Reactions of Zirconocene Bis(trimethylsilyl)acetylene Complexes with Fluorinated Pyridines: C–H vs. C–F Bond Activation

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The zirconocene complexes $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1a**: L = THF; **1b**: L = pyridine) and the ethylene bis(tetrahydroindenyl) complex *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**) react with 2,3,5,6-tetrafluoropyridine with C–H bond activation to produce the 4-substituted pyridyl complexes with agostic alkenyl groups $Cp'_2Zr(4\text{-}C_5NF_4)[\text{–}C(SiMe_3)=CH(SiMe_3)]$ ($Cp'_2 = Cp_2$) (**3**) and (Cp'_2 = ebthi) (**4**). With 2,3,4,6-tetrafluoropyridine, after C–H bond activation, complex **2** yields two isomers of the 5-substituted pyridyl complex *rac*-(ebthi)$Zr(3\text{-}C_5NF_4)[\text{–}C(SiMe_3)=CH(SiMe_3)]$ with agostic alkenyl groups, **5a** and **5b**. With pentafluoropyridine complex **1b** gives, after dissociation of the bis(trimethylsilyl)acetylene (btmsa), C–F bond activation at the 4-position and formation of $Cp_2Zr(4\text{-}C_5NF_4)F$ (**6**). Complex **1b** reacts with 3-chloro-2,4,5,6-tetrafluoropyridine by means of a preferred C–Cl activation to give $Cp_2Zr(3\text{-}C_5NF_4)Cl$ (**7**). These results are in contrast to the reactions of the titanium complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ which, with 2,3,5,6-tetrafluoropyridine, gave C–F activation in preference to C–H activation. With pentafluoropyridine, C–F bond activation at the 2-position was found rather than at the 4-position.

Introduction

Among reactions of different titanocene and zirconocene complexes of bis(trimethylsilyl)acetylene $Cp_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (M = Ti, without L; M = Zr, L = THF, pyridine), the activation of seemingly unreactive bonds by the pentamethylcyclopentadienyl complexes $Cp^*_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (M = Ti, Zr) and the ethylene bis(tetrahydroindenyl) complexes *rac*-(ebthi)$M(\eta^2\text{–}Me_3SiC_2SiMe_3)$ (M = Ti, Zr) has been described by us in some reviews.[1–10] For example, cleavage of C–H, C–C (Cp-ring opening, cleavage of butadiynes), Si–C, P–C, N–H, N–C, N–N, Si–O, N–O, C–O, C–S and C–B bonds gave complexes with potential applications in stoichiometric and catalytic reactions.

The inertness of fluorocarbons is a consequence of the great strength of the C–F bond which arises from the small size and the high electronegativity of the fluorine atom. Nevertheless, the activation of several types of carbon–fluorine bonds by transition metal complexes has been summarised in many reviews.[11–16]

Examples of the activation of C–F bonds by electron-deficient group 4 transition-metal species of zirconium and titanium with subsequent C–F bond cleavage are relatively rare. One of the first examples for titanium was reported by Stone et al. who isolated $Cp_2Ti(C_6F_5)F$ upon pyrolysis of $Cp_2Ti(C_6F_5)_2$.[17] Later Burk and coworkers described the elimination of a cyclopropane $(CH_2)_2CR_2$ and the formation of a titanocene-fluoro-dienone complex $Cp_2Ti(F)[(O\text{–}C(CCF_3)_3C=CF_2)]$ by F-abstraction in the reaction of a tetrakis(trifluoromethyl)cyclopentadienone-titanacyclobutane complex $[Cp_2Ti(CH_2)_2CR_2][O=C(CCF_3)_4]$.[18] Beckhaus and coworkers described the complete defluorination of trifluoromethyl-substituted Cp-ligands by titanium amide complexes.[19] More recently similar reactions were described by Deck et al. for the corresponding pentafluorophenyl substituents of cyclopentadienyl and indenyl ligands.[20] Hessen and coworkers reported that the complex $[Cp^*_2Ti(\eta^1\text{-}FC_6H_5)][BPh_4]$ reacts with trifluorotoluene to yield 1,2-diphenyl-1,1,2,2-tetrafluoroethane and $Cp^*_2TiF_2$.[21] Stoichiometric and catalytic C–F bond activations for the aromatisation of cyclic perfluorocarbons were achieved using titanocene and zirconocene, generated from Cp_2MCl_2 (M = Ti, Zr) and $Mg/HgCl_2$ or Cp_2ZrCl_2 and $Al/HgCl_2$.[22]

Zirconocene generating systems such as Cp_2ZrPh_2 or $Cp_2ZrCl_2/2\ n$BuLi can defluorinate perfluorodecalin to perfluoronaphthalene.[23] 2-Fluoro- and 3-fluoropyridine can also be defluorinated by various complexes such as Cp'_2MCl_2 (M = Ti, Zr, Hf; Cp′ = Cp, Cp*) in combination with different aluminium compounds acting as reducing agents.[24] In a series of outstanding papers, Jones and co-

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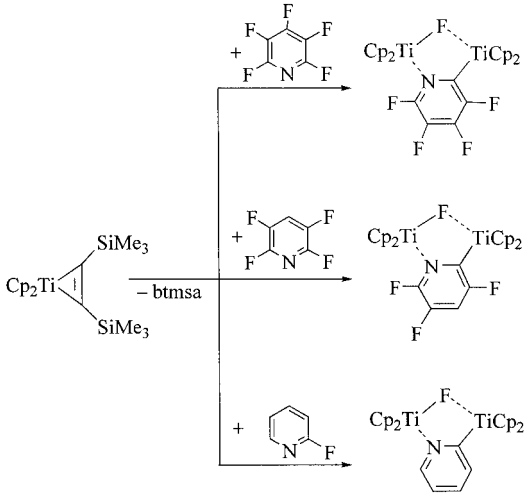
workers described the activation of several types of C–F bonds in alkanes, arenes and olefins using $Cp^*_2ZrH_2$. The published mechanistic investigations showed different pathways depending on the substrate used.[25–31] Caulton et al. showed that Cp_2ZrHCl reacts with fluoroethylene with formation of Cp_2ZrFCl, $Cp_2Zr(CH_2CH_3)Cl$ and Cp_2ZrF_2.[32] In the case of zirconium, hydride complexes were mostly used in C–F bond activation reactions. One exception was the reaction of *rac*-(ebthi)Zr(Me)(NH*t*Bu) with pentafluoropyridine published by Bergman and coworkers. Using the monomeric imidozirconocene complex [*rac*-(ebthi)-Zr=N*t*Bu], they observed activation of the *ortho* C–F bond and the formation of an amininopyridinato complex *rac*-(ebthi)ZrF(-N*t*Bu-2-C_5NF_4).[33]

In the light of the surprising results concerning zirconocene difluorides and alkyl monofluorides in the catalytic polymerisation of olefins,[34–37] we began to question whether the above mentioned alkyne complexes could activate C–F bonds to form the zirconocene fluoro complexes by C–F bond cleavage. These investigations were also extended to cover the question of whether hydride complexes (Zr–H systems, formed by reactions of systems containing Zr–F and Al–H bonds) could cleave the C–F bonds of $B(C_6F_5)_3$.[38,39]

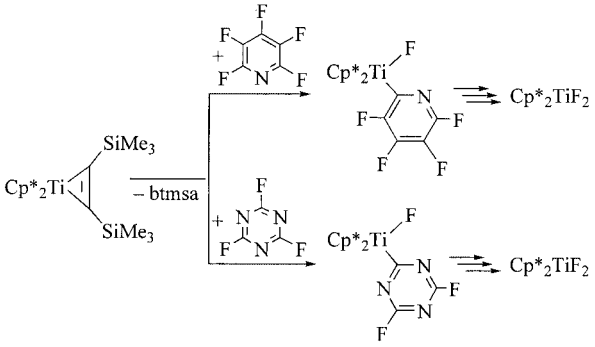
In this work we extended and compared the investigations of Beckhaus and his group concerning reactions of our titanium reagents[1–10] $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and $Cp^*_2Ti(\eta^2\text{–}Me_3SiC_2SiMe_3)$ towards pyridine and fluorinated pyridines with the reactions of the corresponding zirconocene complexes. In this paper we describe the reactions of the zirconocene complexes $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1a**: L = THF, **1b**: L = pyridine) and the ethylene bis(tetrahydroindenyl) complex *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ towards fluorinated pyridines. These reactions were used to probe any differences in the behaviour between the bis(trimethylsilyl)acetylene complexes of Ti and Zr.

Results and Discussion

Very recently, Beckhaus and coworkers published a series of excellent examples of reactions of titanocene bis(trimethylsilyl)acetylene complexes with different N-heterocyclic compounds.[40–43] In these reactions, the complexes $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ act as sources of titanocene "Cp_2Ti" and permethyltitanocene "Cp^*_2Ti" after dissociation of the alkyne. They react differently with pyridine and fluorinated pyridines (Scheme 1 and Scheme 2). Under C–H activation, $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and pyridine give an H-bridged binuclear titanium fulvalene derivative. 2-Fluoropyridine reacts with $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ by means of C–F activation to give an F-bridged binuclear titanium complex. It is remarkable that no C–H activation product was found in this case. With $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$, pentafluoropyridine gives a similar perfluorinated product.



Scheme 1.

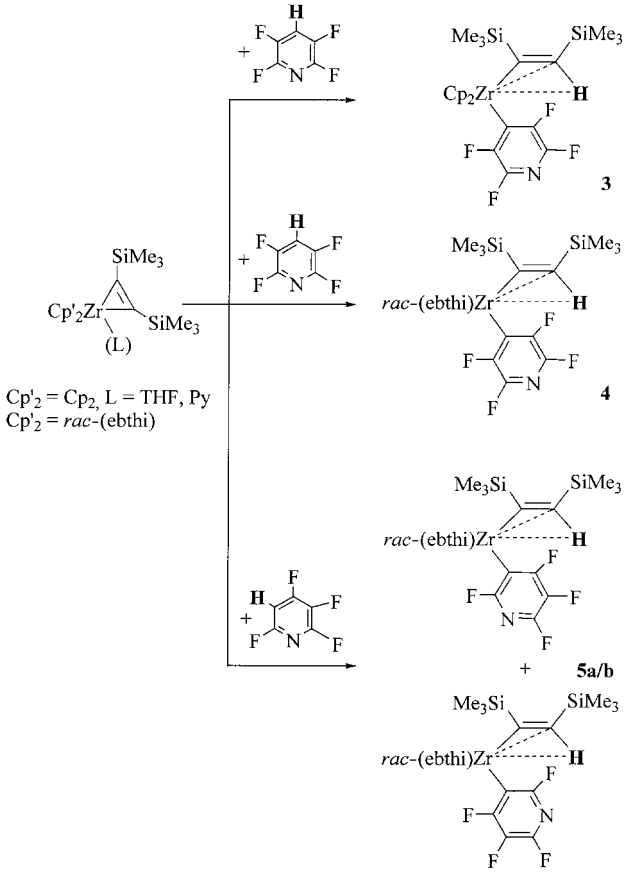


Scheme 2.

With $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ the pentafluoropyridine forms, after C–F activation, a mononuclear titanium(IV) monofluoro complex $Cp^*_2Ti(2\text{-}C_5NF_4)F$ as an intermediate, as demonstrated by ^1H and ^{19}F NMR spectroscopic measurements. The latter complex reacts with an excess of the substrate to give the difluoride complex $Cp^*_2TiF_2$. A similar reaction was found for the cyanuric fluoride (Scheme 2).

In addition to C–F activation after elimination of the bis(trimethylsilyl)acetylene, there is another pathway for the reactions of the corresponding zirconocene complexes **1** and **2** with fluorinated pyridines. Upon C–H activation and without alkyne elimination, formation of agostic alkenyl complexes was observed. Both possibilities represent the typical reactions of these metallocene bis(trimethylsilyl)-acetylene complexes (Scheme 3).

The zirconocene complex $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1a**) and the ethylene bis(tetrahydroindenyl) complex *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**) react with 2,3,5,6-tetrafluoropyridine by means of C–H bond activation to produce the complexes $Cp'_2Zr(4\text{-}C_5NF_4)$[–C(SiMe$_3$)=CH(SiMe$_3$)] ($Cp'_2 = Cp_2$) (**3**) and ($Cp'_2$ = ebthi) (**4**) (Scheme 3) containing both fluorosubstituted pyridyl groups metallated in the 4-position and agostic alkenyl groups. With 2,3,4,6-tetrafluoropyridine complex **2** yields,



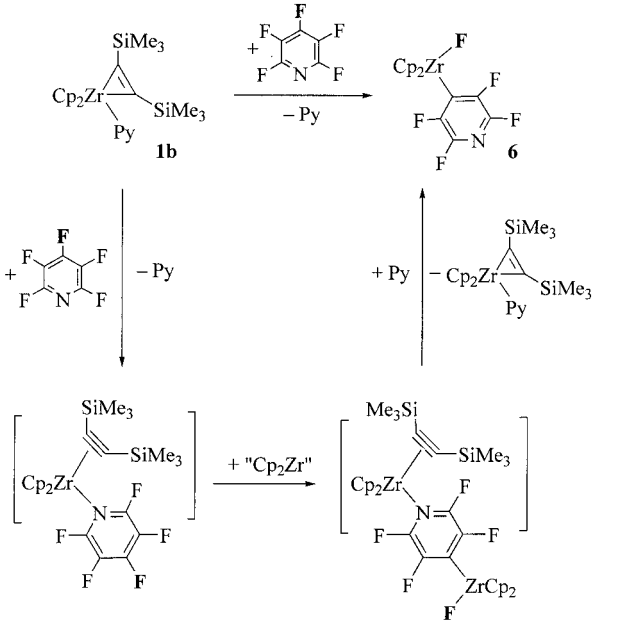
Scheme 3.

after C–H bond activation, two isomers **5a** and **5b** (1 to 2 ratio) of the corresponding complex *rac*-(ebthi)Zr(3-C_5NF_4)[–C($SiMe_3$)=CH($SiMe_3$)] bearing fluorosubstituted pyridyl substituents metallated in the 5-position as well as agostic alkenyl groups (Scheme 3).

With pentafluoropyridine and **1b**, elimination of bis(trimethylsilyl)acetylene and C–F bond activation in the 4-position was observed with subsequent formation of Cp_2Zr(4-C_5NF_4)F (**6**) (Scheme 4). As described in this work, in the case of zirconium such a species was isolated whereas in the above mentioned reaction of $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with pentafluoropyridine the respective C–F activation reaction resulted in formation of a similar mononuclear titanium(IV) mono-fluoro complex $Cp^*_2Ti(2\text{-}C_5NF_4)F$ only as an intermediate which reacts to give the difluoride $Cp^*_2TiF_2$ (see Scheme 2).

According to these results, C–H activation is preferable to C–F activation for zirconium. For zirconium, the attack for C–F bond activation occurs in the 4-position and not in the 2-position as described for titanium. Both positions are activated but in the case of zirconium the 4-position is favoured.

It is possible to explain the favoured reaction at the 4-position for zirconium by invoking a bimolecular reaction with precoordination of the pentafluoropyridine as an N-donor and a subsequent attack of a second zirconocene moiety at the 4-position (Scheme 4). Coordination of the

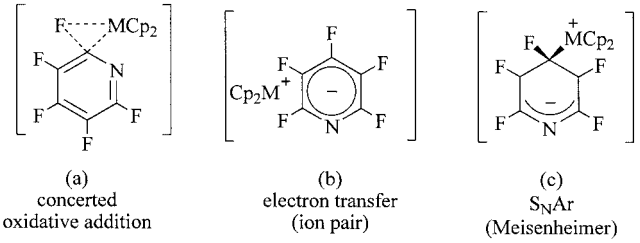


Scheme 4.

pyridine or such a precoordination of the pentafluoropyridine is generally impossible for the complex $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ because of the smaller sized titanium atom.

It is reasonable to assume that the above mentioned C–H bond activation of 2,3,5,6-tetrafluoropyridine in complexes containing a fluorosubstituted pyridyl metallated in the 4-position could also proceed via a similar precoordination. In contrast, the unsubstituted pyridine in complex **1b** did not show such reactivity since it has no H-atoms in the 4-position which could be activated.

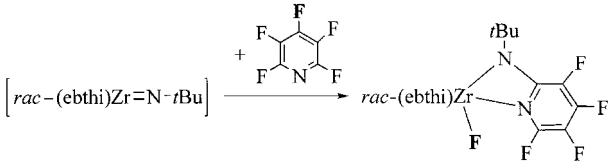
Another explanation for the favoured reaction at the 4-position follows from suggestions by Jones, Braun and Perutz (Scheme 5).[15,44] The observed preference for C–F bond activation in the 2-position for titanium provides evidence for concerted oxidative addition of the pyridine by means of a three-centred transition state (a). An electron transfer reaction pathway through a tight ion pair (b) or an S_NAr type nucleophilic mechanism via a Meisenheimer intermediate (c) would result in an attack at the 4-position of the pentafluoropyridine as found for zirconium.



Scheme 5.

These results for the activation in the 4-position are also in contrast to the above mentioned reaction very recently described by Bergman[33] in which *rac*-(ebthi)Zr(Me)(NH*t*Bu) reacts with pentafluoropyridine via the monomeric imidozirconocene complex [*rac*-(ebthi)Zr=N*t*Bu]

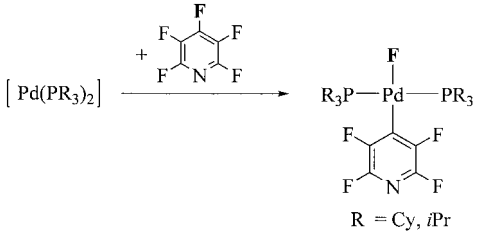
to afford the amininopyridinato complex *rac*-(ebthi)ZrF-(–N*t*Bu-2-C_5NF_4) with activation of the *ortho* C–F bond (Scheme 6).



Scheme 6.

On the other hand, Bergman described only N-donor coordination for the unsubstituted pyridine and no C–H bond activation whereas the imidozirconocene complex [*rac*-(ebthi)Zr=N*t*Bu] reacted, for example with benzene, with activation of the C–H bond and formation of the complex *rac*-(ebthi)Zr(Ph)NH*t*Bu.[33]

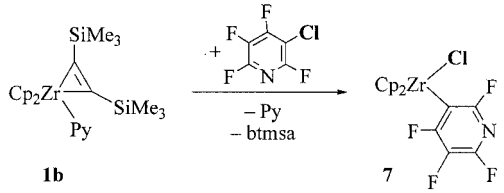
The activation of pentafluoropyridine in the 4-position with formation of $L_nM(4\text{-}C_5NF_4)F$ complexes was shown by Perutz and Braun to be typical for Ni,[44] Pd,[45] Rh[46] and Pt.[47] An example of reactions of this type is shown in Scheme 7.



Scheme 7.

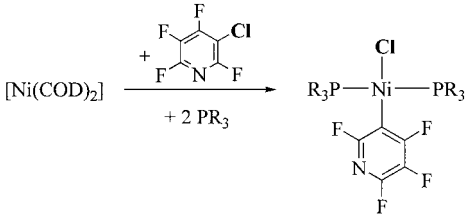
One can conclude from these results that the chemo- and regioselectivity of the C–H and C–F bond activations in reactions of fluorinated pyridines depends on the *metals* (C–F for Ti, C–H for Zr; 2-position for Ti, 4-position for Zr and Ni) and the *ligands* (Zr: 2-position for L = imido, 4-position for L = alkyne).

For the purpose of comparing the different reactivities of C–F and C–Cl bonds in halogenated pyridines, we found that complex **1b** reacts with 3-chloro-2,4,5,6-tetrafluoropyridine by means of a preferred C–Cl activation to give $Cp_2Zr(3\text{-}C_5NF_4)Cl$ (**7**) (Scheme 8). This result is very similar to that described by Perutz and Braun for the reaction of Ni^0 complexes with 3-chloro-2,4,5,6-tetrafluoro-pyridine (Scheme 9).[44]



Scheme 8.

In general, the preferred reactivity of C–Cl bonds over C–F bonds is not restricted to the 3-position of the 3-chloro-2,4,5,6-tetrafluoro-pyridine. Traces of 2-chloro-3,4,5,6-tetrafluoro-pyridine contained in our batch of pentafluoro-pyridine also reacted with complex **2** with preferred C–Cl bond activation to give the complex *rac*-(ebthi)-$Zr(2\text{-}C_5NF_4)Cl$.[48]



Scheme 9.

NMR-Spectroscopic and Molecular Structure Data

Unfortunately, all of the new compounds are only sparingly soluble in aromatic hydrocarbons so that in most cases the detection of the fluorinated carbon atoms was unsuccessful. However, the presence of the fluorinated pyridines is evident from their ^{19}F NMR signals. The most characteristic NMR spectroscopic and molecular structural feature of compounds **3** and **4** is the agostic interaction of the alkenyl group Zr–Cα=CβH. This alkenyl unit shows ^1H-NMR signals at rather low fields and the ^{13}C-NMR signals of Cα appear at low field whereas the Cβ signals are located upfield of the normal olefinic range. Typical for the additional agostic interaction is the very small coupling constant $^1J_{C\beta\text{-}H}$ (96 Hz in **3**, 97 Hz in **4** and 100 Hz in **5**). In the molecular structure, acute Zr–Cα–Cβ angles and short Zr–Cβ bond lengths reflect this special type of interaction. All these features have been previously observed in similar complexes such as $[Cp_2Zr\{-C(SiMe_3)=CH(SiMe_3)\}]_2[\mu\text{-}C\equiv C]$ (**A**),[49] [*rac*-(ebthi)Zr(C≡C-2-Py){–C(SiMe$_3$)=CH(SiMe$_3$)}] (**B**)[49] and the β-propiolactamate $[Cp_2Zr(-NC_3H_4O)\{-C(SiMe_3)=CH(SiMe_3)\}]$ (**C**)[50] which are all typical zirconocene σ-alkenyl complexes with agostic Cβ–H···Zr interactions (Table 1).

Table 1. Comparison of spectroscopic and structural data of complexes with agostic interactions $Cp'_2Zr(R)[C\alpha(SiMe_3)=C\beta H\text{-}(SiMe_3)]$.

Compound	**3**	**4**	A	B	C
Cp′$_2$	Cp_2	ebthi	Cp_2	ebthi	Cp_2
R	4-C_5NF_4	4-C_5NF_4	[μ-C≡C]	C≡C-2-Py	NC_3H_4O
^1H-NMR [ppm]					
δ(Cβ-H)	6.65	6.27	7.94	7.69	8.04
^{13}C-NMR					
δ(Cα)	218.8	223.6	236.4	227.6	227.0
δ(Cβ)	101.1	115.4	149.1	114.5	106.3
$^1J_{C\beta\text{-}H}$ [Hz]	96	97	125	98	101
Bond lengths [Å]					
d(Zr–Cα)	2.247(2)	2.257(2)	2.235(7)	2.262(3)	2.242(3)
d(Zr–Cβ)	2.554(2)	2.556(2)	2.530(7)	2.530(4)	2.543(3)
d(Cα = Cβ)	1.323(3)	1.331(3)	1.329(9)	1.319(5)	1.330(4)
Angles [°]					
ZrCαCβ	87.3(2)	86.8(2)	86.5(5)	85.6(2)	86.9(2)

Table 2. Crystallographic data.

	3	4	6	7
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a [Å]	9.961(2)	9.520(2)	9.484(2)	7.716(2)
b [Å]	10.544(2)	25.141(5)	7.845(2)	9.007(2)
c [Å]	13.207(3)	13.741(3)	19.025(4)	20.755(4)
α [°]	108.51(3)			
β [°]	99.85(3)	106.40(3)	101.94(3)	
γ [°]	104.00(3)			
V [Å^3]	1229.1(4)	3155.0(11)	1384.9(5)	1442.4(6)
Z	2	4	4	4
Density [g cm^{-3}]	1.467	1.425	1.873	1.874
μ(Mo-K_α) [mm^{-1}]	0.586	0.472	0.845	0.985
T [K]	200	200	200	200
Reflections (measured)	3658	11391	3952	6273
Reflections (independent)	3658	6180	2142	1843
Reflections (observed)	3165	5116	1834	1620
No. parameters	284	372	183	199
R_1 [$I > 2\sigma(I)$]	0.0248	0.0335	0.0276	0.0266
wR_2 (all data)	0.0606	0.0921	0.0714	0.0552

In the ^{19}F NMR spectra of complexes **3**, **4**, **5**, **6** and **7** the shifts for the fluorine substitutents on the pyridine ring are in the low field region for uncoordinated fluoroaromatics (ca. –100 ppm) and are not shifted to the extreme high field as found for the fluoro bridged Zr–F–C groups (ca. –200 ppm).[51] The signal for the fluoride at zirconium was found at 1.3 ppm for complex **6**. This is in the range typically seen for other zirconocene fluorides (ca. 20–30 ppm).[52]

The increased steric demand of the *rac*-ebthi ligand system is responsible for restricted rotation of the pyridyl group about the Zr–C bond. For the Cp complex **3** only two ^{19}F resonances were found whereas the ebthi complex **4** exhibits four (an exchange between the otherwise equivalent *ortho* or *meta* fluoro substituents by pyridyl rotation does not occur). Therefore, two possible and different orientations of the asymmetric 5-pyridyl substituent are the most probable explanation for the presence of two isomeric forms

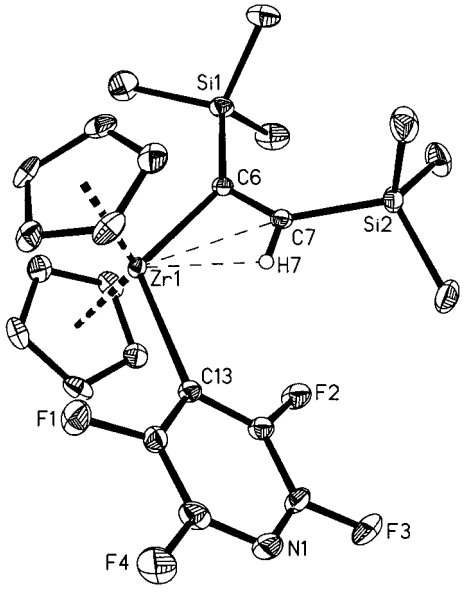


Figure 1. Molecular structure of complex **3**. Hydrogen atoms (except H7) are omitted for clarity. The thermal ellipsoids correspond to the 30% probability level. Selected bond lengths [Å] and angles [°]: Zr1–C6 2.247(2), Zr1–C7 2.554(2), Zr1–H7 2.14(2), Zr1–C13 2.432(2); Zr1–C6–C7 87.3(2), C7–C6–Si1 131.8(2), C6–C7–Si2 137.4 (2).

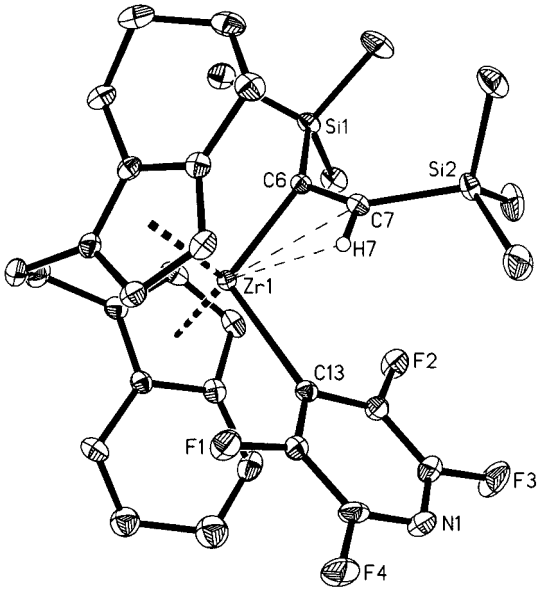


Figure 2. Molecular structure of complex **4**. Hydrogen atoms (except H7) are omitted for clarity. The thermal ellipsoids correspond to the 30% probability level. Selected bond lengths [Å] and angles [°]: Zr1–C6 2.257(2), Zr1–C7 2.556(2), Zr1–H7 2.16(3), Zr1–C13 2.426(2); Zr1–C6–C7 86.8(2), C7–C6–Si1 128.0(2), C6–C7–Si2 137.6 (2).

of **5** (Scheme 3). Accordingly, differences show up for the proton signal of the agostic CH group: it appears as a *triplet* in **3** (coupling to two fluorine atoms made equivalent by pyridyl rotation) but only as a *doublet* in **4** and **5**.

Complexes **3**, **4**, **6** and **7** were investigated by X-ray crystallography. The crystallographic data are presented in Table 2 and the molecular structures are shown in Figure 1, Figure 2, Figure 3 and Figure 4, respectively. Complexes **3**, **4**, **6** and **7** display the general feature of bent metallocenes and show no interactions between the fluoro substituents of the pyridine ring and the central atom. Complexes **3** and **4** are characterised by a molecular geometry typical for species containing agostic interactions of the alkenyl group Zr–Cα=CβH (Table 1). Notable features are Zr–Cα bonds in the range of a single bond, Cα–Cβ distances in the range typical for double bonds and a very small Zr–Cα–Cβ angle which indicates the additional interaction of the H(Cβ) with the central zirconium atom (Figure 1 and Figure 2). The tetrafluoropyridyl ring σ-bonded at the 4-position exhibits relatively long Zr–C single bond lengths [Zr1–C13 = 2.432(2) Å in **3** and 2.426(2) Å in **4**].

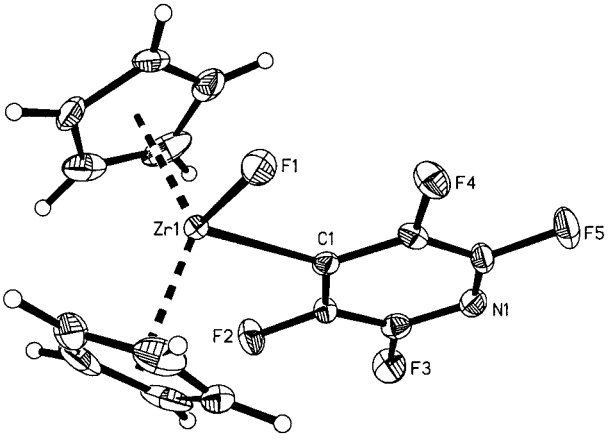


Figure 3. Molecular structure of complex **6**. The thermal ellipsoids correspond to the 30% probability level. Selected bond lengths [Å] and angles [°]: Zr1–C1 2.347(3), Zr1–F1 1.946(2); F1–Zr1–C1 99.38(9).

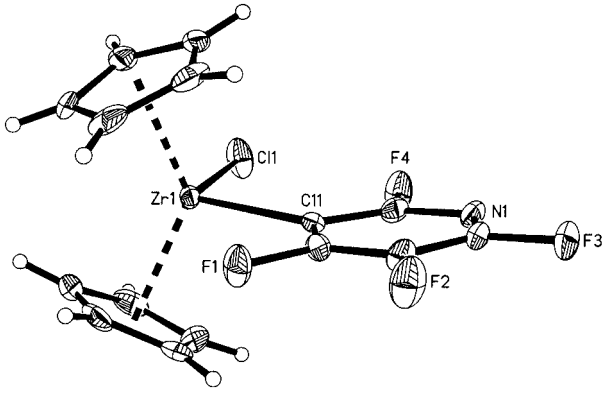


Figure 4. Molecular structure of complex **7**. The thermal ellipsoids correspond to the 30% probability level. Selected bond lengths [Å] and angles [°]: Zr1–C11 2.353(5), Zr1–Cl1 2.422(1); Cl1–Zr1–C11 104.9(1).

The molecular structure of complex **6** is depicted in Figure 3. The tetrafluoropyridyl ring σ-bonded at the 4-position in the molecule has shorter Zr–C bond lengths [Zr1–C13 = 2.347(3) Å] compared with **3** and **4** mentioned above. The observed Zr1–F1 bond length of 1.946(2) Å and the C1–Zr1–F1 angle of 99.38(9)° are in the same range as found in other zirconocene fluoro complexes. For example, some bond lengths were observed in the complex $Cp_2Zr(F)(C_6F_5)$ [Zr–C = 2.346 Å and Zr–F = 1.946 Å].[25] The monofluoride [(η^5-tetrahydroindenyl)$_2$Zr(F)(CH_2CH_2-2-Py)] [Zr–C = 2.377(3) Å] and the difluoride [(η^5-tetrahydroindenyl)$_2ZrF_2$] [Zr–F = 1.946(2) and 1.974(2) Å] exhibit comparable bond lengths.[52]

In the molecular structure of complex **7** (Figure 4), the bond length for Zr1–C11 [2.353(5) Å] is the same as that found for complex **6**. The observed Zr1–Cl1 bond length of 2.422(1) Å corresponds well with that found in other complexes of this type, e.g. Cp*$_2$Zr(Cl)($CH_2CH{=}CH_2$) (Zr–C = 2.324 Å and Zr–Cl =2.436 Å).[53]

Conclusions

Using the reactions presented we have documented that zirconocene bis(trimethylsilyl)acetylene complexes are able to activate C–H, C–F and C–Cl bonds of differently substituted pyridines. Whereas the corresponding titanocene bis(trimethylsilyl)acetylene complexes react with elimination of the alkyne and preferential C–F bond activation with formation of binuclear Ti^{III} complexes, an additional reaction possibility exists for zirconium in which the alkyne can remain part of the complex and form, after C–H bond activation, Zr^{IV} complexes with agostic σ-alkenyl groups. The latter is a typical example of the different reactivity between titanocene and zirconocene bis(trimethylsilyl)acetylene complexes. For titanium, a favourable elimination of the alkyne with formation of Ti^{III} complexes can be observed whereas for zirconium no elimination of the alkyne occurs but, instead, the formation of Zr^{IV} complexes.

Experimental Section

General: All operations were carried out under argon with standard Schlenk techniques. Prior to use, solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvents were treated with sodium or sodium tetraethylaluminate then distilled and stored under argon. Fluorinated pyridines were dried over molecular sieves and degassed before use. The following spectrometers were used: Mass spectrometry: AMD 402; NMR spectroscopy: Bruker ARX 400 (^{1}H, ^{13}C) and Bruker AC 250 (^{19}F) instruments. Chemical shifts were referenced to signals of the solvents used which were [D_6]benzene (δ_H = 7.16, δ_C = 128.0 ppm) and [D_8]toluene (δ_H = 2.03, δ_C = 20.4 ppm). The ^{19}F NMR spectra were referenced to external $CFCl_3$. The spectra were assigned with the help of DEPT experiments. Melting points were measured in sealed capillaries using a Büchi 535 apparatus. Elemental analyses were performed using a Leco CHNS-932 elemental analyser.

X-ray Crystallographic Study of Complexes 3, 4, 6 and 7: Data were collected with a STOE-IPDS-diffractometer using graphite-mono-

chromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS-86)[54] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[55] XP (BRUKER AXS) was used for structure representations.

CCDC-263968 (for **3**), -263969 (for **4**), -263970 (for **6**) and -263971 (for **7**) 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.

Preparation of Complex 3: Complex **1a** (266 mg, 0.5 mmol) was dissolved in THF/*n*-hexane (ca. 1 to 3, 10 mL) and treated with 2,3,5,6-tetrafluoropyridine (115 μL, 1.14 mmol) while stirring. After 2 h at 60 °C the brown solution had become green and a grey precipitate had formed. After filtration, the precipitate was recrystallised from THF/*n*-hexane at –32 °C. Filtration gave a yield of 160 mg of colourless crystals (51%). M.p. 147 °C (dec.). $C_{23}H_{29}F_4NSi_2Zr$ (542.87): calcd. C 50.89, H 5.38, N 2.58; found C 50.98, H 5.30, N 2.55. ^{1}H NMR (C_6D_6): δ = 0.15 (t, $J_{H,F}$ = 0.7 Hz, 9 H, β-$SiMe_3$), 0.25 (s, 9 H, α-$SiMe_3$), 5.34 (s, 10 H, Cp), 6.65 (t, $J_{H,F}$ = 3.9 Hz, 1 H, CH) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 0.2 (t, $J_{C,F}$ = 1.6 Hz, β-$SiMe_3$), 2.0 (α-$SiMe_3$), 101.1 ($^1J_{C,H}$ = 96.2, $J_{C,F}$ = 1.8 Hz, β-CH), 108.1 (Cp), 146.0, 143.6 (2 m, CF), 162.8 (t, $^2J_{C,F}$ = 57 Hz, *p*-C), 218.8 (t, $J_{C,F}$ = 1.5 Hz, α-C) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ = –96.5 (AA′XX′), –110.5 (AA′XX′) ppm. ^{29}Si NMR (C_6D_6): δ = –3.2 ($^2J_{Si,H}$ = 3 Hz (CH) and 6.6 Hz (Me), β-Si), –6.9 ($^2J_{Si,H}$ = 6.4, $^3J_{Si,H}$ = 19 Hz, α-Si) ppm. MS (70 eV): *m*/*z* 541 $[M]^+$, 391 $[M - C_5F_4N]^+$, 370 $[M - Me_3SiC{=}CHSiMe_3]^+$, 220 $[M - C_5F_4N - Me_3SiC{=}CHSiMe_3]^+$.

Preparation of Complex 4: This was prepared as described above starting from complex **2** (300 mg, 0.57 mmol) and 2,3,5,6-tetrafluoropyridine (230 μL, 2.3 mmol) in *n*-heptane. At 80 °C the solution became red-brown and a yellow precipitate formed which was filtered off to give complex **4**. The yield was 161 mg (42%). M.p. 197 °C (dec.). $C_{33}H_{43}F_4NSi_2Zr$ (675.19): calcd. C 58.54, H 6.40, N 2.07; found C 58.28, H 6.62, N 1.99. ^{1}H NMR (C_6D_6): δ = 0.14 (d, $J_{H,F}$ = 0.7 Hz, 9 H, β-$SiMe_3$), 0.40 (s, 9 H, α-$SiMe_3$), 0.65–2.59 (20 H, CH_2), 5.15 (t, $J_{H,F} \approx {}^3J_{H,H} \approx$ 2.4 Hz, 1 H, CH), 5.87 (t, $J_{H,F} \approx {}^3J_{H,H} \approx$ 3.0 Hz, 1 H, CH), 5.97 (dd, $J_{H,F} \approx$ 1.5, $^3J_{H,H} \approx$ 2.7 Hz, 1 H, CH), 6.27 (d, $J_{H,F}$ = 4.5 Hz, 1 H, =CHβ), 6.45 (d, $^3J_{H,H}$ = 2.7 Hz, 1 H, CH) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 0.9 (β-$SiMe_3$), 3.4 (α-$SiMe_3$), 21.8, 22.1, 22.3, 22.7, 23.3 (2 C), 24.1, 25.6 (d, $J_{C,F} \approx$ 1 Hz), 27.7, 28.5 (10×CH_2), 100.1, 103.3 (d, $J_{C,F}$ = 4.0 Hz), 105.3, 106.4 (d, $J_{C,F}$ = 10.5 Hz) (4×CH), 115.4 ($^1J_{C,H}$ = 96.8, $J_{C,F}$ = 4.4 Hz, β-CH), 120.8, 122.1 (d, $J_{C,F} \approx$ 1 Hz), 122.7 (d, $J_{C,F} \approx$ 1 Hz), 125.7, 129.4, 129.6 (6×quat. C), 223.6 (d, $J_{C,F}$ = 4.4 Hz, α-C) ppm; the C atoms of the pyridine were not found. ^{19}F{^{1}H} NMR (C_6D_6): δ = –95.7 (m), –97.4 (m), –112.6 (m), –114.6 (m) ppm. MS: *m*/*z* 675 $[M]^+$, 524 $[M - C_5F_4N]^+$, 504 $[M - C_8H_{19}Si_2]^+$, 354 $[M - C_5F_4N - C_8H_{19}Si_2]^+$.

Preparation of Complexes 5a/b: These were prepared as described above starting from complex **2** (243 mg, 0.43 mmol) and 2,3,4,6-tetrafluoropyridine (49 μL, 0.48 mmol) in *n*-heptane (10 mL). After 1.5 h at 60 °C the green solution had become red-brown and a yellow precipitate had formed which was filtered off to give a 1:2 mixture of complexes **5a** and 5**b**. Yield 233 mg (75%). M.p. 180–181 °C (dec.). $C_{33}H_{43}F_4NSi_2Zr$ (675.19): calcd. C 58.54, H 6.40, N 2.07; found C 58.30, H 6.28, N 2.01. ^{1}H NMR (C_6D_6): **5a**: δ = 0.15 (s, 9 H, β-$SiMe_3$), 0.40 (s, 9 H, α-$SiMe_3$), 0.6–2.7 (20 H, CH_2), 5.17 (t, $J_{H,F} \approx {}^3J_{H,H} \approx$ 2.6 Hz, 1 H, CH), 5.83 (t, $J_{H,F} \approx {}^3J_{H,H} \approx$ 3.0 Hz, 1 H, CH), 5.99 (dd, $J_{H,F} \approx$ 1.5, $^3J_{H,H} \approx$ 2.9 Hz, 1 H, CH), 6.40 (d, $J_{H,F}$ = 3.7 Hz, 1 H, =CHβ), 6.42 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, CH) ppm. **5b**: δ = 0.18 (s, 9 H, β-$SiMe_3$), 0.41 (s, 9 H, α-$SiMe_3$), 0.6–2.7 (20 H, CH_2), 5.18 (t, $J_{H,F} \approx {}^3J_{H,H} \approx$ 2.6 Hz, 1 H, CH), 5.80 (t, $J_{H,F} \approx {}^3J_{H,H} \approx$ 3.0 Hz, 1 H, CH), 5.95 (dd, $J_{H,F} \approx$ 1.6, $^3J_{H,H} \approx$ 2.6 Hz, 1 H, CH), 6.39 (d, $J_{H,F}$ = 3.7 Hz, 1 H, =CHβ), 6.45 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, CH) ppm. ^{13}C{^{1}H} NMR (C_6D_6): **5a**: δ = 0.9 (β-$SiMe_3$), 3.4 (α-$SiMe_3$), 21.9, 22.2, 22.4, 22.8, 23.3 (2 C), 23.9, 25.6, 27.8, 28.3 (10×CH_2), 99.7, 104.2 (d, $J_{C,F}$ = 4.2 Hz), 105.1, 106.7 (d, $J_{C,F}$ = 11.0 Hz) (4×CH), 116.1 (d, $J_{C,F}$ = 3.3 Hz, =CHβ), 120.5, 121.7 (d, $J_{C,F} \approx$ 1 Hz), 122.9 (d, $J_{C,F} \approx$ 1 Hz), 125.7, 129.5, 129.6 (6×quat. C), 225.2 (d, $J_{C,F}$ = 4.0 Hz, α-C) ppm; **5b**: δ = 1.0 (β-$SiMe_3$), 3.4 (α-$SiMe_3$), 21.8, 22.3, 22.4, 22.7, 23.4 (2 C), 24.2, 25.2 (d, $J_{C,F} \approx$ 1 Hz), 27.8, 28.5 (10×CH_2), 99.9, 103.0 (d, $J_{C,F}$ = 3.9 Hz), 105.1, 105.9 (d, $J_{C,F}$ = 10.0 Hz) (4×CH), 116.7 ($^1J_{C,H} \approx$ 100, $J_{C,F}$ = 3.5 Hz, =CHβ), 119.9, 121.8 (d, $J_{C,F} \approx$ 1 Hz), 122.4 (d, $J_{C,F} \approx$ 1 Hz), 125.6, 129.2, 129.6 (6×quat. C), 222.9 (d, $J_{C,F}$ = 4.7 Hz, α-C) ppm; the C-atoms of the pyridine were not found. ^{19}F{^{1}H} NMR (C_6D_6): **5a**: δ = –43.9 (m), –88.0 (m), –92.7 (m), –171.5 (m) ppm. **5b**: δ = –41.9 (m), –90.0 (m), –93.7 (m), –170.3 (m) ppm. The molar ratio **a/b** is about ½. MS: *m*/*z* 675 $[M]^+$, 354 $[M - C_5F_4N - C_8H_{19}Si_2]^+$.

Preparation of Complex 6: This was prepared as described above starting from complex **1b** (553 mg, 1.2 mmol) and pentafluoropyridine (142 μL, 1.3 mmol) in *n*-hexane (15 mL). The violet solution became red-brown after 16 h at 60 °C and a dark precipitate formed which was filtered, washed with *n*-hexane and recrystallised from benzene. Yield 308 mg (67%). M.p. 134 °C (dec.). $C_{15}H_{10}F_5NZr$ (388.98): calcd. C 46.14, H 2.58, N 3.59; found C 45.99, H 2.30, N 3.36. ^{1}H NMR (C_6D_6): δ = 5.67 (s, 10 H, Cp) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 113.59 (Cp) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ = 1.3 (s, Zr–F), –89.8 (br), –138.4 (m) ppm. MS: *m*/*z* 389 $[M]^+$, 370 $[M - F]^+$, 239 $[M - C_5F_4N]^+$.

Preparation of Complex 7: This was prepared as described above starting from complex **1b** (667 mg, 1.42 mmol) and 3-chloro-2,4,5,6-tetrafluoropyridine (168 μL, 1.48 mmol) in *n*-heptane (20 mL). The violet solution immediately became brown and a beige precipitate formed. The solvent was removed in a vacuum and the residue was recrystallised from benzene. Yield 251 mg (73%). M.p. 162 °C (dec.). $C_{15}H_{10}ClF_4NZr$ (404.95): calcd. C 44.27, H 2.48, N 3.44; found C 44.44, H 2.55, N 3.25. ^{1}H NMR (C_6D_6): δ = 5.73 ppm; ([D$_8$]toluene, 90 °C): δ = 5.84 (s, 10 H, Cp) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 113.9 ppm; ([D$_8$]toluene, 90 °C): δ = 114.3 (Cp), 133.7, 151.0, 157.1, 161.9 (4×d, C–F) ppm; Zr–C atom not found. ^{19}F{^{1}H} NMR (C_6D_6): δ = –43.5 (br), –88.0 (br), –91.4 (m), –169.4 (m) ppm. MS: *m*/*z* 405 $[M]^+$, 370 $[M - Cl]^+$, 255 $[M - C_5F_4N]^+$, 131 $[M - ZrC_5F_4NCl]^+$.

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