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Reactions of Zirconocene 2-Vinylpyridine Complexes with Diisobutylaluminum Hydride and Fluoride

Perdita Arndt,* Anke Spannenberg, Wolfgang Baumann,
Vladimir V. Burlakov,[†] and Uwe Rosenthal*

*Leibniz-Institut für Organische Katalyse an der Universität Rostock e. V.,
Buchbinderstrasse 5-6, D-18055 Rostock, Germany*

Sigurd Becke and Thomas Weiss

Bayer AG, Bayer Polymers, BPO-IIS-INN-SYR-SE, Q 18, D-51368 Leverkusen, Germany

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*Summary: In reactions of the zirconocene 2-vinylpyridine complex $Cp_2Zr(2\text{-vipy})$ (**1**) with $^iBu_2AlH$ and $^iBu_2AlF$ the isostructural complexes $[Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}2\text{-}CH_2CH{-}C_5H_4N)(\mu\text{-}H)][^iBu_2Al]$ (**3**) and $[Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}2\text{-}CH_2CH{-}C_5H_4N)(\mu\text{-}F)][^iBu_2Al]$ (**5**) were formed. These complexes can serve as models for the transfer of fluorine from zirconium to aluminum (Zr−F with Al−H to Zr−H and Al−F) found in the reaction of rac-(ebthi)ZrF_2 with $^iBu_2AlH$ to form the dimeric complex [rac-(ebthi)$ZrH(\mu\text{-}H)]_2$ (**6**). The compounds are important in obtaining an understanding of the activation of zirconocene fluoro complexes by $^iBu_3Al$ and of the role of $^iBu_2AlH$ in activation processes for the catalytic polymerization of olefins.*

Introduction

Metallocene-type Ziegler−Natta catalysts, used frequently in catalytic olefin polymerization, are formed by the reaction of metallocene complexes Cp'_2MX_2 (Cp′ = substituted η^5-cyclopentadienyl, X = R, H, etc.) with various Lewis acid activators (Lewis acids = methylalumoxane, tris(perfluoro)arylborane, etc.) in which metallocenium ion pair complexes with noncoordinating anions $[Cp'_2MX]^+[(\mu\text{-}X)\text{-}LA]^-$ are formed by abstraction of X.[1] Activators such as methylalumoxane and fluorinated boranes play an important role in metallocene activation. However, these compounds are expensive and, at least in the case of methylalumoxane, must be used in large excess relative to the amount of the metallocene.[1,2]

For economic reasons, there is great interest in finding cheaper catalyst systems. The easier abstraction of a fluorine ligand from the metal center of the starting precatalyst results in a more active system.[3] This was successfully demonstrated by catalysts for ethylene polymerization with $^iBu_3Al$ as the sole activating cocatalyst. In contrast to the reactive fluorine-containing *rac*-(ebthi)ZrF_2, the analogous dichloride *rac*-(ebthi)$ZrCl_2$ (ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)) was found to be totally inactive under comparable reaction conditions![4a−c] A transfer of the fluoride substituent from zirconium to aluminum with formation of Zr−H bonds seems to be the reason for this special "*fluoride effect*".

The marked counterion dependence of polymerization activity was also investigated for some fluoroaluminates with Zr−F−Al bridges.[4d−f] This and the extraordinary effects of the fluorine anions[5] prompted us to investigate as a model the reactions of selected zirconocene complexes of 2-vinylpyridine with $^iBu_2AlH$ and $^iBu_2AlF$, as well as complexes of *rac*-(ebthi)ZrF_2 with $^iBu_2AlH$, in detail.

Results and Discussion

It is already known that the reaction of titanocene and zirconocene alkyne complexes $Cp'_2M(\eta^2\text{-}Me_3SiCCSiMe_3)$ ($Cp'_2 = Cp_2$ = bis(η^5-cyclopentadienyl); $(thi)_2$ = bis(η^5-tetrahydroindenyl), ebthi, etc.; M = Ti, Zr) with $^iBu_3Al$, with formation of isobutene and $^iBu_2AlH$, gives heterobinuclear complexes with planar tetracoordinated carbon atoms.[6a] These complexes are prepared more readily by the direct reaction of the alkyne complexes $Cp'_2M(\eta^2\text{-}Me_3SiCCSiMe_3)$ with $^iBu_2AlH$.[6a] Related reactions have been studied by Erker and Binger.[6b−d]

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* To whom correspondence should be addressed. E-mail: uwe.rosenthal@ifok.uni-rostock.de.

[†] On leave from the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov St. 28, 117813, Moscow, Russia.

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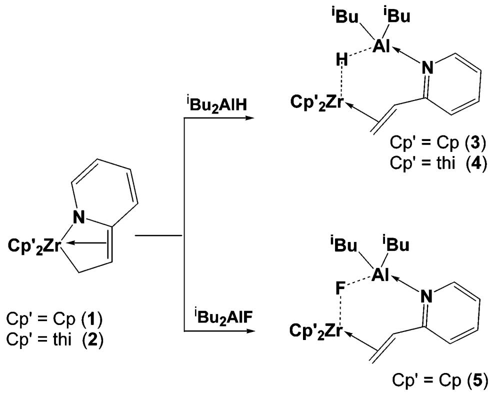
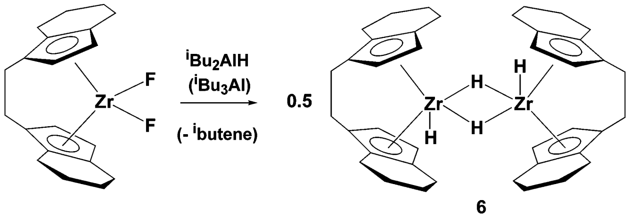
Scheme 1



Scheme 2



One must conclude from these results that ${}^{i}Bu_3Al$ very smoothly forms isobutene and ${}^{i}Bu_2AlH$ in such systems. For this reason we investigated the reactions of ${}^{i}Bu_2AlH$ as the actual activator in detail. When the 2-vinylpyridine complexes Cp_2Zr(2-vipy) (**1**)[7a] and $(thi)_2Zr$(2-vipy) (**2**)[7b] were treated with ${}^{i}Bu_2AlH$, the 1:1 complexes **3** and **4** were obtained (Scheme 1).

In the reaction of **1** with ${}^{i}Bu_2AlF$, the complex **5**, isostructural with the hydride complex **3** (Scheme 1), was produced. We did no experiments to convert complex **5** to **3** with ${}^{i}Bu_2AlH$ and to convert complex **3** to **5** with ${}^{i}Bu_2AlF$. Also, the reaction of a mixture of ${}^{i}Bu_2AlH$ and ${}^{i}Bu_2AlF$ with complex **1** was not investigated.

In the reaction of *rac*-(ebthi)ZrF_2[7] with 2 equiv of ${}^{i}Bu_2AlH$ the fluoride substituents were replaced by hydrogen and the dimeric complex containing two terminal and two bridging H atoms [*rac*-(ebthi)ZrH(μ-H)]$_2$ (**6**) was formed (Scheme 2). Buchwald and co-workers obtained this complex in 1991 by treating *rac*-(ebthi)-$ZrCl_2$ with $NaBEt_3H$ in benzene at room temperature.[8]

Interestingly, in the analogous reaction of *rac*-(ebthi)-$ZrCl_2$ with ${}^{i}Bu_2AlH$ under analogous conditions the chloride ligands were not replaced by hydrogen. Only unchanged starting material was isolated. Fluoride obviously is the more labile ligand compared with chloride.

NMR Investigations. As described earlier, 2-vinylpyridine coordinates to the zirconocene core as what is described best as a monoazadiene ligand, thus forming a metallaazacyclopentene complex (Scheme 1).[7a] 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 ${}^{3}J_{H,H}$ across "single" and "double" bonds). The species formed by addition of ${}^{i}Bu_2AlH$ or ${}^{i}Bu_2AlF$ (complexes **3** and **5**) preserve a small amount of this electronic modification of the 2-vinylpyridine. Their ${}^{1}H$ NMR spectra resemble those of the 2-vinylpyridine complex **1**, but the ${}^{13}C$ NMR spectra show that this electronic modification is less pronounced than that in **1**.[7a]

Chart 1

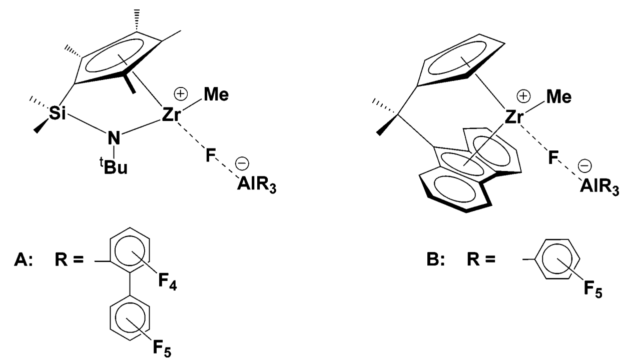


Table 1. Crystallographic Data for 3, 5, and 6

	3	5	6
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$C2/c$
a (Å)	11.008(2)	10.955(2)	14.045(3)
b (Å)	13.164(3)	13.275(3)	17.604(4)
c (Å)	17.199(3)	17.147(3)	30.080(6)
β (deg)			92.18(3)
V (Å^3)	2492.3(8)	2493.6(8)	7432(3)
Z	4	4	8
density (g cm^{-3})	1.249	1.296	1.407
μ(Mo Kα) (mm^{-1})	0.486	0.494	0.594
T (K)	293	200	200
no. of rflns (measd)	9134	9166	7113
no. of rflns (indep)	2647	2576	3841
no. of rflns (obsd)	2042	1661	2721
no. of params	227	182	399
R1 ($I > 2\sigma(I)$)	0.038	0.049	0.046
wR2 (all data)	0.075	0.087	0.109

The ${}^{19}F$ NMR signal at δ −255 ppm of complex **5** is downfield shifted, compared to the similar complexes $[Me_2Si(\eta^5\text{-}Me_4C_5)({}^{t}BuN)ZrMe]^+[PBA]^-$ (PBA = tris(2,2′,2″-nonafluorobiphenyl)fluoroaluminate) (**A**; −109 ppm)[4d] and $[Me_2C(Flu)(Cp)ZrMe]^+[(\mu\text{-}F)Al(C_6F_5)_3]^-$ (**B**; −122 ppm),[4e] which also contain $Zr^+\cdots F{-}Al^-$ units (Chart 1).

X-ray Crystal Structures. Complexes **3**, **5**, and **6** were investigated by X-ray crystal structure analysis. The crystallographic data are listed in Table 1, and the molecular structures are shown in Figures 1−3.

Complexes **3** and **5** consist of a typical bent zirconocene having a monomeric structure.

The isostructural complexes **3** and **5** differ from the structure of the starting complex **1** (1-zircona-2-azacyclopent-3-ene),[7] although they possess the same C−C−2-py structural element. They are best described as stabilized olefin complexes (zirconacyclopropanes). On the basis of the structural data, there is no compelling evidence for a "localization" of the double bonds within the pyridine ring with dearomatization and formation of a bridging 1-monoazadiene between Zr and Al.

The most important feature with respect to the aforementioned fluoride effect is the competition of zirconium

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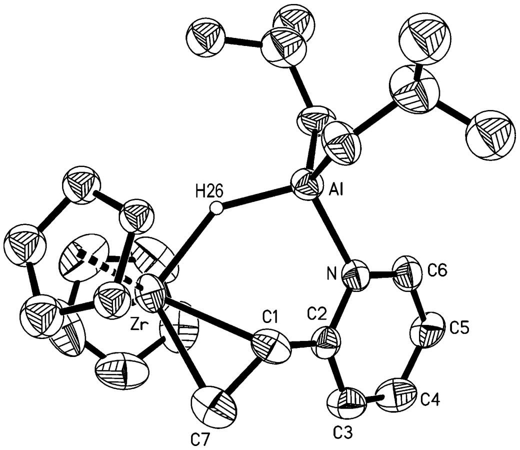

Figure 1. ORTEP plot of complex **3**. Hydrogen atoms except the bridging hydrogen atom and one position of the disordered groups are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å): Zr−C7 = 2.323(9), Zr−C1 = 2.341(8), Zr−H26 = 1.92(4), Al−H26 = 1.66(4), Al−N = 1.964(5), C1−C7 = 1.433(10), C1−C2 = 1.438(10), N−C2 = 1.359(7), N−C6 = 1.357(8), C2−C3 = 1.409(9), C3−C4 = 1.359(9), C4−C5 = 1.390(9), C5−C6 = 1.343(9).

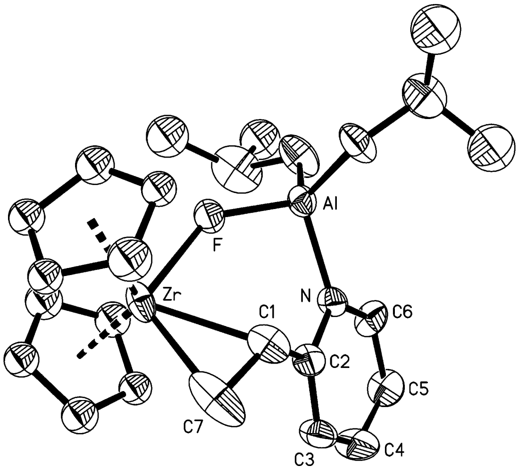

Figure 2. ORTEP plot of complex **5**. Hydrogen atoms and one position of the disordered groups are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å): Zr−C7 = 2.271(4), Zr−C1 = 2.301(11), Zr−F = 2.237(4), Al−F = 1.736(5), Al−N = 1.918(8), C1−C7 = 1.435(10), C1−C2 = 1.463(13), N−C2 = 1.380(10), N−C6 = 1.359(11), C2−C3 = 1.414(13), C3−C4 = 1.354(13), C4−C5 = 1.355(13), C5−C6 = 1.398(13).

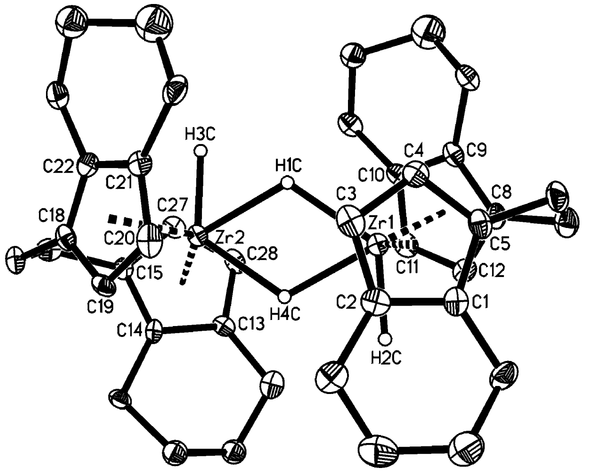

Figure 3. ORTEP plot of complex **6**. Hydrogen atoms, except the terminal and bridging hydrogen atoms, and one position of the disordered groups are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Zr1−H2c = 1.75(6), Zr2−H3c = 1.69(7), Zr1−H4c = 1.96(7), Zr1−H1c = 2.02(6), Zr2−H4c = 2.08(7), Zr2−H1c = 2.01(6); Zr1−H4c−Zr2 = 116.2, Zr1−H1c−Zr2 = 116.4, X1a−Zr1−X1b = 125.4 (X1a and X1b are centroids of C1−C5 and C8−C12, respectively), X1c−Zr2−X1d = 125.8 (X1c and X1d are centroids of C13, C14, C15, C27, C28 and C18−C22, respectively).

and aluminum in their interactions with the bridging fluoride ligand in complex **5** (Zr−F = 2.237(4); Al−F = 1.736(5) Å; Zr−F−Al = 136.5(3)°). Both of the metals interact with the fluoride ligand, and one can use this complex as a model to understand the transfer of F from Zr to Al (substitution of fluoride substituents by hydrogen, Scheme 2). The relatively short Al−F bond distance indicates the high affinity of Al for F. Complexes such as **5** (but with H at the tetracoordinated Al) are assumed as intermediates in the formation of **6**.

Similar complexes, for instance the aforementioned $[Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)ZrMe]^+[PBA]^-$ (**A**) (Scheme 3) with $Zr^+\cdots F-Al^-$ units, were found to have bond lengths of Zr−F = 2.123(6) Å and Al−F = 1.780(6) Å and an angle Zr−F−Al of 175.4(4)°, but in this case the Al−F bond distance is longer and Al has no H substituents for the aforementioned substitution reaction (Scheme 2).[4d]

The structure of the binuclear complex [*rac*-(ebthi)-$ZrH(\mu\text{-}H)]_2$ (**6**) consists of a Zr_2H_4 core, in which two terminal and two bridging hydrogens interact with the zirconium centers Zr1 and Zr2.

The angles between the plane defined by the centroids and zirconium and the neighboring planes of Zr with the two bridging H atoms are 79.6 and 77.3°. The latter planes form an angle of 11.3°. Structures of this $[Cp'_2ZrH(\mu\text{-}H)]_2$ type have been described for various substituted Cp derivatives[9a−c] and for ansa ligands.[9d−f] A dimeric zirconium complex with unsubstituted Cp ligands having two bridging H atoms has also been reported.[9g] The titanium(III) complex [*rac*-(ebthi)Ti(μ-H)]$_2$ with the ebthi ligand exists without terminal hydrogen atoms.[9h]

Conclusion

The present results give some hints regarding the aforementioned “fluoride effect”[4] on group 4 metallocene polymerization catalysts. Complex **5** can serve as a model for the abstraction of F from Zr by the $^iBu_3Al/^iBu_2AlH$ system to form Zr−H and Al−F bonds, as shown for the formation of **6**. This can be summarized by the following simplified schematic presentation: $[Zr]\cdots F-AlR_2$ and $[Zr]-H\cdots AlR_2$. These features are

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based on the well-known high affinity of aluminum for fluorine (diatomic bond enthalpies (Zr−F, 616 kJ/mol; Al−F, 664 kJ/mol),[10] show the competition of zirconium and aluminum in the interaction with the bridging fluorine in complex **5**, and serve to explain the observed activation of Zr−F complexes by Al−H compounds in polymerization catalysis.

Experimental Section

General Considerations. All operations were carried out under argon with standard Schlenk techniques. Prior to use, solvents were distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, 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 solvent used: benzene-d_6 (δ_H 7.16, δ_C 128.0); 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.

The complexes Cp_2Zr(2-vipy) (**1**)[7a] and $(thi)_2Zr$(2-vipy) (**2**)[7b] were described before and prepared in analogy to the published methods.[7a]

Preparation of Complex 3. To a solution of Cp_2Zr(2-vipy) (**1**; 211 mg, 0.65 mmol) in toluene (10 mL) was added $^{i}Bu_2AlH$ (0.65 mmol, 0.65 mL of a solution in toluene (1.0 M)). The mixture was stirred for 2 h at ambient temperature, and the color changed to deep red. After evaporation to dryness, the residual red oil was dissolved in a small amount of *n*-hexane. Red crystals were formed upon cooling to −40 °C for 48 h. Filtration gave **3** (210 mg, 68%), mp 136 °C. Anal. Calcd for $C_{25}H_{36}AlNZr$ (468.78): C, 64.06; H, 7.74; N, 2.99. Found: C, 63.74; H, 7.56; N, 2.87. ^{1}H NMR (benzene-d_6): δ −4.46 (br, 1 H, μ-H), 0.18, 0.51, 0.60, 0.67 (4 m, 4 H, CH_2 ^{i}Bu), 0.99 (d, 2 H, CH_2 vipy), 1.17, 1.22, 1.27, 1.31 (4 d, 12 H, CH_3), 2.20 (m, 2 H, CH−Al), 3.76 (t, 1H, CH vipy), 5.20, 5.40 (2 s, 10 H, Cp), 5.66 (t, 1 H, py), 6.49 (dd, 1 H, py), 6.56 (t, 1 H, py), 7.32 (d, 1 H, py). ^{13}C{^{1}H} NMR (benzene-d_6): δ 20.6 (CH_2 vipy), 23.5, 24.8 (br, CH_2 ^{i}Bu), 27.2, 27.4 (*C*H ^{i}Bu), 28.3 (2), 28.6, 28.8 (CH_3), 42.3 (CH_2*C*H vipy), 102.3, 102.8 (Cp), 112.4, 119.5 139.1, 144.4 (CH, py), 176.5 (C_q py). MS (70 eV; *m/z*): 467 [Cp_2Zr(vipy)(H)Al($^{i}Bu)_2]^+$, 325 [$Cp_2Zr(vipy)]^+$, 220 [$Cp_2Zr]^+$.

Preparation of Complex 4. To a solution of $(thi)_2Zr$(2-vipy) (**2**; 241 mg, 0.55 mmol) in toluene (10 mL) was added $^{i}Bu_2AlH$ (0.55 mmol, 0.55 mL of a solution in toluene (1.0 M)). The same procedure described for **3** gave **4** (151 mg, 47%), mp 129−130 °C. Anal. Calcd for $C_{33}H_{48}AlNZr$ (576.95): C, 68.71; H, 8.40; N, 2.44. Found: C, 68.31; H, 8.15; N, 2.02. ^{1}H NMR (benzene-d_6): δ −3.92 (br, 1 H, μ-H), 0.48, 0.66 (m, 4 H, CH_2 ^{i}Bu), 1.17, 1.22, 1.30, 1.33 (4 d, 12 H, CH_3), 2.19 (m, 2 H, CH−Al), 1.42−1.75 (m, 8 H, CH_2 thi), 2.12−2.31 (m, 10 H, CH_2 thi, CH_2 vipy), 3.80 (dd, 1H, CH vipy), 4.32, 4.66, 4.93, 5.36, 5.59 (6 m, 6 H, Cp thi), 5.68 (m, 1H, py), 6.62 (m, 2 H, py), 7.38 (dd, 1 H, py). ^{13}C{^{1}H} NMR (benzene-d_6): δ 25.7, 25.2, 24.9, 24.3, 23.8, 23.7 (2), 23.5 (*C*H_2 thi), 20.5, 22.8 (br, CH_2 ^{i}Bu), 27.2, 27.3 (*C*H ^{i}-Bu), 28.3, 28.5, 28.7, 28.8 (CH_3), 31.4 (CH_2 vipy), 48.3 (*C*H vipy), 98.8, 101.9, 102.0 (2), 102.4, 102.5 (CH thi), 115.5, 118.0 (2), 119.3 (C_q thi), 112.0, 120.1, 138.8, 144.2 (CH, py), 176.1 (C_q py). MS (70 eV; *m/z*): 575 [$(thi)_2Zr$(vipy)(H)Al($^{i}Bu)_2]^+$, 433 [$(thi)_2Zr(vipy)]^+$, 328 [$(thi)_2Zr]^+$, 105 [$C_7H_7N]^+$.

Preparation of Complex 5. To a solution of Cp_2Zr(2-vipy) (**1**; 170 mg, 0.52 mmol) in toluene (10 mL) was added $^{i}Bu_2AlF$ (0.52 mmol, 0.52 mL of a solution in toluene (1.0 M)). The mixture was stirred for 4 h at ambient temperature, and the color changed to deep red. After evaporation to dryness, the orange oil was dissolved in a small amount of *n*-hexane. When this solution was cooled to −40 °C for 48 h, a red oil was formed. After filtration of the mother liquor the orange oil was dissolved again in a small amount of ether; after 1 week light orange crystals of **5** (10 mg) were formed, suitable for X-ray crystal structure analysis. An additional yield of 80 mg of an orange oil (38%) was obtained. For oil and crystals nearly identical spectroscopic results were obtained. Oil: ^{1}H NMR (benzene-d_6) δ 0.35−0.45 (m, 4 H, CH_2 ^{i}Bu), 0.93 (d, 2 H, CH_2 vipy), 1.14, 1.16, 1.17, 1.20 (4 d, 12 H, CH_3), 2.08 (m, 2 H, CH−Al), 3.16 (m, 1H, CH vipy), 5.31, 5.62 (2 d, 10 H, Cp), 5.75 (t, 1 H, py), 6.66 (dd, 1 H, py), 6.70 (t, 1 H, py), 7.36 (d, 1 H, py); ^{13}C{^{1}H} NMR (benzene-d_6) δ 36.3 (CH_2 vipy), 20.7, 23.5 (br, CH_2 ^{i}Bu), 26.5 (2) (*C*H ^{i}Bu), 28.3, 28.4, 25.5 (2) (CH_3), 54.0 (CH_2*C*H vipy), 107.8, 108.0 (Cp), 110.1, 118.2, 137.1, 141.3 (CH, py), 169.4 (C_q py); ^{19}F NMR (benzene-d_6) δ −255. $C_{25}H_{35}$-AlFNZr (467.76). The oil was not pure enough, and elemental analysis of the crystals was not possible due to the small amounts.

Preparation of Complex 6. To a solution of *rac*-(ebthi)-ZrF_2[7] (405 mg, 1.16 mmol) in 10 mL of toluene was added $^{i}Bu_2AlH$ (2.1 mmol, 2.1 mL of a solution in *n*-heptane (1.0 M)). The mixture was stirred for 2 h at room temperature, and the color changed to light green-brown. After evaporation to dryness, the residue was washed twice with 1 mL of cold *n*-hexane and dissolved in a small amount of toluene. After filtration the solvent was removed in vacuo until the first colorless crystals formed. When the mixture was cooled to −78 °C for 72 h, a colorless precipitate formed, which was filtered, washed with cold *n*-pentane, and dried in vacuo to give **6** (250 mg, 69%). The substoichiometric amounts of $^{i}Bu_2AlH$ given here are necessary. Smaller amounts of $^{i}Bu_2AlH$ gave lower yields and 3 equiv of $^{i}Bu_2AlH$ gave a violet oil and no complex **6**. This complex was obtained by another method described earlier with very similar characterization data.[8] Mp: 136 °C. Anal. Calcd for $C_{40}H_{52}Zr$ (715.29): C, 67.17; H, 7.33. Found: C, 67.21; H, 7.15. ^{1}H NMR (benzene-d_6): δ −1.28 (t, $J = 7.2$ Hz, 2 H, μ-H); 1.3−2.0 (8 H), 2.25−2.6 (10 H), 2.67 (dt, 1 H), 2.75 (dt, 1 H), 3.12 (dt, 1 H), 3.62 (dt, 1 H, all CH_2 ebthi); 5.07, 5.27, 6.37, 6.56 (4 d, $J = 2.8$ Hz, 2 H each, CH ebthi); 5.17 (t, $J = 7.2$ Hz, 2 H, Zr−H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 23.9, 23.9 (2C), 24.0, 25.0, 25.2, 26.2, 26.8, 27.7, 28.9 (all CH_2); 99.2, 99.9, 102.0, 102.9 (all CH); 114.4, 120.8, 121.5, 122.1, 124.0, 129.2 (all C_{quart}). MS (70 eV; *m/z*): 357 [$C_{20}H_{26}Zr]^+$. Crystals for X-ray: solution of THF/*n*-hexane 1:3.

X-ray Crystallographic Study of Complexes 3, 5, and 6. Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97)[11] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[12] XP (BRUKER AXS) was used for structure representations.

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Supporting Information Available: Tables of crystallographic data in CIF file format, including bond lengths and angles of compound **3** (data_260), **5** (data_261), and **6** (data_267). This material is available free of charge via the Internet at http://pubs.acs.org.

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