Selective C–H and C–F Bond Activation Reactions of Pyridine and Fluoropyridines – Formation of Binuclear μ-X Titanocene Complexes (X = H, F) with α-Functionalized N-Heterocycles

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Keywords: Titanium / Bridging ligand / Fluorinated ligands / Nitrogen heterocycles / C–H activation / C–F activation

Titanocene synthons react with pyridine (**2**), fluorosubstituted pyridines [pentafluoropyridine (**3**), 2-fluoropyridine(**4**)] and cyanuric fluoride, by C–H and C–F bond activation, respectively, to afford interesting novel binuclear titanium(III) complexes. C–H bond activation requires high temperatures (110 °C), whereas C–F bond activation occurs at room temperature. X-ray structure analysis showed that the two titanium(III) centres are hydride-bridged when pyridine was reacted with the titanocene fragment and fluoride-bridged if a 2-fluoro-substituted derivative of pyridine was used. The reactivities of a C–F and a C–H bond in the 2-position toward the titanocene fragment have been compared in a competition experiment using 2-fluoropyridine – revealing a preference for C–F bond cleavage. Primary mononuclear C–F bond activation products have been proved in solution by NMR measurements using $[Cp^*{}_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}]$ instead of the non-methylated titanocene source.

Introduction

We recently reported that N-heterocycles such as pyrimidine, pyrazine and triazine may undergo amazing C–C couplings when reacted with the titanocene fragments $[Cp_2Ti]$ or $[Cp^*{}_2Ti]$.[1] With this kind of reaction we presume a single electron transfer from the titanium(II) centre to the N-heterocycles, as in the case of 2,2′-bipyridine and comparable chelating ligands.[2–4] Here we report reactions of low valent titanium complexes with pyridines. Examples of C–C coupling reactions of pyridine via low valent early transition metal complexes are rare.[5] As well as simple pyridine (C_5H_5N) we also wanted to use fluorinated pyridines. The electronegative fluorine substituents lower the energy of the LUMOs and increase the electron affinities,[6] which could be helpful in C–C coupling reactions. In particular, C–H or C–F bond activation reactions could also be possible.

Carbon–fluorine bond activation of several fluoroaromatics mediated by transition metal complexes has been thoroughly investigated in the last two decades. Especially, late transition metal complexes have been employed to cleave aromatic carbon–fluorine bonds by oxidative addition.[7] There are few examples for C–F bond activation reactions via electron-deficient transition metal complexes.[7–26] For titanium compounds, Burk and co-workers showed, as one of the first examples, that tetrakis(trifluoromethyl)cyclopentadienone reacts with d^0 bis(cyclopentadienyl)-titanacyclobutanes to produce titanium fluoride products.[26] Our group has given an example of complete defluorination of a CF_3 moiety, employing a titanium amide.[18] Kiplinger and Richmond reported the first hydrogenolysis of an aromatic C–F bond at ambient temperature, using an in situ generated, low-valent zirconocene fragment $[Cp_2Zr]$.[25] They also reported the conversion of several saturated perfluorohydrocarbon compounds into the corresponding aromatic derivatives by reductive defluorination, using the $Cp_2TiF_2/Al/HgCl_2$ system.[25] Jones et al. found that zirconocene hydrides ($[Cp_2ZrH_2]_2$, $[Cp^*{}_2ZrH_2]$) can activate a C–F bond of perfluorobenzene at room temperature.[22,27] They suggested the reaction proceeded by oxidative addition to a low valent zirconocene intermediate[22] and an S_NAr2 of fluorinated aromatics to give either reduced fluoroaromatics or new zirconium-aryl bonds.[12] Metallation of polyfluorinated pyridines and other fluorine-containing N-heterocycles in the 2-position via C–F activation is of special interest. Perutz et al. prepared the nickel complex $[NiF(2\text{-}C_5NF_4)(PEt_3)_2]$ by reacting pentafluoropyridine with $[Ni(COD)(PEt_3)_2]$[28] and provided new pathways for the synthesis of uncommon tetrafluoropyridines substituted at the 2-position.[29] Substitution reactions of unsubstituted pyridines at the 2-position are common and well known.[30] There are fewer examples of the synthesis of 2-

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substituted pyridines mediated by early transition metal complexes.[31,32] Teuben et al. have also synthesized a 6-substituted 2-methylpyridine by hydrogen transfer using a titanium complex.[33]

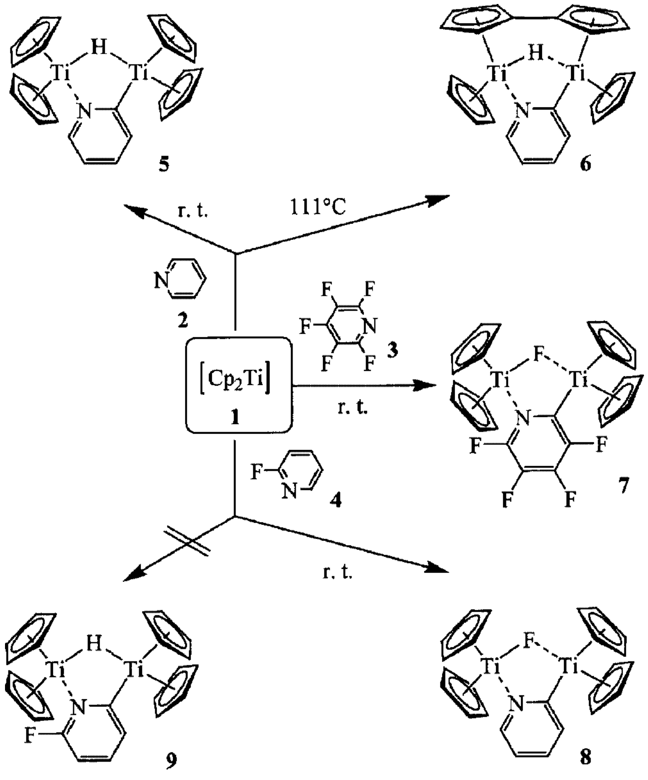
This paper describes the reactions of pyridine (**2**) and fluorosubstituted pyridines [pentafluoropyridine (**3**), 2-fluoropyridine (**4**)] with the titanocene fragments [Cp_2Ti] and [Cp^*_2Ti], generated in situ by using the corresponding bis(trimethylsilyl)acetylene complexes **10** and **13**.[34]

We also report the structure and facile synthesis of complexes **5**–**8** by activation of the 2-C–H and 2-C–F bonds of pyridine (**2**) and the fluorosubstituted pyridines **3** and **4**, respectively, using an in situgenerated titanocene fragment [Cp_2Ti] (**1**). Due to the facile preparation and its versatility the titanocene complex of bis(trimethylsilyl)acetylene (**10**)[34] was used as well as the reaction between magnesium and titanocene dichloride to generate the titanocene fragment.

Results and Discussion

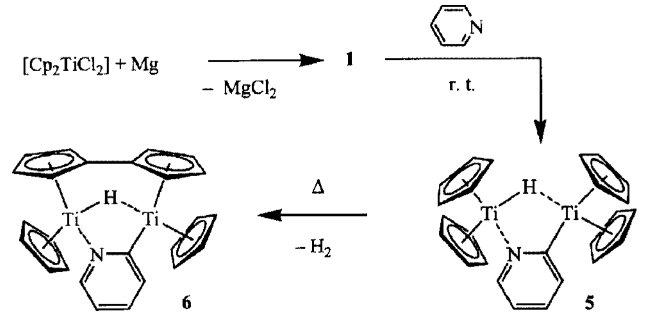
Reactivity

Upon refluxing for 3 h, a solution of [$Cp_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}$] (**10**) and C_5H_4N (**2**) in toluene the color changes from yellow to red-brown. Slow evaporation leads to precipitation of dark brown crystals of the fulvalene titanium complex **6** (Scheme 1). Stirring a suspension of [Cp_2TiCl_2], Mg and an excess of **2** in THF for 48 h yields a brown solution. Brown crystals of the binuclear titanocene complex **5** can then be obtained after filtration from the magnesium chloride pyridine adduct, removal of the solvent and recrystallization of the residue from toluene. Treatment of a solution of **10** in *n*-hexane with pentafluoro- (**3**) and monofluoropyridine (**4**)at ambient temperature leads to a color change from yellow to slightly green and to the slow crystallization of the fluoride-bridged binuclear titanium derivatives **7** and **8**, respectively. All these compounds were isolated as thermally robust solids with high melting points (207–217 °C) but they decomposed rapidly upon exposure to air and moisture. Complexes **5**–**8**, isolated in 25–75% yield, have been characterized by X-ray structure analysis, mass spectrometry and elemental analysis.



Scheme 1. Reaction of **1** (generated in situ from [$Cp_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}$] or [$Cp_2TiCl_2$]/Mg) with pyridines **2**–**4**.

In all reactions of the in situ generated titanocene fragment **1** and N-heterocycles **2**–**4** we observed C–H or C–F bond activation at the 2-position and transfer of hydrogen or fluorine, respectively, into the titanium coordination sphere. The titanium(III) centres of the resulting dimeric complexes are bridged by a hydride and a fluoride, respectively, and the metallated pyridyl ligand. As expected for compounds with unpaired electrons the ^1H NMR spectra (300 MHz, 25 °C, C_6D_6) of the Ti^{III} complexes show either no or paramagnetically broadened signals. The positions of the signals are reproducible and provide a characteristic fingerprint. For the syntheses of complexes **6**–**8** the titanocene complex of bis(trimethylsilyl)acetylene (**10**) was used as the source of titanocene fragment **1**.[35] The reaction of **10** with pyridine (**2**) requires higher temperatures and results in the coupling of two Cp ligands, leading to fulvalene complex **6**. Conversely, **2** reacts with the titanocene generating system [Cp_2TiCl_2/Mg] at room temperature[36] to give complex **5** with no Cp ligand coupling (Scheme 2).



Scheme 2. Formation of fulvalene-bridged titanocene complex **6**.

Complex **5** has been isolated as an intermediate in the hydrosilylation of pyridines with silanes catalyzed by low valent titanocene complexes.[37] In this reaction the silane provides the bridging hydride of **5**, and the pyridine undergoes the ortho-metallation under liberation of H_2. The reaction between the titanocene fragment (**1**) and pyridine (**2**) shows that **5** can also be synthesized by C–H activation without an external hydride source. Several facts indicate that the reaction to **6** probablyproceeds via a preliminary hydride transfer from the pyridine and a subsequent coupling of the Cp ligands. The mass spectrum of **5** has no molecular peak, but one at [$M^+ - H_2$] (40% intensity) shows that this complex easily loses H_2, which suggests that the higher reaction temperature could explain the Cp ligand coupling and the formation of **6** instead of **5** if acetylene complex **10** is used to generate titanocene **1**. This is supported by the spectra of the product isolated after refluxing a solution of **5** for 3 h in toluene. IR and ^{1}H NMR spectra are identical to those of the fulvalene-bridged complex **6**, while the characteristic signals of **5** have vanished. For **5** a broad signal at δ = 31 ppm in the ^{1}H NMR spectrum is consistent with investigations by Harrod and Samuel, who assigned this signal to Cp ligands.[37] The ^{1}H NMR spectrum of **6** shows weaker broad signals at δ = 8.9,9.5, 10.9, 11.1,16.2 and 21.5 ppm. Accordingly, it seems reasonable to propose **5** as an intermediate in the reaction of **10** with **2** to give **6** because the coupling reaction follows its formation if the reaction is carried out at a higher temperature (Scheme 2).

The fact that [$Cp_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}$] (**10**) reacts with perfluorinated pyridine (**3**) to afford complex **7** at room temperature, whereas pyridine only reacts at >100 °C, indicates that fluorine transfer is a favored reaction pathway. This has been confirmed by a C–H/C–F competition experiment with 2-fluoropyridine (**4**), which bears hydrogen as well as fluorine in the 2-position. In this reaction the selective transfer of fluorine occurs, and only the C–F activation product **8** is observed. The alternative C–H activation product **7** is not found. Under preparative conditions **8** could be isolated in 71% yield. A comparison of C–F and C–H bond activation by zerovalent nickel and platinum complexes shows, by DFT calculation, a preferred exothermic C–F bond activation, owing to a strong thermodynamic preference for C–F over C–H bond activation and a relatively low kinetic barrier.[38] Generally, ortho-substituted aryl fluorides undergo C–F bond activation. In such a way [$Cp^*_2Zr(o\text{-}C_6H_4F)H$] reacts by β-fluoride elimination to give [$Cp^*_2Zr(C_6H_5)F$].[20] The selectivity of C–F versus C–H activation depends on the nature of the transition metal system. Late transition metal complexes (Rh,[39] Os[40,41]) often prefer C–H over C–F activation reactions, whereas [$Ru(dmpe)_2H_2$] and partially fluorinated arenes produce only C–F bond activation products.[42] The insertion of tungsten in a C–F bond in the presence of C–H bonds was one of the first examples.[43]

Crystal Structures of 6–8

Crystals suitable for X-ray structure analysis were obtained either directly from the reaction mixtures or after recrystallization from toluene for complex **5** and from fluorobenzene for complex **7**. Figure 1, Figure 2 and Figure 3 show the molecular structures of **6**–**8**, respectively.

Due to slight disorder of the pyridyl ligands in **6**–**8**, the Ti1–C1 and Ti2–N1 bond lengths could not be determined reliably. The asymmetric unit of **7** contains two independent molecules, A and B. Since the two molecules do not exhibit significant differences only the structure of A will be discussed. The bridging H-atom of **6** could be freely refined and the bond lengths between titanium and hydrogen, which average 1.82(3) Å, are in the same range as in the published structure of **5**[37] but shorter than in the analogue fulvalene hydrido chloride complex.[44] Ti–F bond lengths for **7** (2.047 Å) and **8** (2.051 Å) (average) are in the range expected for bent bridging Ti–F–Ti bonds.[45–48] The Ti–Ti distance in **6** (3.324 Å) is considerably shorter than in **7** (3.829 Å) and **8** (3.788 Å), probably due to the minor steric

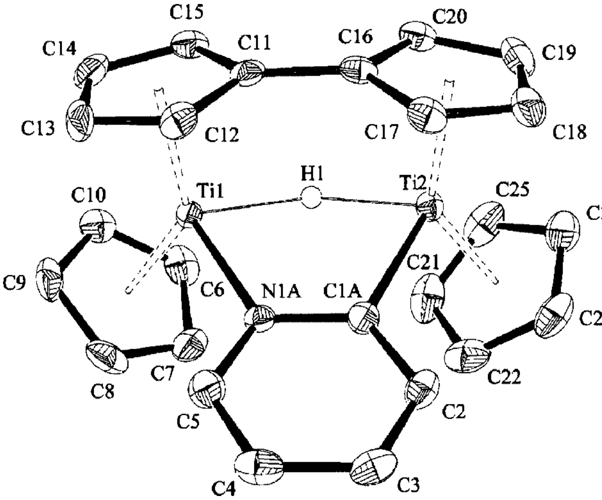


Figure 1. Molecular structure of **6**: ORTEP plot with 50% probability thermal ellipsoids; hydrogen atoms omitted for clarity.Thebridging H-atom has been freely refined. Selected bond lengths [Å] and angles [°]: Ti1–Ti2 3.324, Ti1–H1 1.85(3), Ti1–N1A 2.205(3), Ti2–H1 1.79(3), Ti2–C1A 2.205(3), Ti1–Ct1 2.062, Ti1–Ct2 2.040, Ti2–Ct3 2.050, Ti2–Ct4 2.065; Ct1–Ti1–Ct2 139.79, Ct3–Ti2–Ct4 137.21, H1–Ti1–N1A 84.6(9), H1–Ti2–C1A 84.7, Ti1–H1–Ti2 131.64, Ct1 = centroid of C6–C10, Ct2 = centroid of C11–C15, Ct3 = centroid of C16–C20, Ct4 = centroid of C21–C25.

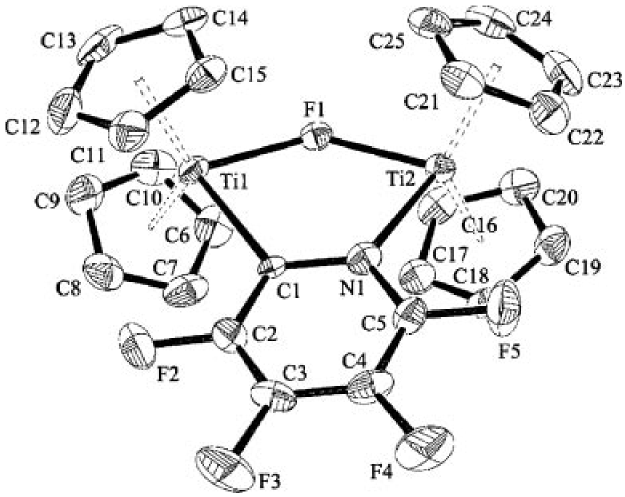


Figure 2. Molecular structure of **7**: ORTEP plot with 50% probability thermal ellipsoids. The asymmetric unit contains two independent molecules A and B; only data for A are given; hydrogen atoms omitted for clarity.Selected bond lengths [Å] and angles [°]: Ti1–Ti2 3.829, Ti1–F1 2.0487(13), Ti1–C1 2.277(2), Ti2–N1 2.288(2), Ti2–F1 2.0448(15), Ti1–Ct1 2.076, Ti1–Cpt 2.075, Ti2–Ct3 2.071, Ti2–Ct4 2.078; Cp1–Ti1–Ct2 132.72, Ct3–Ti2–Ct4 131.86, F1–Ti1–C1 78.31(7), F1–Ti2–N1 77.79(7), Ti1–F1–Ti2 138.62(8), Ct1 = centroid of C6–C10, Ct2 = centroid of C11–C15, Ct3 = centroid of C16–C20, Ct4 = centroid of C21–C25.

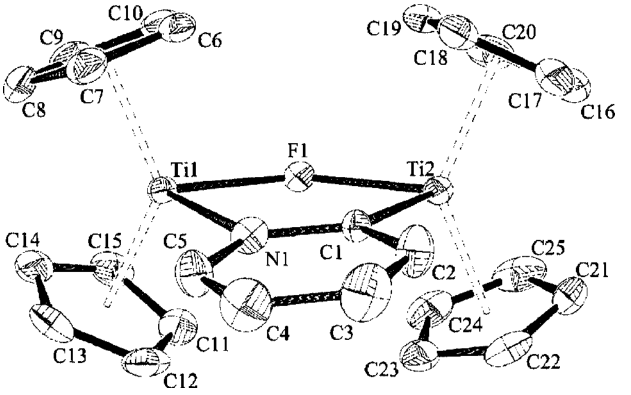


Figure 3. Molecular structure of **8**. ORTEP plot with 50% probability thermal ellipsoids; hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–Ti2 3.788, Ti1–F1 2.0507(11), Ti1–N1 2.2271(18), Ti2–F1 2.0504(11), Ti2–C1 2.2252(18), Ti1–Ct1 2.081, Ti1–Ct2 2.078, Ti2–Ct3 2.084, Ti2–Ct4 2.083; Ct1–Ti1–Ct2 131.67, Ct3–Ti2–Ct4 132.91, F1–Ti1–N1 79.27(5), F1–Ti2–C1 79.60(6), Ti1–F1–Ti2 134.91, Ct1 = centroid of C6–C10, Ct2 = centroid of C11–C15, Ct3 = centroid of C16–C20, Ct4 = centroid of C21–C25.

demand of the hydride and the presence of the fulvalene bridge. In all three complexes the distance is beyond the range of a direct Ti–Ti interaction.

Reaction of 10 with Cyanuric Fluoride

Reactions between **10** and fluorinated and non-fluorinated triazine further support the cleavage of a C–F bond as a favored pathway in reactions of fluorinated N-heterocycles and low-valent titanium complexes. Scheme 3 shows the two reaction pathways.

Triazine reacts with **10**, through C–C coupling, to give a dimeric chelate ligand,[1] whereas the fluorinated analogue reacts through α-F-activation to form a complex similar to those obtained in the reactions with pyridines (Scheme 3).

Crystal Structure of 11

Figure 4 shows the molecular structure of **11**. Unlike the disordered pyridyl ligands in **6**–**8**,the N-heterocyclic ligand in **11** showed no disorder. The fluoride-bridge in **11** is approximately symmetric. Ti–F distances [Ti1–F1 = 2.0413(18) Å; Ti2–F1 2.0619(18) Å] are typical for fluoride-bridged Ti complexes[45] (Ti–F = 2.046 Å in $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}F)]_2(\mu\text{-}\ \eta5\text{:}\ \eta5\text{-}C_{10}H_8)]$;[48] Ti–F = 2.092 Å in $[(C_5H_4Me)_2\text{-}TiF]_2$[49]). The Ti–Ti distance (3.831 Å) is similar to those in **6**–**8**. The Ti2–C1 bond [2.229(3) Å] is slightly shorter than the Ti1–C1 bond [2.293(3) Å]. Generally, **11** has the same structural characteristics as **6**–**8**.

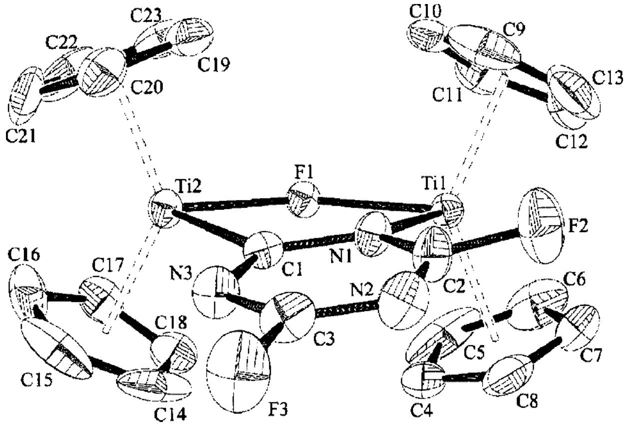
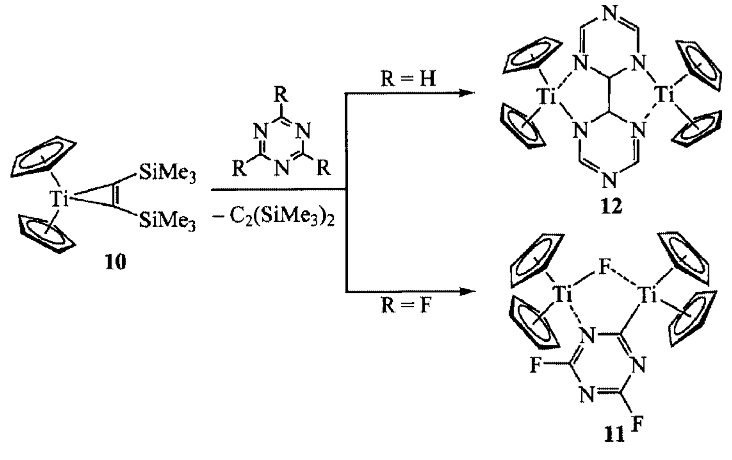


Figure 4. Molecular structure of **11**: ORTEP plot with 50% probability thermal ellipsoids; hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti1–Ti2 3.831, Ti1–F1 2.0413(18), Ti1–N1 2.293(3), Ti2–F1 2.0619(18), C1–N1 1.391(4), N1–C2 1.324(4), C2–N2 1.310(4), N2–C3 1.318(5), C3–N3 1.299(4), N3–C1 1.373(4), Ti2–C1 2.229(3), Ti1–Ct1 2.067, Ti1–Ct2 2.073, Ti2–Ct3 2.067, Ti2–Ct4 2.072; Ct1–Ti1–Ct2 132.18, Ct3–Ti2–Ct4 133.66, F1–Ti1–N1 77.39, F1–Ti2–C1 78.62, Ti1–F1–Ti2 138.02(9), Ct1 = centroid of C4–C8, Ct2 = centroid of C9–C13, Ct3 = centroid of C14–C18, Ct4 = centroid of C19–C23.

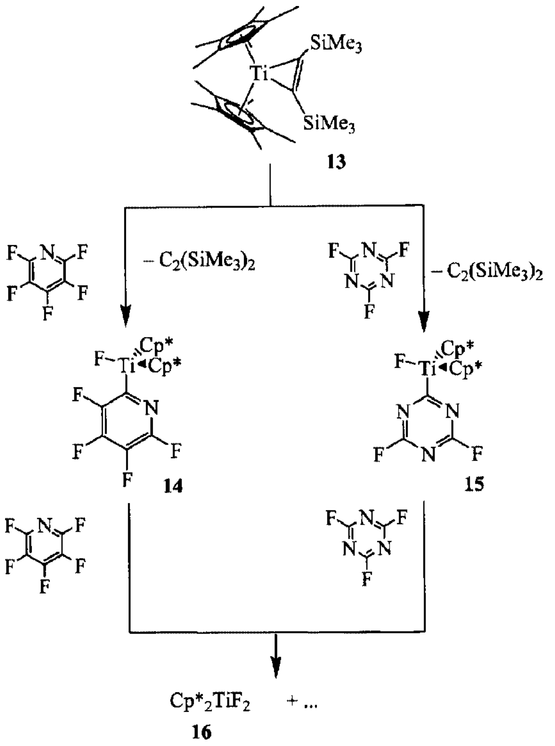
Reactions of $[Cp^*_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}]$ (13) with Fluorinated N-Heterocycles

To understand the formation of binuclear complexes **7**, **8** and **11** reactions were performed using the permethylated complex $[Cp^*_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}]$ (**13**)[34] instead of the non-methylated analogue **10**.



Scheme 3. Reaction of **10** with triazine and cyanuric fluoride.

Both fluorosubstituted pyridines and cyanuric fluoride react with **13** to give [$Cp^*_2TiF_2$] (**16**) as the final product and not binuclear, fluoride-bridged titanocene complexes. Mass spectroscopic investigations, as well as ^1H, ^{13}C and ^{19}F NMR experiments, revealed the intermediate formation of mononuclear Ti^{IV} complexes, which react further with fluorinated starting material to form **16** (Scheme 4).



Scheme 4. Reaction of [$Cp^*_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}$] (**13**) with pentafluoropyridine and cyanuric fluoride, with intermediate formation of mononuclear complexes **14** and **15**.

^1H, ^{13}C and ^{19}F NMR spectroscopic data of **14** were obtained by recording NMR spectra of a corresponding reaction mixture. Therefore, the acetylene complex **13** was reacted with pentafluoropyridine for 2 h at 60 °C in *n*-hexane. The volatiles were then removed and the resulting solid was redissolved in C_6D_6. The ^{19}F NMR spectrum of the reaction mixturedisplaysfour multiplets of equal integration in the fluoroaromatic region at δ = –170.31, –147.48, –130.08 and –87.61, which are assignable to the fluoro nuclei of the pyridyl ligand of complex **14**. These δ are in excellent agreement with ^{19}F NMR spectroscopic data given for the complex [$NiF(2\text{-}C_5NF_4)(PEt_3)_2$], which contains a fluorosubstituted pyridyl ligand with an analogous substitution pattern (δ –173.38, –150.75, –131.33, –84.70).[50] The spectrum also shows a singlet for the metal fluoride of **14** at δ = 128.82. Another ^{19}F resonance at δ = 74.14 was assigned to the final product [$Cp^*_2TiF_2$] (**16**), which is consistent with the NMR spectroscopic data of pure **16** in C_6D_6 prepared according to the literature.[51] The proton spectrum of the reaction mixture shows a singlet at δ = 1.56, assigned to **14**, and, as expected, a further singlet at δ = 1.82, which was assigned to **16**. The single resonance seen for the protons of **14** reveals that the Cp*–Ti–Cp* plane is orthogonal to that of the pyridyl ligand. Consistently, only two signals assigned to the Cp* ligands of **14** arise in the ^{13}C NMR spectrum, at δ = 11.3 and 124.4, respectively. Two further signals, at δ = 11.2 and 124.9, are as expected for **16**. To determine that **14** is formed as an intermediate that reacts with pentafluoropyridine to give the final product **16** the reaction was monitored by following the increase of the ^1H resonance of **14** at δ = 1.56 as the reaction starts and the decrease of this resonance while that assigned to **16** at δ = 1.82 increases. Analogues NMR investigations revealed the formation of the intermediate complex **15** and, subsequently, **16** in the reaction between **13** and cyanuric fluoride (Scheme 4). Besides **16**, NMR investigations could characterize no further products. The fate of the fluoroaromatic ligands could not be clarified. The fluoroaromatic region of the ^{19}F spectra showed several additional signals of very low intensity, probably due to the formation of multiple compounds in low concentration. Table 1 summarizes the ^1H and ^{19}F NMR spectroscopic data of intermediates **14** and **15**.

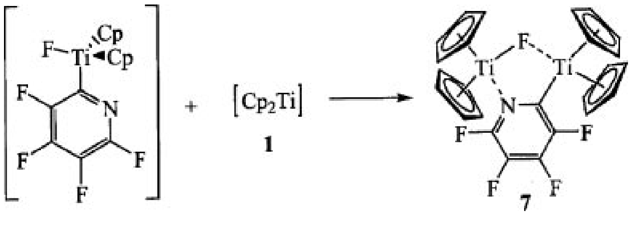
Table 1. NMR spectroscopic data of **14**, **15** (C_6D_6, 298 K).[a]

Complex	^1H	^{19}F
14	1.56 (s, 30 H, CH_3)	128.82 (s, 1 F, Ti–F) –87.61 (m, 1 F) –130.08 (m, 1 F) –147.48 (m, 1 F) –70.31 (m, 1 F)
15	1.53 (s, 30 H, CH_3)	128,71 (s, 1 F, Ti–F) –41.00 (d, J_{FF} = 12, 1 F) –45.31 (d, J_{FF} = 12, 1 F)

[a] Reported in ppm (δ) and *J* values in Hz.

Mass spectra (MS CI, *iso*-butane) of reaction mixtures prepared analogously to those used for the NMR investigations also showed evidence for the intermediate formation of mononuclear Ti^{IV} complexes **14** and **15**. The spectra show the characteristic fragments $[M + 1]^+$, $[M - F]^+$, $[Cp^*_2TiF_2]^+$, $[Cp^*_2TiF]^+$ and $[Cp^*]^+$ (M = molecular mass of **14** and **15**, respectively). Due to their similarly high solubilities, **14** and **15** could not be separated from the final product **16**.

Intermediate formation of mononuclear Ti^{IV} complexes can also be assumed in the reactions to **6**–**8**, and **11**. The Ti^{IV} species might subsequently react further with in situ generated titanocene [Cp_2Ti^{II}] in terms of a comproportion reaction that results in Ti^{III} complexes **6**–**8** and **11** (Scheme 5).



Scheme 5. Proposed formation of binuclear Ti^{III} complex **7**.

The observed preference for C–F activation at the 2-position of the fluoropyridines provides indirect evidence for concerted oxidative addition of the heterocycles via a three-centered transition state, as proposed for nickel-mediated C–F bond activation reactions.[52] A primary electron transfer reaction pathway, as expected from the reducing properties of titanium(II) derivatives, can be excluded due to the absence of reactions at the 4-position, which are found as a result of the formation of ion pairs or Meisenheimer type intermediates.[53–56]

Conclusions

Titanocene-generating systems can selectively activate 2-C–H and 2-C–F bonds of pyridine and fluorosubstituted pyridines, respectively, in reactions that yield dimeric, hydride-bridged Ti^{III} complexes. C–F activation reactions at room temperature between the titanocene source $[Cp_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}]$ and the fluorosubstituted N-heterocycles pentafluoropyridine and 2-fluoropyridine, as well as cyanuric fluoride, afforded dimeric, fluoride-bridged titanocene complexes that were isolated in good yields. The reaction of $[Cp_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}]$ with 2-fluoropyridine showed that 2-C–F activation is preferred over 2-C–H activation. The ease synthesis of polyfluorinated pyridines metallated at the 2-position, via C–F activation reactions, may offer new opportunities to synthesize polyfluorinated pyridines substituted at the 2-position. Such compounds are very difficult to prepare by either electrophilic or nucleophilic substitution.[53,57–60]

Experimental Section

General Remarks: All operations were performed under nitrogen with rigorous exclusion of oxygen and moisture using glove box or Schlenk techniques. Solvents were thoroughly dried and saturated with nitrogen. ^1H and ^{19}F NMR spectra were recorded with a Bruker AVANCE 300 spectrometer (^1H, 300.1 MHz; ^{19}F, 282.4 MHz). ^1H NMR chemical shifts were referenced to residual protons of the solvent; ^{13}C and ^{19}F NMR spectra were referenced to C_6D_6 and $CFCl_3$ (externally), respectively. Electron impact (EI) mass spectra were recorded with a Finnigan-MAT 95 Spectrometer. IR spectra were recorded with a BIO-RAD FTS-7 Spectrometer using KBr pellets. Elemental analyses were carried out by the Analytischen Laboratorien in Lindlar (Germany). $[Cp_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}]$ (**10**) and $[Cp^*{}_2Ti\{\eta^2\text{-}C_2(SiMe_3)_2\}]$ (**13**) were prepared according to the literature.[34] All heterocyclic compounds (Aldrich) were used as received.

Preparation of Complex 5: A suspension of Cp_2TiCl_2 (1 g, 4 mmol), magnesium (96 mg, 4 mmol) and pyridine (2 mL, excess) in THF (40 mL) was stirred for 48 h. The solution turned dark brown and a white solid precipitated. The mixture was then concentrated and the resultant brown solid was dissolved in toluene (20 mL) and filtered. Concentrating the solution to a few mL afforded 420 mg (48%) of **5** as brown crystals that were washed with *n*-hexane and dried in vacuo. M.p. 217–219 °C; ^1H NMR (C_6D_6): δ = 31.0, 16.3, 14.0, 11.1, 10.9 ppm broad signals. IR (KBr): $\tilde{\nu}$ = 3075, 1601, 1441, 1217, 1067, 1009, 793, 758, 698, 629 cm^{-1}. $C_{25}H_{25}NTi_2$ (435.24 $g\,mol^{-1}$); MS (70 eV): *m/z* (rel. intensity) 433 (40) $[M^+ - H_2]$, 354 (100) $[M^+ - C_5H_7N_2]$, 288 (20), 260 (15), 178 (85) $[Cp_2Ti]^+$, 113 (20) $[CpTi]^+$, 66 (15) $[CpH]^+$ The experimental data, including the molecular structure determined by single crystal X–ray diffraction, agree with published results.[37]

Preparation of Complex 6: A solution of **10** (1 g, 2.87 mmol) and pyridine (2 mL, excess) in toluene (30 mL), heated under reflux for 3 h, turned dark brown. Concentrating the solution to a few mL afforded 150 mg (24%) of **6** as brown crystals that were washed with *n*-hexane and dried in vacuo. M.p. 203–205 °C; ^1H NMR (C_6D_6): δ = 16.2, 11.0, 10.9, 9.5, 8.9 ppm broad paramagnetic signals. IR (KBr): $\tilde{\nu}$ = 3079, 1576, 1520, 1435, 1242, 1042, 1009, 8097, 799, 735, 631, 586 cm^{-1}. MS (70 eV): *m/z* (rel. intensity) 433 (50) $[M^+]$, 354 (100) $[M^+ - C_5H_5N]$, 288 (25), 260 (18), 178 (25) $[Cp_2Ti]^+$, 113 (25) $[CpTi]^+$. HR-MS: calcd 433.0789; found 433.0793. $C_{25}H_{23}NTi_2$ (433.22 $g\,mol^{-1}$): calcd H 5.35, C 69.31, N 3.23; found H 5.39, C 69.06, N 3.11.

Preparation of Complex 7: **10** (300 mg, 0.86 mmol) and pentafluoropyridine (**3**) (72.8 mg, 0.43 mmol) were dissolved in *n*-hexane (60 mL) at room temperature. After 24 h crystals precipitated, and the reaction was complete after one week. The mixture changed from yellow to slightly green during the reaction. Crystals, separated from the solution by decanting, were washed twice with *n*-hexane (20 mL) and subsequently dried in vacuo. The yield of **7** was 158 mg (70%) as green-yellow crystals. Crystals suitable for X-ray structure analysis were obtained from fluorobenzene. M.p. 207 °C, IR (KBr): $\tilde{\nu}$= 3937, 3090, 2955, 1715, 1620, 1588, 1505, 1478, 1437, 1373, 1252, 1090, 1013, 795, 691, 592, 471, 395, 226 cm^{-1}. MS (70 eV): *m/z* (rel. intensity) 328 (95) $[M^+ - Cp_2TiF]$, 197 (80) $[Cp_2TiF]^+$, 178 (85) $[Cp_2Ti]^+$, 132 (100) $[CpTiF]^+$. $C_{25}H_{20}F_5NTi_2$ (525.19 $g\,mol^{-1}$): calcd. H 3.84, C 57.18, F 18.09; found H 3.78, C 56.97, F 18.01.

Preparation of Complex 8: **10** (300 mg 0.86 mmol) and 2-fluoropyridine (41.8 mg 0.43 mmol) (**4**) were dissolved in *n*-hexane (60 mL) at room temperature. After one week, the solution was cooled to 0 °C and tawny crystals precipitated. During the reaction the mixture changed from yellow to slightly green. Crystals, separated from the solution by decanting, were washed twice with *n*-hexane (20 mL) and subsequently dried in vacuo. The yield of **8** was 139 mg (71%) as tawny crystals. Crystals suitable for X-ray structure analysis were obtained from the reaction mixture. M.p. 211 °C, IR (KBr): $\tilde{\nu}$= 3090, 2955, 2724, 2367, 2276, 2081, 1651, 1578, 1532, 1449, 1441,1398,1362, 1260, 1154, 1065, 1013, 795, 727, 667, 590, 485, 451, 422, 378 cm^{-1}. MS (70 eV): *m/z* (rel. intensity) 256 (100) $[M^+ - Cp_2TiF]$, 197 (70) $[Cp_2TiF]^+$, 178 (60) $[Cp_2Ti]^+$, 132 (95) $[CpTiF]^+$. $C_{25}H_{24}FNTi_2$ (453,23 $g\,mol^{-1}$): calcd. H 5.34, C 66.26, F 4.02; found H 5.23, C 65.91, F 4.19.

Preparation of Complex 11: **10** (300 mg, 0.86 mmol) and cyanuric fluoride (**9**) (58.1 mg, 0.43 mmol) were dissolved in *n*-hexane (60 mL) at room temperature. After 6 h a brown solid and dark brown crystals precipitated; the reaction was completed after 3 days. The solid, separated from the solution by decanting, was washed twice with *n*-hexane (20 mL) and subsequently dried in vacuo. The yield of **9** was 148 mg (70%) as a brown solid. Crystals suitable for X-ray structure analysis were obtained from the reaction mixture. M.p. 160 °C (dec.), IR (KBr): $\tilde{\nu}$= 3740, 3104, 2955, 2864, 2733, 2517, 2367, 2338, 1615, 1580, 1495, 1398, 1260, 1094, 1017, 804, 689, 590, 463, 397, 328, 303, 280 cm^{-1}. MS (70 eV): *m/z* (rel. intensity) 197 (60) $[Cp_2TiF]^+$, 178 (20) $[Cp_2Ti]^+$, 132 (100) $[CpTiF]^+$, 65 (50) $[Cp]^+$. $C_{23}H_{20}F_3N_3Ti_2$ (491.19 $g\,mol^{-1}$): H 4.10, C 56.24, F 11.60; found H 4.13, C 55.99, F 11.32.

Crystal Structure Determinations: Data for structures **6**–**8** and **11** were collected with a STOE-IPDS diffractometer with graphite-

Table 2. Crystal structure data for complexes **6**–**8**, and **11**.

	6	**7**	**8**	**11**
Empirical formula	$C_{25}H_{23}NTi_2$	$C_{56}H_{45}F_{11}N_2Ti_4$	$C_{28}H_{31}FNTi_2$	$C_{23}H_{20}F_3N_3Ti_2$
Formula mass	433.24	1146.54	496.34	491.22
Diffractometer	STOE IPDS	STOE IPDS	STOE IPDS	STOE IPDS
Crystal dimensions [mm]	0.5 × 0.13 × 0.04	0.88 × 0.11 × 0.06	1.00 × 0.18 × 0.08	0.17 × 0.11 × 0.06
Color, habit	brown	yellow	tawny	brown
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
a [Å]	14.1436(7)	7.9100(2)	17.7395(5)	14.5571(9)
b [Å]	16.1737(4)	18.2720(4)	17.3790(5)	9.7461(3)
c [Å]	17.2637(7)	33.6745(12)	7.81280(10)	15.5543(9)
α [°]	90	90	90	90
β [°]	90	90	90	114.017(7)
γ [°]	90	90	90	90
V [Å^3]	3949.1(3)	4867.0(2)	2408.65(10)	2015.71(18)
Space group	$Pbca$	$P2_12_12_1$	$\mathrm{P}2_12_12$	$P2_1/c$
Z	8	4	4	4
$D_{\mathrm{calcd.}}$ [Mg m^{-3}]	1.457	1.565	1.369	1.619
ν [mm^{-1}]	0.819	0.716	0.686	0.835
F_{000}	1792	2328	1036	1000
λ (Mo-$K\alpha$, graphite) [Å]	0.71073	0.71073	0.71073	0.71073
Temp. [K]	193(2)	193(2)	193(2)	193(2)
θ Range for collection [°]	2.25 to 25.94	2.13 to 26.01	2.30 to 26.01	2.53 to 25.96
No. reflns. collected	327242	42160	25102	20089
No. obsd. reflns. [$I > 2\sigma(I)$]	2186	7586	3919	2199
No. independent reflns.	3649	9058	4506	3921
Absorption corr. method	numerical	none	numerical	none
Max., min. transmission	0.9680, 0.6850	0.9583, 0.5713	0.9471, 0.5469	0.9516, 0.8710
No. data/restraints/parameters	3649/0/344	9058/0/662	4506/0/382	3921/0/280
R indices (all data)	$R1 = 0.0801$, $wR2 = 0.0663$	$R1 = 0.0410$, $wR2 = 0.0644$	$R1 = 0.0308$, $wR2 = 0.0538$	$R1 = 0.0959$, $wR2 = 0.0808$
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0368$, $wR2 = 0.0586$	$R1 = 0.0305$, $wR2 = 0.0618$	$R1 = 0.0241$, $wR2 = 0.0522$	$R1 = 0.0395$, $wR2 = 0.0694$
GoF on F^2	0.837	0.939	0.968	0.801
Fleck parameter	–	–0.003(15)	–0.001(18)	–
Largest diff. peak, hole [e Å^{-3}]	0.268, –0.264	0.229, –0.266	0.333, –0.203	0.316, –0.370

monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Table 2 summarizes the crystal data and intensity collection and refinement parameters. Intensity measurements were performed at 193(2) K. The structure of each complex was solved by direct phase determination (SHELXL 97)[61] and refined on F^2 (SHELXL 97)[61] with anisotropic thermal parameters for all non-hydrogen atoms. CCDC-223097 (**6**), -223098 (**7**), -223099 (**8**), and CCDC-243696 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Fonds der Chemischen Industrie and by the Karl-Ziegler-Stiftung der Gesellschaft Deutscher Chemiker.

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Received: March 29, 2004