Synthesis and Reactivity of Cyclopentadienyl and Indenyl Ligands Bearing ω-Fluorinated Pendant Groups. Crystal Structure of (*ortho*-F-C_6H_4)-CPh_2-$C_5H_4SiMe_3$

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Z. Naturforsch. **57 b,** 1207–1214 (2002); received November 29, 2001

Half-Sandwich Complex, Intra-molecular Stabilisation, Transmetallation

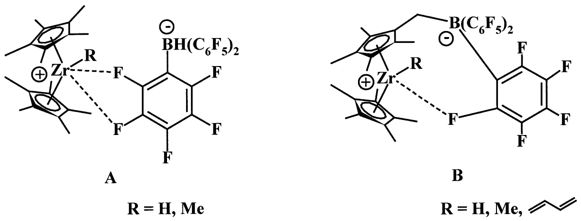
A series of cyclopentadienes and indenes with ω-fluorinated pendant groups have been synthesised and their reactivity towards metallating agents *n*-BuLi, NaH, TlOEt, Me_3SiCl, Me_3SnCl, $TiHal_4$, ZrX_4 (X = Cl, NMe_2) has been investigated. The crystal structure of 1-trimethylsilyl-3-(diphenyl-*ortho*-fluorophenyl-methyl)-cyclopentadiene (**3**) was determined.

1. Introduction

Half-sandwich complexes of early transition metals with bulky substituents are interesting as potential catalysts for olefin polymerisation [1 - 5]. The efficiency of such catalysts depends on the stability of the cationic complexes formed in the process of catalysts activation [6]. Modifying the ligand environment of the metal centre one can control the stability of the complexes and have an influence on the physic-chemical properties of the resulting polymers.

One of the possibilities to achieve stabilisation of cationic species consists of the modification of the Cp-ligand with pendant substituents, which can provide protection of the metal centre by weak coordination. Such a substituent should not have strong s- or p-donor character in order not to depress the Lewis-acidity and the catalytic properties of the transition metal centre. Groups bearing ω-fluorine atoms seem to be likely candidates for exerting this stabilising effect.

Marks and co-workers [8] have stabilised the zirconocene system by interaction with tris(pentafluorophenyl)borane (**A**). It has been proved that coordination of fluorine to a metal centre favours the stabilisation, but this interaction is rather weak and does not neutralise the electrophilic properties of the cationic species. Erker [9] and Piers and co-workers [10] have modified this system by creating Zr-F intramolecular interactions on the basis of metallocene zwitterionic species (**B**).



Scheme 1.

Our aim was the creation and further investigation of certain systems with intra-molecular F→M

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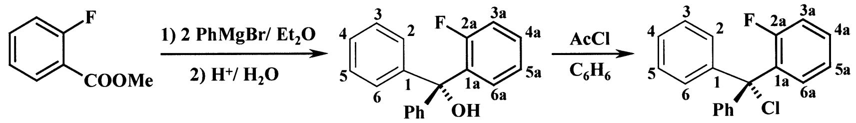
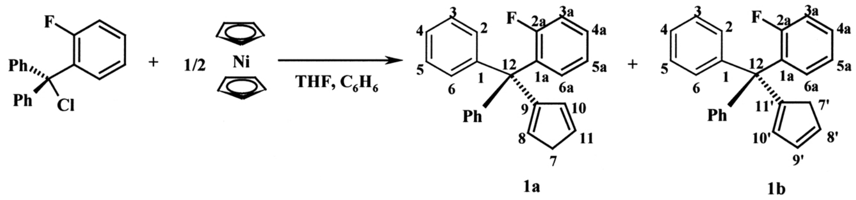
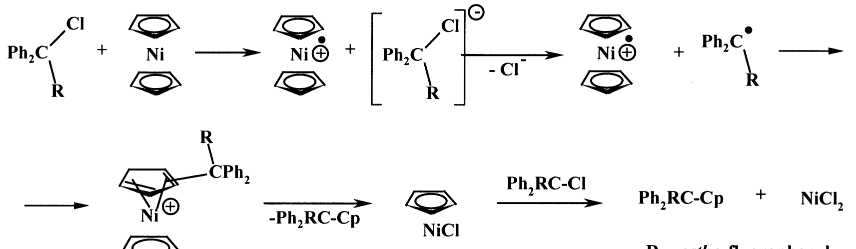


Scheme 2.



Scheme 3.



R = *ortho*-fluorophenyl
Cp = cyclopentadienyl

Scheme 4.

interaction, where the fluorine atom is in the tail-position of the organic ligand.

Results and Discussion

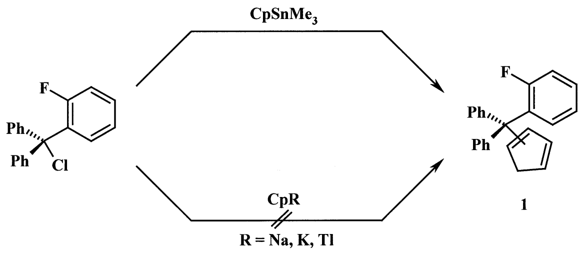
ortho-*Fluorophenyl-diphenylmethyl-cyclopentadiene (***1***)*

For the synthesis of this ligand we synthesised the corresponding tritylchloride (Scheme 2) by reaction of *ortho* -fluoromethylbenzoate with 2 equivalents of phenylmagnesium bromide followed by S_N1 OH/Cl exchange with an excess of acetyl chloride [11].

Subsequent substitution of halogen by cyclopentadienyl has been achieved by the previously developed method [6, 7] using nickelocene as a Cp-source (Scheme 3).

The process affords good yields and occurs probably via a radical mechanism including the steps of Scheme 4.

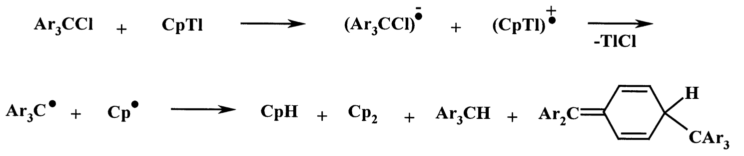
The product is a white crystalline solid consisting of two isomers **1a** and **1b** in a ratio 3.5÷1. Alternatively this ligand can be synthesised by metathesis reaction of diphenyl-*ortho*-fluorophenyl-methylchloride with CpSnMe$_3$, while direct substitutions with CpNa, CpK or even CpTl in THF were found to be unsuccessful (Scheme 5).



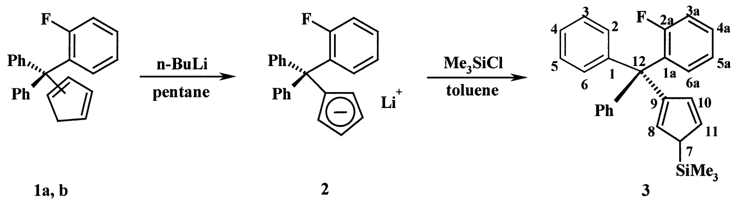
Scheme 5.

According to TLC a mixture of at least 3-4 compounds was obtained in the reaction of tritylchloride with CpTl excluding the target product. We speculate that the possible mechanism of this reaction is that of Scheme 6.

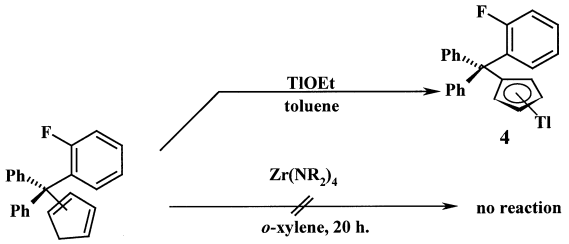
This mechanism would explain the red colour of the reaction mixture, which is characteristic for systems containing Cp- and trityl- radical species. Attempts to deprotonate **1** with several bases such as n-BuLi or NaH in ethereal solvents (Et$_2$O, THF, DME) have failed, while the parent Ph$_3$CCp is smoothly deprotonated under these conditions [12]. However **1** reacts with n-BuLi in pentane to give the lithium salt of the ligand. After 30 h the Li-salt **2** was quenched by addition of Me$_3$SiCl converting it into the trimethylsilyl derivative **3**, which was obtained as a white crystalline powder. This compound exists



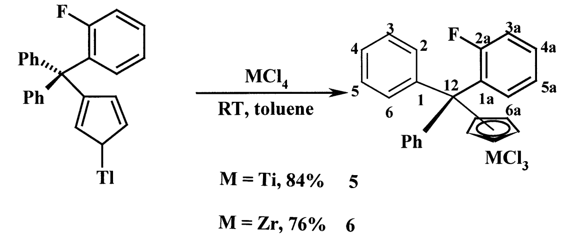
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

in the form of one isomer (3-Me_3Si-Cp). Obviously the bulky Me_3Si-group rules out the formation of the 2-substituted isomer (Scheme 7).

Direct metallation of **1** was achieved in reactions with Me_3SnNMe_2 and with TlOEt. The grey precipitate of the Tl-salt **4** is formed quantitatively, while the trimethyltin derivative is formed only after heating the toluene solution of **1** with Me_3SnNMe_2 under reflux for 12 h. However, even in this case the reaction is incomplete and the yield is very poor. Further attempts of a direct metallation of **1** with zirconium amides ($Zr(NR_2)_4$, R = Me, Et) also failed (Scheme 8).

Transmetallation of **3** with TiX_4 (X = Cl, Br) was not successful. Immediate colour change from yellow to brown-red occurs just after the addition of **3** to a solution of the titanium halide. The only product isolated in these reactions was TiX_3 (X = Cl, Br). Reduction occurs even at –100 °C. A possible reason for this may be the pre-coordination of TiX_4 forming an adduct with a Ti-F bond, in which the position of the Me_3Si-group at the Cp-ring is unfavourable for further substitution, whereas the double bond is available and, therefore, a fast halogen transfer from Ti can readily occur.

By contrast the Tl-salt **4** smoothly reacts with both $TiCl_4$ and $ZrCl_4$ providing the corresponding half-sandwich complexes **5** and **6** with good yields (Scheme 9).

The products are yellow micro-crystalline powders, slowly decomposing in the presence of moisture, but stable in an inert atmosphere. According to the ^{19}F NMR chemical shifts data there is no interaction between the metal atoms and the fluorine atom in **5** and **6**. The possible reason for this observation lies in the bulkiness of the ligand system.

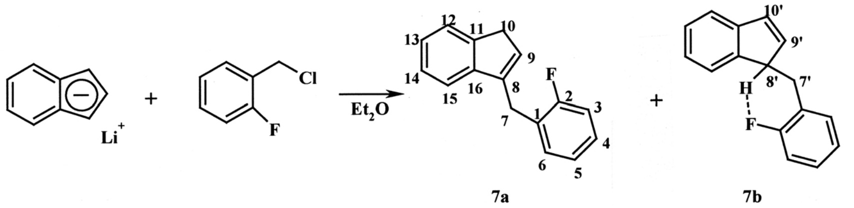
1-(ortho-Fluorobenzyl)-indene

1-(*ortho*-Fluorobenzyl)-indene **7** was obtained by interaction of indenyl-lithium with *ortho*-fluorobenzylchloride in diethylether (Scheme 10).

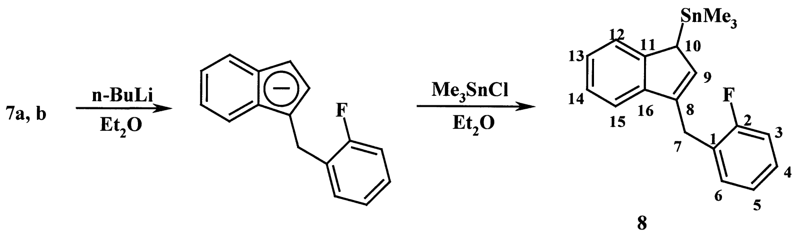
The product was purified by distillation in a vacuum and obtained as an intensively green oily liquid, slowly darkening on air. It consists of a mixture of two isomers **7a** and **7b** in the ratio 3:10 according to the ^{19}F-NMR data. The possible reason for this distribution may be a H···F hydrogen bond formation in **7b**, which makes this isomer more stable.

In order to obtain a soft transmetallation agent we synthesised the stannyl-derivative **8** by metallation of **7** with *n*-BuLi and subsequent quenching of the Li-salt with trimethyltin chloride (Scheme 11).

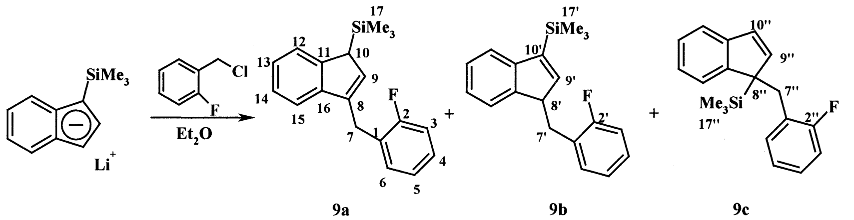
Compound **8**, a dark-red oil, sensitive to air moisture, exists as only one isomer.



Scheme 10.



Scheme 11.

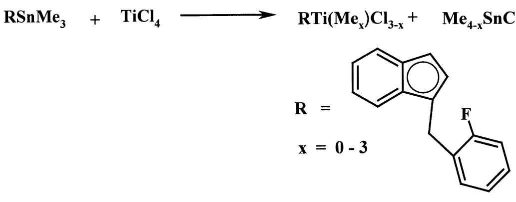


Scheme 12.

The analogous Me_3Si-derivative **9** was obtained in good yield (81%) by interaction of the lithium salt of 1-trimethysilylindene with *ortho*-fluorobenzylchloride (Scheme 12). The product **9** consists of a mixture of three isomers **9a-c** in the ratio of 3.5:5:1. The formation of the isomer **9c** was unexpected.

By reaction of **8** with $TiCl_4$ in petroleum ether at room temperature we obtained several products, as suggested by the mass-spectrum (Scheme 13). The mechanism of this reaction was not investigated. An exchange of methyl groups with chlorine atoms of one of the indenyl-groups with chlorine atoms between organotin and titanium species are proposed in this case.

Changing the reaction conditions to the inverted order of reagents mixing [13] gave the same result (even under very mild reaction conditions: –100 °C, petroleum ether).



Scheme 13.

The trimethylsilyl derivative **9** does not react with $TiCl_4$ even in boiling toluene. The NMR spectrum of the product was identical with that of the starting material **9**.

Interaction of two equivalents of **8** with 1 eq. of $ZrCl_4$ leads to a mixture of two products – slightly yellow crystals and a red oil, which according to NMR data are half-sandwich and sandwich species. Since an analogous product with a *para*-fluorobenzyl substituent was easily obtained [14], we conclude that after addition of the first equivalent of the ligand to zirconium a coordination of the fluorine to the metal atom takes place and hinders the addition of the second equivalent.

Structure Determination

The molecular structure of **3** has been determined by X-ray diffraction. The trimethylsilyl moiety occupies exclusively the allilyc σ-bonded position in the cyclopentadiene ring. There is no interaction between the trimethylsilyl and the fluoro substituents. The C(4) atom is tetrahedral with angles Si(1)-C(4)-C(3) = 109.2(1)°, Si(1)-C(4)-C(5) = 110.0(1)°, C(5)-C(4)-C(3) = 102.9(2)°. The bond length Si(1)-C(4) is 190.7(2) pm, nearly equal to the bond length $Si\text{-}C_{Cp}$ in its unsubstituted analogue

Table 1. Selected bond lengths (pm) and bond angles (°) for **3**.

Si(1)-C(7)	185.9(2)	C(10)-C(11)	135.6(3)
Si(1)-C(8)	186.3(3)	C(2)-C(3)	135.0(3)
Si(1)-C(9)	186.2(3)	C(1)-C(2)	153.1(3)
Si(1)-C(4)	190.7(2)	C(3)-C(4)	148.7(3)
F(1)-C(11)	133.7(3)	C(2)-C(6)	145.9(3)
C(1)-C(10)	154.4(3)	C(5)-C(6)	134.0(3)
C(1)-C(20)	155.0(3)	C(4)-C(5)	148.2(3)
C(1)-C(30)	154.6(3)		
C(7)-Si(1)-C(8)	112.1(1)	C(2)-C(1)-C(20)	106.3(2)
C(9)-Si(1)-C(8)	108.0(1)	C(2)-C(1)-C(10)	109.69(2)
C(7)-Si(1)-C(9)	110.7(1)	C(5)-C(4)-C(3)	102.9(2)
C(4)-Si(1)-C(9)	109.3(1)	C(3)-C(4)-Si(1)	109.2(1)
C(7)-Si(1)-C(4)	108.3(1)	C(6)-C(2)-C(1)	123.3(2)
C(8)-Si(1)-C(4)	108.4(1)	C(10)-C(1)-C(20)	110.5(2)
F(1)-C(11)-C(10)	119.3(2)	C(5)-C(4)-Si(1)	110.0(1)
C(1)-C(10)-C(11)	120.2(2)	C(2)-C(3)-C(4)	109.9(2)
C(3)-C(2)-C(1)	128.8(2)	C(6)-C(5)-C(4)	109.5(2)
C(5)-C(6)-C(2)	109.7(2)	C(30)-C(1)-C(20)	110.1(2)
C(2)-C(1)-C(30)	112.4(2)	C(3)-C(2)-C(6)	107.8(2)

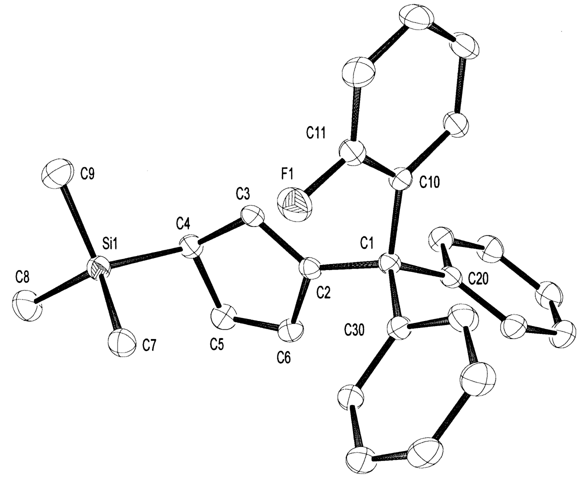


Fig. 1. Crystal structure of 1-[$(C_6H_5)_2$(*ortho*-F-C_6H_4)]-C(C_5H_3-3-$SiMe_3$) (**3**).

(trityltrimethylsilylcyclopentadiene) [6]. The double bonds of the cyclopentadiene ring in **3** differ in their length, (C(2)-C(3) = 135,0(3) pm, C(5)-C(6) = 134,0(3) pm, indicating double bonds similar to the unsubstituted analogue (136.0(2) and 133.4(3) pm).

Experimental Section

All experiments were carried out in an argon atmosphere. All solvents were purified by standard methods and were freshly distilled prior to use. Me_3SiCl and $TiCl_4$ were distilled over Al_2O_3. $ZrCl_4$ was purchased from Aldrich and degassed several times before use. Zirconium amides were received in-house. Nickelocene was obtained according to [15]. Cyclopentadienyltrimethyltin was distilled twice under argon prior to use. The Grignard reagent and ^{n}BuLi hexane solutions were prepared by routine procedures. CpTl was prepared by interaction of a mixture of thallium formiate and thallium malonate with cyclopentadiene in aqueous KOH solution.

The NMR spectra were recorded with Bruker AC 300 (^{1}H, ^{19}F: 300 MHz, ^{13}C: 75 MHz) and Varian VXR-400 (^{1}H, ^{19}F: 400 MHz, ^{13}C: 100 MHz) spectrometers. As internal standard for ^{19}F spectroscopy the chemical shift of $CFCl_3$ was used. The elemental analysis was performed on a Carlo-Erba analyser. Mass-spectra were recorded on a Varian CH-7a MAT spectrometer (EI-MS, E = 70 eV). Melting points were determined in sealed capillaries and are uncorrected.

Diphenyl-ortho-fluorophenyl-methanol

An ethereal solution of phenylmagnesium bromide (0.245 mol) was added to a solution of methyl-*ortho*-fluoro-benzoate (19.1 g, 0.124 mol), the mixture refluxed for 1h, and then poured on ice cold water. After extraction with Et_2O (at pH ~ 5.5) and washing of the ethereal phase with water the solution was dried over $MgSO_4$, solvent was evaporated and the product obtained washed with petroleum ether and dried. White powder. Yield 63% (21.75 g).

M. p. 123 °C. – ^{1}H NMR (400 MHz, d^6-acetone): δ = 5.23 (d, $^4J_{H-F}$ = 33.44 Hz, 1H, OH), 7.03 - 7.16, 7.24 - 7.39 (m, m, 14H, CH_{Ar}). – ^{13}C NMR (100 MHz, d^6-acetone): δ = 81.32 (COH), 116.79 (d, $^2J_{C-F}$ = 22.2 Hz, C-3a), 124.46 (d, $^4J_{C-F}$ = 3.7 Hz, C-5a), 127.79 (C-4), 128.33 (C-3), 128.44 (C-2), 130.25 (d, $^3J_{C-F}$ = 3.6 Hz, C-6a), 130.40 (d, $^3J_{C-F}$ = 8.4 Hz, C-4a), 135.58 (d, $^2J_{C-F}$ = 11.6 Hz, C-1a), 147.19 (C-1), 161.14 (d, $^1J_{C-F}$ = 245.9 Hz, C-1a). – ^{19}F NMR (400 MHz, d^6-acetone): δ = –108.52 (C*F*). – MS (EI, 70 eV): *m/z* (%) = 278 (23) [M$^+$], 261 (67) [M$^+$-OH], 201 (47) [M$^+$-Ph]. – $C_{19}H_{15}FO$ (278.3): calcd. C 81.99, H 5.43; found C 81.26, H 5.94.

Diphenyl-ortho-fluorophenyl-methylchloride

A benzene solution of diphenyl-ortho-fluorophenyl-methanol (11.1 g, 40 mmol) was added to acetyl chloride (2.9 ml, 40 mmol) with vigorous stirring. After 10 min the rest (4.3 ml, 60 mmol) was added. After 40 min. of reflux benzene was evaporated to ~30 ml and the product crystallised from benzene-petroleum ether at –20 °C. Then precipitate was separated by filtration and dried in a vacuum. White crystalline powder. Yield 62% (7.3 g).

M. p. 102 °C. – ^{1}H NMR (300 MHz, d^6-acetone): δ = 6.78 - 7.51 (m, 14H, CH_{Ar}). – ^{13}C (75 MHz, d^6-acetone):

δ = 80.33 (CCl), 116.81 (d, $^1J_{C-F}$ = 22.5 Hz, C-3a), 117.50 (d, $^2J_{C-F}$ = 22.5 Hz, C-1a), 127.82 (C-2), 128.41 (C-3), 129.62 (C-4), 131.91 (d, $^4J_{C-F}$ = 8.7 Hz, C-5a), 133.31 (d, $^3J_{C-F}$ = 9.8 Hz, C-4a), 135.58 (d, $^3J_{C-F}$ = 11.3 Hz, C-6a), 144.54 (C-1), 162.32 (d, $^1J_{C-F}$ = 248.6, C-2a). – ^{19}F NMR (300 MHz, d^6-acetone): δ = –98.68 (C*F*). – MS (EI, 70 eV): *m/z* (%) = 261 (82) [M$^+$-Cl], 183 (32) [M$^+$-Cl-Ph-H]. – $C_{19}H_{14}ClF$ (296.8): calcd. C 76.90, H 4.75; found C 76.53, H 5.16.

*Diphenyl-ortho-fluorophenyl-methyl-cyclopentadiene (**1**)*

Nickelocene (2.3 g, 12.5 mmol) dissolved in THF was added to the benzene solution (30 ml) of diphenyl-*ortho*-fluorophenyl-methylchloride (7.3 g, 25 mmol). A brown precipitate was observed. After 25 min the mixture was filtered and the solvent evaporated. The product was purified through recrystallisation from heptane and was obtained as a white crystalline solid. Yield 82% (6.69 g).

M. p. 185 °C. – ^{1}H NMR (300 MHz, C_6D_6): δ = 2.82, 2.85 (q, q', *J* = 1.5 Hz, 2H, H-7, H-7', the ratio q/q' is 3.5/1), 6.10-6.20, 6.23-6.29, 6.30-6.35 (m, m, m, 3H, -C_{Cp}H=), 6.60-6.94, 6.98-7.15, 7.28-7.44 (m, m, m, 14H, C_{Ar}H). – ^{13}C (75 MHz, C_6D_6): δ = 40.90 (C-7), 44.33 (C-7'), 59.23 (C-12), 116.43 (C-3a), 116.84 (C-6a), 123.93 (C-3), 127.93 (C-4), 132.31 (C-11), 129.92 (d, $^4J_{C-F}$ = 8.4 Hz, C-5a), 133.15 (C-2), 135.50 (d, $^3J_{C-F}$ = 11.2 Hz, C-4a), 137.31 (C-10), 144.59 (C-9), 145.90 (C-1), 146.00 (d, $^2J_{C-F}$ = 37.7 Hz, C-1a), 150.88 (C-11'), 161.55 (d, $^1J_{C-F}$ = 249.8 Hz, C-2a). – ^{19}F NMR (300 MHz, C_6D_6): δ = –102.56 (C*F*, **1a**), –100.88 (C*F*, **1b**) (ratio **1a**/**1b** is 3.5/1). – MS (EI, 70 eV): *m/z* (%) = 326 (89) [M$^+$], 261 (54) [M$^+$-Cp], 184 (31) [M$^+$-Cp-Ph]. – $C_{24}H_{19}F$ (326.4): calcd. C 88.31, H 5.87; found C 88.12, H 6.23.

*1-Trimethylsilyl-3-(diphenyl-ortho-fluorophenyl-methyl)-cyclopentadiene (**3**)*

A ^{n}BuLi solution in hexane (15 mmol) was dropped to a suspension of **1** (3.26 g, 10 mmol) in petroleum ether at room temperature. The mixture was stirred for 30 h, then the solution was filtered, the precipitate washed with pentane (2∗25 ml) and dried. The lithium salt obtained was used without further purification and analysis. It was suspended in toluene and trimethylsilylchloride (2.5 ml, 15 mmol) was added at room temperature. After 12 h the mixture was filtered, the solvent evaporated and the residue was dried in a vacuum. The product (orange oil) was crystallised from pentane. Yield 63% (2.50 g).

M. p. 89 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.1 (s, 9H, Si*Me*$_3$), 3.14 (t, *J* = 1.4 Hz, 1H, H-7), 6.45, 6.30-6.21 (br. t, br. dt, 1H, 2H, H-8, H-10, H-11), 7.42-7.39, 7.16-7.00, 6.92-6.68 (m, 14H, C*H*$_{Ar}$). – ^{13}C (75 MHz, C_6D_6): δ = –1.71 (Si*Me*$_3$), 50.29 (C-7), 59.6 (C-12), 116.2 (C-8), 116.6 (d, $^2J_{C-F}$ = 22.9 Hz, C-3a), 126.7 - 128.3 (C_{Ar}), 130.54 (d, $^3J_{C-F}$ = 20.2 Hz, C-4a), 131.03 (d, $^2J_{C-F}$ = 4.7 Hz, C-1a), 134.63 (C-11), 145.32 (C-9), 149.26 (C-1), 162.93 (C-2). – ^{19}F NMR (400 MHz, $CDCl_3$): δ = –99.03. – MS (EI, 70 eV): *m/z* (%) = 398 (48) [M$^+$], 325 (29) [M$^+$-SiMe$_3$], 303 (25) [M$^+$-FC$_6$F$_4$], 261 (97) [M$^+$-CpSiMe$_3$]. – $C_{27}H_{27}FSi$ (398.6): calcd. C 81.36, H 6.83; found C 80.97, H 7.04.

*Diphenyl-ortho-fluorophenyl-methyl-cyclopentadienyl-thallium (**4**)*

Thallium ethylate (0.5 ml, 6.87 mmol) was added to the saturated solution of **1** (2.24 g, 6.87 mmol) in toluene. After 30 h stirring at room temperature the solution was filtered and the grey precipitate obtained was washed with toluene (2∗10 ml) and dried in a vacuum. Yield 100%. MS (EI, 70 eV): *m/z* (%) = 530 (10) [M$^+$+H], 325 (68) [M$^+$-Tl].

*Diphenyl-ortho-fluorophenyl-methyl-cyclopentadienyl-titanium trichloride (**5**)*

$TiCl_4$ (0.33 ml, 3 mmol) was added to the suspension of **4** (3 mmol) in toluene. The reaction mixture was left overnight. Then the solution was filtered and the solvent evaporated. The product was recrystallised from toluene-pentane. Greenish yellow powder, yield 84% (1.20 g).

^{1}H NMR (400 MHz, d^8-toluene): δ = 6.52, (dt, J_1 = 1.6 Hz, J_2 = 78.2 Hz, 4H, C*H*$_{Cp}$), 6.72 - 7.43 (m, 14H, C*H*$_{Ar}$). – ^{13}C (100 MHz, d^8-toluene): δ = 45.83 (C-12), 109.16 (*C*$_{Cp}$H), 117.18 (d, $^2J_{C-F}$ = 20.5 Hz, C-3a), 123.52 (d, $^4J_{C-F}$ = 3.8 Hz, C-5a), 127.53 (C-4), 128.63 (C-3), 131.05 (d, $^3J_{C-F}$ = 8.2 Hz, C-6a), 130.53 (d, $^3J_{C-F}$ = 8.3 Hz, C-4a), 136.25 (C-2), 136.73 (d, $^2J_{C-F}$ = 11.6 Hz, C-1a), 147.19 (C-1), 160.32 (d, $^1J_{C-F}$ = 248.4 Hz, C-2a). – ^{19}F NMR (400 MHz, d^8-toluene): δ = –100.33 (C*F*). – MS (EI, 70 eV): *m/z* (%) = 478 (36) [M$^+$-H], 443 (26) [M$^+$-HCl], 406 (63) [M$^+$-2Cl-H]. – $C_{24}H_{18}Cl_3FTi$ (479.7): calcd. C 60.10, H 3.78; found C 59.88, H 3.98.

*Diphenyl-ortho-fluorophenyl-methyl-cyclopentadienyl-zirconium trichloride (**6**)*

The product was obtained in a same way as **5**. Rose powder, yield 76%.

^{1}H NMR (300 MHz, d^8-toluene): δ = 6.11, (dt, J_1 = 1.8 Hz, J_2 = 83.6 Hz, 4H, C*H*$_{Cp}$), 6.69 - 7.38 (m, 14H, C*H*$_{Ar}$). – ^{13}C (75 MHz, d^8-toluene): δ = 43.64 (C-12), 115.16 (C_{Cp}H), 127.91 (C-4), 128.23 (C-3), 137.43 (C-2), 160.32 (d, $^1J_{C-F}$ = 259.6 Hz, C-2a) – ^{19}F NMR (400 MHz, d^8-toluene): δ = –100.06 (C*F*). – MS (EI, 70 eV): *m/z* (%) = 487 (87) [M$^+$-Cl], 468 (34) [M$^+$-Cl-F], 452 (43)

[M^+-2Cl], 433 (48) [M^+-2Cl-C_6H_4F]. – $C_{24}H_{18}Cl_3FZr$ (523.0): calcd. C 55.12, H 3.47; found C 54.67, H 4.05.

1-(ortho-Fluorobenzyl)-indene (**7**)

A hexane solution of ^{n}BuLi (35 mmol) was added to a cooled (–35 °C) ethereal solution of freshly distilled indene (35 mmol). After coming to room temperature (~30 min) a solution of *ortho*-fluorobenzylchloride was dropped to the reaction mixture. 10 min after addition a white precipitate was observed. The mixture was stirred overnight. Then it was mixed with NH_4Cl-saturated water solution and extracted with Et_2O (2∗10 ml). The combined organic fraction was washed with water and dried over $MgSO_4$. The solvent was evaporated and the dark green oil distilled in a vacuum (B. p. 150 - 160 °C / 1 Torr). Green oily liquid, slowly decomposing on air, yield 77% (5.65 g). ^{1}H NMR (400 MHz, d^8-toluene): δ = 2.57 (dd, J_1 = 3.6 Hz, J_2 = 9.0 Hz, 2H, H-7), 3.00 (dd, J_1 = 7.7 Hz, J_2 = 6.6 Hz, 2H, H-7'), 3.62 (dd, J_1 = 2.0 Hz, J_2 = 8.3 Hz, 2H, H-8'), 3.76 (s, 2H, H-10), 5.87 (s, 1H, H-9), 6.24, 6.59 (dd, dd, J_1 = 3.8 Hz, J_2 = 1.7 Hz, 1H, 1H, H-9', H-10'), 6.72 - 6.88, 6.96 - 7.25 (m, m, 16H, CH_{Ar}) (ratio **7a**/**7b** = 3:10). – ^{13}C (100 MHz, d^8-toluene): δ = 27.29 (C-7), 31.29 (C-7'), 37.72 (C-10), 50.70 (C-8'), 115.28 (C-9'), 115.51 (C-10'), 119.42 (C-9), 121.40 (C-13), 123.41 (C-14), 123.94 (C-8), 125.03 (C-5), 127.00 (C-6), 127.67 (C-12), 127.91 (C-15), 128.14 (C-4), 131.50 (C-3), 144.61 (C-11), 147.05 (C-16), 161.73 (d, $^1J_{C-F}$ = 247.0 Hz, C-2). – ^{19}F NMR (400 MHz, d^8-toluene): δ = –118.47 (C*F*). – MS (EI, 70 eV): *m/z* (%) = 224 (17) [M^+], 115 (30) [Ind]. – $C_{16}H_{13}F$ (224.3): calcd. C 85.69, H 5.84; found C 85.34, H 5.95.

1-(ortho-Fluorobenzyl)-3-trimethylstannyl-indene (**8**)

A hexane solution of ^{n}BuLi (40 mmol) was added to the cooled (–35 °C) ethereal solution of **7** (9 g, 40 mmol). After coming to room temperature (~30 min) the suspension of the salt was cooled down to 0 °C and the ethereal solution of trimethyltinchloride (8 g, 40 mmol) dropped to the mixture. After 12 h the dark red solution was decanted from the precipitate of LiCl, the solvent was evaporated and the product thoroughly dried in a vacuum (80 °C, 10^{-2} Torr). Dark red oily liquid, decomposing at contact with air and moisture. Yield 97% (15.0 g). ^{1}H NMR (400 MHz, C_6D_6): δ = –0.21 (s, 9H, Sn*Me*$_3$), 3.69 (s, 1H, H-10), 3.98 (s, 2H, H-7), 6.25 (s, 1H, H-9), 6.75 - 7.52 (m, 8H, CH_{Ar}). – ^{13}C (100 MHz, C_6D_6): δ = –9.58 (Sn*Me*$_3$), 27.25 (d, $^3J_{C-F}$ = 3.2 Hz, C-7), 42.87 (C-10), 115.44 (d, $^3J_{C-F}$ = 20 Hz, C-6), 119.58 (C-15), 121.68 (C-13), 121.74 (C-12), 123.75 (C-14), 124.15 (d, $^4J_{C-F}$ = 3.7 Hz, C-5), 131.73 (d, $^2J_{C-F}$ = 56.2 Hz, C-3), 135.78 (C-8), 142.08 (C-11), 147.03 (C-16), 161.59 (d, $^1J_{C-F}$ = 243.5 Hz, C-2). – ^{19}F NMR (400 MHz, C_6D_6): δ = –120.30 (C*F*). – MS (EI, 70 eV): *m/z* (%) = 287 (72) [M^+], 372 (87) [M^+-Me], 342 (62) [M^+-3Me], 223 (58) [M^+-$SnMe_3$]. – $C_{19}H_{21}FSn$ (387.1): calcd. C 58.96, H 5.47; found C 58.24, H 6.02.

Table 2. Crystallographic data for 1-[$(C_6H_5)_2$ (*ortho*-F-C_6H_4)]C(C_5H_3-3-$SiMe_3$) (**3**).

Chemical formula	$C_{27}H_{27}FSi$
Crystal system	monoclinic
Mol. wt.	398.58
Cell dimensions	
a [pm]	1584.8(1)
b [pm]	1225.1(2)
c [pm]	1149.7(1)
β [deg]	91.785
V [10^{-30} m^3]	2231.2(4)
Scan range 2θ, deg	17.52 - 22.37
Number of reflections	4058
For $\|I_0\| > 2\sigma(\|I_0\|)$	3542
Space group	$P2_1/c$
Z	4
R_w	0.1732

Trimethylsilyl-1-(ortho-fluorobenzyl)-indene (**9**)

^{n}BuLi in hexane (10 mmol) was added to the solution of trimethylsilylindene (1.9 g, 10 mmol) in Et_2O at –35 °C. After coming to room temperature (~30 min) *ortho*-fluorobenzyl-chloride (1.2 g, 10 mmol) was added via a syringe. Formation of a white precipitate of LiCl was observed directly after adding Me_3SiCl. After 12 h stirring the mixture was poured into water, extracted with Et_2O (2∗10 ml) and the combined organic phase dried over $MgSO_4$. Then the solvent was evaporated and the residue was distilled in a vacuum. Slightly green oily liquid, slowly darkening on air. Yield 81% (2.40 g). B. p. 170 - 175 °C/1 Torr. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 9H, Si*Me*$_3$, H-17'), 0.11 (s, 9H, Si*Me*$_3$, H-17''), 0.41 (s, 9H, Si*Me*$_3$, H-17), 3.08 (dq, J_1 = 4.8 Hz, J_2 = 9.6 Hz, J_3 = 122.3 Hz, 2H, H-7'), 3.09 (s, 2H, H-7''), 3.56 (d, J = 3.2 Hz, 2H, H-7), 3.91 (t, J = 6.8 Hz, H-10), 4.12 (t, J = 20.0 Hz, 1H, H-8'), 6.74 (dd, J_1 = 92.3 Hz, J_2 = 2.4 Hz, 2H, H-9'', H-10'') 6.75 (dd, J_1 = 4.4 Hz, J_2 = 2.6 Hz, 1H, H-9'), 7.03 (dd, J_1 = 2.9 Hz, J_2 = 1.7 Hz, 1H, H-9), 7.13 - 7.60 (m, CH_{Ar}), ratio **9a**/**9b**/**9c** is 3.5/5/1. – ^{13}C (100 MHz, $CDCl_3$): δ = –2.56 (Si*Me*$_3$, C-17''), –2.44 (Si*Me*$_3$, C-17), –1.15 (Si*Me*$_3$, C-17'), 27.96 (C-7'), 29.69 (C-7''), 31.18 (C-7), 44.73 (C-8'), 50.40 (C-8''), 51.64 (C-10), 114 - 159 (C_{Ar} and C_{Ind}), 161.08 (d, $^1J_{C-F}$ = 247.4 Hz, C-2), 161.17 (d, $^1J_{C-F}$ = 248.6 Hz, C-2''), 161.35 (d, $^1J_{C-F}$ = 245.6 Hz, C_{Ar}-2'). – ^{19}F NMR (400 MHz, $CDCl_3$): δ = –120.07 (C*F*, **9a**), –120.37 (C*F*, **9b**), –121.39 (C*F*, **9c**). – MS (EI, 70 eV): *m/z* (%) = 296 (18) [M^+], 233 (24) [M^+-$SiMe_3$]. – $C_{19}H_{21}FSi$ (296.5): calcd. C 76.98, H 7.14; found C 76.22, H 7.63.

Structure determination

Data collection was performed at room temperature with an Enraf-Nonius CAD-4 diffractometer using graphite monochromatic Mo-K_α radiation (λ = 71.073 pm) and ω scans. 4058 unique reflections were measured in the range $17.52° < 2\theta < 22.37°$. The R_w value was 0.0583 for 3542 observed reflections ($I > 2\sigma(I)$). Approximate positions for the Si atom were obtained using direct methods (SHELXS-97 program) and the remaining non-hydrogen atoms were located by successive difference Fourier syntheses. In the anisotropic refinement of non-hydrogen atoms the hydrogen atoms were included as fixed contributions using a riding model.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC-166431. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk

Acknowledgements

We thank Drs. E. V. Avtomonov (Bayer AG), A. V. Churakov (Kurnakov-Institute of General and Inorganic Chemistry, Moscow), M. V Borzov (Department of Chemistry, Lomonosov State University, Moscow) and V. V. Kotov (Universität Münster, Germany) for intellectual support and helpful discussions.

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