

REACTIONS OF TITANOCENE- AND ZIRCONOCENE-BIS(TRIMETHYLSILYL)ACETYLENE COMPLEXES WITH SELECTED HETEROCYCLIC AND AROMATIC NH AND OH ACID COMPOUNDS

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Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of organometallic synthesis and catalysis.

The titanocene complexes $\text{Cp}'_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ ($\text{Cp}' = \text{Cp}$ (**1**), Cp^* (**2**)) react with pyrrole under the formation of the titanium(III) mono-*N*-pyrrolides $\text{Cp}'_2\text{Ti}(\text{NC}_4\text{H}_4)$ ($\text{Cp}' = \text{Cp}$ (**6**), Cp^* (**7**)); whereas the corresponding zirconocene system $\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)(\text{thf})$ (**3**) forms in a different reaction pathway first the $\text{Cp}_2\text{Zr}(\text{NC}_4\text{H}_4)[\text{C}(\text{SiMe}_3)=\text{CH}(\text{SiMe}_3)]$ (**8**) and then the zirconium(IV) bis-*N*-pyrrolide $\text{Cp}_2\text{Zr}(\text{NC}_4\text{H}_4)_2$ (**11**). With $\text{Cp}^*_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ (**4**) and pyrrole, the zirconium(IV) mono-*N*-pyrrolide with an agostic alkenyl group $\text{Cp}^*_2\text{Zr}(\text{NC}_4\text{H}_4)[\text{C}(\text{SiMe}_3)=\text{CH}(\text{SiMe}_3)]$ (**9**) was obtained. In the reaction of the ethylene-bistetrahydroindenyl (ebthi) complex *rac*-(ebthi) $\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ (**5**) with 2,3,5,6-tetrafluoroaniline under N–H bond activation, a complex with an agostic alkenyl group *rac*-(ebthi) $\text{Zr}(\text{NH-C}_6\text{HF}_4)[\text{C}(\text{SiMe}_3)=\text{CH}(\text{SiMe}_3)]$ (**10**) was formed. Compound **10** reacts with additional 2,3,5,6-tetrafluoroaniline to give the bisanilide *rac*-(ebthi) $\text{Zr}(\text{NH-C}_6\text{HF}_4)_2$ (**12**) which was obtained directly from **5** with two equivalents of 2,3,5,6-tetrafluoroaniline. In reactions of complex **5** with unsubstituted aniline to *rac*-(ebthi) $\text{Zr}(\text{NH-C}_6\text{H}_5)_2$ (**13**) and with pentafluorophenol to bisphenolate *rac*-(ebthi) $\text{Zr}(\text{O-C}_6\text{F}_5)_2$ (**14**), no intermediates could be isolated. The new reaction products **6**, **9**, **10**, **12**, **13** and **14** were investigated by X-ray crystallography.

Keywords: Metallocenes; Titanocenes; Zirconocenes; Organometallics; Heterocycles; Aromatics.

In reactions of different titanocene and zirconocene complexes of bis(trimethylsilyl)acetylene $\text{Cp}_2\text{M}(\text{L})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ ($\text{M} = \text{Ti}$, $\text{L} = \text{nil}$ (**1**); $\text{M} = \text{Zr}$, $\text{L} = \text{THF}$ (**3**)), and the pentamethylcyclopentadienyl complexes $\text{Cp}^*\text{M}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ ($\text{M} = \text{Ti}$ (**2**), Zr (**4**)) or the *rac*-ethylenebistetrahydroindenyl (ebthi) complex *rac*-(ebthi) $\text{M}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ ($\text{M} = \text{Zr}$ (**5**)), activation of several bonds was described in some reviews¹⁻¹⁰. 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, C-F and C-B bonds gave complexes of potential applicability in stoichiometric and catalytic reactions.

Beckhaus and coworkers published very recently a series of excellent examples for reactions of titanocene-bis(trimethylsilyl)acetylene complexes with different N-heterocyclic compounds¹¹⁻¹⁵. In these reactions the complexes $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ and $\text{Cp}^*\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ act, after dissociation of the alkyne, as sources of titanocene Cp_2Ti and permethyltitanocene Cp^*Ti , which dimerize and trimerize heterocycles to exciting compounds, e.g., with a cyclohexane or benzene core.

In this work we tried to extend such investigations about reactions of titanocene- and zirconocene-bis(trimethylsilyl)acetylene complexes to selected heterocyclic and aromatic NH and OH acidic compounds to find out differences in the behavior between the bis(trimethylsilyl)acetylene complexes of Ti and Zr.

Several metallocene amido complexes $\text{Cp}'_2\text{M}(\text{NRR}')_2$ ($\text{M} = \text{Zr}$: $\text{Cp}' = \text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{R} = \text{H}$, $\text{R}' = t\text{-Bu}$, $\text{C}_6\text{H}_4\text{-}t\text{-Bu}$, $2,6\text{-Me}_2\text{C}_6\text{H}_3$, $\text{NRR}' = \text{NC}_4\text{H}_4$, $\text{Cp}'_2 = \text{rac}(\text{ebthi})$, $\text{R} = \text{H}$, $\text{R}' = 2,6\text{-MeC}_6\text{H}_3$, C_6H_5 , C_6F_5 ¹⁶⁻¹⁹; $\text{M} = \text{Ti}$: $\text{Cp}' = \text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{NRR}' = \text{NC}_4\text{H}_4$ ¹⁹, $\text{Cp}'_2 = [\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]$, $\text{NRR}' = \text{NC}_4\text{H}_4$ ²⁰) were synthesized starting from Cp_2MX_2 ($\text{X} = \text{Cl}$, Br) and an alkali (Na, Li) amide or by heating of Cp_2MMe_2 ($\text{M} = \text{Zr}$, Ti) in the presence of the corresponding amine in THF. Also the Ti(III) amide complex $\text{Cp}^*\text{Ti}(\text{NMePh})$ was obtained by the reaction of Cp^*TiX with lithium amide²¹.

In 1988 Bergman et al.^{17,22} found that complexes $\text{Cp}_2\text{Zr}(\text{NHR})_2$ eliminate 1 equivalent of RNH_2 (by heating) giving very reactive zirconocene imido derivatives $\text{Cp}_2\text{Zr}=\text{NR}$ which show an extensive reaction chemistry. For example, [2+2]cycloadditions with alkynes led to azametallacyclobutenes which gave (after protonation and reaction with an additional amine) enamines and regenerated the starting zirconocene bisamide complexes. Based on this investigations, Bergman et al. developed a hydroamination of alkynes with zirconocene bisamides $\text{Cp}_2\text{Zr}(\text{NHR})_2$ as catalysts¹⁷.

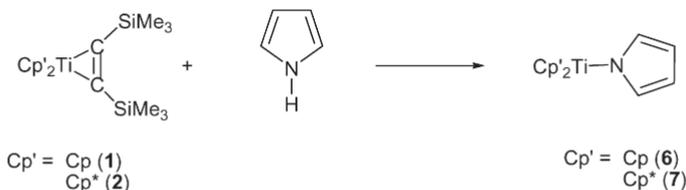
Related hydroamination processes were reported with catalysts such as CpTiCl_3 ²³ and the titanocene-alkyne complex $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ (**1**) used by Beller et al.²⁴.

We investigated and compared titanocene- and zirconocene-alkyne complexes $\text{Cp}'_2\text{M}(\text{L})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ ($\text{M} = \text{Ti}$: $\text{L} = \text{nil}$, $\text{Cp}'_2 = \text{Cp}_2 = (\eta^5\text{-C}_5\text{H}_5)_2$ (**1**), $\text{Cp}'^*_2 = (\eta^5\text{-C}_5\text{Me}_5)_2$ (**2**); $\text{M} = \text{Zr}$: $\text{L} = \text{THF}$, $\text{Cp}'_2 = \text{Cp}_2$ (**3**), Cp'^*_2 (**4**), *rac*-(*ebthi*) = **5**) in their reactions with amines like anilines ($\text{H}_2\text{N-C}_6\text{H}_5$ and $\text{H}_2\text{N-C}_6\text{HF}_4$) and their aromatic cyclic counterpart pyrrole (HNC_4H_4).

RESULTS AND DISCUSSION

Reactions of titanocene complexes $\text{Cp}'_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ with nitrogen bases like aldimines and ketimines^{25a}, oxazoles, isoxazoles, thiazoles^{25b} and siloximes^{25c} were detailed investigated and give Ti(IV) products of oxidative addition and a release of the acetylene $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$. On the other hand, with 2,2'-bipyridyl and 4,5-diazafluorene, an electron transfer from a titanocene species gives Ti(III) compounds with a bipyridyl radical anion and under separation of hydrogen a diazafluorenyltitanocene complex²⁶. $\text{Cp}'^*_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ (**2**) gives with $\text{Me}_2\text{C}=\text{N}=\text{N}=\text{CMe}_2$ recondensed by the splitting of the acetone azine also a Ti(III) complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{N}=\text{CMe}_2)$ ²⁷.

We report here, that the titanocene complexes $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ (**1**) and $\text{Cp}'^*_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ (**2**) react with pyrrole under gas (probably hydrogen) evolution and formation of paramagnetic Ti(III) mono-*N*-pyrrolides **6** and **7**²⁸ (Scheme 1).

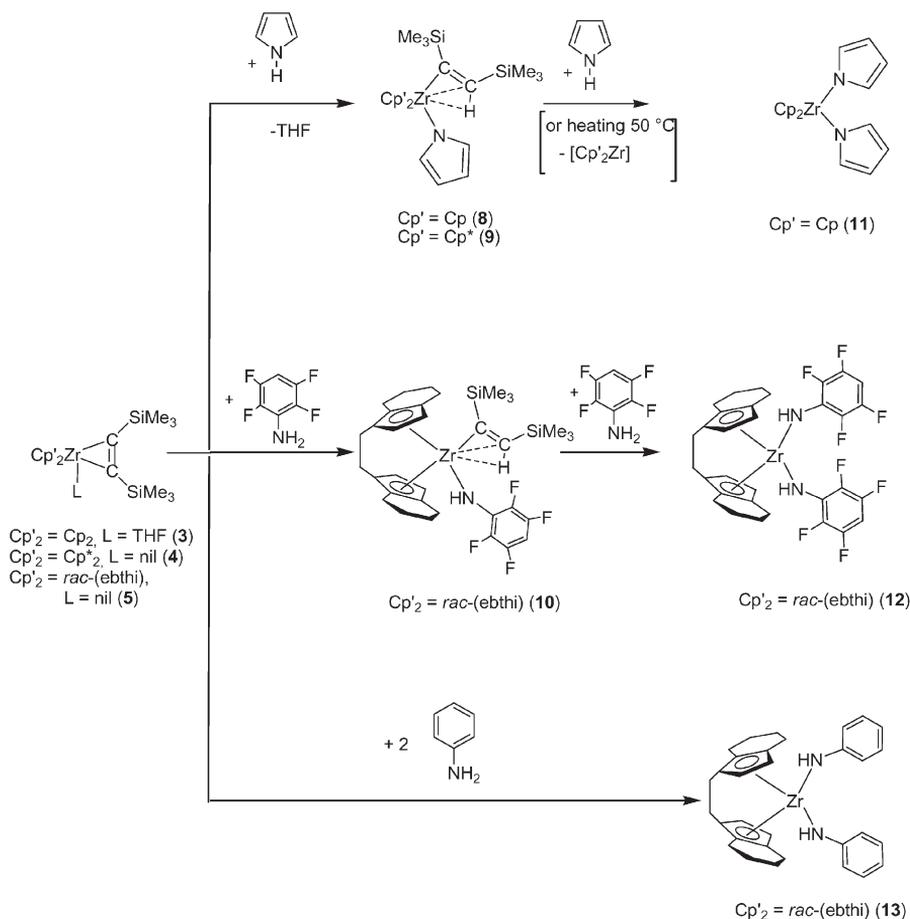


SCHEME 1

Reactions of the corresponding zirconocene-bis(trimethylsilyl)acetylene complexes **3** and **4** with pyrrole followed another pathway. Upon N-H activation and without alkyne elimination, the formation of the alkenyl complexes **8** and **9** with an agostic interaction was observed in a first step (Scheme 2).

When complex **8** is heated or treated with an equimolar amount of pyrrole, the alkenyl group gets lost and a bispyrrolide-zirconocene complex **11** is formed (Scheme 2). This bisamide **11** was described before as the product of the reaction of a zirconocene dihalogenide with 2 equivalents of alkali pyrrolide^{16,19}. NMR investigations of the conversion of **8** in solution (C_6D_6 , 50 °C) demonstrate that, besides the bisamide **11**, also free bis(trimethyl-

silyl)acetylene and further silyl species are obtained (there is good evidence for the generation of (*E*)-Me₃SiCH=CHSiMe₃, but neither this nor a formal hydroamination product like C₄H₄N-C(SiMe₃)=CH(SiMe₃) were proven). With Cp*₂Zr(η²-Me₃SiC₂SiMe₃) (**4**) and pyrrole, under the same conditions, only the mono-*N*-pyrrolide with an agostic alkenyl group (**9**) was obtained.



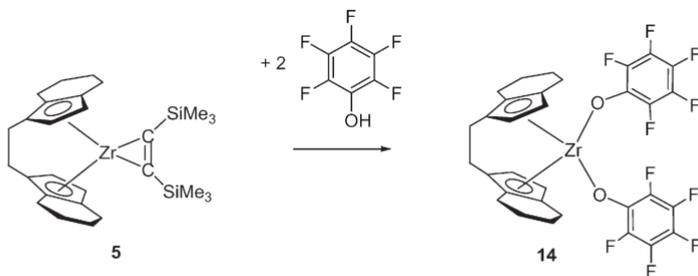
SCHEME 2

In the reaction of the ethylenebis(tetrahydroindenyl) complex *rac*-(ebthi)Zr(η²-Me₃SiC₂SiMe₃) (**5**) with 2,3,5,6-tetrafluoroaniline under N-H bond activation, the complex with an agostic alkenyl group *rac*-(ebthi)Zr(NH-C₆HF₄)[C(SiMe₃)=CH(SiMe₃)] (**10**) was formed. Compound **10** reacts with an excess 2,3,5,6-tetrafluoroaniline to the bisanilide

rac-(*ebthi*)Zr(NH-C₆HF₄)₂ (**12**) which was also obtained directly from **5** with two equivalents of 2,3,5,6-tetrafluoroaniline (Scheme 2).

Complex **5** reacted with unsubstituted aniline to give the bisamide *rac*-(*ebthi*)Zr(NH-C₆H₅)₂ (**13**); in contrast to 2,3,5,6-tetrafluoroaniline, no alkenyl complex as intermediate could be isolated.

In the same manner, in the reaction of **5** with pentafluorophenol, the alkyne was eliminated and the corresponding *rac*-(*ebthi*)Zr(O-C₆F₅)₂ (**14**) was formed (Scheme 3).



SCHEME 3

A similar bis(pentafluorophenolate) complex was described for the Cp-zirconocene system Cp₂Zr(O-C₆F₅)₂.²⁹

NMR and Molecular Structure Data

The most characteristic NMR and molecular structural feature of the alkenyl compounds **8**, **9** and **10** is the agostic interaction of the alkenyl group with zirconium Zr-C^α=C^β-H. These alkenyl units show ¹H NMR signals at rather low fields (**8**: 8.04, **9**: 6.67, **10**: 7.20 ppm) and the ¹³C NMR signals of C^α appear always downfield, but those for C^β in most cases slightly upfield compared with the normal olefin range. Typical of the additional agostic interaction is the especially small coupling constant ¹J(C^β-H) (**8**: 100, **9**: 101, **10**: 105 Hz). In the molecular structure, acute Zr-C^α-C^β angles and short Zr-C^β bond lengths reflect this special type of interaction. All these features were found before in selected similar complexes such as: [CpZr(μ-η¹:η⁵-C₅H₄)(C(SiMe₃)=CH(SiMe₃))₂] (**A**)³⁰, [Cp*₂Zr(C(CMe₃))(C(SiMe₃)=CH(SiMe₃))] (**B**)³¹ and the propane-3-lactamate [Cp₂Zr(NC₃H₄O)(C(SiMe₃)=CH(SiMe₃))] (**C**)³², which are all typical examples of zirconocene σ-alkenyl complexes with agostic C^β-H...Zr interactions (Table I).

In the ^{19}F NMR spectra of complex **10**, the chemical shifts on the fluorine substituents at the aromatic ring are in the region of uncoordinated fluoroaromatics (ca. -150 ppm) and not shifted to an extremely high field, as found for fluoro-bridged Zr-F-C groups (ca. -200 ppm)³³. Differences show up for the proton signal of the agostic CH group: it appears as singlet for **8** or **9**, but as triplet for **10** (coupling to two fluorine atoms, made equivalent by phenyl rotation). The steric demand of the *rac*-ebthi ligand system seems to force alkenyl and phenyl group close together, and hence spin-spin coupling through space becomes operative. Further steric effects are evident from a comparison of complex **9** (with the Cp* ligand) to the Cp complex **8**: only one signal for each pair of pyrrolide α - and β -CH groups appears for the latter, but four nonequivalent groups are observed for the former (broad signals at room temperature which coalesce pairwise at about 35 °C; see Experimental) and indicate that the rotation around the N-Zr bond is hindered for **9**.

TABLE I

Comparison of spectroscopic and structural data of complexes with agostic interactions $[\text{Cp}'_2\text{Zr}(\text{R})\{\text{C}^\alpha(\text{SiMe}_3)=\text{C}^\beta\text{-H}(\text{SiMe}_3)\}]$

Compounds	8	9	10	A	B	C
Cp' ₂	Cp ₂	Cp* ₂	ebthi	Cp	Cp* ₂	Cp ₂
R	NC ₄ H ₄	NC ₄ H ₄	HN-C ₆ HF ₄	(μ - η^1 : η^5 -C ₅ H ₄) ³⁰	C=CCMe ₃ ³¹	NC ₃ H ₄ O ³²
^1H NMR, ppm						
$\delta(\text{C}^\beta\text{-H})$	8.04	6.67	7.20	7.52/7.28	7.04	8.04
^{13}C NMR						
$\delta(\text{C}^\alpha)$	232.9	230.6	227.0	230.2/230.3	223.7	227.0
$\delta(\text{C}^\beta)$	105.4	112.8	123.1	101.7/100.4	111.3	106.3
$^1J(\text{C}^\beta\text{-H}), \text{Hz}$	100	101	105	97/96	95	101
Bond length, Å						
$d(\text{Zr}-\text{C}^\alpha)$		2.296(3)	2.271(3)	2.244(3)	2.298(2)	2.242(3)
$d(\text{Zr}-\text{C}^\beta)$		2.570(3)	2.591(3)	2.566(3)	2.534(2)	2.543(3)
$d(\text{C}^\alpha=\text{C}^\beta)$		1.327(4)	1.326(4)	1.318(5)	1.340(4)	1.330(4)
$d(\text{Zr}-\text{N})$		2.297(2)	2.238(3)			2.238(3)
Angle, °						
Zr-C ^{α} -C ^{β}		85.97(19)	88.1(2)	88.2(2)	83.9(1)	86.9(2)

The bisamide complexes **11**, **12** and **13** as well as the bisphenolate **14** exhibit in the NMR spectra, besides the resonances of the Cp or ebthi ligand system, only one set of signals of aromatic rings, which indicates that the arylamido and aryloxo ligands, respectively, are equivalent.

The complexes **6**, **9**, **10**, **12**, **13** and **14** were investigated by X-ray crystallography; they display the general feature of bent metallocenes. The crystallographic data are presented in Table II and the molecular structures are depicted in Figs 1–6.

TABLE II
Crystallographic data (compounds **6**, **9**, **10**, **12**, **13**, and **14**)

Parameter	6	9	10	12	13	14
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$
<i>a</i> , Å	7.885(2)	19.505(4)	14.616(3)	8.894(2)	12.759(3)	17.501(4)
<i>b</i> , Å	9.526(2)	9.969(2)	12.404(2)	34.307(7)	14.361(3)	10.212(2)
<i>c</i> , Å	15.323(3)	18.469(4)	19.515(4)	9.385(2)	13.776(3)	15.592(3)
α , °	90	90	90	90	90	90
β , °	90	117.54(3)	109.87(3)	98.23(3)	96.94(3)	93.49(3)
γ , °	90	90	90	90	90	90
<i>V</i> , Å ³	1151.0(4)	3184.4(11)	3327.4(11)	2833.7(11)	2505.5(9)	2781.4(10)
<i>Z</i>	4	4	4	4	4	4
Density, g cm ⁻³	1.409	1.250	1.380	1.603	1.431	1.724
μ (MoK α), mm ⁻¹	0.712	0.441	0.449	0.467	0.463	0.494
<i>T</i> , K	200(2)	200(2)	200(2)	293(2)	200(2)	200(2)
Number of reflections (measured)	19 200	51 954	11 826	6 858	19 825	22 549
Number of reflections (independent)	2 650	7 309	6 534	3 589	2 883	3 203
Number of reflections (observed)	2 447	6 328	4 301	2 692	2 567	2 843
Number of parameters	145	329	391	403	163	204
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>))	2.41	2.75	3.94	3.39	1.97	2.10
<i>wR</i> 2 (all data)	5.55	8.13	8.49	9.20	5.46	5.63

The structure of the paramagnetic compounds **6** (Fig. 1) and **7**²⁸ show behind the two cyclopentadienyl rings the pyrrolide ligand N-coordinated to the central metal atom. The Ti–N distances [2.090(1) (**6**) and 2.096(4)/2.100(3) Å (**7**)²⁸] are in the same range as described for Ti amide complexes such as the Ti(IV) bispyrrolide $\text{Cp}_2\text{Ti}(\text{NC}_4\text{H}_4)_2$ ¹⁹ (Ti–N 2.070(5), 2.100(4) Å) and the Ti(IV) fulvenide pyrrolide $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)](\text{C}_5\text{Me}_3\text{CH}_2)\text{Ti}(\text{NC}_4\text{H}_4)\}$ ²⁰ (Ti–N 2.072(4) Å).

Complexes **9** and **10** are characterized by molecular structural geometry typical for agostic interactions of the alkenyl group $\text{Zr}-\text{C}^\alpha=\text{C}^\beta-\text{H}$ (Table I). These are Zr–C^α bonds in the range of a single bond, C^α–C^β distances in the range of typical double bonds and a small angle Zr–C^α–C^β which indicates an additional interaction of the H(C^β) with the central zirconium atom (Table I, Figs 2 and 3)³¹.

For structure **12** (Fig. 4), different Zr–N distances for the amide ligands (Zr–N1: 2.164(3) Å or Zr–N2: 2.128(4) Å) were obtained, probably due to weak intermolecular interactions of the fluoro substituents of the benzene rings with hydrogen atoms of the ebthi ligand. The bisanilide **13** (Fig. 5) cannot form such a “network” and exhibits Zr–N distances of 2.1148(11) Å. Comparable Zr–N bonds were found in compounds such as $(\text{Cp}_2\text{Zr}(\text{NC}_4\text{H}_4)_2$: 2.171(2)/2.167(2)¹⁹ and *rac*-(ebthi)Zr(HN-2,6-Me₂C₆H₃)₂: 2.137(3) Å¹⁸).

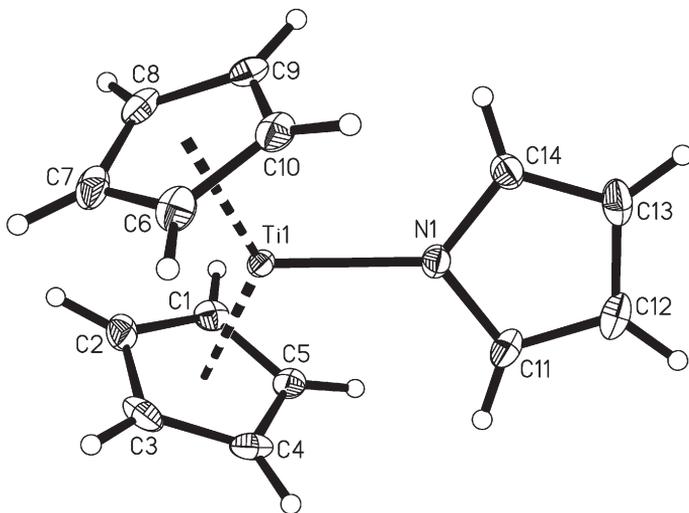


FIG. 1

Molecular structure of complex **6** in the crystal. The thermal ellipsoids correspond to 30% probability

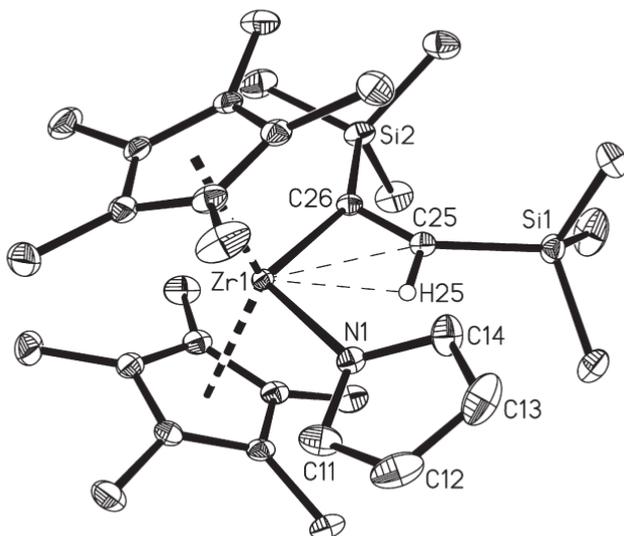


FIG. 2

Molecular structure of complex **9** in the crystal. Hydrogen atoms (except H25) are omitted for clarity. The thermal ellipsoids correspond to 30% probability

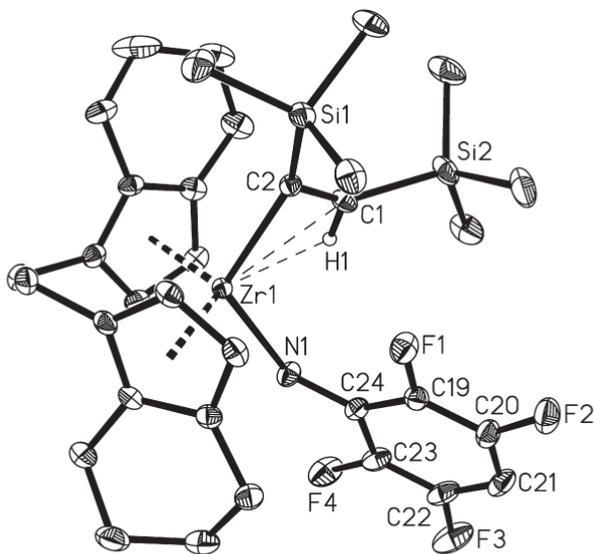


FIG. 3

Molecular structure of complex **10** in the crystal. Hydrogen atoms (except H1) are omitted for clarity. The thermal ellipsoids correspond to 30% probability

The molecular structure of **14** (Fig. 6) displays behind the ebthi ligand two equivalent phenolate rings with a Zr–O distance of 2.0334(10) Å which is slightly elongated in comparison with corresponding bonds in $\text{Cp}_2\text{Zr}(\text{O}-\text{C}_6\text{F}_5)_2$ ²⁹ (Zr–O: 1.991(2) Å). The most interesting feature of this structure is the arrangement of C_6F_5 rings. The angle between the plane O–Zr–O1A and the plane defined by the atoms of the pentafluorophenyl ring amounts to 33.3° in contrast to compound $\text{Cp}_2\text{Zr}(\text{O}-\text{C}_6\text{F}_5)_2$ ²⁹ where this angle is only 9.7°.

The structures of complexes **12** and **14** with fluoro-substituted phenyl ligands show no interactions between the fluoro substituents of the aromatic rings and the central atom. This is of interest with regard to catalytic reactions of early transition metal complexes in which such interactions and subsequent C–F bond cleavage reactions with the formation of metal fluorides are reported. With this process, deactivation was often discussed. For instance, in the polymerization of ethene by cationic zirconocene complexes a nucleophilic aromatic substitution of $\text{B}(\text{C}_6\text{F}_5)_3$ was found³⁴. A very low activity was observed in the hydroamination with $\text{Ti}(\text{O}-\text{C}_6\text{F}_5)_4$ as a catalyst, compared with other substituted Ti(IV) tetrakisphenolates³⁵. Here one could assume an interaction or cleavage of C–F bonds as the reason for this

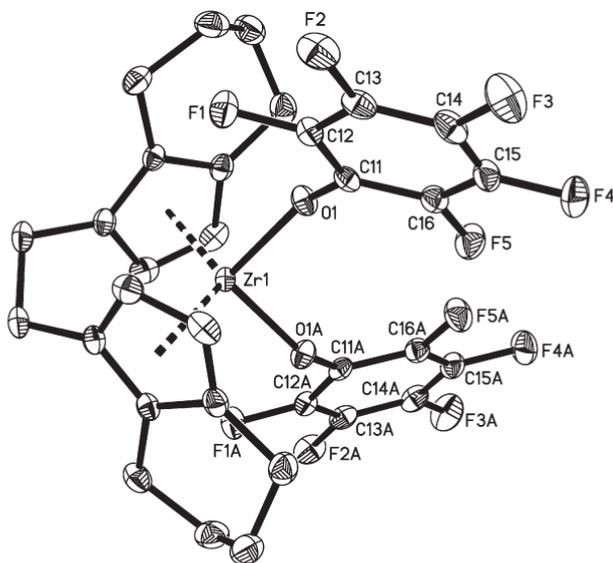


FIG. 6

Molecular structure of complex **14** in the crystal. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability

result. Additionally, for the case of $\text{H}_2\text{N}-\text{C}_6\text{HF}_4$ as a substrate in hydroamination reactions, such interactions must be excluded. From this point of view the structures of compounds **12** and **14** are important.

CONCLUSION

By the reactions presented here, it is well documented that titanocene- and zirconocene-bis(trimethylsilyl)acetylene complexes are able to activate heterocyclic and aromatic N-H and O-H acid compounds.

Whereas the titanocene-bis(trimethylsilyl)acetylene complexes react with loss of the alkyne and N-H bond activation with formation of Ti(III) monopyrrolide complexes, the corresponding zirconocene systems end up with Zr(IV) complexes. In a first step, zirconocene complexes with agostic σ -alkenyl groups are formed by H transfer from the pyrrole to the alkyne which yield in the second step bisamide complexes under elimination of several silylated compounds, among them the recovered alkyne.

This is a typical different reaction behavior of titanocene- and zirconocene-bis(trimethylsilyl)acetylene complexes, affording for titanium, a favored release of the alkyne with the formation of Ti(III) complexes and, for zirconium, no elimination of the alkyne but the formation of Zr(IV) complexes. Attempts to obtain an olefin such as $\text{C}_4\text{H}_4\text{N}-\text{C}(\text{SiMe}_3)=\text{CH}(\text{SiMe}_3)$ by coupling of the pyrrolide with the alkenyl group have failed so far.

EXPERIMENTAL

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 (C_6D_6 , toluene- d_8) were treated with sodium or sodium tetraethylaluminate, distilled and stored under argon. Fluorinated pyridines were dried over molecular sieves and degassed before use. The following spectrometers were used: MS: AMD 402; NMR: Bruker AV 300 and Bruker AV 400. Chemical shifts (δ , ppm) were referenced to signals of the used solvents: C_6D_6 (δ_{H} 7.16, δ_{C} 128.0), toluene- d_8 (δ_{H} 2.03, δ_{C} 20.4). The ^{19}F NMR spectra were referenced externally to CFCl_3 . The spectra were assigned using DEPT experiments. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Complexes $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)^{36}$ (**1**), $\text{Cp}^*\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)^{36}$ (**2**), $\text{Cp}_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)(\text{thf})^{30}$ (**3**), $\text{Cp}^*\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)^{37}$ (**4**) and $\text{rac}[\text{Zr}(\text{ebthi})(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]^{38}$ (**5**) were prepared by the literature methods.

$[\text{Cp}_2\text{Ti}(\text{NC}_4\text{H}_4)]$ (**6**)

To a solution of $\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$ (**1**; 1.260 g, 3.61 mmol) in 10 ml of hexane was added pyrrole (0.50 ml, 7.21 mmol). Within a few minutes the solution slightly darkened and crystals were formed at the bottom and on walls of the reaction tube. After 1 day the

crystals were separated from the mother liquor by decanting, washed with cooled hexane, and dried in vacuum to give 0.833 g (94.3%) of complex **6**, m.p. 170–172 °C. For $C_{14}H_{14}NTi$ (244.1) calculated: 68.88% C, 5.78% H, 5.74% N; found: 68.52% C, 5.45% H, 5.37% N.



Complex $[Cp_2Zr(\eta^2-Me_3SiC_2SiMe_3)(thf)]$ (**3**; 1.083 g, 2.33 mmol) was dissolved in pyrrole (2.0 ml, 28.8 mmol). The color instantly turned to light yellow. After 5 min the mixture was evaporated in vacuum and the residue was dissolved in 15–20 ml of toluene. From the filtered solution a light yellow solid precipitated after 1 day at -78 °C which was separated from the mother liquor by decanting, washed with cooled toluene, and dried in vacuum to give 0.790 g (73.8%) of **8**, m.p. 126–127 °C (dec.). 1H NMR (300 MHz, C_6D_6 , 297 K): 0.20 s, 9 H (β -SiMe₃); 0.23 s, 9 H (α -SiMe₃); 5.49 s, 10 H (Cp); 6.82 "t", 2 H (β -pyrrolide); 6.91 "t", 2 H (α -pyrrolide); 8.04 s, 1 H (=CH $^\beta$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6 , 297 K): 0.6 (β -SiMe₃); 2.0 (α -SiMe₃); 105.4, $J_{C,H} = 100$ (=CH $^\beta$); 110.1 (Cp); 110.1 (β -pyrrolide); 132.3 (α -pyrrolide); 232.9 (Zr-C=C). ^{29}Si NMR (79 MHz, C_6D_6 , 297 K): -9.0 , $^3J_{Si,H} = 19.8$, $^2J_{Si,H} = 6.4$ (α -SiMe₃); -5.5 , $^2J_{Si,H} = 6.6/3.0$ (β -SiMe₃). For $C_{22}H_{33}NSi_2Zr$ (458.9) calculated: 57.58% C, 7.25% H, 3.05% N; found: 57.36% C, 7.01% H, 2.98% N.



Complex $[Cp^*_2Zr(\eta^2-Me_3SiC_2SiMe_3)(thf)]$ (**4**; 0.545 g, 1.02 mmol) was dissolved in 5 ml of toluene and pyrrole was added (0.20 ml, 2.88 mmol). After 2 days the light yellow solution was evaporated in vacuum and the residue was dissolved in 30 ml of warm hexane (55 °C). The solution was filtered and allowed to stand at -78 °C. After 1 day light yellow crystals were formed which were separated from the mother liquor by decanting, washed with cooled hexane, and dried in vacuum to give 0.378 g (61.6%) of **9**, m.p. 249–250 °C (dec.). 1H NMR (400 MHz, toluene- d_8 , 297 K): 0.35 s, 9 H (β -SiMe₃); 0.44 s, 9 H (α -SiMe₃); 1.55 s, 30 H (C_5Me_5); 6.50, 6.65 2 \times br, 2 \times 1 H (β -pyrrolide); 6.67 s, 1 H (=CH $^\beta$); 6.70, 6.81 2 \times br, 2 \times 1 H (α -pyrrolide). 1H NMR (400 MHz, toluene- d_8 , 357 K, the compound starts decomposing!): 0.34 s, 9 H (β -SiMe₃); 0.43 s, 9 H (α -SiMe₃); 1.57 s, 30 H (C_5Me_5); 6.38 "t", 2 H (β -pyrrolide); 6.69 "t", 2 H (α -pyrrolide); 6.69 s, 1 H (=CH $^\beta$). $^{13}C\{^1H\}$ NMR (100 MHz, toluene- d_8 , 297 K): 2.7 (β -SiMe₃); 6.6 (α -SiMe₃); 12.3 (C_5Me_5); 107.6, 108.9 (2 \times β -pyrrolide); 112.8, $J_{C,H} = 101$ (=CH $^\beta$); 119.2 (C_5Me_5); 132.1, 133.0 (2 \times α -pyrrolide); 230.6 (Zr-C=C). ^{29}Si NMR (79 MHz, toluene- d_8 , 297 K): -9.4 , $^3J_{Si,H} = 21.3$, $^2J_{Si,H} = 6.2$ (α -SiMe₃); -5.8 , $^2J_{Si,H} = 6.5/3.8$ (β -SiMe₃). MS (70 eV, m/z): 462 $[Cp^*_2Zr(C_4H_5N)]^+$. For $C_{32}H_{53}NSi_2Zr$ (597.3) calculated: 64.15% C, 8.92% H, 2.34% N; found: 63.95% C, 9.25% H, 2.45% N.



Complex $rac-Zr(ebthi)(\eta^2-Me_3SiC_2SiMe_3)$ (**5**; 0.300 g, 0.57 mmol) and 2,3,5,6-tetrafluoroaniline (0.113 g, 0.68 mmol) were dissolved in 10 ml of hexane and stirred at room temperature. The color of the solution changed and after two hours the formation of orange crystals started. The orange crystals were separated from the mother liquor, washed with hexane and dried in vacuo. Yield 118 mg (30%) of **10**, m.p. 105 °C (dec.). 1H NMR (400 MHz, C_6D_6 , 297 K): 0.18 s, 9 H (SiMe₃); 0.42 s, 9 H (SiMe₃); 1.0–1.8, 8 H (ebthi-CH₂); 1.9–2.8, 12 H (ebthi-CH₂); 3.83 br, 1 H (NH); 5.17 d, 1 H, $^3J_{H,H} = 2.9$ (ebthi-CH); 5.41 d, 1 H, $^3J_{H,H} = 2.9$ (ebthi-CH); 5.60 m, 1 H (ebthi-CH); 5.84 tt, 1 H, $J_{F,H} = 10.3/6.9$ (aniline-CH);

6.34 d, 1 H, $^3J_{\text{H,H}} = 2.6$ (ebthi-CH); 7.20 t, 1 H, $J_{\text{F,H}} = 1.8$ (=CH $^\beta$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 297 K): 0.8 (SiMe $_3$); 3.6 (SiMe $_3$); 21.4, 22.5, 22.6, 22.9, 23.7, 23.9, 24.8 (2 C); 28.0, 28.9 (10 \times ebthi-CH $_2$); 86.0 t, $J_{\text{C,F}} = 24$ (aniline-CH); 102.7, 105.8, 106.4, 110.0 (4 \times ebthi-CH); 123.1, $^1J_{\text{C,H}} = 105.1$, $J_{\text{C,F}} = 2.4$ (=CH $^\beta$); 118.3, 118.4, 126.1, 127.4, 130.1, 134.8 (6 \times ebthi-C); 227.0 (Zr-C=C); CF were not detected. ^{19}F NMR (282 MHz, C_6D_6 , 297 K): -143.4 (CF); -160.7 (CF). MS (70 eV, m/z): 518 ($\text{M}^+ - \text{Me}_3\text{SiC}_2\text{SiMe}_3$). For $\text{C}_{34}\text{H}_{45}\text{F}_4\text{NSi}_2\text{Zr}$ (691.1) calculated: 59.09% C, 6.56% H, 2.03% N; found: 58.93% C, 6.45% H, 2.01% N.

[Cp $_2$ Zr(NC $_4$ H $_4$) $_2$] (**11**)

To complex [Cp $_2$ Zr(η^2 -Me $_3$ SiC $_2$ SiMe $_3$)(thf)] (**3**; 0.735 g, 1.58 mmol) was added pyrrole (2.5 ml, 36.0 mmol) and the mixture was stirred at 90 $^\circ\text{C}$ for 1 day. The resulting yellow-orange solution was evaporated in vacuum to dryness. The residue was dissolved in 10–15 ml of toluene giving a yellow solution, which was filtered and allowed to stand at -30 $^\circ\text{C}$. After 3 days yellow crystals were separated from the mother liquor by decanting, washed with cooled toluene, and dried in vacuum to give 0.373 g (66.6%) of **11**, m.p. 178–180 $^\circ\text{C}$. ^1H NMR (300 MHz, C_6D_6): 5.72 s, 10 H (Cp); 6.52 "t", 4 H (β -pyrrolide); 6.64 "t", 4 H (α -pyrrolide). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 297 K): 114.2 (Cp); 110.1, 129.2 (β - and α -pyrrolide). For $\text{C}_{18}\text{H}_{18}\text{N}_2\text{Zr}$ (353.5) calculated: 61.15% C, 5.13% H, 7.92% N; found: 61.07% C, 4.98% H, 7.53% N.

Formation in the NMR tube: [Cp $_2$ Zr(NC $_4$ H $_4$){C(SiMe $_3$)=CH(SiMe $_3$)}] (**8**; 150 mg, 0.328 mmol) was dissolved in 0.5 ml of C_6D_6 and heated to 50 $^\circ\text{C}$. The color of the solution gradually turned to deep green during 6 h and a mixture of the bisamide **11** together with free bis(trimethylsilyl)acetylene and further silyl species was observed by NMR monitoring. Almost half of the silyl intensity was found in the free alkyne ($\delta(^1\text{H})$ 0.16, $\delta(^{13}\text{C})$ -0.1, $\delta(^{29}\text{Si})$ -19.4), a further large amount in a species characterized by $\delta(^1\text{H})$ 0.11 and 6.80, $\delta(^{13}\text{C})$ -1.5 and 151.1, $\delta(^{29}\text{Si})$ -7.9. This might be (*E*)-Me $_3$ SiCH=CHSiMe $_3$, reference data³⁹: ^1H (CDCl $_3$) 0.06 and 6.56, ^{13}C (CDCl $_3$) -1.2 and 150.7, ^{29}Si (neat) -8.9. Some more signals were growing in the spectra, but a loss of overall intensity in the Cp and pyrrole region indicated that unobservable compounds may be generated. Free hydrogen (expected at about 4.5 ppm) was not found.

rac-[Zr(ebthi)(NH-C $_6$ HF $_4$) $_2$] (**12**)

The complex *rac*-[Zr(ebthi)(η^2 -Me $_3$ SiC $_2$ SiMe $_3$)] (**5**) (0.300 g, 0.57 mmol) and 2,3,5,6-tetrafluoroaniline (0.226 g, 1.37 mmol) were dissolved in 10 ml of hexane and stirred at room temperature. The color of the solution changed and after a few hours crystallization started. Yellow crystals were separated from the mother liquor, washed with hexane and dried in vacuo. Yield 233 mg (60%) of **12**, m.p. 220 $^\circ\text{C}$ (dec.). ^1H NMR (400 MHz, C_6D_6 , 297 K): 1.37 m, 4 H, 1.70 m, 4 H, 2.30 m, 6 H, 2.66 dt, 2 H (all ebthi-CH $_2$); 2.48 AA'BB', 4 H (ebthi-ethylene); 5.14 d, 2 H, $^3J_{\text{H,H}} = 3.2$ (ebthi-CH); 5.35 s, 2 H (NH); 5.83 m, 2 H (ebthi-CH); 5.96 tt, 2 H, $J_{\text{F,H}} = 10.2/7.1$ (aniline-CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 297 K): 22.6, 22.7, 23.2, 23.9, 27.4 (5 \times ebthi-CH $_2$); 91.7 t, $J_{\text{C,F}} = 24$ (aniline-CH); 106.1, 112.4 (2 \times ebthi-CH); 122.1, 130.9, 131.2 (3 \times ebthi-C); 138.2 m (NH-C); 138.7 m, $^1J_{\text{C,F}} = 235$; 147.0 m, $^1J_{\text{C,F}} = 243$ (2 \times CF). ^{19}F NMR (282 MHz, C_6D_6 , 297 K): -142.4 (CF); -156.8 (CF). MS (70 eV, m/z): 354 ($\text{M}^+ - 2 \text{NH-C}_6\text{F}_4$). For $\text{C}_{32}\text{H}_{28}\text{F}_8\text{N}_2\text{Zr}$ (683.8) calculated: 56.20% C, 4.12% H, 4.09% N; found: 56.46% C, 4.51% H, 3.81% N.

rac-[Zr(ebthi)(NH-C₆H₅)₂] (**13**)

The complex *rac*-[Zr(ebthi)(η^2 -Me₃SiC₂SiMe₃)] (**5**; 0.400 g, 0.76 mmol) was dissolved in 10 ml of hexane and aniline was added (0.140 ml, 1.5 mmol). The color of the solution changed and yellow crystals of **13** were immediately formed, which were separated from the mother liquor by decanting. Yield 302 mg (74%) of **13**, m.p. 243 °C (dec.). ¹H NMR (C₆D₆, 297 K): 1.3–2.9 m, 20 H (ebthi-CH₂); 5.07 d, 2 H, ³J_{HH} = 2.9 (ebthi-CH); 5.86 d, 2 H, ³J_{HH} = 2.9 (ebthi-CH); 5.96 s, 2 H (NH); 6.75 m, 2 H (*p*-CH_{aniline}); 6.84 m, 4 H (*o*-CH_{aniline}); 7.16 m, 4 H (*m*-CH_{aniline}). ¹³C{¹H} NMR (C₆D₆, 297 K): 23.2, 23.3, 23.6, 24.2, 27.4 (5 × CH₂); 103.8, 110.3 (2 × ebthi-CH); 119.4, 128.7, 129.4 (3 × ebthi-C); 117.8, 118.6, 128.9, 156.4 (4 × aniline). MS (70 eV, *m/z*): 355 (M⁺ – 2 NH-C₆H₅). For C₃₂H₃₆N₂Zr (538.2) calculated: 71.19% C, 6.72% H, 5.19% N; found: 71.12% C, 6.66% H, 4.99% N.

rac-[Zr(ebthi)(OC₆F₅)₂] (**14**)

To a solution of *rac*-[Zr(ebthi)(η^2 -Me₃SiC₂SiMe₃)] (**5**; 0.250 g, 0.475 mmol) in 15 ml of THF was added pentafluorophenol (0.175 g, 0.951 mmol) in 5 ml of diethyl ether under stirring. After 24 h the yellow solution was evaporated to dryness and the residue was dissolved in hexane. The solution was filtered and reduced in vacuum. At room temperature colorless crystals of **14** were formed. Yield 122 mg (36%) of **14**, m.p. 132–134 °C. ¹H NMR (300 MHz, C₆D₆, 298 K): 1.30 m, 4 H, 1.50 m, 4 H, 2.21 m, 4 H, 2.43 m, 4 H (all ebthi-CH₂); 2.69 AA'BB', 4 H (ebthi-ethylene); 5.51 d, 2 H, ³J = 3 (ebthi-CH); 5.75 d, 2 H, ³J = 3 (ebthi-CH). ¹³C{¹H} NMR (75 MHz, C₆D₆, 298 K): 22.2, 22.6, 23.4, 23.5 (4 × ebthi-CH₂); 28.0 (ebthi-ethylene); 108.2, 114.8 (2 × ebthi-CH); 123.1, 133.2, 133.9 (3 × ebthi-C); CF not detected. ¹⁹F NMR (282 MHz, C₆D₆, 298 K): –162.3 m, 4 F; –165.5 m, 4 F; –172.1 tt, 2 F (*para*). MS (70 eV, *m/z*): 720 (M⁺), 537 (M⁺ – OC₆F₅). For C₃₂H₂₄F₁₀O₂Zr (721.7): 53.25% C, 3.35% H; found: 52.86% C, 3.19% H.

X-ray Crystallography

Data were collected with a STOE-IPDS-diffractometer using graphite-monochromatized MoK α radiation. The structures were solved by direct methods (SHELXS97)⁴⁰ and refined by full-matrix least-squares techniques against *F*² (SHELXL97)⁴¹. XP (Bruker AXS) was used for structure representations.

CCDC 634160 (for **6**), 634161 (for **9**), 634162 (for **10**), 634163 (for **12**), 634164 (for **13**), 634165 (for **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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