Novel Synthesis of Zirconocene Difluoride and Alkyl Monofluoride Complexes

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Starting from zirconocene bis(trimethylsilyl)acetylene complexes $Cp'_2Zr(L)(\eta^2\text{-btmsa})$ via the 2-vinylpyridine complexes $Cp'_2Zr(2\text{-vipy})$ a novel synthetic method for zirconocene difluoride and alkyl monofluoride complexes was elaborated. Examples with selected different ligand systems Cp'_2 $[Cp_2 = \text{bis}(\eta^5\text{-cyclopentadienyl})$; ebthi = 1,2-ethylene-1,1'-bis(η^5-tetrahydroindenyl); $(\text{thi})_2 = \text{bis}(\eta^5\text{-tetrahydroindenyl})$; $Me_2Si(\eta^5\text{-}C_5H_4)_2 = \text{dimethylsilylbis-}$($\eta^5$-cyclopentadienyl); $(\text{i})_2 = \text{bis}(\eta^5\text{-indenyl})$; ebi = 1,2-ethylene-1,1'-bis(η^5-indenyl); and $Me_2Si(\eta^5\text{-}C_9H_{10})_2 = \text{dimethylsilyl-1,1'-bis}(\eta^5\text{-tetrahydroindenyl})]$ were synthesized. In the series of these investigations new complexes $(\text{i})_2Zr(THF)(\eta^2\text{-btmsa})$ (**1**), *rac*-(ebi)Zr(THF)(η^2-btmsa) (**2**), $(\text{thi})_2Zr(2\text{-vipy})$ (**3**), $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(2\text{-vipy})$ (**4**), $(\text{i})_2Zr(2\text{-vipy})$ (**5**), and *rac*-(ebthi)-Zr(2-Ph-vipy) (**6**) were prepared as starting materials. Different methods for preparation of the zirconocene difluorides *rac*-(ebthi)ZrF_2 (**7**), $(\text{thi})_2ZrF_2$ (**8**), $Me_4C_2(\eta^5\text{-}C_5H_4)_2ZrF_2$ (**9**), and $Me_2Si(\eta^5\text{-}C_9H_{10})_2ZrF_2$ (**10**) and the monofluorides $Cp_2Zr(F)(CH_2CH_2\text{-2-Py})$ (**11**), *rac*-(ebthi)-Zr(F)(CH_2CH_2\text{-2-py}) (**12**), $(\text{thi})_2Zr(F)(CH_2CH_2\text{-2-py})$ (**13**), $Me_2Si(\eta^5\text{-}C_5H_4)_2Zr(F)(CH_2CH_2\text{-2-py})$ (**14**), and $Me_2Si(\eta^5\text{-}C_9H_{10})_2ZrF(Me)$ (**15**) are reported and compared. The molecular structures of the bis-η^5-tetrahydroindenyl complexes **3**, **8**, and **13** were confirmed by X-ray crystal structure analysis.

Introduction

The metallocene-type Ziegler–Natta catalysts frequently used in catalytic olefin polymerization typically consist of a complex of two cyclopentadienyl anion-based ligands with a metal cation.[1] This metallocene is not able to polymerize olefins; it needs activation.[1,2] Methylaluminoxane is the activator generally used in industry, although there is no detailed knowledge about its specific role in the polymerization processes. As an alternative to methylalumoxane, noncoordinating bor-

ate counterions were used.[2c–e] Most compounds developed for this purpose are based on perfluorophenyl-boron compounds, e.g., tris(pentafluorophenyl)borane, $B(C_6F_5)_3$.[2f–i]

For economic reasons, there is a great interest in finding cheaper catalyst systems. This could be achieved by tuning the metallocene ligand and/or finding a cheaper cocatalyst.[2j] Isobutylalumoxane[2k,l] as well as hydroxy-isobutylalumoxane[2j] have been published recently as alternative cocatalysts in metallocene activation.

Recently we claimed that zirconocene difluoride and zirconocene monofluoride alkyl complexes, among them *rac*-(ebthi)ZrF_2 (**7**),[4c] are active catalysts for ethylene polymerization with $^iBu_3Al$ as the sole activating cocatalyst.[5] In contrast to fluorine-containing **7**, the dichloride *rac*-(ebthi)$ZrCl_2$ was found to be totally inactive under comparable reaction conditions!

These results and the extraordinary effects of the fluoride[3,6] prompted us to investigate zirconocene fluoro complexes. From our point of view the activation of zirconocene catalysts depends both on the nature of the

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Scheme 1

**Scheme 2**

Scheme 3

Scheme 4
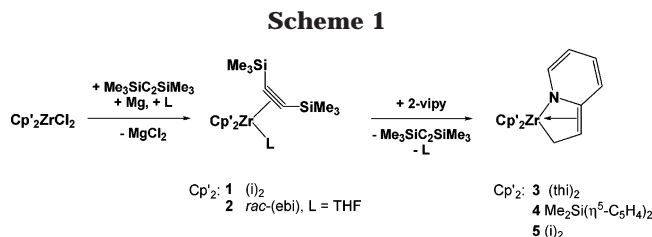
leaving ligand when forming the active species and on the character and stability of the resulting counterpart (anion). For this purpose we elaborated synthetic methods to obtain zirconocene difluoride and alkyl monofluoride complexes as metallocene components.

Results and Discussion

Preparation of the Starting Materials. Zirconocene Complexes of Bis(trimethylsilyl)acetylene and 2-Vinylpyridine. Both groups of complexes with bis(trimethylsilyl)acetylene (btmsa) and 2-vinylpyridine (2-vipy) were known before. In addition to the already known alkyne complexes $Cp'_2Zr(L)(\eta^2$-btmsa)[4b,7a−c] the new complexes with $Cp'_2 =$ (i)$_2$ (**1**) and $Cp'_2 = rac$-(ebi) (**2**) with L = THF were prepared following the same procedure of reduction of the corresponding dichlorides with magnesium in the presence of btmsa. These complexes were used as starting materials for subsequent investigations (Scheme 1).[8]

Zirconocene complexes with 2-vinylpyridine Cp'_2Zr-(2-vipy) ($Cp'_2 = Cp_2$, ebthi) are already known.[4c] The new complexes (thi)$_2$Zr(2-vipy) (**3**), Me$_2$Si(η^5-C$_5$H$_4$)$_2$Zr-(2-vipy) (**4**), and (i)$_2$Zr(2-vipy) (**5**) were prepared following the same method of substitution of btmsa by 2-vipy (Scheme 1). This procedure did not work to prepare the corresponding rac-(ebi)Zr(2-vipy) because intractable mixtures of complexes were formed.

The complex rac-(ebthi)Zr(2-Ph-vipy) (**6**) was prepared directly by reduction starting from rac-(ebthi)ZrCl$_2$, 2-(2-phenylvinyl)pyridine, and lithium in THF at −40 °C (Scheme 2),[9] but this procedure failed to produce rac-(ebi)Zr(2-vipy) from rac-(ebi)ZrCl$_2$ and 2-vinylpyridine, giving again a mixture of complexes.
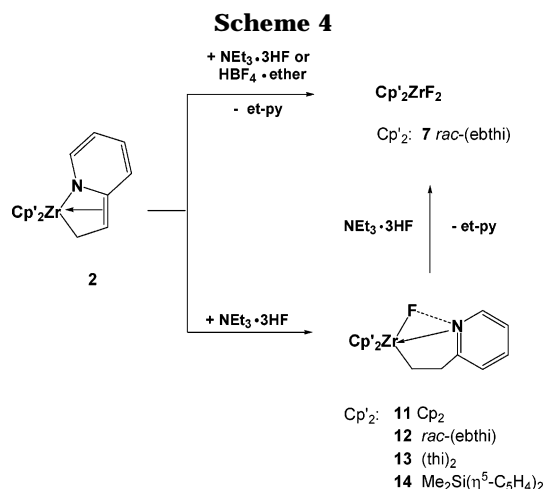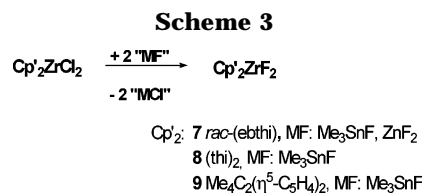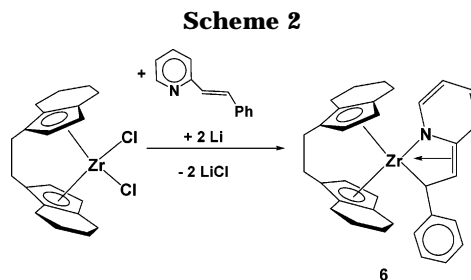
Zirconocene Difluorides. There are many published methods for the preparation of *metallocene difluorides*, mostly based on *exchange reactions* with Me$_3$-SnF as a versatile reagent.[10] We prepared a number of such complexes like rac-(ebthi)ZrF$_2$ (**7**), (thi)$_2$ZrF$_2$ (**8**), and Me$_4$C$_2$(η^5-C$_5$H$_4$)$_2$ZrF$_2$ (**9**) by using of 3 equiv of Me$_3$-SnF for **7** and 2.1 equiv of Me$_3$SnF in the case of **8** and **9**, both in dichloromethane solution. Alternatively, we used ZnF$_2$ as a cheaper fluorinating agent in acetone to obtain rac-(ebthi)ZrF$_2$ (**7**) (Scheme 3).

Another method for the preparation of metallocene difluorides is the *acidolysis reaction* starting from suitable starting materials[4c] (Scheme 4).

For rac-(ebthi)Zr(2-vipy) this was proven first by reaction with HBF$_4$ etherate to obtain rac-(ebthi)ZrF$_2$ (**7**, poorly reproducible).[4c] Better suited is NEt$_3$·3HF as reagent for this reaction,[11] which gives the difluoride **7** starting from rac-(ebthi)Zr(2-vipy) or from rac-(ebthi)-ZrMe$_2$. Also NH$_4$BF$_4$ can be used to produce the difluoride Me$_2$Si(η^5-C$_9$H$_{10}$)$_2$ZrF$_2$ (**10**) from Me$_2$Si(η^5-C$_9$H$_{10}$)$_2$-ZrMe$_2$ (Scheme 5).

Zirconocene Alkyl Monofluorides. Regarding the *metallocene alkyl monofluorides*, it was impossible to obtain the monofluoride rac-(ebthi)Zr(F)(CH$_2$CH$_2$-2-Py) (**12**) starting from rac-(ebthi)Zr(2-vipy) by using HBF$_4$ etherate because only rac-(ebthi)ZrF$_2$ (**7**) was obtained.[4c]

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(9) We thank Dr. Kahlert, Bayer AG, for information concerning this synthetic procedure.

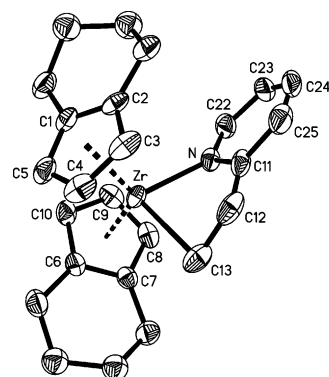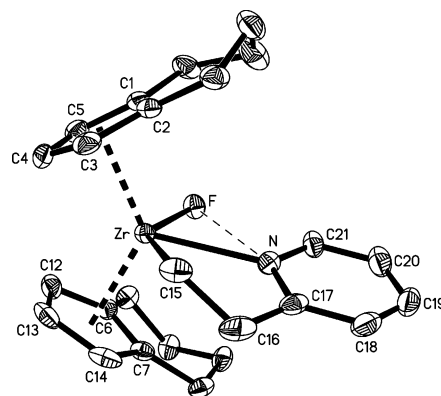(10) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425.

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Scheme 5

Figure 1. Molecular structure of complex **3** in the crystal. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Zr−C13 2.282(4), Zr−C12 2.604(5), Zr−C11 2.687(4), Zr−N 2.163(3), C12−C13 1.442-(8), C11−C12 1.379(7), N−C11 1.393(6), N−C22 1.364(5), C22−C23 1.366(6), C23−C24 1.413(9), C24−C25 1.340(9), C11−C25 1.424(7); N−Zr−C13 82.3(2); X1a-Zr-X1b 127.8 (X1a, X1b are centroids of C1−C5 and C6−C10, respectively).

The reaction of *rac*-(ebthi)Zr(2-vipy) with NH₄F often gave mixtures of the monofluoride **12** and the difluoride **7**. A suitable reagent to prepare such monofluorides is NEt₃·3HF,[11] provided one takes great care of the exact stoichiometry. The reaction of Cp₂Zr(2-vipy) with NEt₃·3HF gives Cp₂Zr(F)(CH₂CH₂-2-Py) (**11**). In the same manner the complexes *rac*-(ebthi)Zr(F)(CH₂CH₂-2-py) (**12**), (thi)₂Zr(F)(CH₂CH₂-2-py) (**13**), and Me₂Si(η⁵-C₅H₄)₂Zr(F)(CH₂CH₂-2-py) (**14**) were formed (Scheme 4). This reagent also works well with zirconocene dimethyl complexes such as Me₂Si(η⁵-C₉H₁₀)₂ZrMe₂ to give Me₂Si(η⁵-C₉H₁₀)₂ZrF(Me) (**15**) (Scheme 5).

It is worth mentioning that all these methods failed to synthesize the corresponding complexes with unsaturated substituents at the Cp ring. There are some hints from NMR spectroscopic investigations of the complicated reaction mixtures on a modification of the unsaturated groups.

NMR Investigations. As described earlier, the coordination of the 2-vinylpyridine to the zirconocene core changes the electronic structure of the ligand so that it is described best as a coordinated monoazadiene which becomes a metallaazacyclopentene.[4c] The aromaticity of the pyridine subunit is reduced, and there is a certain discrimination of bond orders within the ring (partially localized double bonds, evidenced by clearly different coupling constants $^3J_{H,H}$ across "single" (C23−C24 in **3**, see Figure 1) and "double" (C24−C25 in **3**) bonds. Upon formation of the complexes **11**−**14** (reaction with HF derivatives), this kind of interaction is released and NMR spectroscopic properties of an undisturbed pyridine system are found again. ^{1}H and ^{13}C NMR spectra of the monofluoro complexes **11**−**14** with a 2-(2-pyridyl)-ethyl group show various scalar couplings to the fluorine atoms, most prominent for the CH group adjacent to nitrogen (C21 in Figure 2). In the solid state, the nitrogen atom is directed toward the metal center; a close proximity to the fluorine results from this orientation. σ-Bonding interactions between halogen, particularly fluorine, and pyridine nitrogen atoms are known[12] and give rise to a low-field shift of the *ortho* protons (δ 9.3 ppm) together with a coupling $^3J_{H,F}$ of 16 Hz. The chemical shifts observed for **11**−**14** are very similar to each other. The coupling constants are smaller (6−7 Hz), so it is not clear whether they do result from such a special bonding situation or wheter they are transmitted "through space", as commonly observed with the fluorine nucleus. However, the chemical shift of fluorine in these complexes should be noted, which is about 100 ppm shifted to lower frequency compared to that of the similar methyl-fluoro complex **15**.

Figure 2. Molecular structure of complex **13** in the crystal. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å]: Zr−C15 2.377(3), Zr−N 2.497(3), Zr−F 2.025-(2), C15−C16 1.524(5), C16−C17 1.489(5), N−C17 1.360-(4), N−C21 1.349(4), C17−C18 1.388(5), C18−C19 1.372(7), C19−C20 1.373(7), C20−C21 1.374(5).

X-ray Crystal Structures. Representative examples of described complexes were investigated by X-ray crystal structure analysis: starting 2-vinylpyridine complex **3**, the monofluoride **13**, and the difluoride **8**. The crystallographic data are listed in Table 1, and the molecular structures are shown in Figures 1−3.

All complexes consist of a typical bent zirconocene in a monomeric structure.

A comparison of **3** and **13** seems worth doing; both molecules have a C−C−2-py subunit. Selected data are presented in Table 2.

The starting point in the discussion of the compared examples is the 2-vinylpyridine complex **3**. The angle between the plane defined by X1a, X1b, and Zr (X1a and X1b are the centroids of C1−C5 and C6−C10, respectively) and the plane defined by Zr, N, and C13 is 88.0°. As described before in similar complexes, the 2-vinylpyridine gives by complexation a five-membered zirconacycle with a fused pyridine ring. With a "localization" of the double bonds within the pyridine ring a 1-zircona-2-azacyclopent-3-ene (1-monoazadiene) is formed. The

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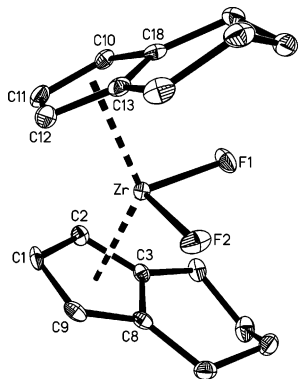
Figure 3. Molecular structure of complex **8** in the crystal. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: F1−Zr 1.946(2), F2−Zr 1.974-(2); F1−Zr−F2 98.66(8), X1a−Zr−X1b 132.3 (X1a, X1b are centroids of C1, C2, C3, C8, C9 and C10, C11, C12, C13, C18, respectively).

Table 1. Crystallographic Data

	3	8	13
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12$	$P2_1/n$	$Pbca$
a [Å]	8.708(2)	7.002(1)	8.753(2)
b [Å]	27.547(6)	18.910(4)	18.251(4)
c [Å]	8.547(2)	11.667(2)	25.778(5)
β [deg]		96.12(3)	
V [Å^3]	2050.2(8)	1536.0(5)	4118.1(15)
Z	4	4	8
density [g·cm^{-3}]	1.408	1.590	1.467
μ(Mo Kα) [mm^{-1}]	0.545	0.728	0.553
T [K]	293	200	200
no. of reflns (measd)	10864	3987	11567
no. of reflns (indep)	3206	2046	3307
no. of reflns (obsd)	2779	1783	2461
no. of params	252	190	278
R1 ($I>2\sigma(I)$)	0.027	0.025	0.034
wR2 (all data)	0.060	0.059	0.085

Table 2. Selected Data of Complexes with the C−C−2-py Subunit in the Molecule

	3	13
Zr−Cα	2.282(4)	2.377(3)
Zr−Cβ	2.604(5)	no bond
Zr−Cβ'(py-ring)	2.687(4)	no bond
Zr−N	2.163(3)	2.497(3)
Cα-Cβ	1.442(8)	1.524(5)
Cβ−(Cβ'-py-ring)	1.379(7)	1.489(5)
pyridine		
N−Cβ'(Zr-ring)	1.393(6)	1.360(4)
N−C(py-ring)	1.364(5)	1.349(4)

Zr−Cα distance is typical for Zr−C σ-bonds, and the Zr−N bond length is in the typical range of zirconium amides and not of pyridine-N coordination. The large distances from Zr to the internal C atoms indicate a weak Zr−π(C=C) interaction. The σ^2,π-interaction adopts the typical "envelope" structure with an angle of 53.9° at the N−C13 axis (Zr, N, C13/C11, C12, C13, N). The different bond lengths in the five-membered ring, the long Cα−Cβ and the short Cβ−(Cβ'-py-ring) bond, are analogous to the *s-cis*-diene complexes. Regarding the difference between the distances in N−Cβ'(Zr-ring)/N−C(py-ring) in **3**, there is no such large difference found in the other examples of previously described complexes of this type, Cp$_2$Zr(2-vipy) and *rac*-(ebthi)Zr(2-vipy) (first $\Delta d = 0.046$, second $\Delta d = 0.041$ Å). Nevertheless the

alternating bond distances in the pyridine ring support the bonding description with dearomatization as a 2-dihydropyridin-2-ylidene in conjugation with the unsaturated zirconacycle. The description as a 1-zircona-2-azacyclopent-3-ene rather than a η^4-1-azadiene complex or an olefin complex stabilized by pyridine N atom coordination is favored.

The five-membered zirconacycle with a fused pyridine ring that is present in the structure of **13** differs clearly from the above-mentioned system in **3**. There is no "localization" of the double bonds within the pyridine ring, and a N-ligand-stabilized σ-alkyl complex is formed. The Zr−Cα and Cα−Cβ are single σ-bonds, both longer than found in **3**. The Zr−N bond length is in the typical range of pyridine-N coordination and not of zirconium amides. There is no bond from Zr to the Cβ and Cβ' atoms. The bonding description as an σ-alkyl complex stabilized by pyridine N atom coordination is favored. Addionally, there is a fluoride coordinated at the metal center. The Zr−F bond length is longer than found in the difluoride **8**. The reason for this could be a F−N interaction (2.662 Å; N−F−Zr 62.7°) or H21−F interaction (2.089 Å), cf. NMR Investigations.

In the structure of (thi)$_2$ZrF$_2$ (**8**) the angle between the planes defined by X1a, X1b, and Zr (X1a and X1b are centroids of C1, C2, C3, C8, C9 and C10, C11, C12, C13, C18, respectively) and Zr, F1, and F2 is 89.1°.

Conclusion

Zirconocene difluorides and zirconocene alkyl monofluorides can be prepared by a route starting from the bis(trimethylsilyl)acetylene complexes via the 2-vinylpyridine complexes and a subsequent reaction with fluorinating reagents. HBF$_4$ etherate, NH$_4$BF$_4$, and NEt$_3$·3HF are well suited to produce the difluorides, whereas the only suitable reagent to prepare monofluorides is NEt$_3$·3HF. All these methods failed to synthesize the corresponding complexes with unsaturated substituents at the Cp ring.

Experimental Section

General Procedures. All operations were carried out under argon with standard Schlenk techniques. Prior to use nonhalogenated solvents were freshly distilled from sodium tetraethylaluminate and stored under argon.

The following spectrometers were used: mass spectra, AMD 402; NMR spectra, Bruker ARX 400 and AC 250 (^{19}F). Chemical shifts (^{1}H, ^{13}C, ^{29}Si) are given relative to SiMe$_4$ and are referenced to signals of the used solvents: benzene-d_6 (δ_H = 7.16, δ_C = 128.0), toluene-d_8 (δ_H = 2.03, δ_C = 20.4), tetrahydrofuran-d_8 (δ_H = 1.73, δ_C = 25.2), chloroform-d (δ_H = 7.27, δ_C = 77.0); chemical shifts (^{19}F) are given relative to CFCl$_3$. The spectra were assigned with the help of DEPT and shift correlation experiments. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Alkyne Complexes. The complexes (thi)$_2$Zr(THF)(η^2-btmsa)[7b] and Me$_2$Si(η^5-C$_5$H$_4$)$_2$Zr(py)(η^2-btmsa)[7c] were prepared according to the published methods.

(i)$_2$Zr(THF)(η^2-btmsa) (1). Bis(trimethylsilyl)acetylene (306 μL, 1.35 mmol) was added to a suspension of (i)$_2$ZrCl$_2$ (531 mg, 1.35 mmol) and magnesium (32 mg, 1.35 mmol) in 25 mL of THF. The resulting deep brown mixture was stirred for 4 h at ambient temperature. After evaporation of the THF,

but not totally to dryness, the residue was dissolved in a 1:3 mixture of THF/*n*-hexane. After filtration deep red crystals were formed upon cooling at −40 °C within 48 h. The crystals were separated to give 309 mg (55%) of **1**, mp 106−110 °C. Anal. Calcd for $C_{30}H_{40}OSi_2Zr$ (564.04): C, 63.88; H, 7.15. Found: C, 63.61; H, 6.87. ^{1}H NMR (THF-d_8): δ 0.11 (s, 18H, SiMe$_3$), 1.78, 3.62 (2 m, 4H each, THF), 5.62, (d, 4H, 1-H and 3-H), 6.08 (t, 2H, 2-H), 6.84, 7.17 (2 m, 4H each, 4-, 5-, 6-, 7-H). ^{13}C{^{1}H} NMR (THF-d_8): δ 2.6 (SiMe$_3$), 26.3, 68.1 (CH$_2$-THF), 90.8, 117.3, 122.9, 124.3 (CH-indenyl), 127.4, 134.8 (C$_q$-indenyl), ≡C−Si not observed due to molecular dynamics.[7] MS (70 eV) *m/z*: 490 [(i)$_2$Zr(Me$_3$SiC$_2$SiMe$_3$)]$^+$.

rac-(ebi)Zr(THF)(η^2-btmsa) (2). The same procedure as described for **1**, but starting from (ebi)$_2$ZrCl$_2$ (639 mg, 1.53 mmol), magnesium (37 mg), and bis(trimethylsilyl)acetylene (346 μL, 1.53 mmol) gives deep red needles (269 mg, 46%) of **2**, mp 98−106 °C. Anal. Calcd for $C_{32}H_{42}OSi_2Zr$ (590.08): C, 65.14; H, 7.17. Found: C, 64.99; H, 7.07. ^{1}H NMR (THF-d_8): δ 0.11 (s, 18H, SiMe$_3$), 1.78, 3.62 (2 m, 4H each, THF), 3.26, 3.55 (2 m, 2H each, CH$_2$), 5.47, 6.60 (2 d, 2H each, 2-H and 3-H), 6.79 (m, 4H, 5-H and 6-H), 6.97, 7.71 (2 d, 2H each, 4-H and 7-H). ^{13}C{^{1}H} NMR (THF-d_8): δ 4.1 (SiMe$_3$), 26.3, 68.1 (CH$_2$ THF), 30.5 (CH$_2$), 91.6, 111.2, 120.4, 122.1, 124.3, 125.3 (CH-indenyl), 117.6, 121.3 (C$_q$-indenyl), further C not observed due to molecular dynamics.[7] MS (70 eV) *m/z*: 517 [(ebi)Zr-(Me$_3$SiC$_2$SiMe$_3$)]$^+$.

2-Vinylpyridine Complexes. The complexes Cp$_2$Zr(2-vipy) and *rac*-(ebthi)Zr(2-vipy) were prepared as described before.[4c] The following complexes were prepared in analogy with the published methods.

(thi)$_2$Zr(2-vipy) (3). 2-Vinylpyridine (57.5 μL, 0.53 mmol) was added by a syringe to a solution of (thi)$_2$Zr(THF)(η^2-btmsa)[7b] (303 mg, 0.53 mmol) in 10 mL of THF/*n*-hexane (1:3). The resulting deep red mixture was stirred at room temperature for 2 h and filtrated, and deep red crystals were formed at −40 °C within 48 h. The crystals were separated to give 189 mg (81%) of **3**, mp 142 °C. Anal. Calcd for $C_{25}H_{29}NZr$ (434.78): C, 69.11; H, 6.75; N, 3.22. Found: C, 68.75; H, 7.15; N, 3.16. ^{1}H NMR (benzene-d_6): δ −0.9 (br, 1H, CH$_2$-vipy), 1.3−1.7, 1.9−2.3 (2 m, 17H, CH$_2$), 4.67 (t, *J* = 9.2 Hz, 1H, CH-vipy), 5.02, 5.28, 5.44 (3 br, 6H, CH-thi), 5.53 (t, *J* = 6.2 Hz, 1.2 Hz, 1H, py-5), 6.23 (m, *J* = 9.1, 6.1, 1.4 Hz, 1H, py-4), 6.61 (m, *J* = 9.1, 6.1 Hz, 1H, py-3), 7.31 (d, *J* = 6.3 Hz, 1H, py-6). ^{13}C{^{1}H} NMR (benzene-d_6): δ 23.9, 24.1, 24.5, 25.2 (CH$_2$-thi), 56.4 (CH$_2$-vipy), 88.2 (CH-vipy), 103.8, 104.4, 105.5 (CH-thi), 117.4, 117.7 (C$_q$-thi), 119.4, 123.9, 139.1, 145.9 (CH, py), 139.9 (C$_q$-py). MS (70 eV) *m/z*: 433 [(thi)$_2$Zr(vipy)]$^+$.

Me$_2$Si(η^5-C$_5$H$_4$)$_2$Zr(2-vipy) (4). Me$_2$Si(η^5-C$_5$H$_4$)$_2$Zr(py)(η^2-btmsa)[7c] (738 mg, 1.4 mmol) was dissolved in THF/*n*-hexane (1:3), and 2-vinylpyridine (151 μL, 1.4 mmol) was added. The color changed immediately to red, and the solution was stirred for 1 h. After filtration red crystals of **4** (420 mg, 78%) were obtained at −78 °C, mp 138 °C. Anal. Calcd for $C_{19}H_{21}NSiZr$ (382.69): C, 59.63; H, 5.53; N, 3.66. Found: C, 59.55; H, 5.32; N, 3.48. ^{1}H NMR (benzene-d_6): δ −0.77, 3.31 (2 br t, 1H each, Zr-CH$_2$); 0.40 (s, 6H, SiMe$_2$); 4.45 (t, 1H, ^3J = 9.7 Hz, metallacyclic CH); 4.95, 5.09, 5.16, 5.45, 5.85 (5 m, 1H each, C$_5$H$_4$); 5.44 (dt, 1H, ^3J = 6.2 Hz, ^4J = 1.0 Hz, Py-5); 5.65 (m, 3H, C$_5$H$_4$); 6.33 (ddd, 1H, ^3J = 8.9 and 6.1 Hz, ^4J = 1.4 Hz, Py-4); 6.46 (d, 1H, ^3J = 8.9 Hz, Py-3); 7.42 (d, 1H, ^3J = 6.4 Hz, Py-6). ^{13}C NMR (benzene-d_6): δ −5.2, −4.8 (2 Si-Me); 51.0 (Zr-CH$_2$); 88.3 (metallacyclic CH); 101.9, 102.5, 103.1, 103.8 (enhanced intensity), 109.4, 110.6, 115.5 (C$_5$H$_4$); 103.8 (Py-5); 122.9 (Py-3); 128.4 (Py-4); 139.3 (Py-2); 146.0 (Py-6). MS (70 eV) *m/z*: 381 [Me$_2$Si(η^5-C$_5$H$_4$)$_2$Zr(2-vipy)]$^+$.

(i)$_2$Zr(2-vipy) (5). 2-Vinylpyridine (78.0 μL, 0.72 mmol) was added by a syringe to a solution of (i)$_2$Zr(THF)(η^2-btmsa) (**1**) (409 mg, 0.72 mmol) in 10 mL of THF/*n*-hexane, 1:3. The resulting deep red mixture was stirred 4 h at room temperature and filtrated, and deep red crystals formed at −40 °C

within 48 h. The crystals were separated to give 171 mg (56%) of **5**, mp 182 °C. Anal. Calcd for $C_{25}H_{21}NZr$ (426.67): C, 70.38; H, 4.96; N, 3.28. Found: C, 69.96; H, 5.12; N, 3.08. ^{1}H NMR (toluene-d_8): δ −3.63, (t, *J* = 9.7 Hz, 1H, CH$_2$-vipy), 1.80 (t, *J* = 9.3 Hz, 1H, CH$_2$-vipy), 3.92 (t, *J* = 9.8 Hz, 1H, CH-vipy), 5.47, 6.23, 6.33, 7.30 (4 m, 4H, CH-vipy), 5.05, 5.06, 5.19, 5.74, 5.87, 6.17 (6H, Cp-indenyl), 6.33, 6.67, 6.76, 6.83, 6.85, 6.97, 7.04 (8H, C6-ring-indenyl). ^{13}C{^{1}H} NMR (toluene-d_8): δ 60.6 (CH$_2$-vipy), 88.9 (CH-vipy), 99.5, 97.9, 92.0, 92.2, 93.7, 111.8 (CH-Cp-indenyl), 128.7, 123.1, 123.5, 122.2, 124.2, 122.8, 123.4, 123.1 (C6-ring-indenyl), 118.5, 118.7, 122.0, 122.9 (C$_q$-indenyl), 123.0, 122.0, 103.8, 146.0 (CH, py), 137.0 (C$_q$-py). MS (70 eV) *m/z*: 425 [(i)$_2$Zr(vipy)]$^+$.

rac-(ebthi)Zr(2-Ph-2-vipy) (6). *rac*-(ebthi)ZrCl$_2$ (806 mg, 1.89 mmol), 2-(2-phenylvinyl)pyridine (342 mg, 1.89 mmol), and lithium (26 mg, 3.78 mmol) were suspended at −40 °C in 20 mL of THF. The reaction mixture was stirred for a further 24 h at −40 °C. The color of the solution turned to dark red/red-brown. After filtration and crystallization at −30 °C crystals of **6** were obtained (578 mg, 57%), mp 248 °C. Anal. Calcd for $C_{33}H_{35}NZr$ (536.87): C, 73.83; H, 6.57; N, 2.61. Found: C, 73.39; H, 6.43; N, 2.60. ^{1}H NMR (benzene-d_6): δ −0.33 (d, 1H, ^3J = 8.5 Hz, Zr-α-CH); 4.81 (d, 1H, CH ebthi); 4.94 (d, 1H, ^3J = 8.5 Hz, Zr-β-CH); 4.97 (d, 1H, CH ebthi); 5.53 (d, 1H, CH ebthi); 5.56 (d, 1H, CH ebthi); 5.61 (t, 1H, ^3J = 6 Hz, py-5); 6.29 (dd, 1H, ^3J = 6 and 9 Hz, Py-4); 6.62 (d, 1H, ^3J = 9 Hz, Py-3); 7.07 (t, 1H, *p*-Ph); 7.24 (d, 2H, *o*-Ph); 7.32 (t, 2H, *m*-Ph); 7.48 (d, 1H, ^3J = 6 Hz, Py-6); CH$_2$ signals not analyzed. ^{13}C NMR (benzene-d_6): δ 23.3, 23.4, 23.4, 24.2, 24.3, 24.6, 24.9, 25.4, 28.8, 29.9 (10 × CH$_2$); 75.5 (Zr-α-CH); 91.6 (Zr-β-CH); 100.9, 101.2, 102.5, 105.3 (4 × CH ebthi); 116.2, 116.7, 119.6, 121.1, 124.3, 125.0 (6 × C ebthi); 108.4 (Py-5); 125.9 (Py-3); 127.2 (Py-4); 137.9 (Py-2); 146.0 (Py-6). MS (70 eV) *m/z*: 535 [(ebthi)Zr(2-Ph-2-vipy)]$^+$.

Difluorides. *rac*-(ebthi)ZrF$_2$ (**7**) was described and characterized before.[4c] New synthetic procedures for **7**: (A) By exchange reactions: (i) *rac*-(ebthi)ZrCl$_2$ (477 mg, 1.12 mmol) and Me$_3$SnF (614 mg, 3.36 mmol) were stirred in dichloromethane at room temperature for 2 h. After filtration the solvent was removed in vacuo, and the remaining Me$_3$SnCl was removed by sublimation at 60 °C (3 × 10^{-1} mbar) to yield **7** as a white product (338 mg, 77%). (ii) *rac*-(ebthi)ZrCl$_2$ (500 mg, 1.17 mmol) and ZnF$_2$ (133 mg, 1.29 mmol) were stirred in acetone at room temperature for 3 days. After filtration the solvent was concentrated in vacuo, ether was added, and the precipitate formed at −78 °C was isolated by filtration and dried in vacuo to yield **7** (97 mg, 21%). (B) By acidolysis reactions: (i) Complex **7** was prepared first[4c] from *rac*-(ebthi)-Zr(2-vipy) with HBF$_4$ etherate (yield 73%, but badly reproduceable). (ii) *rac*-(ebthi)Zr(2-vipy) (195 mg, 0.42 mmol) was dissolved in toluene, and NEt$_3$·3HF (46 μL, 0.28 mmol) was added. The solution was stirred for 5 h. After filtration the filtrate was concentrated in vacuo and *n*-hexane was added. At −78 °C white crystals of **7** (70 mg, 42%) appeared. (iii) *rac*-(ebthi)ZrMe$_2$ (322 mg, 0.83 mmol) was dissolved in toluene, and NEt$_3$·3HF (91 μL, 0.56 mmol) was added. The solution was stirred for 5 h, and after filtration the filtrate was concentrated in vacuo. *n*-Hexane was added, and white crystals of **7** (65 mg, 20%) appeared at −78 °C.

(thi)$_2$ZrF$_2$ (8). (thi)$_2$ZrCl$_2$ (684 mg, 1.71 mmol) and Me$_3$SnF (656, 3.59 mmol) were stirred in dichloromethane at room temperature for 4 h. After filtration the filtrate was concentrated in vacuo and *n*-hexane was added. A white product, **8** (163 mg, 26%), crystallized at −30 °C, mp 128 °C. Anal. Calcd for $C_{18}H_{22}F_2Zr$ (367.59): C, 58.82; H, 6.03. Found: C, 58.75; H, 6.05. ^{1}H NMR (CDCl$_3$): δ 1.67 (m, 2H, 5- and 6-H); 1.75 (m, 2H, 5- and 6-H); 2.51 (dt, 2H, 4- and 7-H); 2.62 (dt, 2H, 4- and 7-H); 5.77 (d, 2H, ^3J = 3.1 Hz, 1- and 3-H); 6.44 (t, 1H, ^3J = 3.1 Hz, 2-H). ^{13}C NMR (CDCl$_3$): δ 22.6 (C5, C6); 23.5 (t, $J_{C,F}$ = 2 Hz, C4, C7); 108.2 (C1, C3); 110.5 (C2); 131.0 (C3a,

C7a). ^{19}F NMR (CDCl$_3$): δ 21.8. MS (70 eV) m/z: 366 [(thi)$_2$ZrF$_2$]$^+$.
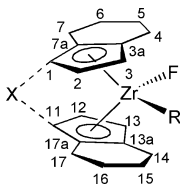
Me$_4$C$_2$(η^5-C$_5$H$_4$)$_2$ZrF$_2$ (9). Me$_4$C$_2$(η^5-C$_5$H$_4$)$_2$ZrCl$_2$ (400 mg, 1.07 mmol) and Me$_3$SnF (410 mg, 2.24 mmol) were stirred in dichloromethane at room temperature for 1 h. Then the reaction mixture was filtered, and the filtrate was concentrated in vacuo. *n*-Hexane was added, and a mixture of Me$_4$C$_2$(η^5-C$_5$H$_4$)$_2$ZrF$_2$ and Me$_3$SnCl crystallized at −30 °C. Me$_3$SnCl was removed by sublimation at 60 °C (3 × 10^{-1} mbar). The white product, **9** (183 mg, 50%), remained, mp 178 °C. Anal. Calcd for C$_{16}$H$_{20}$F$_2$Zr (341.55): C, 56.27; H, 5.90. Found: C, 56.09; H, 5.81. ^{1}H NMR (benzene-d_6): δ 1.08 (s, 12H, Me); 5.78 (m, 4H, α-H Cp); 6.30 (m, 4H, β-H Cp). ^{13}C NMR (benzene-d_6): δ 28.3 (Me); 44.5 (CMe$_2$); 108.2 (α-C Cp); 120.5 (β-C Cp); 143.0 (quart.). ^{19}F NMR (benzene-d_6): δ 25. MS (70 eV) m/z: 340 [Me$_4$C$_2$Cp$_2$ZrF$_2$]$^+$.

Me$_2$Si(η^5-C$_9$H$_{10}$)$_2$ZrF$_2$ (10). A suspension of Me$_2$Si(η^5-C$_9$H$_{10}$)$_2$ZrMe$_2$ (500 mg, 1.2 mmol) and NH$_4$BF$_4$ (126 mg, 1.2 mmol) in toluene was stirred at 90 °C for 48 h. Then the reaction mixture was filtered, and the filtrate was concentrated in vacuo. *n*-Hexane was added, and **10** (153 mg, 30%) crystallized at −30 °C, mp 234 °C. Anal. Calcd for C$_{20}$H$_{26}$F$_2$SiZr (423.73): C, 56.69; H, 6.18. Found: C, 56.35; H, 6.03. ^{1}H NMR (benzene-d_6): δ 0.48 (s, 9H, SiMe$_2$); 1.40 (m, 2H, 5-H); 1.45 (m, 2H, 6-H); 1.78 (m, 2H, 6-H); 1.89 (m, 2H, 5-H); 2.34 ("t", 4H, 7-H); 2.40 (dt, 2H, ^2J = 16 Hz, ^3J = 6 Hz, 4-H); 2.81 (ddd, 2H, ^2J = 16 Hz, ^3J = 6 and 8 Hz, 4-H); 5.44 (d, ^3J = 3.0 Hz, 2-H); 6.33, (dt, $^3J_{H,H}$ = 3.0 Hz, $J_{H,F}$ = 1.5 Hz; 3-H). ^{13}C NMR (benzene-d_6): δ −2.1 (SiMe$_2$); 22.4 (C5); 23.1 (C6); 24.0 (t, $J_{C,F}$ = 1.5 Hz, C4); 26.3 (C7); 105.7 (C1); 111.8 (t, $J_{C,F}$ = 1.5 Hz, C2); 121.5 (t, $J_{C,F}$ = 1 Hz, C3); 126.7, 136.5 (C3a, C7a). ^{19}F NMR (benzene-d_6): δ 29.6. ^{29}Si NMR (benzene-d_6): δ −14.1 ($^2J_{Si,H}$ = 6.9 Hz). MS (70 eV) m/z: 422 [Me$_2$Si(η^5-C$_9$H$_{10}$)$_2$ZrF$_2$]$^+$.

Monofluorides: Cp$_2$Zr(F)(CH$_2$CH$_2$-2-Py) (11). NEt$_3$·3HF (83 μL, 0.51 mmol) was added to Cp$_2$Zr(2-vipy)^{4c} (**2a**) (500 mg, 1.53 mmol), dissolved in 20 mL of toluene. The reaction mixture was stirred at 60 °C until the solution became colorless. After filtration the filtrate was concentrated in vacuo, *n*-hexane was added, and **11** (154 mg, 29%) crystallized at −30 °C, mp 98 °C. Anal. Calcd for C$_{17}$H$_{18}$FNZr (346.56): C, 58.92; H, 5.24; N, 4.04. Found: C, 58.59; H, 4.97; N, 3.65. ^{1}H NMR (benzene-d_6): δ 1.03 ("t", 2H, Zr-CH$_2$); 3.33 ("t", 2H, Py-CH$_2$); 5.82 (d, 10H, $^2J_{H,F}$ = 1.6 Hz, Cp); 6.55 (dd, 1H, ^3J = 7.3 and 5.6 Hz, Py-5); 6.71 (d, 1H, ^3J = 7.7 Hz, Py-3); 6.90 (dt, 1H, ^3J = 7.3 and 7.7 Hz, ^4J = 1.8 Hz, Py-4); 9.13 ("dd", 1H, ^3J = 5.6 Hz, $J_{H,F}$ = 7.2 Hz, Py-6). ^{13}C NMR (benzene-d_6): δ 40.3 ($^1J_{C,H}$ = 120 Hz, $J_{C,F}$ = 10 Hz, Zr−CH$_2$); 40.4 ($^1J_{C,H}$ = 127 Hz, Py-CH$_2$); 110.9 ($J_{C,F}$ = 2 Hz, Cp); 120.8 ($J_{C,F}$ = 4 Hz, Py-5); 121.9 (Py-3); 137.8 (Py-4); 149.8 ($J_{C,F}$ = 29 Hz, Py-6); 170.3 (Py-2). ^{19}F NMR (benzene-d_6): δ −68.4.

rac-(ebthi)Zr(F)(CH$_2$CH$_2$-2-Py) (12). NEt$_3$·3HF (42 μL, 0.26 mmol) was added to *rac*-(ebthi)Zr(2-vipy)^{4c} (359 mg, 0.78 mmol), dissolved in 20 mL of toluene. The reaction mixture was stirred until the solution became colorless. After filtration the filtrate was concentrated in vacuo, *n*-hexane was added, and **12** (199 mg, 53%) crystallized at −30 °C. Mp: 135 °C. Anal. Calcd for C$_{27}$H$_{32}$FNZr (480.78): C, 67.45; H, 6.71; N, 2.91. Found: C, 67.16; H, 6.81; N, 2.81. ^{1}H NMR (benzene-d_6, CH$_2$ signals omitted): δ 0.83, 1.23 (2 m, 1H each, Zr-CH$_2$); 3.35, 3.61 (2 m, 1H each, Py-CH$_2$); 5.14 (d, 1H, ^3J = 3.0 Hz, 2-H); 5.76 (dd, 1H, ^3J = 3.2 Hz, $J_{H,F}$ = 3.9 Hz, 13-H); 5.87 (d, 1H, ^3J

= 3.0 Hz, 3-H); 5.96 (dd, 1H, ^3J = 3.2 Hz, $J_{H,F}$ = 4.8 Hz, 12-H); 6.52 (dd, 1H, ^3J = 5.7 and 7.5 Hz, Py-5); 6.73 (d, 1H, ^3J = 7.5 Hz, Py-3); 6.88 (dt, 1H, ^3J = 7.5 Hz, ^4J = 1.7 Hz, Py-4); 9.13 ("t", 1H, ^3J = 7.7 Hz, ^4J = 1.7 Hz, $J_{H,F}$ = 6.4 Hz, Py-6). ^{13}C NMR (benzene-d_6): δ 22.8 ($J_{C,F}$ = 2.4 Hz), 22.9, 23.2, 23.3 ($J_{C,F}$ = 1.9 Hz), 23.4, 23.8 ($J_{C,F}$ = 4.4 Hz), 24.3 ($J_{C,F}$ = 2.0 Hz), 24.7, 26.9, 28.2 (10 × CH$_2$ ebthi); 40.4 ($^1J_{C,H}$ = 125 Hz, Py-CH$_2$); 41.8 ($^1J_{C,H}$ = 119 Hz, $J_{C,F}$ = 8.0 Hz, Zr-CH$_2$); 104.1 (C2); 105.9 ($J_{C,F}$ = 4.4 Hz, C12); 110.7 (C3); 112.0 ($J_{C,F}$ = 4.7 Hz, C13); 116.7 ($J_{C,F}$ = 2.6 Hz), 122.2 ($J_{C,F}$ = 2.3 Hz), 124.7 ($J_{C,F}$ = 2.4 Hz), 125.3, 128.3, 128.8 (6 × quart.); 120.4 ($J_{C,F}$ = 2.7 Hz, Py-5); 121.7 (Py-3); 137.5 ($J_{C,F}$ = 1.7 Hz, Py-4); 149.7 ($J_{C,F}$ = 24.9 Hz, Py-6); 170.1 ($J_{C,F}$ = 0.9 Hz, Py-2). ^{19}F NMR (benzene-d_6): δ −52. MS (70 eV) m/z: 479 [(ebthi)Zr(F)(CH$_2$CH$_2$-2-Py)]$^+$.

(thi)$_2$Zr(F)(CH$_2$CH$_2$-2-Py) (13). NEt$_3$·3HF (37 μL, 0.23 mmol) was added to (thi)$_2$Zr(2-vipy) (**3**) (300 mg, 0.69 mmol), dissolved in 20 mL of toluene. The solution was stirred until the solution became colorless. Then the solution was filtered, the filtrate was concentrated in vacuo, *n*-hexane was added, and **13** (100 mg, 32%) crystallized at −30 °C, mp 119 °C. Anal. Calcd for C$_{25}$H$_{30}$FNZr (454.74): C, 66.03; H, 6.65; N, 3.08. Found: C, 66.00; H, 6.95; N, 3.03. ^{1}H NMR (benzene-d_6): δ 1.11 ("t", 2H, Zr-CH$_2$); 1.28, 1.38, 1.46, 1.62 (4 m, 2H each, 4-H and 5-H); 2.07, 2.31, 2.50, 2.89 (4 ddd, 2H each, 4-H and 7-H); 3.44 ("t", 2H, Py-CH$_2$); 5.39, 5.59 (2 dd, 2H each, ^3J = 3.1 Hz, $J_{H,F}$ = 2.2 Hz, 1-H and 3-H); 5.52 (t, 2H, ^3J = 3.1 Hz, 2-H); 6.53 (dd, 1H, ^3J = 7.3 and 5.3 Hz, Py-5); 6.71 (d, 1H, ^3J = 7.5 Hz, Py-3); 6.87 (dt, 1H, ^3J = 7.5 Hz, ^4J = 1.5 Hz, Py-4); 9.08 ("t", 1H, ^3J = 5.6 Hz, ^4J = 1.5 Hz, $J_{H,F}$ = 6.7 Hz, Py-6). ^{13}C NMR (benzene-d_6): δ 23.4, 23.4 (C5/6); 24.3 ($J_{C,F}$ = 2.9 Hz); 24.7 ($J_{C,F}$ = 8.4 Hz, C4/7); 39.3 ($^2J_{C,F}$ = 10.1 Hz, Zr-CH$_2$); 40.6 (Py-CH$_2$); 101.6, 105.8, 111.5 (C1/2/3); 122.9 ($J_{C,F}$ = 1.5 Hz), 126.8 ($J_{C,F}$ = 2.7 Hz, C3a/7a); 120.4 ($J_{C,F}$ = 3.3 Hz, Py-5); 122.2 (Py-3); 137.8 ($J_{C,F}$ = 2.1 Hz, Py-4); 149.5 ($J_{C,F}$ = 28.2 Hz, Py-6); 170.9 ($J_{C,F}$ = 1 Hz, Py-2). ^{19}F NMR (benzene-d_6): δ −47.2. MS (70 eV) m/z: 453 [(thi)$_2$Zr(F)(CH$_2$CH$_2$-2-Py)]$^+$.

Me$_2$Si(η^5-C$_5$H$_4$)$_2$Zr(F)(CH$_2$CH$_2$-2-Py) (14). NEt$_3$·3HF (60 μL, 0.37 mmol) was added to Me$_2$Si(η^5-C$_5$H$_4$)$_2$Zr(2-vipy) (**4**) (425 mg, 1.11 mmol) in 20 mL of toluene. The reaction mixture was stirred for 2 h. After filtration the filtrate was concentrated in vacuo, *n*-hexane was added, and **14** (94 mg, 21%) crystallized at −30 °C, mp 185 °C. Anal. Calcd for C$_{19}$H$_{22}$FNSiZr (402.69): C, 56.67; H, 5.51; N, 3.48. Found: C, 56.34; H, 5.47; N, 3.07. ^{1}H NMR (benzene-d_6): δ 0.28, 0.49 (2 s, 3H each, Me$_2$-Si); 1.05 ("t", 2H, Zr-CH$_2$); 3.34 ("t", 2H, Py-CH$_2$); 5.56, 6.01, 6.23, 6.34 (4 m, 2H each, C$_5$H$_4$); 6.56 (dd, 1H, ^3J = 7.5 and 5.5 Hz, Py-5); 6.74 (d, 1H, ^3J = 7.5 Hz, Py-3); 6.91 (dt, 1H, ^3J = 7.5 Hz, ^4J = 1.2 Hz, Py-4); 9.20 (dd, 1H, ^3J = 5.5 Hz, $J_{H,F}$ = 7 Hz, Py-6). ^{13}C NMR (benzene-d_6): δ −6.2, −3.5 (2 Me); 40.5 (Py-CH$_2$); 42.6 ($J_{C,F}$ = 9.4 Hz, Zr-CH$_2$); 104.7, 107.5, 114.6, 114.9 ($J_{C,F}$ = 2 Hz), 125.8 ($J_{C,F}$ = 4.8 Hz, 5 × C$_5$H$_4$); 120.9 ($J_{C,F}$ = 3.5 Hz, Py-5); 122.0 (Py-3); 137.7 ($J_{C,F}$ = 2 Hz, Py-4); 149.4 ($J_{C,F}$ = 28.5 Hz, Py-6); 169.9 (Py-2). ^{19}F NMR (benzene-d_6): δ −57.7. MS (70 eV) m/z: 401 [Me$_2$Si(η^5-C$_5$H$_4$)$_2$Zr(F)(CH$_2$CH$_2$-2-Py)]$^+$.

Me$_2$Si(η^5-C$_9$H$_{10}$)$_2$ZrF(Me) (15). NEt$_3$·3HF (60 μL, 0.37 mmol) was added to Me$_2$Si(η^5-C$_9$H$_{10}$)$_2$ZrMe$_2$ (461 mg, 1.11 mmol), dissolved in 20 mL of toluene. The solution was stirred for 2 h. Then the solution was filtered, the filtrate was concentrated in vacuo, *n*-hexane was added, and **15** (186 mg, 40%) crystallized at −30 °C. Me$_2$Si(η^5-C$_9$H$_{10}$)$_2$ZrF$_2$ (**10**) may form as a side product and must be removed by sublimation (90 °C, 3 × 10^{-1} mbar). Mp: 172 °C. Anal. Calcd for C$_{21}$H$_{29}$FSiZr (419.77): C, 60.09; H, 6.96. Found: C, 60.47; H, 6.75. ^{1}H NMR (benzene-d_6): δ 0.34, 0.49 (2 s, 3H each, Me$_2$Si); 0.40 (d, 3H, $^3J_{H,F}$ = 2.5 Hz, Zr-Me); 4.88 (d, 1H, ^3J = 3.0 Hz); 5.69 (d, 1H, ^3J = 3.1 Hz); 6.01 (dd, 1H, ^3J = 3.1 Hz, $J_{H,F}$ = 2.1 Hz); 6.53 (d, 1H, ^3J = 3.0 Hz); CH$_2$ not analyzed. ^{13}C NMR (benzene-d_6): δ −2.2, −2.2 (2 Si-Me); 28.7 (Zr-Me); 22.6 ($J_{C,F}$ = 3.7 Hz), 22.7, 23.3, 23.4, 23.9 ($J_{C,F}$ = 3.0 Hz), 24.7, 26.1, 26.3 (8 × CH$_2$); 100.0, 102.4 (2 × Si−C); 111.1, 111.2, 117.7, 121.5 (4 × CH);

125.0, 127.0, 131.5, 133.8 (4 × quart.). ^{19}F NMR (benzene-d_6): δ 51.7. ^{29}Si NMR (benzene-d_6): δ 14.8 ($^2J_{\text{Si,H}}$ = 6.8 Hz). MS (70 eV) m/z: 403 [Me$_2$Si(η^5-C$_9$H$_{10}$)$_2$ZrF]$^+$.

X-ray Crystallographic Study of Complexes 3, 8, and 13. Data were collected with a STOE-IPDS-diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97)[13] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[14] XP (Bruker AXS) was used for structure representations. The absolute structure of **3** was determined through the Flack parameter x = −0.03(5).

Supporting Information Available: Tables of crystallographic data in cif file format, including bond lengths and angles of compounds **8** (data_813), **13** (data_817), and **3** (data_820). This material is available free of charge via the Internet at http://pubs.acs.org.

OM049745U

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(14) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Germany, 1997.