45.69 (CH), 49.45 (C-10), 53.52 (C-2), 65.24 (C-1), 123.35 (C-3), 130.87 (=CH), 137.59 (=CH) 155.48 (C-4) ppm. IR (KBr): $\tilde{\nu}$ = 3064 (m), 2961 (vs), 2900 (vs), 2864 (vs), 1474 (m), 1460 (m), 1391 (m), 1362 (s), 1248 (m), 862 (m), 837 (s), 809 (m), 744 (m), 725 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 244 (5) [M$^+$], 122 (79) [$C_9H_{14}^+$], 107 (100) [$C_8H_7^+$], 91 (14), 57 (12) [*t*-Bu$^+$]. Anal. Calcd. for $C_{18}H_{28}$ (244.42): C 88.45, H 11.55. Found: C 88.28, H 11.61%.

3.6. Preparation of ferrocene **8**

At 0 °C *n*-BuLi (4.00 mmol, 2.5 cm^3 of a 1.6-mol dm^{-3} solution in hexane) was added dropwise to a solution of **6** (1.639 g, 3.194 mmol) in THF (2 cm^3) followed by addition of $FeCl_2$ (204 mg, 1.60 mmol), and the reaction mixture was stirred for 1.5 h. After addition of ice (20 g), the reaction mixture was neutralized with 20% citric acid–H_2O and extracted with CH_2Cl_2 (3×15 cm^3). The combined organic layers were dried ($MgSO_4$) and concentrated. The residue was chromatographed (SiO_2, PE/EA = 20:1) to give a red-colored fraction containing **8** (383 mg, red oil) as a mixture of several species.

3.7. Bis[η^5-1-(tert-butyl)-3-(3-tributylstannylpropyl)-cyclopentadienyl]iron(II) (**9**)

Under N_2 atmosphere and exclusion of moisture at 0 °C *n*-BuLi (8.00 mmol, 5.0 cm^3 of a 1.6-mol dm^{-3} solution in hexane) was added dropwise to a solution of **8** (383 mg) in THF (1.0 cm^3), and the reaction mixture was stirred at room temperature for 3 days. After acidifying with 20% citric acid–H_2O, the aqueous layer was extracted with CH_2Cl_2 (3×10 cm^3). The combined organic layers were dried ($MgSO_4$) and concentrated. The residue was chromatographed (SiO_2, PE, R_f = 0.54–0.63) to give **9** (300 mg, 0.312 mmol) as a red oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.77–0.85 (m, 16H, CH_2), 0.89 (t, ^3J = 7.2 Hz, 18H, CH_3), 0.86–0.91 (m, 4H, CH_2), 1.19–1.21 (m, 6H, CH_2), 1.23–1.36 (m, 26H, *t*-Bu, CH_2), 1.42–1.55 (m, 14H, CH_2), 3.60–4.04 (m, 6H, CpH) ppm. IR (film): $\tilde{\nu}$ = 2956 (s), 2924 (s), 2854 (m), 2360 (m), 2341 (m), 1459 (m), 1376 (w), 1359 (w), 1131 (m), 1109 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 962 (<1) [M$^+$], 671 (<1) [M$^+$ − $SnBu_3$], 382 (4) [$C_{19}H_{34}Sn^+$], 291 (100) [$SnBu_3^+$], 234 (63) [$HSnBu_2^+$], 179 (71) [H_2SnBu^+], 121 (31) [HSn^+], 57 (5) [$C_4H_9^+$]. HRMS Calcd. 962.4436 (for $C_{48}H_{90}{}^{56}Fe^{120}Sn_2$). Found: 962.4457 (M$^+$). Anal. Calcd. for $C_{48}H_{90}FeSn_2$ (960.51): C 60.02, H 9.44. Found: C 60.60, H 9.60%.

3.8. Bis[η^5-1-(tert-butyl)-3-(3-triphenylstannylpropyl)-cyclopentadienyl]iron(II) (**10**)

Under exclusion of moisture and air at 0 °C PhLi (2.41 mmol, 1.50 cm^3 of a 1.6 mol dm^3 solution in cyclohexane/Et_2O = 70:30) was added dropwise to a solution of **6** (990 mg, 1.93 mmol) in THF (1.5 cm^3), and the reaction mixture stirred at room temperature for 15 min. Then powdered iron(II) chloride (122 mg, 0.965 mmol) was added, and the reaction mixture stirred for 3 h. After acidifying with 20% citric acid–H_2O (ice-cooling), the aqueous layer was extracted with CH_2Cl_2 (4×10 cm^3), and the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (SiO_2, PE/EA = 20:1). In a first fraction starting material **6** (268 mg, 0.522 mmol, 27%) was reisolated. In a second fraction [R_f(PE/EA = 20:1) = 0.00–0.05] product **10** (488 mg, 0.452 mmol, 47%) was isolated as a red oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.12–1.18 (m, 18H, *t*-Bu), 1.40–1.58 (m, 4H, 3-CH_2), 1.69–2.01 (m, 4H, 2-CH_2), 2.15–2.55 (m, 4H, 1-CH_2), 3.39–3.88 (m, 6H, CpH), 7.31–7.38 (m, 18H, ArH), 7.44–7.63 (m, 12H, ArH) ppm. IR (film): $\tilde{\nu}$ = 3062 (m), 3012 (s), 2953 (m), 2858 (m), 1428 (s), 1074 (m), 727 (vs), 698 (vs), 658 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 1082 (82) [M$^+$], 731 (4) [M$^+$ − Ph_3Sn], 674 (18) [M$^+$ − Ph_3Sn − C_5H_9], 569 (18) [$C_{30}H_{33}FeSn^+$], 351 (100) [Ph_3Sn^+], 279 (19), 197 (22) [$PhSn^+$], 78 (100) [$C_6H_6^+$]. Anal. Calcd. for $C_{60}H_{66}FeSn_2$ (1080.45): C 66.70, H 6.16. Found: C 66.70, H 6.15%.

3.9. Bis[η^5-1-(tert-butyl)-3-(3-triphenylstannylpropyl)-cyclopentadienyl]dichlorozirconium(IV) (**11**)

PhLi (1.51 mmol, 0.84 cm^3 of a 1.8 mol dm^3 solution in cyclohexane/Et_2O = 70:30) was added dropwise to a solution of **6** (776 mg, 1.51 mmol) in THF (3 cm^3) at −78 °C, and the reaction mixture stirred for 15 min. Then a solution of $ZrCl_4 \cdot 2THF$ in THF [prepared by adding $ZrCl_4 \cdot 2THF$ (285 mg, 0.755 mmol) to THF (5 cm^3) at −78 °C and warming the suspension to room temperature] was added dropwise at −78 °C, and the reaction mixture allowed to warm up to room temperature (16 h). After removal of all volatile materials, the residue was extracted with boiling toluene (15 cm^3). Concentration of the extract gave **11** (349 mg, 0.294 mmol, 39%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.03–1.27 (m, 18H, *t*-Bu), 1.37–1.68 (m, 4H, CH_2), 1.75–2.12 (m, 4H, CH_2), 2.38–2.61 (m, 2H, CH_2), 2.65–2.80 (m, 2H, CH_2), 5.56–6.21 (m, 6H, CpH), 7.32–7.37 (m, 20H, Ph), 7.41–7.61 (m, 10H, Ph) ppm. IR (film) $\tilde{\nu}$ = 3063 (m), 3047 (m), 2959 (s), 2905 (m), 2866 (m), 1462 (m), 1428 (s), 1362 (m), 1259 (m), 1201 (m), 1074 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 1109 (20) [M$^+$ − Ph], 1067 (7), 723 (23), 633 (41), 436 (65), 308 (100), 274 (43), 196 (40), 154 (95),

119 (39). HRMS Calcd. 1109.1236 (for $^{12}C_{48}H_{61}$-$^{35}Cl_2{}^{120}Sn_2{}^{90}Zr$). Found: 1109.1233 ($M^+ - Ph$).

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