# Fluorosilyl-Substituted Cyclopentadienyltitanium(IV) Complexes: Synthesis, Structure, and Styrene Polymerization Behavior[#]

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The synthesis and characterization of new halo-silyl-substituted titanium(IV) derivatives [$TiCl_3(\eta^5$-$C_5H_4SiCl_3)$] (**9**), [$TiCl_3(\eta^5$-$C_5H_4SiMe_2F)$] (**10**), [$TiCl_3(\eta^5$-$C_5H_4SiMeF_2)$] (**11**), [$TiCl_3(\eta^5$-$C_5H_4SiF_3)$] (**12**), and [$TiF_3(\eta^5$-$C_5H_4SiMe_2F)$] (**13**) are reported. The reaction of lithiated trimethylsilylcyclopentadienide with $Me_2SiCl_2$, $MeSiCl_3$, or $SiCl_4$ gave chlorosilyl(trimethylsilyl)cyclopentadienes that were fluorinated with $Me_3SnF$ to yield fluorosilyl derivatives $C_5H_4(SiMe_2F)SiMe_3$ (**4**), $C_5H_4(SiMeF_2)SiMe_3$ (**5**), and $C_5H_4(SiF_3)SiMe_3$ (**6**), respectively. Addition of disilylated compounds **4**−**6** to a solution of $TiCl_4$ gave the respective half-sandwich titanium complexes **10**−**12**, which could be alternatively prepared by selective fluorination of the corresponding chlorosilyl-substituted cyclopentadienyltitanium(IV) trichlorides with $Me_3SnF$. Completely fluorinated [$TiF_3(C_5H_4SiMe_2F)$] (**13**) was prepared from [$TiCl_3(C_5H_4SiMe_2Cl)$] (**7**) and 4 equiv of $Me_3SnF$. The molecular structures of the pentameric **13** and the monomeric **10** were determined by X-ray diffraction analysis. The $^{47,49}$Ti NMR and UV−vis spectroscopy showed the electron-releasing nature of the $SiMe_2Cl$, $SiMe_2F$, $SiMeCl_2$, and $SiMeF_2$ substituents, whereas $SiCl_3$ and $SiF_3$ groups had electron-withdrawing properties. The catalytic behavior of these half-sandwich titanium compounds in styrene polymerization was studied in the presence of excess methylaluminoxane.

## Introduction

Group 4 metallocenes represent an important class of organometallic compounds that are applicable as catalysts in homogeneous polymerization[1] of olefins. The substitution on the cyclopentadienyl ring is the main route used for modifying the properties of these complexes.[2] Whereas the initial step of the catalytic process is the attack of the electron-rich olefin on the electron-deficient metal center,[3] one can anticipate that decreasing the electron density at the central metal atom will lead to an increased polymerization activity of the modified catalyst. In 1986, Gassman and Winter reported preparation and characterization of the first titanocene complex bearing a strongly electron-withdrawing $CF_3$ substituent.[4] Since that time the syntheses of Group 4 compounds with electron-withdrawing chloro,[5] carbomethoxy,[6] carboxamide,[7] or perfluoroaryl[8] substituents on the cyclopentadienyl ring have been published, and some of these complexes were used as olefin polymerization catalysts.[9] Recently, the synthesis[10−12] and reactivity studies[13,14] of chlorosilyl-substituted cyclopentadienyltitanium(IV) compounds were published, but their electronic properties were not investigated.

We report here the syntheses of novel titanium complexes bearing trichlorosilyl-, fluoro(dimethyl)silyl-, difluoro(methyl)-silyl-, and trifluorosilyl-substituted cyclopentadienyl ligands. All compounds were characterized by spectroscopic methods in order to determine electronic effects of the halosilyl substituents on the titanium atom. We also present results of our studies of styrene polymerization catalyzed by these complexes in the presence of an excess of methylaluminoxane.

## Results and Discussion

**Synthesis and Characterization of Ligands.** 1-(Trichlorosilyl)-1-(trimethylsilyl)cyclopentadiene (**3**) was prepared by

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[#] Dedicated to Dr. Karel Mach on the occasion of his 70th birthday.

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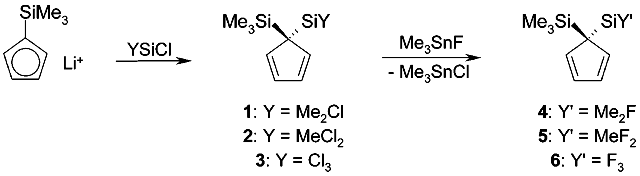
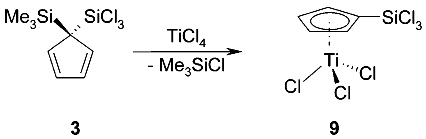
10.1021/om070098r CCC: $37.00

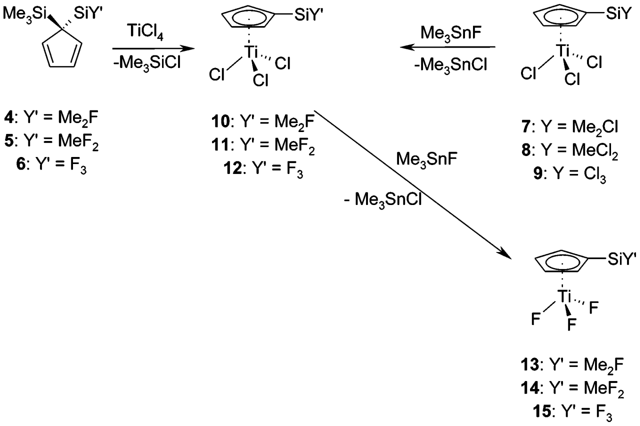
**Scheme 1**



**Scheme 2**



**Scheme 3**



the reaction of (trimethylsilyl)cyclopentadienyllithium with silicon tetrachloride in hexane according to the methods described for the chloro(dimethyl)silyl[10] and dichloro(methyl)silyl[11] derivatives **1** and **2**, respectively; see Scheme 1.

Scheme 1 depicts the reactions of the silyl-disubstituted cyclopentadienes **1**−**3** with a common fluorinating agent, $Me_3SnF$,[23] to give the respective fluorosilyl derivatives $C_5H_4(SiMe_2F)SiMe_3$ (**4**), $C_5H_4(SiMeF_2)SiMe_3$ (**5**), and $C_5H_4(SiF_3)SiMe_3$ (**6**). $^1H$ and $^{19}F$ NMR spectroscopic studies showed that the irreversible replacement of chlorine atom(s) by fluorine is complete in 30 min at ambient temperature.

$^{19}F$ NMR spectroscopy showed that the reaction of **3** with $Me_3SnF$ proceeded rapidly and completely at ambient temperature giving 1-(trifluorosilyl)-1-(trimethylsilyl)cyclopentadiene (**6**). However, purification of **6** by vacuum distillation was only partially successful since large amounts of the $Me_3SnCl$ produced in the reaction always contaminated the product. Hence we used $Bu_3SnF$ instead of $Me_3SnF$. Thus, after vacuum distillation, analytically pure product could be isolated.

**Preparation of Titanium(IV) Complexes.** Treatment of $C_5H_4(SiCl_3)SiMe_3$ (**3**) with $TiCl_4$ in dichloromethane or toluene gave $[TiCl_3(\eta^5\text{-}C_5H_4SiCl_3)]$ (**9**) with selective elimination of $Me_3SiCl$ (Scheme 2). The yellow product **9** is moderately soluble in organic solvents and was easily purified by crystallization from hexane or vacuum sublimation. Titanium complex **9** is air- and moisture-sensitive but could be stored as a solid under inert atmosphere. Toluene or dichloromethane solutions of **9** slowly turned green-yellow on standing in direct light under argon at ambient temperature. Similar behavior of related half-metallocenes $[TiCl_3(\eta^5\text{-}C_5H_4SiMe_2Cl)]$ (**7**) and $[TiCl_3(\eta^5\text{-}C_5H_4SiMeCl_2)]$ (**8**) was described by Royo et al.[11]

The fluorosilyl-substituted cyclopentadienes **4**−**6** reacted with titanium tetrachloride to give new half-sandwich titanium(IV) trichlorides **10**−**12** bearing fluorosilyl substituents on the Cp ring. Compounds **10**−**12** are moisture-sensitive bright yellow microcrystalline solids that can be purified by crystallization from hexane or, better, by vacuum sublimation. The multinuclear NMR spectra were consistent with their proposed structures. For details see the Experimental Section.

An alternative method for the preparation of complexes **10**−**12** is the selective fluorination of the corresponding chlorosilyl-substituted metallocenes **7**−**9** by $Me_3SnF$ (Scheme 3). NMR spectroscopy showed that fluorination is very selective, and Ti−Cl bonds remain untouched when the molar amount of $Me_3SnF$ used is less than or equal to the number of Si−Cl bonds. Selectivity of the fluorination process was also confirmed by the determination of the molecular structure of **10**.

If an excess of the fluorination agent is used, fluorides readily replace all chlorine atoms in the molecule. We isolated and characterized the compound $[TiF_3(\eta^5\text{-}C_5H_4SiMe_2F)]$ (**13**) and determined its molecular structure. The oligomeric nature of **13** in a solution was evidenced by very broad signals in the $^1H$, $^{13}C$, and $^{19}F$ NMR spectra. A broad $^{19}F$ resonance at 173.42 ppm corresponds to fluorine nuclei bonded to the titanium atom. All attempts to prepare fluorosilyl-cyclopentadienyl titanium(IV) trifluorides of the formula $[TiF_3(\eta^5\text{-}C_5H_4SiMeF_2)]$ (**14**) and $[TiF_3(\eta^5\text{-}C_5H_4SiF_3)]$ (**15**) led to completely insoluble orange solids that could not be satisfactorily characterized.

**$^{47,49}$Ti NMR and Electronic Absorption Spectra.** It was demonstrated previously[16,17] that the introduction of electron-releasing groups (alkyl, trimethylsilyl, trimethylstannyl, etc.) on the cyclopentadienyl ring leads to a decrease of the HOMO−LUMO energy gap and results in an increase of $\lambda_{max}$ (wavelength of the first CT band in the electronic spectra) as well as in a downfield shift of the $\delta$(Ti) signal in the $^{47,49}$Ti NMR spectrum. We used Ti NMR and UV−vis spectroscopy to assess the electronic effects of halosilyl substituents on the metal nucleus. Table 1 lists $^{47,49}$Ti NMR data and $\lambda_{max}$ values for the studied complexes together with corresponding data for related half-sandwich titanium(IV) trichlorides. We note that no interactions between $^{47,49}$Ti and $^{19}F$ nuclei were observed in the NMR spectra of fluorosilyl complexes **10** and **11**.

When parent complex $CpTiCl_3$ is considered to be a reference, all substituted compounds with higher $\lambda_{max}$ and $\delta$(Ti) values have greater electron density at the titanium atom; that is, the substituent on the cyclopentadienyl ring has an electron-donating effect. From obtained data it is evident that $SiMe_2Cl$, $SiMe_2F$, $SiMeCl_2$, and $SiMeF_2$ groups show features typical for electron-releasing substituents. The introduction of the $SiCl_3$ group causes a high-field shift of $\delta$(Ti) by 4.1 ppm. Analogously, the electron-withdrawing properties of $SiCl_3$ and $SiF_3$ groups cause a blue-shift of $\lambda_{max}$ values by 4 and 19 nm, for complexes **9** and **12**, respectively.

Chart 1 shows the dependence of $\delta(^{49}Ti)$ and $\lambda_{max}$ on the nature of the substituent bonded to the cyclopentadienyl ring; data for complex $[TiCl_3(\eta^5\text{-}C_5H_4SiMe_3)]$ and reference compound $CpTiCl_3$ are included for the purpose of comparison. The properties of the substituent on the cyclopentadienyl ring change from electron-releasing to electron-withdrawing in the order

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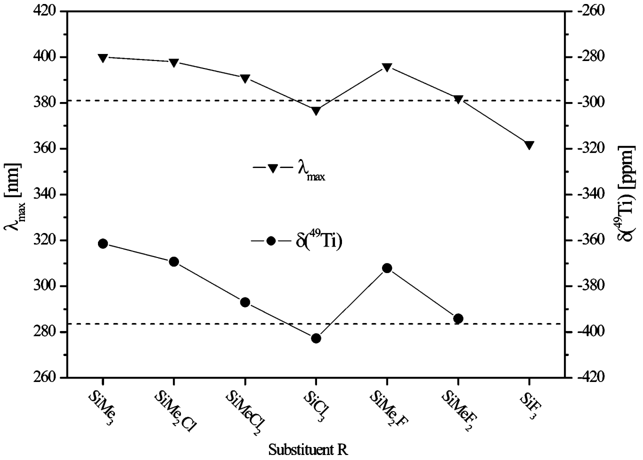
**Table 1. $^{47,49}$Ti NMR Data and Absorption Maxima of the First CT Transition in Electronic Spectra**

| compound | $\delta(^{49}Ti)$ [ppm] | $\Delta\nu_{1/2}(^{49}Ti)$ [Hz] | $\delta(^{47}Ti)$ [ppm] | $\Delta\nu_{1/2}(^{47}Ti)$ [Hz] | $\lambda_{max}$ [nm] | ref |
|---|---|---|---|---|---|---|
| **7** | −369.3[a] | 69 | −635.8 | 172 | 398 | 16 |
| **8** | −387.0[b] | 97 | −652.7 | 255 | 391 | this work |
| **9** | −402.3[b] | 211 | −668.8 | 923 | 377 | this work |
| **10** | −372.1[b] | 81 | −639.5 | 229 | 396 | this work |
| **11** | −394.1[b] | c | d | d | 382 | this work |
| **12** | d | d | d | d | 362 | this work |
| $CpTiCl_3$ | −396.5[e] | 49 | −662.7 | 74 | 381 | 16 |
| $(Me_3SiCp)TiCl_3$ | −361.4[a] | 36 | −628.0 | 85 | 400 | 16 |

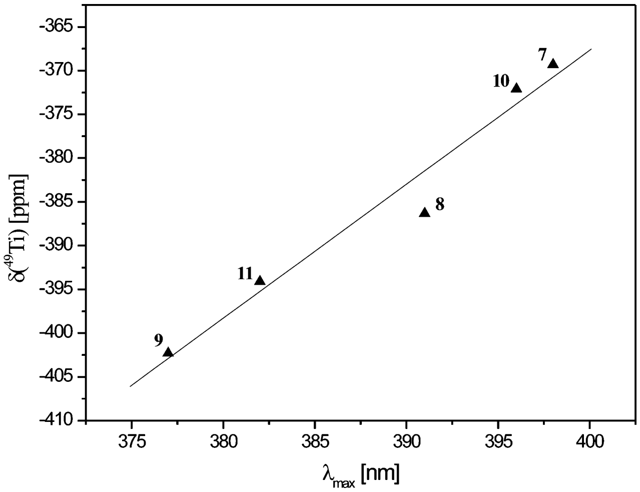
[a] $CD_2Cl_2$. [b] Toluene-$d_8$. [c] Not determined. [d] Too broad to be observed. [e] $CDCl_3$.

**Chart 1. Dependence of $\lambda_{max}$ and $\delta(^{49}Ti)$ on the Nature of the Substituent R in the Series of $RC_5H_4TiCl_3$ Complexes[a]**



[a] Dashed lines correspond to data for reference compound $CpTiCl_3$.

**Chart 2. Correlation between $\delta(^{49}Ti)$ and $\lambda_{max}$ for the Complexes 7−11**



$SiMe_3 > SiMe_2Cl > SiMe_2F > SiMeCl_2 > SiMeF_2 \approx H > SiCl_3 > SiF_3$.

Similar to the other half-sandwich titanium(IV) trihalides, a nearby linear relationship (correlation coefficient = 0.9808) between the $^{49}$Ti NMR chemical shift and $\lambda_{max}$ was found; see Chart 2. The principles of this phenomenon were explained elsewhere in terms of variation in the paramagnetic contribution to the Ti nucleus shielding.[17] For the series of the presently studied compounds this implies a similar character of their frontier orbitals.

The next NMR parameter observed, $^{47,49}$Ti resonance half-width at half-height ($\Delta\nu_{1/2}$), is usually attributed to the symmetry or asymmetry of the electronic environment at the titanium atom. Since the electronic environment at the titanium atom is affected by substituents bonded to the cyclopentadienyl ring, it is not surprising that the changes in the number of halogen atoms bonded to the Si atom cause variation in $\Delta\nu_{1/2}$. In the series of studied complexes $^{47,49}$Ti resonance half-widths increase with an increasing number of halide atoms on the silyl group and increase on going from a less electronegative chlorosilyl to a more electronegative fluorosilyl substituent. The largest $\Delta\nu_{1/2}$ value was observed for trichlorosilyl complex **9**, and significant line broadening prevented the Ti nucleus resonance signal for $[TiCl_3(\eta^5\text{-}C_5H_4SiF_3)]$ (**12**) from being observed.

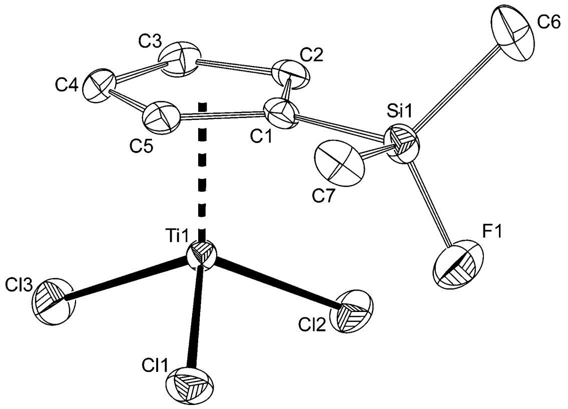


**Figure 1.** Thermal ellipsoid plot (50% probability) of **10**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ti1−Cg1, 2.001(1); Ti1−Cl1, 2.2320(9); Ti1−Cl2, 2.2230(9); Ti1−Cl3, 2.2336(9); Cl1−Ti1−Cl2, 104.76(4); Cl2−Ti1−Cl3, 101.89(4); Cl1−Ti1−Cl3, 102.98(4).

**Crystal Structure.** In the crystals of **10**, two crystallographically independent but essentially identical molecules are present. The structure of one of them is depicted in Figure 1, together with the atomic numbering scheme. Crystallographic data are listed in Table 4. In the molecule of **10** the cyclopentadienyl ring is almost planar, with no carbon atom deviating more than 0.01 Å. The coordination of the Ti atom can be described as a three-legged piano-stool configuration, with geometrical parameters very close to those reported for $[TiCl_3(C_5H_5)]$, $[TiCl_3(C_5H_4SnMe_3)]$, or $[TiCl_3(C_5H_4SiMe_2Ph)]$.[18] The fluorine atom is located below the cyclopentadienyl ring plane. The Ti···F separation is 3.652(2) Å [3.575(2) Å] (hereafter, the values in brackets refer to the second independent molecule). The dihedral angle between the cyclopentadienyl ring plane and the $C_{ipso}$−Si bond vector is 1.5(2)° [0.1(2)°].

There are two independent (**13A** and **13B**) molecules with minor structural differences in the unit cell of **13**. Table 2 lists selected geometric parameters for **13A** that will be used in the subsequent discussion. Crystallographic data are summarized

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**Table 2. Selected Geometric Parameters for 13 (species A)**

| | | | | | |
|---|---|---|---|---|---|
| | | Bond Lengths (Å) | | | |
| Ti1−Cg1 | 2.025(2) | Ti1−F12 | 1.813(2) | Ti2−F13 | 1.975(2) |
| Ti2−Cg2 | 2.054(1) | Ti1−F13 | 2.037(2) | Ti2−F23 | 1.967(2) |
| Ti3−Cg3 | 2.076(1) | Ti1−F14 | 1.805(2) | Ti2−F22 | 2.035(1) |
| Ti4−Cg4 | 2.067(1) | Ti1−F15 | 1.939(2) | Ti1···Ti2 | 3.3100(7) |
| Ti5−Cg5 | 2.030(1) | Ti2−F15 | 2.159(2) | Ti3···Ti4 | 3.3039(6) |
| | | Bond Angles (deg) | | | |
| F12−Ti1−F13 | 72.15(7) | Cg2−Ti2−F15 | 172.54(6) | F16−Ti2−F22 | 151.35(7) |
| F12−Ti1−F14 | 80.48(8) | Cg2−Ti2−F16 | 104.88(7) | Ti1−F15−Ti2 | 107.63(7) |
| F13−Ti1−F15 | 90.94(10) | F13−Ti2−F23 | 150.04(7) | Ti2−F23−Ti4 | 148.98(8) |

**Table 3. Results of Styrene Polymerization Catalyzed by Studied Compounds[a)]**

| catalyst | Al/Ti | conversion [%] | A[b] | $M_n$[c] [kg·mol$^{-1}$] | $M_w/M_n$[c] | $T_m$[d] [°C] |
|---|---|---|---|---|---|---|
| $CpTiCl_3$ | 800 | 98 | 89 | 8.6 | 2.47 | 252.7 |
| **7** | 800 | 99 | 89 | 16.1 | 2.34 | 266.1 |
| **8** | 800 | 93 | 84 | *e* | *e* | 264.6 |
| **9** | 800 | 89 | 81 | *e* | *e* | 265.1 |
| **10** | 800 | 81 | 73 | 64.0 | 2.32 | 263.9 |
| **11** | 800 | 99 | 89 | 57.4 | 2.35 | 264.3 |
| **12** | 800 | 87 | 79 | *e* | *e* | 265.1 |
| **13** | 400 | 51 | 46 | 17.5 | 2.24 | 266.5 |
| | 800 | 47 | 42 | | | |
| | 1600 | 53 | 48 | | | |

[a] Polymerization conditions: [Ti] = 300 $\mu$M, [styrene] = 0.52 M, reaction time 2 h, toluene, 50 °C, total volume 30 mL. [b] Activity: kg PS/(mol$_{Ti}^{-1}$ × h$^{-1}$). [c] Determined by SEC. [d] Melting temperature of polystyrene. [e] Not determined due to insolubility of polymer in 1,2,4-trichlorobenzene.

**Table 4. Crystallographic Data for 10 and 13**

| | **10** | **13** |
|---|---|---|
| empirical formula | $C_7H_{10}Cl_3FsiTi$ | $C_{35}H_{50}F_{20}Si_5Ti_5$ |
| cryst syst | triclinic | monoclinic |
| space group | $P\bar{1}$ (No. 2) | $P2_1/c$ (No. 14) |
| *a* (Å) | 6.4370(3) | 14.0743(1) |
| *b* (Å) | 12.5910(5) | 26.4287(2) |
| *c* (Å) | 14.9830(10) | 26.6932(2) |
| α (deg) | 96.361(5) | 90 |
| β (deg) | 12.5910(5) | 93.2874(5) |
| γ (deg) | 92.040(5) | 90 |
| *Z* | 4 | 8 |
| *V* (Å$^3$) | 1168.54(11) | 9912.61(13) |
| $D_c$ (g cm$^{-3}$) | 1.680 | 1.649 |
| cryst size (mm) | 0.3 × 0.25 × 0.075 | 0.3 × 0.25 × 0.15 |
| cryst shape | yellow plate | orange plate |
| $\mu$ (mm$^{-1}$) | 1.486 | 0.994 |
| *F*(000) | 592 | 4960 |
| *h*; *k*; *l* range | −8, 8; −16, 16; −19, 19 | −18, 18; −34, 34; −34, 34 |
| $\theta$ range (deg) | 1.37−27.5 | 1.45−27.5 |
| no. of reflns measd | 17 673 | 149 981 |
| no. of indep reflns ($R_{int}$)[a] | 5358 (0.016) | 22 749 (0.056) |
| no. of obsd reflns [$I>2\sigma(I)$] | 3284 | 16 586 |
| no. of params refined | 235 | 1191 |
| max./min. $\Delta\rho$ (e Å$^{-3}$) | 0.576/−0.733 | 0.508/−0.432 |
| GOF[b] | 1.228 | 1.076 |
| $R$[c]/$wR$[c] | 0.035/0.0893 | 0.0385/0.0929 |

[a] $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$. [b] GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ for all data. [c] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{1/2}$ for all data.

in Table 4. The molecular structure of **13** in the solid state consists of a pentameric unit (Figure 2) in which three titanium atoms are coordinated in a distorted octahedral fashion, whereas the remaining two titanium atoms, Ti1 and Ti5, have a coordination environment near that of a tetragonal pyramid. The $Ti_4F_{12}$ core has geometric parameters similar to those reported for the tetrameric compound $[TiF_3(\eta^5\text{-}C_5Me_4Et)]_4$.[19] The fifth molecule in **13** is connected to this core through two bridging fluorine atoms, F13 and F15. The terminal (mean 1.822 Å) and bridging Ti−F bond lengths (mean 2.010 Å) show the expected differences. The complete structure involving substituted cyclopentadienyl rings is depicted in Figure 3. Silicon-bonded fluorine atoms do not participate in the formation of bridges. The metal−ring distances at titanium atoms Ti1 and Ti5 are slightly shorter than those found for the hexacoordinated metal centers Ti2, Ti3, and Ti4. Silicon-bonded fluorine atoms F11, F21, F41, and F51 are located above their parent cyclopentadienyl ring planes, away from the titanium center. Only F31 is placed below the cyclopentadienyl ring plane due to its weak interaction with the adjacent titanium atom; the distance F31···Ti5 is 2.974(2) Å [3.037(2) Å]. The pentacoordinate Ti1 atom has the sum of F−Ti−F angles of 329°, whereas hexacoordinate Ti2, Ti3, and Ti4 atoms have a corresponding parameter (sum of the angles generated by four equatorial fluorine atoms) in the range 346−349°. Titanium atom Ti5 with the sum of the F−Ti−F angles of 335° represents an intermediate between hexa- and pentacoordinate Ti atoms. The shortest observed metal−metal separations Ti1···Ti2 and Ti3···Ti4 were found to be 3.3100(7) and 3.3039(6) Å, respectively [3.3083(7) and 3.3061(6) Å].

**Polymerization of Styrene.** Styrene polymerizations with half-sandwich titanium(IV) complexes **7**−**13** as catalysts and methylaluminoxane (MAO) as cocatalyst were carried out in toluene solution at 50 °C. The polymerization results together with data for reference complex $CpTiCl_3$ are summarized in Table 3. Under the given reaction conditions halosilyl-substituted complexes **7**−**12** exhibited catalytic activity comparable to that of $CpTiCl_3$. Most of the monomer was converted to polystyrene (PS). All polystyrenes prepared with **7**−**12**/MAO systems are significantly more stereoregular than that obtained using the reference $CpTiCl_3$/MAO system, as expressed by a >10 °C increase in melting temperature of the PS. Observed melting points were in the range 264−267 °C and reflect the polymer crystallinity rather than their molecular weight. The polymers soluble in 1,2,4-trichlorobenzene were characterized by size-exclusion chromatography (SEC). The molecular weights of the prepared PS were in the range reported for those for which other half-metallocene catalysts had been used under similar conditions.[20] An introduction of a halosilyl group on the cyclopentadienyl ring led to an increase of the PS molar mass in comparison with $CpTiCl_3$, probably due to steric effects. In addition, silicon-bonded halide atoms can interact with bulky methylaluminoxane oligomers, producing greater hindrance at the cyclopentadienyl ligand.[14] The PS obtained when fluorosilyl-

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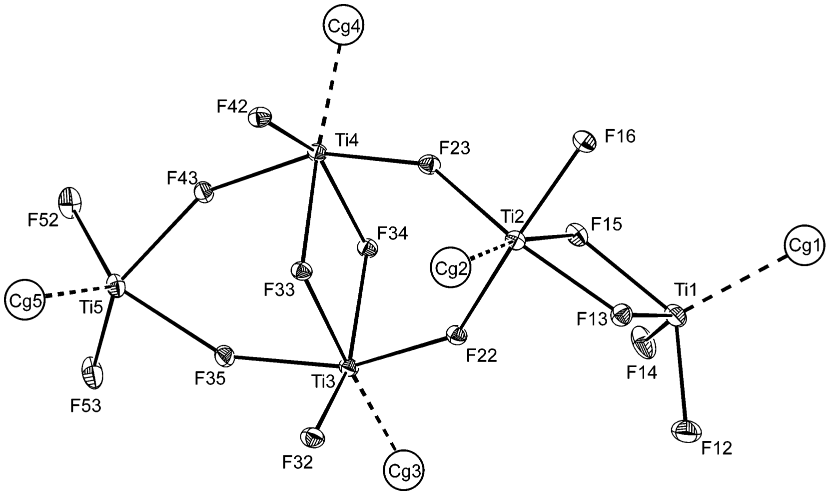

**Figure 2.** ORTEP style plot of the pentameric core of **13** at the 30% probability level. Circles labeled Cg1−Cg5 denote substituted cyclopentadienyl rings defined by carbons C11−C15, C21−C25, C31−C35, C41−C45, and C51−C55, respectively.

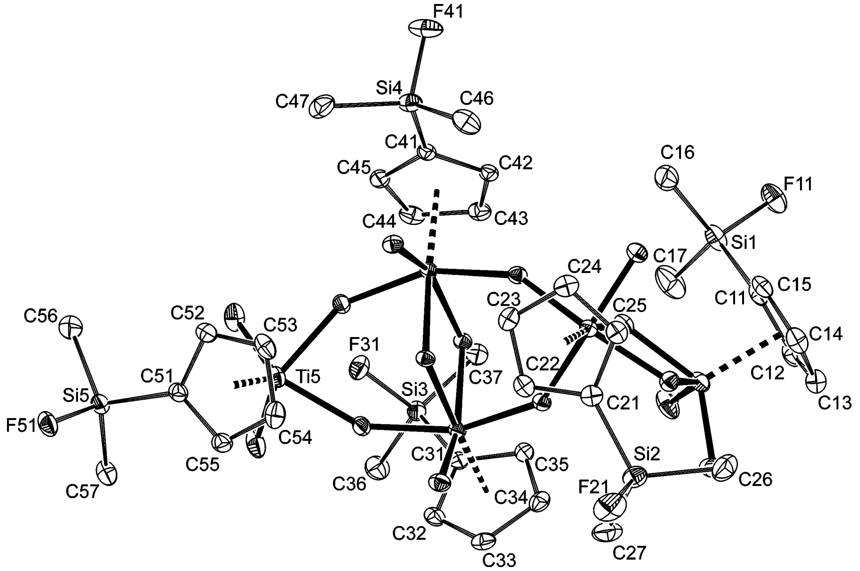

**Figure 3.** View of the molecular structure of **13** with the atom-labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. Orientation of the pentameric molecule is in accordance with Figure 2. H atoms are omitted for clarity.

substituted complexes were used had higher molar mass than the PS prepared using analogous chlorosilyl-substituted derivatives (compare catalysts **7** and **10** in Table 3). Polystyrenes prepared using complexes **8**, **9**, and **12** could not be characterized by SEC due to their complete insolubility in 1,2,4-trichlorobenzene, caused by their high molar mass together with their high stereoregularity. The relatively narrow molar mass distributions ($M_w/M_n = 2.32-2.47$) imply that the polymer preparation involved single-site catalysts. In the series of tested catalysts, complex **13** had the lowest catalytic activity owing to its oligomeric nature. This complex contains coordinatively saturated titanium atoms that cannot act as active sites. Styrene polymerizations catalyzed by **13** were performed at different Al/Ti ratios, and we established that the catalytic activity of this compound is not significantly dependent on MAO concentration, in contrast with the parent $CpTiF_3$/MAO system.[20]

## Summary

In this work, we have described the reactions of chlorosilyl-substituted cyclopentadienes and the corresponding cyclopentadienyl titanium(IV) trichlorides with $Me_3SnF$, which gave novel fluorosilyl-substituted compounds. In the case of complexes $[TiCl_3(\eta^5\text{-}C_5H_4SiMe_{(3-x)}Cl_x)]$, where $x = 1-3$, the fluorination was very selective, giving compounds of the type $[TiCl_3(\eta^5\text{-}C_5H_4SiMe_{(3-x)}F_x)]$. Further fluorination with $Me_3SnF$ gave oligomeric and polymeric products of general formula $[TiF_3(\eta^5\text{-}C_5H_4SiMe_{(3-x)}F_x)]$, where $x = 1-3$. Electronic and $^{47,49}$Ti NMR spectroscopy showed the electron-withdrawing properties of the trihalosilyl substituent, whereas dihalo(methyl)-silyl and halo(dimethyl)silyl groups showed electron-donating features. All studied half-sandwich titanium complexes have catalytic activity in styrene polymerization, giving polystyrenes with significantly higher molecular weight and crystallinity than those prepared with reference compound $CpTiCl_3$.

## Experimental Section

**Materials.** All manipulations were performed under an argon atmosphere using standard Schlenk and vacuum-line techniques. Solvents were dried and deoxygenated by common methods and distilled just before use. $C_5H_5(SiMe_3)$,[21] $CpTiCl_3$,[22] $C_5H_4(SiMe_2$-

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Cl)$SiMe_3$,[10] [$TiCl_3(\eta^5$-$C_5H_4SiMe_2Cl)$],[10] $C_5H_4(SiMeCl_2)SiMe_3$,[11] and [$TiCl_3(\eta^5$-$C_5H_4SiMeCl_2)$][12] were prepared by known procedures. $Me_3SnF$ was prepared according to the literature[23] and was sublimed at 110 °C/0.1 Pa before use. $Bu_3SnF$, $SiCl_4$, *n*-BuLi, and $TiCl_4$ were obtained commercially (Aldrich) and used without further purification.

**Methods.** NMR spectra were recorded on Bruker AMX 360 and Bruker 500 Avance spectrometers equipped with a 5 mm broadband probe at 300 K (solutions in $CD_2Cl_2$, $CDCl_3$, or toluene-$d_8$), and the chemical shifts were referenced to external TMS, $CFCl_3$, and $TiCl_4$, respectively. Electronic absorption spectra were obtained using a Hewlet-Packard 8453 spectrometer (solvent $CH_2Cl_2$; $10^{-2}$−$10^{-4}$ M solutions in a 2 cm cuvette). Infrared spectra were measured as Nujol mulls (KBr cuvette) or neat (NaCl cuvette) under an argon atmosphere on a Perkin-Elmer 684 spectrophotometer. Melting points of **7**−**13** were determined in argon-sealed capillaries using a Stuart SMP-3 melting point apparatus and are uncorrected. Elemental C, H analyses were carried out on a Fisions EA1108 microanalyzer.

**Crystallography.** The X-ray data for both crystals of **10** and **13** were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the $\varphi$ and $\omega$ scan mode. Data reductions were performed with DENZO-SMN.[24] The absorption was neglected. Structures were solved by direct methods (Sir92)[25] and refined by full matrix least-square based on $F^2$ (SHELXL97).[26] All hydrogen atoms were positioned geometrically and refined on their parent carbon atoms, with C−H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for cyclopentadienyl H atoms and C−H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl hydrogen atoms.

**Polymerization Studies.** Styrene polymerizations were carried out in a 100 mL thermostated glass reactor equipped with a magnetic stirrer under nitrogen atmosphere. Toluene was freshly distilled under vacuum from sodium benzophenone ketyl prior to use. Styrene (Aldrich) was dried over calcium hydride, vacuum distilled, and immediately used for polymerization runs. Toluene, styrene, and MAO (10 wt % in toluene from Crompton) were introduced into the reactor, the temperature was adjusted to 50 °C, and the polymerization was initiated by injection of the catalyst (freshly prepared toluene solution). The total volume of the polymerization mixture was 30 mL for each run. The polymerizations were performed for a 120 min period. After this time the reaction was quenched by the addition of *sec*-butanol, and to the resulting mixture was added methanolic HCl. Polystyrene was collected by filtration, washed with methanol (3 × 50 mL), and dried in vacuum oven to a constant weight. The reproducibility of the amount of polymer was estimated to be ±5%. Melting points of obtained polystyrenes were determined on DSC 2920 (TA Instruments) under a nitrogen atmosphere with a heating rate of 10 °C/min. Both molar masses and molar dispersities ($M_w/M_n$) of the polymers were determined by high-temperature SEC (Polymer Laboratories PL-GPC 220) equipped with RI and viscometric detectors in 1,2,4-trichlorobenzene at 160 °C against atactic PS standards. The tacticity of the PS could not be studied by NMR spectroscopy due to poor solubility of prepared polymers.

**$C_5H_4(SiCl_3)SiMe_3$ (3).** Silicon tetrachloride (12.91 g, 76.0 mmol) was added at once to a suspension of Li[$C_5H_4(SiMe_3)$] (10.96 g, 76.0 mmol) in 200 mL of hexane at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 24 h to ensure completion of the reaction. After 24 h of stirring, the precipitated LiCl was allowed to settle and the supernatant liquid was filtered through the Celite. Solvent was removed under reduced pressure, yielding a yellow, oily residue. Distillation at 40 °C/1 Pa gave **3** as a colorless liquid (14.67 g, 54.0 mmol, 71% yield) that crystallized on cooling at −15 °C. $^1$H NMR ($CDCl_3$): $\delta$ 0.19 (s, 9H, $SiMe_3$), 3.43 (s, sp$^3$-C bonded proton, isomers), 6.68 (m, 2H, $C_5H_4$), 7.01 (m, 2H, $C_5H_4$). $^{13}$C NMR: $\delta$ −0.9 (s, $SiMe_3$), 60.3 (s, $C_{ipso}$), 132.5 (s, $C_5H_4$), 135.5 (s, $C_5H_4$). IR (neat, cm$^{-1}$): 3111w, 3094w, 3070m, 2960s, 2902m, 1656br-m, 1466 m, 1411m, 1283m, 1254vs, 1121s, 1083m, 1047m, 976vs, 949s, 844br-vs, 739vs, 695m. Anal. Found: C, 35.78; H, 4.91. Calc for $C_8H_{13}Cl_3Si_2$: C, 35.36; H, 4.82.

**$C_5H_4(SiMe_2F)SiMe_3$ (4).** To a solution of $C_5H_4(SiMe_2Cl)SiMe_3$, **1** (3.00 g, 13.0 mmol), in 30 mL of $CH_2Cl_2$ was added $Me_3SnF$ (2.38 g, 13.0 mmol), and the reaction mixture was stirred at room temperature for 24 h. After removing volatiles under reduced pressure the resulting yellow oil was distilled at 50 °C/400 Pa to give **4** as a moisture-sensitive colorless liquid (1.56 g, 7.3 mmol, 56% yield). The $^1$H NMR spectrum of **4** is in agreement with that reported[15] by Borisova et al. $^1$H NMR ($CDCl_3$): $\delta$ 0.00 (s, 9H, $SiMe_3$), 0.02 (d, $^3J_{H-F} = 7.1$ Hz, 6H, $SiMe_2F$), 6.54 (m, 2H, $C_5H_4$), 6.78 (m, 2H, $C_5H_4$). $^{13}$C NMR: $\delta$ −2.0 (d, $^2J_{C-F} = 15.1$ Hz, $SiMe_2F$), −1.4 (s, $SiMe_3$), 58.8 (d, $^2J_{C-F} = 13.2$ Hz, $C_{ipso}$), 132.7 (s, $C_5H_4$), 133.5 (s, $C_5H_4$). $^{19}$F NMR: $\delta$ −151.62 (sep, $^3J_{F-H} = 6.8$ Hz, $^1J_{F-Si} = 290$ Hz, $SiMe_2F$). IR (neat, cm$^{-1}$): 3098w, 3083m, 3069w, 2961s, 2902m, 1656br-m, 1431m, 1406m, 1285w, 1257vs, 1192w, 1122vs, 1078w, 1025m, 975vs, 921s, 876vs, 841s, 791s, 737vs, 691m, 660s, 625m. Anal. Found: C, 56.46; H, 9.21. Calc for $C_{10}H_{19}FSi_2$: C, 56.01; H, 8.93.

**$C_5H_4(SiMeF_2)SiMe_3$ (5).** Moisture-sensitive liquid **5** was prepared analogously from diene $C_5H_4(SiMeCl_2)SiMe_3$ (**2**; 3.26 g, 13.0 mmol) and 2 equiv of $Me_3SnF$. Distillation at 50 °C/670 Pa gave colorless **5** (1.79 g, 8.2 mmol, 63% yield). $^1$H NMR ($CDCl_3$): $\delta$ −0.18 (t, $^3J_{H-F} = 5.6$ Hz, 3H, $SiMeF_2$), 0.08 (s, 9H, $SiMe_3$), 6.64 (m, 2H, $C_5H_4$), 6.93 (m, 2H, $C_5H_4$). $^{13}$C NMR: $\delta$ −8.7 (t, $^2J_{C-F} = 17.6$ Hz, $SiMeF_2$), −1.8 (s, $SiMe_3$), 57.7 (t, $^2J_{C-F} = 14.0$ Hz, $C_{ipso}$), 132.1 (s, $C_5H_4$), 134.1 (s, $C_5H_4$). $^{19}$F NMR: $\delta$ −129.30 (q, $^3J_{F-H} = 5.4$ Hz, $^1J_{F-Si} = 298$ Hz, $SiMeF_2$). IR (neat, cm$^{-1}$): 3101w, 3088m, 3070w, 2962m, 2911m, 1654br-m, 1407br-m, 1267s, 1253vs, 1125s, 1026m, 984s, 906s, 878vs, 828s, 744vs, 705m, 627m. Anal. Found: C, 49.96; H, 7.58. Calc for $C_9H_{16}F_2Si_2$: C, 49.50; H, 7.38.

**$C_5H_4(SiF_3)SiMe_3$ (6).** Neat **3** (1.36 g, 5 mmol) was added to 4.64 g (15 mmol) of solid $Bu_3SnF$, and the suspension was stirred until all of the $Bu_3SnF$ had dissolved (reaction was rather exothermic). The product was removed from the reaction mixture at 670 Pa to a trap cooled to −80 °C, leaving an oily residue of $Bu_3SnCl$. Subsequent distillation of the crude product at 36 °C/670 Pa gave 0.47 g of colorless liquid **6** (yield 42%). $^1$H NMR ($CDCl_3$): $\delta$ 0.14 (s, 9H, $SiMe_3$), 6.67 (m, 2H, $C_5H_4$), 7.02 (m, 2H, $C_5H_4$). $^{13}$C NMR: −2.2 (s, $SiMe_3$), 50.6 (q, $^2J_{C-F} = 14.4$ Hz, $C_{ipso}$), 130.3 (s, $C_5H_4$), 134.9 (s, $C_5H_4$). $^{19}$F NMR: $\delta$ −138.44 (s, $^1J_{F-Si} = 281$ Hz, $SiF_3$). IR (neat, cm$^{-1}$): 3104m, 3087m, 2965s, 1656br-m, 1436m, 1266vs, 1114m, 1028m, 1001m, 949s, 896m, 846m, 812m, 743vs, 706s, 667m. Anal. Found: C, 43.68; H, 6.14. Calc for $C_8H_{13}F_3Si_2$: C, 43.21; H, 5.89.

**[$TiCl_3(\eta^5$-$C_5H_4SiMe_2Cl)$] (7).** Compound **7** was prepared according to the published procedure[10] and purified by repeated sublimation at 70 °C/1 Pa. Mp: 83 °C. IR (Nujol mull, cm$^{-1}$): 3112m, 3096m, 3087m, 1408s, 1369s, 1315m, 1262vs, 1182s, 1071m, 1049s, 960vs, 913m, 896s, 839vs, 795vs, 685s, 628s, 504s, 457vs, 426vs, 360m. UV−vis ($CH_2Cl_2$, nm): 398, 289, 246.

**[$TiCl_3(\eta^5$-$C_5H_4SiMeCl_2)$] (8).** Compound **8** was prepared according to the literature[12] and purified by repeated sublimation at 70 °C/1 Pa. Mp: 92 °C. IR (Nujol mull, cm$^{-1}$): 3112m, 3098m, 3086m, 1409s, 1370s, 1316m, 1261s, 1189s, 1071m, 1048s, 914m,

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895m, 844vs, 796vs, 748s, 626s, 565vs, 525vs, 458s, 424vs, 354m. UV−vis ($CH_2Cl_2$, nm): 391, 286, 246.

**[$TiCl_3(\eta^5$-$C_5H_4SiCl_3)$] (9).** A solution of $TiCl_4$ (4.17 g, 22.0 mmol) in $CH_2Cl_2$ (40 mL) was cooled to −80 °C, and diene **3** (5.98 g, 22.0 mmol) was added at once. The reaction mixture was slowly warmed to room temperature, stirred for 12 h, and finally heated at reflux for 3 h to ensure complete reaction. Volatiles were removed under vacuum to give an orange residue, which was crystallized from hexane (20 mL). The crystals obtained on cooling of the orange filtrate to −80 °C were subsequently sublimed at 70 °C/1 Pa, yielding **9** as a yellow solid (5.12 g, 14.5 mmol, 66% yield). Mp: 99 °C. $^1$H NMR (toluene-$d_8$): $\delta$ 6.14 (m, 2H, $C_5H_4$), 6.56 (m, 2H, $C_5H_4$). $^{13}$C NMR ($CDCl_3$): $\delta$ 126.0 (s, $C_5H_4$), 126.6 (s, $C_{ipso}$), 128.2 (s, $C_5H_4$). IR (Nujol mull, cm$^{-1}$): 3112m, 3100m, 3086m, 1411s, 1369s, 1318m, 1193s, 1072m, 1048vs, 913m, 843vs, 630s, 612vs, 597vs, 553vs, 457s, 430vs, 384m. UV−vis ($CH_2Cl_2$, nm): 377, 284sh, 246. Anal. Found: C, 17.24; H, 1.21. Calc for $C_5H_4Cl_6SiTi$: C, 17.02; H, 1.14.

**[$TiCl_3(\eta^5$-$C_5H_4SiMe_2F)$] (10). Method A.** The diene **4** (1.29 g, 6.0 mmol) was added at once to a solution of $TiCl_4$ (1.14 g, 6.0 mmol) in 40 mL of toluene at −20 °C. The reaction mixture was slowly warmed to room temperature and stirred for 16 h in the dark. After evaporation of volatiles under vacuum, the yellow residue was dissolved in hot hexane (25 mL), filtered through glass wool, and cooled to −80 °C, giving a microcrystalline solid. The isolated crystals were purified by sublimation at 40 °C/1 Pa, yielding yellow **10** (0.69 g, 2.8 mmol, 47% yield). Vacuum sublimation in a sealed ampule gave crystals of **10** suitable for X-ray crystallographic analysis.

**Method B.** Complex **7** (0.94 g, 3.0 mmol) was dissolved in toluene (25 mL), 1 equiv of $Me_3SnF$ (0.55 g, 3.0 mmol) was added, and the mixture was stirred in the dark for 24 h at room temperature. Solvent and $Me_3SnCl$ were removed under vacuum, and the yellow residue was purified as described above. Yield: 0.39 g (1.59 mmol, 53% yield). Mp: 69 °C. $^1$H NMR ($CD_2Cl_2$): $\delta$ 0.62 (d, $^3J_{H-F} = 7.3$ Hz, 6H, $SiMe_2F$), 7.17 (m, 2H, $C_5H_4$), 7.37 (m, 2H, $C_5H_4$). $^{13}$C NMR: $\delta$ −0.5 (d, $^2J_{C-F} = 14.9$ Hz, $SiMe_2F$), 127.7 (s, $C_5H_4$), 130.3 (s, $C_5H_4$), 135.7 (d, $^2J_{C-F} = 20.5$ Hz, $C_{ipso}$). $^{19}$F NMR: $\delta$ −155.21 (sep, $^3J_{F-H} = 7.5$ Hz, $^1J_{F-Si} = 282$ Hz, $SiMe_2F$). IR (Nujol mull, cm$^{-1}$): 3098m, 3088m, 1412s, 1315m, 1257vs, 1183s, 1049vs, 921m, 899s, 872vs, 843vvs, 827vs, 806vs, 774m, 666s, 631m, 461s, 430vs, 416vs, 360m. UV−vis ($CH_2Cl_2$, nm): 396, 283, 243. Anal. Found: C, 28.71; H, 3.43. Calc for $C_7H_{10}Cl_3FSiTi$: C, 28.45; H, 3.41.

**[$TiCl_3(\eta^5$-$C_5H_4SiMeF_2)$] (11). Method A.** Yield: 0.99 g (3.30 mmol, 55%). Yellow crystalline **11** was purified by repeated sublimation at 50 °C/3 Pa.

**Method B.** Yield: 0.62 g (2.07 mmol, 69% yield). Mp: 61 °C. $^1$H NMR ($CD_2Cl_2$): $\delta$ 0.76 (t, $^3J_{H-F} = 6.1$ Hz, 3H, $SiMeF_2$), 7.21 (m, 2H, $C_5H_4$), 7.41 (m, 2H, $C_5H_4$). $^{13}$C NMR: $\delta$ −3.6 (t, $^2J_{C-F} = 15.3$ Hz, $SiMeF_2$), 126.7 (t, $^2J_{C-F} = 23.7$ Hz, $C_{ipso}$), 127.3 (s, $C_5H_4$), 130.2 (s, $C_5H_4$). $^{19}$F NMR: $\delta$ −131.52 (q, $^3J_{F-H} = 6.2$ Hz, $^1J_{F-Si} = 291$ Hz, $SiMeF_2$). IR (Nujol mull, cm$^{-1}$): 3103m, 1409m, 1318w, 1272s, 1195s, 1050s, 972m, 915m, 877vs, 840vs, 787s, 769s, 720vs, 699s, 635m, 449s, 430s, 377m. UV−vis ($CH_2Cl_2$, nm): 382, 281, 244. Anal. Found: C, 24.33; H, 2.41. Calc for $C_6H_7Cl_3F_2SiTi$: C, 24.07; H, 2.36.

**[$TiCl_3(\eta^5$-$C_5H_4SiF_3)$] (12). Method A.** Yield: 0.95 g (3.12 mmol, 52%). Bright yellow **12** was purified by sublimation at 40 °C/1 Pa.

**Method B.** Yield: 0.52 g (1.71 mmol, 57% yield); benzene was used instead of toluene. Mp: 47 °C. $^1$H NMR ($CDCl_3$): $\delta$ 7.27 (m, 2H, $C_5H_4$), 7.48 (m, 2H, $C_5H_4$). $^{13}$C NMR ($C_6D_6$): $\delta$ 125.4 (s, $C_5H_4$), 129.2 (s, $C_5H_4$). $^{19}$F NMR: $\delta$ −135.57 (s, $^1J_{F-Si} = 259$ Hz, $SiF_3$). IR (Nujol mull, cm$^{-1}$): 3109br-m, 1418s, 1373s, 1328m, 1212vs, 1170s, 1053s, 1023m, 967br-s, 922s, 832vs, 775br-vs, 709s, 635s, 594m, 504vs, 454s, 425vs, 383s. UV−vis ($CH_2Cl_2$, nm): 362, 273sh, 241. Anal. Found: C, 19.56; H, 1.26. Calc for $C_4H_4Cl_3F_3SiTi$: C, 19.72; H, 1.33.

**[$TiF_3(\eta^5$-$C_5H_4SiMe_2F)$] (13).** To a solution of **7** (1.12 g, 3.6 mmol) in toluene was added $Me_3SnF$ (2.63 g, 14.4 mmol), and the mixture was stirred at ambient temperature for 48 h. A change of color from yellow to orange was gradually observed. After evaporation of solvents, the orange solid was washed with 10 mL of cold pentane and dried in vacuum. The crude product was extracted with boiling hexane on a frit. Cooling of the light yellow extract to −80 °C gave an orange solid (0.84 g, 3.4 mmol, 94% yield), which was characterized as **13**. Single crystals suitable for X-ray crystal structure determination were grown from a saturated toluene solution layered with a double volume of hexane at −30 °C. Mp: 92 °C (dec). $^1$H NMR (toluene-$d_8$): $\delta$ 0.37 (d, $^3J_{H-F} = 6.0$ Hz, 6H, $SiMe_2F$), 6.27 (br-m, 2H, $C_5H_4$), 6.45 (br-m, 2H, $C_5H_4$). $^{13}$C NMR: $\delta$ −0.8 (d, $^2J_{C-F} = 14.7$ Hz, $SiMe_2F$), 124−131 (br-m, $C_5H_4$). $^{29}$Si NMR: $\delta$ 9.6 (d, $^1J_{Si-F} = 277$ Hz). $^{19}$F NMR: $\delta$ −155.64, −155.01, −130.40, 173.42. IR (Nujol mull, cm$^{-1}$): 3127m, 1655m, 1534s, 1504vs, 1494vs, 1468s, 1386vs, 1270w, 1232w, 1141w, 1103m, 1081m, 1053s, 986vs, 934w, 831m, 784s, 694m, 625m, 555s. UV−vis ($CH_2Cl_2$, nm): 339sh, 246. Anal. Found: C, 34.27; H, 4.01. Calc for $C_7H_{10}F_4SiTi$: C, 34.16; H, 4.09.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 634117 (**10**) and 634649 (**13**).

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**Supporting Information Available:** Crystallographic data for the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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