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Articles

Trimethylsilylcyclopentadienes with Polyfluorinated Ponytails and Mono- and Bis(η^5-cyclopentadienyl)titanium(IV) Complexes Derived from Them

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Cyclopentadienes containing one or two (perfluorooctyl)ethyldimethylsilyl groups and a trimethylsilyl or trimethylstannyl group were prepared by the reaction of $C_8F_{17}CH_2CH_2Si(CH_3)_2Cl$ with LiC_5H_5 ($C_5H_5Si(CH_3)_2CH_2CH_2C_8F_{17}$, **1**; $C_5H_4\{Si(CH_3)_2CH_2CH_2C_8F_{17}\}_2$, **2**) or with $LiC_5H_4Si(CH_3)_3$ ($C_5H_4\{Si(CH_3)_2CH_2CH_2C_8F_{17}\}\{Si(CH_3)_3\}$, **3**) or by the reaction of **1** with butyllithium followed by $(CH_3)_3SnCl$ addition ($C_5H_4\{Si(CH_3)_2CH_2CH_2C_8F_{17}\}\{Sn(CH_3)_3\}$, **4**). All the cyclopentadienes were found, in analogy with similar known compounds, to be mixtures of isomers between which prototropic and on the NMR time scale fast metallotropic shifts occurred, as confirmed by variable-temperature ^1H and ^{13}C NMR. The reaction of **4** with $TiCl_4$ gave Ti(IV) complex $[\{\eta^5\text{-}C_5H_4Si(CH_3)_2CH_2CH_2C_8F_{17}\}TiCl_3]$ (**5**), whereas the reaction of $[(C_5H_4SiMe_3)TiCl_3]$ with lithium salts of **1** and **2** yielded complexes $[\{\eta^5\text{-}C_5H_4Si(CH_3)_2CH_2CH_2C_8F_{17}\}\{\eta^5\text{-}C_5H_4Si(CH_3)_3\}TiCl_2]$ (**6**) and $[\{\eta^5\text{-}C_5H_3(Si(CH_3)_2CH_2CH_2C_8F_{17})_2\}\{\eta^5\text{-}C_5H_4Si(CH_3)_3\}TiCl_2]$ (**7**), respectively. Complex $[\{\eta^5\text{-}C_5H_4Si(CH_3)_2CH_2CH_2C_8F_{17}\}_2TiCl_2]$ (**8**) was synthesized by the reaction of 2 equiv of lithium salt of **1** with $TiCl_3\cdot 3THF$, followed by $PbCl_2$ oxidation. An X-ray crystal and molecular structure of titanocene dichloride substituted by fluorous ponytails, **8**, was determined. The results show the applicability of fluorous chemistry methodology in early transition metal organometallic chemistry.

Introduction

Synthesis and catalysis in fluorous biphase systems[1] is rapidly becoming one of the well-established methods of reagent or catalyst recycling. Cyclopentadienyl complexes, despite their high importance in organometallic chemistry,[2] were studied only marginally in this respect.[3] As a part of our continuing effort to broaden the choice of available cyclopentadienyl ligands with fluorous ponytails, the syntheses of two new ligand types were reported,[4] their transition metal complexes with Fe(II),[4d] Rh(III),[4a] and Rh(I)[4a,d] were prepared, and the fluorophilic properties of some of them were measured. Although the (perfluoroalkyl)tetramethylcyclopentadienyls are quite stable on Rh(III) and Rh(I),[4a] other fluorine-containing cyclopentadienyl anions, even those with ethylene spacers separating the perfluorinated chain from the ring, decomposed at room temperature.[4d] Beckhaus et al.[5] reported the complete defluorination of (trifluoromethyl)tetramethylcyclopentadiene by $[Ti(NMe_2)_4]$ in an attempt to prepare its Ti complex.

A wide range of nonfluorous cyclopentadienyl ligands is known, including, for example, side-chain-functionalized ones[6] or bulky cyclopentadienyls,[2,7] which should allow “tuning“ of the steric hindrance in the coordination sphere around metal centers. We sought inspiration in trimethylsilyl-substituted cyclopentadienyls hoping that the defluorination of ponytails would be suppressed by the presence of a silylcarbyl spacer between the ponytail and the ring, which was indeed true.

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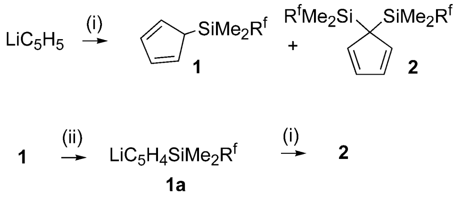
Scheme 1[a]



[a] $R^f = CH_2CH_2C_8F_{17}$, only major isomer of cyclopentadienes shown; (i) $ClSiMe_2R^f$; (ii) BuLi.

Therefore, the synthesis and characterization of cyclopentadienyls substituted with $C_8F_{17}CH_2CH_2Si(CH_3)_2$ groups are reported here, as well as the preparation of their Ti(IV) complexes.

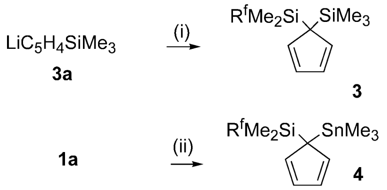
Results and Discussion

The reaction of $C_8F_{17}CH_2CH_2Si(CH_3)_2Cl$[8] with LiCp gave a mixture of mono- and disubstituted cyclopentadienes **1** and **2** (Scheme 1), respectively, from which **1** was separated by distillation. Disubstituted cyclopentadiene was also obtained by the reaction of an isolated lithium salt **1a** with another equivalent of $C_8F_{17}CH_2CH_2Si(CH_3)_2Cl$. Both **1** and **2** were obtained as mixtures of isomers, as expected. It is known that $C_5H_5Si(CH_3)_3$ exists in mixtures of 1-, 2-, and 5-isomers,[9a,b] the latter being the major product at room temperature. While the former two isomers form by nondegenerate prototropic hydrogen shift at higher temperatures,[9c] the 5-isomer undergoes degenerate metallotropic shift at a rate comparable to the NMR time scale at room temperature, so that the signals of ring protons are broad. Compound **1** behaves highly analogously in this respect: three isomers were identified, their proportions at room temperature being approximately 1:3:10 (1:2:5-isomer, obtained by the integration of ring aliphatic proton signals). On cooling to −40 °C, broad signals of ring atoms in both ^{1}H and ^{13}C NMR spectra became narrow, which confirmed the metallotropic equilibrium.

The disubstituted cyclopentadiene **2** can, in theory, exist in seven different isomers[10] between which the proto- and metallotropic shifts can again take place. Indeed, in ^{1}H spectra we observed in the region of ring aliphatic protons six signals, two of which were broad. The seventh isomer (5,5-) shows no signal in this area of the spectrum, and its proportion in the mixture (major isomer) can be estimated from the integral of the AA′XX′ spin system in the aromatic region. At room temperature the isomer composition of the mixture is approximately 41:31:13:3:4:2:6, the first value belonging to the 5,5-isomer and the second and third probably to the 2,5- and 1,5-isomers. Using the integrals of methyl groups on silicon for the determination of the isomer composition[9b] appeared less useful here owing to the overlap of these signals.

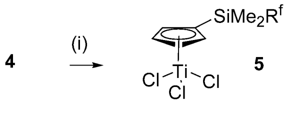
Since the trimethylsilyl group itself was suggested as compatible with fluorous biphase systems,[11] cyclopentadiene **3** with both fluorinated and nonfluorinated silyl groups was also synthesized (Scheme 2) by the reaction of isolated $LiC_5H_4SiMe_3$ with $C_8F_{17}CH_2CH_2Si(CH_3)_2Cl$. In theory, cyclopentadienes with two different substituents can appear in mixtures of up to 10 isomers between which sigmatropic shifts can occur. The presence of the isomers was noted; it was, however, impossible even to count them all properly. It was clear from the proton and carbon spectra that the major isomer was again the 5,5-isomer, in keeping with the reported data on its close analogue $C_5H_4(SiMe_3)(SiMe_2Cl)$.[10]

Scheme 2[a]



[a] $R^f = CH_2CH_2C_8F_{17}$, only major isomer of cyclopentadienes shown; (i) $ClSiMe_2R^f$; (ii) $ClSnMe_3$.

Scheme 3[a]



[a] $R^f = CH_2CH_2C_8F_{17}$; (i) $TiCl_4$.

Cyclopentadiene **4**, with one fluorinated silyl group and one trimethylstannyl group (see below), was also synthesized by the reaction of lithium salt **1a** with trimethylchlorostannane.

For the synthesis of monocyclopentadienyltrichlorotitanium(IV) complex **5** with one fluorinated silyl substituent, we applied the well-known method of $(CH_3)_3Si$ group removal. However, in the reaction of **3** with $TiCl_4$ both $(CH_3)_3Si$ and $C_8F_{17}CH_2CH_2Si(CH_3)_2$ groups were removed, resulting in a mixture of **5** with its $(CH_3)_3Si$ analogue in a ratio of about 1:1. When **4** was used instead of **3**, product **5** was pure (Scheme 3).

Dicyclopentadienyldichlorotitanium complexes are generally prepared by the reaction of (cyclopentadienyl)trichlorotitanium(IV) complexes with cyclopentadienides; this method allows preparing complexes with unequally substituted rings or by the reaction of 2 equiv of cyclopentadienide with $TiCl_3$ followed by the oxidation of the resulting dicyclopentadienyl Ti(III) complex. Both methods worked with our compounds. To prepare asymmetrically substituted titanocene dichlorides, we started from the $[\{C_5H_4Si(CH_3)_3\}TiCl_3]$ complex.[12] Reactions with isolated lithium salts **1a** and **2a** gave complexes **6** and **7**, with one of the rings substituted by $(CH_3)_3Si$ and the other with one or two $C_8F_{17}CH_2CH_2Si(CH_3)_2$ groups, respectively (Scheme 4).

Substituted titanocene dichloride **8** was synthesized by the second route, employing $PbCl_2$ as an oxidant. The orange-red crystalline product is stable in the air and melts at 181−182 °C. Suprisingly, at room temperature this compound is almost insoluble in many organic solvents, including perfluorinated ones. Crystals suitable for X-ray diffraction were obtained directly from

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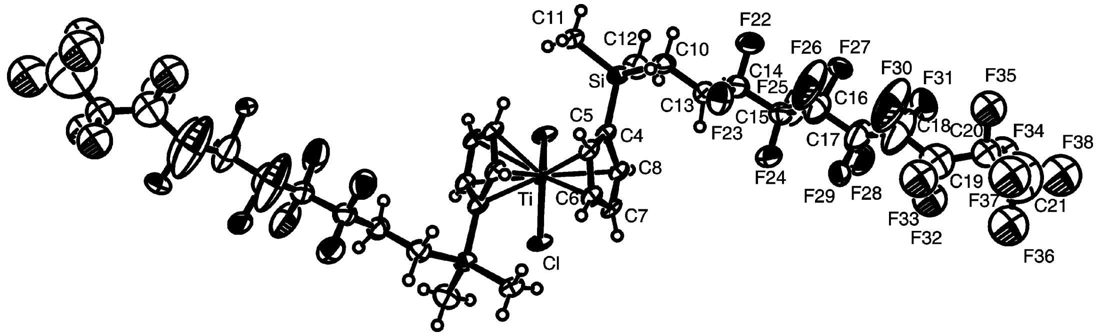
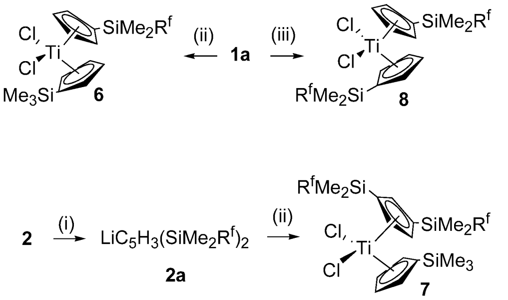


Figure 1. Structure of **8**. The disorder in the perfluoroalkyl chain is omitted for clarity (see Experimental Section). Selected bond distances (Å) and angles (deg): Ti−Cl 2.371(1), Ti−C(4) 2.402(5), Ti−C(5) 2.368(4), Ti−C(6) 2.360(4), Ti−C(7) 2.415(4), Ti−C(8) 2.396(5), Cl−Ti−Cl′ 94.58(6), Ti−C(4)−Si−C(10) 158.6(3), the angle between the normals of Cp rings is 51.1(2).

Scheme 4[a]



[a] $R^f = CH_2CH_2C_8F_{17}$; (i) BuLi; (ii) $[(C_5H_4SiMe_3)TiCl_3]$; (iii) $TiCl_3{\cdot}3THF$, then $PbCl_2$.

the reaction mixture. Only one structure of a cyclopentadienyl complex with fluorous ponytails, $[\{C_5Me_4C_6F_{13}\}RhCl_2]_2$, has been reported previously.[4a] The compound (Figure 1) has a pseudo-tetrahedral ligand arrangement around the Ti atom. The two Cp rings are in a staggered conformation, and the two silyl substituents are opposite each other, as is common in similar structures;[13] the differences in the bond lengths and angles of titanocene dichloride moieties in comparison with the published structures are generally insignificant. The fluoroalkyl chains are oriented toward themselves in neighboring molecules, thus creating separated domains that contain either fluoroalkyl chains or titanocene units. Intermolecular contacts between CH_2CH_2 groups and the second and the fourth members of the perfluoroalkyl chain in fluorous domains (2.56 and 2.80 Å, respectively) and also bridges $SiCH_3{\cdots}Cl$ and Cp-H···Cl in the titanocene domains (2.97 and 2.76 Å, respectively) are the most significant intermolecular interactions in the molecular packing of **8**.

We believe that a rather disappointing absence of solubility of **8** in perfluorinated solvents is caused by the above-mentioned strong organophilic interactions of chlorine atoms, borne out by the shape of the molecule, which in the solid state adopts the conformation of an almost linear rod, polyfluorinated at the ends. The asymmetrically substituted complexes **6** and **7** do show solubility in (perfluoro)methylcyclohexane despite their lower fluorine content (39.1 and 48.6% F, respectively, vs 51.4% F for **8**), and their partition coefficients are being measured.

In conclusion, several examples of a new class of cyclopentadienyl ligand precursors with polyfluorinated carbon chains were prepared. Fluorous ponytails in these compounds are separated from the cyclopentadiene ring by $SiMe_2CH_2CH_2$ spacers. Subsequent synthesis of both mono- and dicyclopentadienyl titanium(IV) complexes opens the possibility to explore fluorous methodology also in catalysis by early transition metal organometallic complexes.

Experimental Section

General Procedures. All the manipulations were carried out in an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Hexane and toluene were distilled from Na; diethyl ether and tetrahydrofuran, from sodium benzophenone ketyl. Solvents were kept under nitrogen. $CDCl_3$ was dried by molecular sieves and stored under nitrogen. Starting dicyclopentadiene, titanium(IV) chloride, titanium(III) chloride, trimethylsilyl chloride, trimethylstannyl chloride, butyllithium, lead(II) chloride (all Aldrich), and (2-perfluorooctyl)ethyldimethylchlorosilane (Apollo Scientific Ltd) were commercial products used without further purification. Trimethylsilylcyclopentadiene[12] and $[(C_5H_4SiMe_3)TiCl_3]$[12] were prepared according to literature methods. ^1H, $^{13}C\{^1H\}$, ^{19}F, $^{119}Sn\{^1H\}$, and $^{29}Si\{^1H\}$ (INEPT technique) spectra were measured on a Varian Mercury 300 spectrometer at 299.98, 75.44, 282.23, 111.82, and 59.60 MHz, respectively, in $CDCl_3$ solvent unless stated otherwise. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to hexamethyldisilane, except ^{119}Sn (relative to external $Sn(CH_3)_4$) and ^{19}F (relative to $CFCl_3$, referenced to external α,α,α-trifluorotoluene at −63.29 ppm). Elementary analyses of cyclopentadienes could not be determined owing to difficulties due to the volatility of polyfluorinated chain fragments. Unfortunately, high-resolution mass spectrometry analysis of the compounds having molecular weights of more than 640 (all compounds but **1** exceed this limit) was not available to us. Cyclopentadienes were very hygroscopic, and a common impurity (10−20%) was $\{Si(CH_3)_2CH_2CH_2C_8F_{17}\}_2O$, which was prepared independently by hydrolysis of $C_8F_{17}CH_2CH_2Si(CH_3)_2Cl$ and identified by ^1H, ^{13}C, and ^{29}Si NMR spectra.

$C_5H_5Si(CH_3)_2CH_2CH_2C_8F_{17}$ (1). (2-Perfluorooctyl)ethyldimethylchlorosilane (3.00 mL, 9.60 mmol) was added to a stirred solution of lithium cyclopentadienide (0.69 g, 9.60 mmol) in tetrahydrofuran (10 mL) at ca. 20 °C. The solution was stirred at 50 °C for 2 h, yielding a yellow solution and a white precipitate. The mixture was left to cool to room temperature, then the solid (LiCl) was filtered off by cannula. The solvent was removed from the filtrate in a vacuum to give a suspension of remaining LiCl in the liquid product, which was then extracted into diethyl ether (15 mL), and the extract

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was filtered. The filtrate was dried under a vacuum to yield a dark yellow liquid (4.43 g), which contains perfluorooctylethyldimethylsilylcyclopentadienes, bis(perfluorooctylethyldimethylsilyl)cyclopentadienes, and perfluorinated siloxane. Distillation gave the product (mixture of isomers) as a colorless liquid with a boiling range of 93−95 °C at 1 mbar (1.97 g, 36%). **5,5-isomer:** ^{1}H NMR (25 °C): 0.02 (s, 6H); 0.68 (m, 2H); 1.85−2.20 (m); 3.40 (bs, 1H); 6.50 (bs, 2H); 6.62 (bs, 2H). ^{1}H NMR (−40 °C): 0.02 (s, 6H); 0.66 (m, 2H); 1.85−2.20 (m); 3.46 (m, 1H); 6.60 (m, 4H). ^{13}C{^{1}H} NMR (25 °C): −4.02 (s, CH_3); 4.22 (s, CH_2); 26.09 (t, J = 23.6 Hz, CH_2); 50.56 (bs, >CH); 104−120 (m, CF_n); 131.00 (bs, CH=); 132.91 (bs, CH=). ^{13}C{^{1}H} NMR (−40 °C): −4.27 (s, CH_3); 3.44 (s, CH_2); 25.42 (t, J = 23.6 Hz, CH_2); 50.49 (bs, >CH); 104−120 (m, CF_n); 130.78 (bs, CH=); 132.68 (bs, CH=). ^{29}Si{^{1}H} NMR (25 °C): 4.03(s). **2,5-isomer:** ^{1}H NMR (25 °C): 0.20 (s, 6H); 0.88 (m); 1.85−2.20 (m); 3.03 (m, 2H); 6.70 (m, 1H); 6.72 (m, 1H); 6.87 (m, 1H). ^{1}H NMR (−40 °C): 0.20 (s, 6H); 0.92 (t, J = 7.2 Hz); 1.85−2.20 (m); 3.05 (m, 2H); 6.74 (m, 1H); 6.76 (m, 1H); 6.89 (m, 1H). ^{13}C{^{1}H} NMR (25 °C): −3.11 (s, CH_3); 5.45 (s, CH_2); 26.06 (t, J = 23.6 Hz, CH_2); 45.23 (s, CH_2); 104−120 (m, CF_n); 132.91 (s, CH=); 138.42 (s, CH=); 143.14 (s, CH=); 144.65 (s, >C=). ^{13}C{^{1}H} NMR (−40 °C): −3.37 (s, CH_3); 4.77 (s, CH_2); 25.39 (t, J = 23.6 Hz, CH_2); 45.04 (s, CH_2); 104−120 (m, CF_n); 138.56 (s, CH=); 142.94 (s, CH=); 144.64(s, >C=). ^{29}Si{^{1}H} NMR (25 °C): −7.45 (s). **1,5-isomer:** ^{1}H NMR (25 °C): 0.16 (s, 6H); 0.84 (m); 1.85−2.20 (m); 3.05 (m, 2H). ^{1}H NMR (−40 °C): 0.16 (s, 6H); 0.84 (m); 1.85−2.20 (m); 3.08 (m, 2H). ^{13}C{^{1}H} NMR (25 °C): −2.52 (s, CH_3); 5.80 (s, CH_2); 26.06 (t, J not resolved, CH_2); 34.85 (s, CH_2); 104−120 (m, CF_n); 136.61 (s, CH=); 142.61 (s, CH=); 144.13 (s, CH=); 145.41 (s, >C=). ^{13}C{^{1}H} NMR (−40 °C): −2.78 (s, CH_3); 4.92 (s, CH_2); 34.54 (s, CH_2); 104−120 (m, CF_n). ^{29}Si{^{1}H} NMR (25 °C): −7.41 (s).

$C_5H_4[Si(CH_3)_2CH_2CH_2C_8F_{17}]_2$ (2). (2-Perfluorooctyl)ethyldimethylchlorosilane (1.93 mL, 6.25 mmol) was added to a stirred solution of lithium (2-perfluorooctyl)ethyldimethylsilylcyclopentadienide (3.60 g, 6.25 mmol) in tetrahydrofuran (5 mL) at ca. 20 °C. The solution was stirred at 20 °C for 2 h and refluxed for 2 h, yielding an orange solution and a white precipitate. The mixture was left to cool to room temperature, then the solid (LiCl) was filtered off by cannula. The solvent was removed from the filtrate in a vacuum to give a suspension of remaining LiCl in the liquid product, which was then extracted into diethyl ether (15 mL), and the extract was filtered. The product was dried under a vacuum to yield the orange liquid (5.31 g, 79%). The product was distilled under a vacuum to yield a colorless liquid with a boiling range of 167−172 °C at 1 mbar (0.7 g, 13%). As a byproduct, 1.31 g of (2-perfluorooctyl)ethyldimethylsilylcyclopentadiene boiling at 93−95 °C at 1 mbar was isolated. **5,5-isomer:** ^{1}H NMR (25 °C): −0.02 (s, 12H); 0.43 (m, 4H); 1.64−2.20 (m); 6.60 (AA′XX′ system, 4H). ^{13}C{^{1}H} NMR (25 °C): −2.63 (s, CH_3); 3.95 (s, CH_2); 26.09 (t, J = 22.8 Hz, CH_2); 56.18 (s, >C<); 104−120 (m, CF_n); 132.12 (s, CH=); 134.96 (s, CH=). ^{29}Si{^{1}H} NMR (25 °C): −0.19(s). ^{19}F NMR (25 °C): −124.7 (s, 2F); −121.8 (s, 2F); −121.2 (s, 2F); −120.4 (s, 6F); −114.7 (s, 2F); −79.5 (s, 3F).

$C_5H_4[Si(CH_3)_2CH_2CH_2C_8F_{17}][Si(CH_3)_3]$ (3). (2-Perfluorooctyl)ethyldimethylchlorosilane (3.84 mL, 12.40 mmol) was added to a stirred solution of lithium (trimethylsilyl)cyclopentadienide (1.79 g, 12.40 mmol) in tetrahydrofuran (10 mL) at approximately 20 °C. The solution was stirred at 50 °C for 2 h, yielding an orange solution and a white precipitate. The mixture was left to cool to room temperature, then the solid (LiCl) was filtered off by cannula. The solvent was removed from the filtrate in a vacuum to give a suspension of remaining LiCl in the liquid product, which was then extracted into diethyl ether (15 mL), and the extract was filtered. The product was dried under a vacuum to yield the orange-brown liquid (6.59 g, 83%). This liquid was distilled under a vacuum to yield a light yellow liquid with a boiling range of 119−123 °C at 1 mbar. **5,5-isomer:** ^{1}H NMR (25 °C): −0.11 (s, 9H); −0.02 (s, 6H); 0.43 (m, 2H); 1.68−2.20 (m); 6.56 (AA′XX′ system, 4H). ^{13}C{^{1}H} NMR (25 °C): −2.20 (s, CH_3); −0.97 (s, CH_3); 4.03 (s, CH_2); 26.35 (t, J = 23.6 Hz,CH_2); 56.53 (s, >C<); 108−120 (m, CF_n); 131.29 (s, CH=); 135.49 (s, CH=). ^{29}Si{^{1}H} NMR (25 °C): −0.47; −1.64.

$C_5H_4[Si(CH_3)_2CH_2CH_2C_8F_{17}][Sn(CH_3)_3]$ (4). A solution of trimethylstannyl chloride (0.23 g, 1.16 mmol) in tetrahydrofuran (5 mL) was added to a stirred solution of lithium (2-perfluorooctyl)ethyldimethylsilylcyclopentadienide (0.67 g, 1.16 mmol) in tetrahydrofuran (5 mL) at approximately 20 °C. The solution was stirred at 20 °C for 2 h and refluxed for 2.5 h, yielding a brown solution and a beige precipitate. The mixture was left to cool to room temperature, then the solid (LiCl) was filtered off by cannula. The solvent was removed from the filtrate in a vacuum to give a suspension of remaining LiCl in the liquid product, which was then extracted into diethyl ether (15 mL), and the extract was filtered. The product was dried under a vacuum to yield a brown liquid (0.62 g, 73%). **5,5-isomer:** ^{1}H NMR (25 °C): 0.02 (s, 9H); 0.18 (s, 6H); 0.63 (m, 2H); 1.72 (m, 2H); 6.50 (bs, 4H). ^{13}C{^{1}H} NMR (25 °C): −7.57 (s, CH_3Sn); −2.60 (s, CH_3Si); 5.60 (s, CH_2Si); 25.79 (t, J = 23.5 Hz, CH_2CF_2); 72.74 (bs, >C<); 108−120 (m, CF_n); 112.72 (s, CH=); 132.29 (s, CH=). ^{29}Si{^{1}H} NMR (25 °C): −2.03. ^{119}Sn{^{1}H} NMR (25 °C): 19.54.

[{η^5-$C_5H_4Si(CH_3)_2CH_2CH_2C_8F_{17}$}$TiCl_3$] (5). The solution of **4** (0.32 g, 0.44 mmol) in 3 mL of toluene was added dropwise to the solution of titanium tetrachloride (0.07 mL, 0.44 mmol) in 2 mL of toluene at room temperature. The reaction mixture was stirred overnight at room temperature. The solid phase, probably titanium(IV) oxide, was filtered off, and the filtrate was dried in a vacuum. The residue was then extracted with hexane (5 mL). Part of the solvent from the collected extracts was removed, and when a solid started to crystallize, the flask was put into a bath (−80 °C). The yellow-orange solid was then filtered off and dried in a vacuum. The pure product was obtained as a yellow-orange solid (0.09 g, 28%). Anal. Calcd for $C_{17}H_{14}Cl_3F_{17}SiTi$: C, 28.22; H, 1.95. Found: C, 28.17; H, 2.02. ^{1}H NMR (25 °C): 0.45 (s, 6H); 0.86 (m); 1.9−2.4 (m); 7.17 (AA′XX′ system, 4H). ^{13}C{^{1}H} NMR (25 °C): −3.08 (s, CH_3); 5.63 (s, CH_2); 25.64 (t, J = 22.2 Hz,CH_2); 108−120 (m, CF_n); 126.53 (s, CH=); 129.28 (s, CH=); 138.35(s, >C=). ^{29}Si{^{1}H} NMR (25 °C): −1.82.

[{η^5-$C_5H_4Si(CH_3)_2CH_2CH_2C_8F_{17}$}{$\eta^5$-$C_5H_4Si(CH_3)_3$}$TiCl_2$] (6). The solution of lithium (2-perfluorooctyl)ethyldimethylsilylcyclopentadienide (0.14 g, 0.24 mmol) in 2 mL of tetrahydrofuran was added dropwise to the solution of [($C_5H_4SiMe_3$)$TiCl_3$] (0.07 g, 0.24 mmol) in 2 mL of tetrahydrofuran. The yellow reaction mixture became reddish and was refluxed for 1.5 h. The mixture was then left to cool to room temperature, the solid (LiCl) was filtered off, and the filtrate was dried in a vacuum. The residue was extracted with hexane (3 mL), and after filtration the solvent was removed under a vacuum. The product was obtained as an orange-red oil (0.18 g, 90%). Anal. Calcd for $C_{25}H_{27}Cl_2F_{17}Si_2Ti$: C, 36.38; H, 3.30. Found: C, 36.30; H, 3.49. ^{1}H NMR (25 °C): 0.29 (s, 9H); 0.38 (s, 6H); 0.99 (m, 2H); 2.00 (m); 6.64 (AA′XX′ system, 4H); 6.69 (AA′XX′ system, 4H). ^{13}C{^{1}H} NMR (25 °C): −2.34 (s, CH_3SiCH_2); −0.09 (s, CH_3); 6.13 (s, CH_2); 25.79 (t, J = 23.7 Hz,CH_2); 109−120 (m, CF_n); 117.66 (s, CH=); 120.14 (s, CH=); 129.66 (s, CH=); 130.41 (s, CH=); 130.96 (s, >C=); 132.73 (s, >C=). ^{29}Si{^{1}H} NMR (25 °C): −4.86; −3.10.

[{η^5-$C_5H_3[Si(CH_3)_2CH_2CH_2C_8F_{17}]_2$}{$\eta^5$-$C_5H_4Si(CH_3)_3$}$TiCl_2$] (7). The solution of lithium bis[(2-perfluorooctyl)ethyldimethylsilyl)]cyclopentadienide (0.81 g, 0.75 mmol) in 4 mL of tetrahydrofuran was added dropwise to the solution of (trimethylsilylcyclopentadienyl)trichlorotitanium(IV) complex (0.22 g, 0.75 mmol) in 3 mL of tetrahydrofuran. The yellow reaction mixture became reddish and was stirred overnight at room temperature and then refluxed for 9 h and left to cool to room temperature. The solid phase was filtered off and the filtrate dried in a vacuum. The residue was then extracted with

Table 1. Crystal Data and Structure Refinement for 8

formula	$C_{34}H_{28}Cl_2F_{34}Si_2Ti_1$		
cryst class	monoclinic	space group	*C*2/*c*
a	52.4839(12) Å	α	90°
b	6.4826(1) Å	*β*	99.784(1)°
c	14.1380(3) Å	*γ*	90°
volume	4740.24(17) $Å^3$	*Z*	4
radiation type	Mo Kα	wavelength	0.710730 cm^{-1}
D_x	1.76	M_r	1257.5
μ	0.506 cm^{-1}	temperature	150 K
size	0.40 × 0.30 × 0.10 mm		
color	deep red	habit	plate
cell from	36 481 reflns	*θ* range	1−26.02°
diffractometer type	KappaCCD	scan type	2*θ*/*ω*
no. of reflns measd	37 247	no. of indep reflns	4694
R_{int}	0.036	θ_{max}	26.14°
h_{min}, h_{max}	0, 64		
k_{min}, k_{max}	0, 8		
l_{min}, l_{max}	−17, 17		
refinement on *F*			
R-factor	0.081	weighted *R*-factor	0.056
max. shift/su	0.0005		
$\Delta\rho_{min}$	−0.67	$\Delta\rho_{max}$	0.95
no. of reflns used	3562	*σ*(*I*) limit	1.96
no. of params	403	goodness of fit	1.050

hexane (10 mL). Part of the solvent from the extract was removed, and when a solid started to crystallize, the flask was put into a freezer (−30 °C). The orange solid was then filtered off and dried in a vacuum. The product was obtained as an orange solid (0.79 g, 79%). Anal. Calcd for $C_{37}H_{36}Cl_2F_{34}Si_3Ti$: C, 33.42; H, 2.73. Found: C, 33.99; H, 2.79. ^1H NMR (25 °C): 0.32 (s, 9H); 0.37 (s, 6H); 0.38 (s, 6H); 0.91 (m, 4H); 1.91 (m, 4H); 6.62 (AA′XX′ system, 4H); 6.78 (d, *J* = 1.8 Hz, 2H); 7.00 (t, *J* = 1.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (25 °C): −2.70 (s, CH_3SiCH_2); −2.66 (s, CH_3SiCH_2); 0.03 (s, CH_3); 6.50 (s, CH_2); 25.67 (t, *J* = 23.8 Hz,CH_2); 109−125 (m, CF_n); 115.80 (s, CH=); 128.67 (s, CH=); 130.78 (s, >C=); 133.05 (s, CH=); 135.20 (s, >C=); 137.90 (s, CH=). $^{29}Si\{^1H\}$ NMR (25 °C): −4.86; −3.34.

[{η^5-$C_5H_4Si(CH_3)_2CH_2CH_2C_8F_{17}$}{$\eta^5$-$C_5H_4Si(CH_3)_2CH_2CH_2C_8F_{17}$}$TiCl_2$] (8). The solution of lithium (2-perfluorooctyl)ethyldimethylsilylcyclopentadienide (0.38 g, 0.66 mmol) in 3 mL of tetrahydrofuran was added dropwise to the slurry of $TiCl_3$·3THF (0.09 g, 0.39 mmol) in 3 mL of tetrahydrofuran. The dark reaction mixture was refluxed for 4 h. Lead(II) chloride (0.05 g, 0.17 mmol) was added into the dark blue reaction mixture at room temperature. The reaction mixture became reddish and was refluxed for 2 h. The mixture was left to cool to room temperature, the solid phase (LiCl and Pb) was filtered off, and the filtrate was put into a freezer (−30 °C). The solid was then filtered off and dried in a vacuum. Red platelike crystals were obtained (0.13 g, 31%). Mp: 181−182 °C. Anal. Calcd for $C_{34}H_{28}Cl_2F_{34}Si_2Ti$: C, 32.47; H, 2.24. Found: C, 31.31; H, 2.41. ^1H NMR ($C_2Cl_4D_2$, 80 °C): 0.41 (s, 12H); 1.05 (m, 4H); 1.98−2.22 (m, 4H); 6.68 (AA′XX′ system, 8H). $^{13}C\{^1H\}$ NMR ($C_2Cl_4D_2$, 80 °C): −2.52 (s, CH_3); 6.06 (s, CH_2); 25.84 (t, *J* not resolved, CH_2); 109−125 (m, CF_n); 118.07 (s, CH=); 129.99 (s, CH=); 131.39 (s, >C=). $^{29}Si\{^1H\}$ NMR ($C_2Cl_4D_2$, 80 °C): −3.13.

Crystal Structure Determination of 8. The data were measured at 150(2) K on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation.[14] The structure was solved by direct methods.[15] The whole structure was refined by full matrix least-squares on *F* values[16] to final *R* = 0.0807 and R_w = 0.0593 using 3562 independent reflections (θ_{max} = 26.02°). The independent part of the unit cell is created by half of the molecule. All heavy atoms until the fifth member of the perfluorinated chain were refined anisotropically. The rest of the molecule was disordered and refined only isotropically. Atoms were localized from the difference Fourier maps. According to similar compounds, the disorder of this group was modeled and restraints were applied to the C−C and C−F bonds, 1.47 and 1.35 Å, respectively. Some of these bonds were still out of the normal ranges for these bonds; this phenomenon was already reported and discussed for similar long and disordered perfluorinated chains.[17] Hydrogen atoms were located from the expected geometry and were refined isotropically. Only one restraint was applied to the one methyl hydrogen; the C−H distance was adjusted to 1.00 Å. The crystal data are summarized in Table 1.

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 204018. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: Details of crystal structure determination. This material is available free of charge via the Internet at http://pubs.acs.org.

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