The Reaction of (Butadiene)zirconocene with Imines

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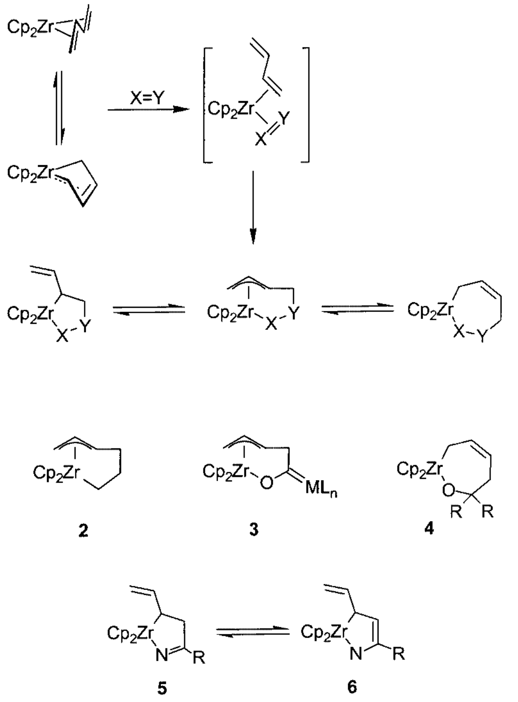
(Butadiene)zirconocene (*s-trans-/s-cis-***1** equilibrium mixture) reacts with the imine MeN=CHPh (**7a**) to form the 1:1 carbon-coupling product [κ*N*-MeN–CHPh–CH_2–η^3-($CHCHCH_2$)]$ZrCp_2$ (**8a**). The X-ray crystal structure analysis of **8a** revealed a metallacyclic structure featuring a distorted π-allyl moiety and a planar-tricoordinate nitrogen atom. Only one of the two possible diastereoisomers is found in the crystal (*cis*-**8a**) as well as in solution. Treatment of **1** with the more bulky aldimine $PhCH_2N$=CHPh (**7b**) selectively gave the corresponding 1:1 addition product *trans*-**8b**. Ketimines $PhCH_2N=C(CH_2)_4$ (**7c**), $HN=CPh_2$ (**7d**), or Δ^1-2-methylpyrroline (**7e**) also reacted selectively with (butadiene)zirconocene to yield the analogous metallacyclic C–C coupling products **8c**–**e**. Treatment of **8e** with $B(C_6F_5)_3$ proceeded cleanly by abstraction of a hydride anion from the carbon atom α to the nitrogen atom to form the intramolecularly coordinated imine product **10a** {with the $[HB(C_6F_5)_3^-]$ anion}. Similarly, Ph_3C^+ abstracts a hydride ion from **8e** to yield **10b** {isolated with the $[B(C_6H_5)_4^-]$ anion}. Proton addition from HNR_3^+ reagents takes place selectively at the Zr–amido nitrogen atom of the complexes **8a** or **8d** to yield the substituted (π-allyl)zirconocene cation complexes **11** or **12**, respectively, The cationic complexes **10**, **11**, and **12** polymerize ethene at room temperature/2 bar of ethene with moderate catalytic activities.

Introduction

(Butadiene)zirconocene (**1**) has been used repeatedly as a reagent in organometallic and organic synthesis[1] as well as in catalysis.[2] Compound **1** is remarkable since it exists as a mixture of the two stereoisomers, (*s-cis-*) and (*s-trans-*η^4-C_4H_6)$ZrCp_2$.[3] It is readily prepared by treatment of the metallocene dihalide with "butadiene−magnesium".[4,5] Several alternative syntheses of **1** have been described in the literature.[3,6]

The (η^4-butadiene)zirconocene system reacts with a variety of unsaturated organic or organometallic reagents with carbon−carbon coupling. In many cases 1:1 or 1:2 addition products were obtained selectively. Their further transformation including hydrolytic workup has opened attractive synthetic pathways to novel Fischer carbene complexes,[1,7] stable conjugated primary enamines,[8] β,γ-unsaturated ε-hydroxycarboxylic acids,[9] and other organic building blocks.[10] Typical examples of organometallic products formed in these addition reactions are shown in Scheme 1.

It is noteworthy that the addition of organic carbonyl compounds leads to seven-membered metallacycles **4** that exhibit a strong metal−oxygen interaction caused by a marked oxygen-to-Zr π-backbonding component,[11] whereas the formally related zirconoxycarbene complexes **3** typically show a metallacyclic π-allyl structure.[7] Five-mem-



Scheme 1

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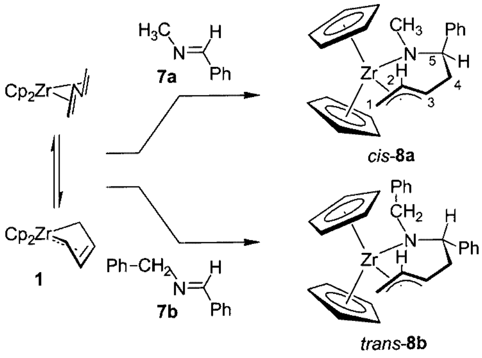
bered tautomeric mixtures ($\mathbf{5} \rightleftarrows \mathbf{6}$) were observed in the case of the 1:1 addition products between **1** and nitriles.[8] The metallacyclic structural type actually favored in such systems thus seems to depend strongly on the specific electronic features of the subunits involved, especially on the π-backbonding ability of the heteroatom that is σ-attached to the zirconocene unit.[2,5] We have now treated (butadiene)-zirconocene with a variety of organic imines and found that the formation of metallacyclic 1:1 addition products is favored. The systems were structurally characterized and their remarkable reaction with some electrophiles was studied.

Results and Discussion

Addition of Aldimines

We have employed the benzaldimines **7a** and **7b** for the addition reaction with (butadiene)zirconocene (**1**). The reactions were carried out in toluene solution at ambient temperature. Both addition reactions required ca. 2 d of reaction time under these conditions to go to completion. The 1:1 addition products **8a** and **8b** were formed selectively (see Scheme 2). We did not observe the formation of any 1:2 addition products, even in the presence of excess imine.[12] The products were isolated as yellow to orange-colored solids in 60% (**8a**) and 45% (**8b**) yield.



Scheme 2

Single crystals of **8a** were obtained from dichloromethane (Figure 1). The structure shows that a new C−C connection has been formed between the heterocarbonyl carbon atom of the imine reagent **7a** and a terminal sp^2-carbon center of the butadiene ligand in **1** [C4−C5: 1.525(4) Å]. The metallocene complex **8a** contains a metallacyclic substructure located in the bent metallocene σ-plane, that contains a distorted η^3-allyl moiety. It exhibits short Zr−C1 [2.472(3) Å] and Zr−C2 [2.487(3) Å] bonds and a markedly longer Zr−C3 contact [2.618(3) Å]. The carbon−carbon bond lengths inside the π-allyl unit are distorted towards a σ,π-type structure [C1−C2: 1.417(4) Å; C2−C3: 1.356(4) Å].[13] The Zr−N bond in **8a** is rather short at 2.157(2) Å. The nitrogen center in complex **8a** is trigonally planar coordinated (sum of bonding angles at N: 354.7°).

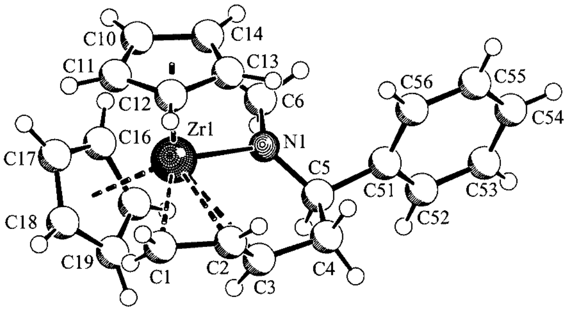


Figure 1. Molecular structure of **8a**; selected bond lengths [Å] and angles [°]: Zr1−N1 2.157(2), Zr1−C1 2.472(3), Zr1−C2 2.487(3), Zr1−C3 2.618(3), C1−C2 1.417(4), C2−C3 1.356(4), C3−C4 1.481(4), C4−C5 1.525(4), C5−N1 1.459(3), N1−C6 1.453(3); N1−Zr1−C1 123.9(1), N1−Zr1−C2 91.7(1), N1−Zr1−C3 67.4(1), C1−Zr1−C2 33.2(1), C1−Zr1−C3 57.3(1), C2−Zr1−C3 30.7(1), Zr1−N1−C5 128.0(2), Zr−N1−C6 116.6(2), Zr1−C1−C2 74.0(2), C1−C2−Zr1 72.8(2), C3−C2−Zr1 80.0(2), C2−C3−Zr1 69.3(2), C4−C3−Zr1 109.1(2), C1−C2−C3 123.7(3), C2−C3−C4 124.3(3), C3−C4−C5 107.6(2), C4−C5−N1 108.0(2), C5−N1−C6 110.1(2); C1−C2−C3−C4 160.9(3)

The formation of a new bond to the former imine sp^2-carbon atom has created a chiral center (C5) in **8a**. In addition, the substituted (π-allyl)ZrCp$_2$ subunit contains an element of planar chirality. Thus, two diastereoisomers could have been formed. However, only one is observed in the crystal. It is characterized by a *cis* orientation of the phenyl group at C5 and the π-allyl "*meso*"-hydrogen atom at C2 (*cis*-**8a**).

Single crystals of **8b** suitable for an X-ray crystal structure analysis were obtained from a toluene solution. In the asymmetric unit there are two crystallographically almost identical enantiomeric molecules. It exhibits an analogous metallacyclic framework to that of **8a**, containing a σ,π-distorted π-allyl unit [Zr−C1: 2.479(5) Å; Zr−C2: 2.511(4) Å; Zr−C3: 2.597(3) Å; C1−C2: 1.409(7) Å; C2−C3: 1.370(6) Å; values taken from molecule A]. The Zr−N σ-bond length in **8b** is found to be 2.185(3) Å and the nitrogen center is coordinated in a trigonally planar manner (sum of bonding angles: 358.0°). The major difference from **8a** is that the phenyl substituent of **8b** at C5 is *trans*-oriented relative to the 2-H at the π-allyl unit (see Figure 2). This may derive from a steric basis: in **8b**, the bulky C_6H_5 group of the *N*-benzyl substituent is found clearly oriented away from the C5 phenyl group.

In solution, only a single diastereoisomer of **8a** was observed, which is probably the *cis*-**8a** isomer. It exhibits a diastereotopic pair of ^{1}H NMR Cp singlets at $\delta = 5.87$ and 5.82 ppm (in CD_2Cl_2 at 298 K). The (*E*)-configured monosubstituted π-allyl unit of **8a** is characterized by ^{13}C NMR signals at $\delta = 42.9$ (C1), 124.7 (C2), and 110.5 (C3) as well as ^{1}H NMR resonances at $\delta = 2.19/1.89$ (1-H, 1-H′), 5.80 (2-H), and 5.02 (3-H) with a characteristic set of coupling constants [^2J(1-H, 1-H′) = 3.0 Hz, ^3J(1-H$_{syn}$, 2-H) = 8.0 Hz, ^3J(1-H$_{anti}$, 2-H) = 14.5 Hz, and ^3J(2-H, 3-H) = 15.0 Hz]. The proton 5-H ($\delta = 4.60$ ppm) shows a

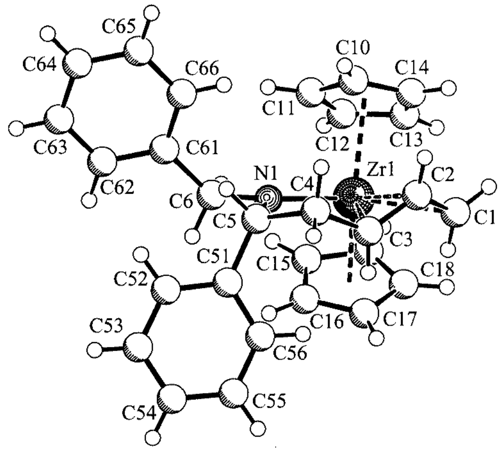


Figure 2. A view of the molecular structure of *trans*-**8b**; selected bond lengths [Å] and angles [°] (molecule A): Zr1−N1 2.185(3), Zr1−C1 2.479(5), Zr1−C2 2.511(4), Zr1−C3 2.597(4), C1−C2 1.409(7), C2−C3 1.370(6), C3−C4 1.487(6), C4−C5 1.535(5), C5−N1 1.473(5), N1−C6 1.462(5); N1−Zr1−C1 123.7(2), N1−Zr1−C2 92.4(2), N1−Zr1−C3 67.2(2), C1−Zr1−C2 32.8(2), C1−Zr1−C3 57.0(2), C2−Zr1−C3 31.1(1), Zr1−N1−C5 129.9(2), Zr−N1−C6 118.2(2), Zr1−C1−C2 74.9(3), C1−C2−Zr1 72.3(3), C3−C2−Zr1 77.9(2), C2−C3−Zr1 71.0(3), C4−C3−Zr1 110.5(3), C1−C2−C3 121.3(5), C2−C3−C4 125.9(4), C3−C4−C5 110.1(3), C4−C5−N1 107.3(3), C5−N1−C6 109.9(3); C1−C2−C3−C4 −162.5(4)

large (anti-periplanar) coupling of ^3J(4-H′, 5-H) = 11.5 Hz and a small (gauche) coupling of ^3J(4-H, 5-H) = 7.2 Hz. Together with the coupling constants at 4-H/4-H′ of ^2J(4-H′, 4-H) = 12.0 Hz, ^3J(4-H′, 3-H) = 11.5 Hz, and ^3J(4-H, 3-H) = 3.5 Hz, this places the C5 phenyl substituent of complex **8a**, in solution, in a *cis* orientation relative to the 2-H *meso*-proton, just as it is found in the solid state structure. The NMR spectroscopic features of complex **8b** are similar (see Tables 1 and 2), but in detail specifically different. In **8b**, the 5-H proton shows only small coupling to 4-H/4-H′ (ca. 7 Hz) which indicates the presence of the *trans*-**8b** isomer in solution, analogously as it is found in the solid state (see Scheme 2).

Table 1. Selected ^{1}H NMR spectroscopic features of the complexes **8**, **10** and **11**

	1-H	1-H′	2-H	3-H	4-H	4-H′	5-H	N−CH$_3$	N−H
8a[a]	2.19	1.89	5.80	5.04	2.41	1.72	4.60	2.24	
8b[b]	2.30	1.88	6.06	5.67	2.33		4.91		
8c[c]	2.22	1.88	5.83	4.87	2.44	1.68			
8d[a]	2.16	1.97	5.43	5.08	3.22	1.45			1.71
8e[a]	2.12	1.83	5.68	5.22	2.27	1.35			
10a[d]	2.05	1.70	5.44	4.34	2.11	1.35			
10b[a]	2.47	2.14	5.93	4.89	2.56	1.78			
11a[e]	2.47	2.26	5.90	4.92	2.64	2.20	4.11	2.15	2.89
11b[a]	2.59	2.35	5.92	4.95	2.85	2.18	4.09	2.27	2.55

[a] Chemical shifts in CD$_2$Cl$_2$ at 298 K. [b] 253 K. [c] 273 K. [d] In [D$_5$]bromobenzene at room temperature. [e] Room temperature [D$_6$] benzene/[D$_8$] THF (4:1).

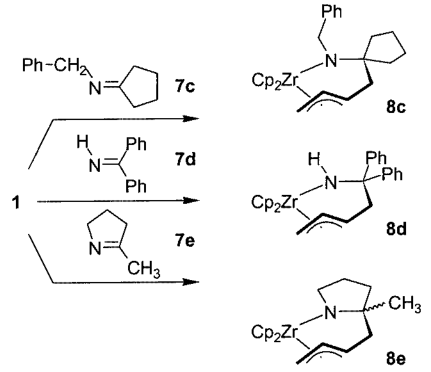
Reaction of (Butadiene)zirconocene with Ketimines

The reaction of **1** with imine **7c** of *N*-benzylcyclopentanone in toluene at room temperature required 2 d to go to completion. Again, only a 1:1 addition product was detected (**8c**), which was isolated in ca. 80% yield. Single crystals of **8c** were obtained from toluene. There are two crystallographically independent but chemically equivalent molecules of **8c** in the asymmetric unit; the values given below correspond to molecule A. The X-ray crystal structure analysis showed the presence of the typical metallacyclic framework (see Figure 3), featuring a nitrogen center that is close to being sp^2-hybridized [sum of bonding angles: 355.3°; angle Zr−N−C5: 128.5(2)°] and bonded to the zirconium atom [Zr−N: 2.178(3) Å], and a distorted η^3-allyl moiety [Zr−C1: 2.473(4) Å; Zr−C2: 2.491(4) Å; Zr−C3: 2.635(4) Å; C1−C2: 1.406(6) Å; C2−C3: 1.373(5) Å] inside a rigid metallacycle. The benzyl substituent at the nitrogen atom in **8c** attains a similar conformational orientation as was observed for **8b** (see above). The spiro-annelated carbocyclic five-membered ring at C5 occupies a pseudoaxial and a pseudoequatorial substituent position with its C−C bonds at the slightly crown-shaped central heterometallacycle.

Table 2. Selected ^{13}C NMR chemical shifts of the framework atoms of the complexes **8** and **11**

	C-1	C-2	C-3	C-4	C-5
8a[a]	42.9	124.7	110.5	46.6	96.4
8b[b]	44.0	126.9	112.7	40.9	88.4
8c[c]	44.9	125.3	109.4	44.0	97.2
8d[a]	41.2	124.8	114.2	47.6	97.3
8e[a]	41.7	125.2	117.4	49.1	98.9
11a[d]	47.6	128.9	103.6	41.6	82.5
11b[a]	47.8	128.6	102.4	41.7	83.1

[a] Chemical shifts in CD$_2$Cl$_2$ at 298 K. [b] 253 K. [c] 273 K. [d] Room temperature [D$_6$] benzene/[D$_8$] THF (4:1).



Scheme 3

In solution, complex **8c** shows the typical ^{1}H/^{13}C NMR spectroscopic features of the metallacyclic π-allyl complex systems (see Tables 1 and 2), so we can assume that the structures of **8c** in solution are similar to that of the solid state.

Imine **7d** of benzophenone also adds cleanly to (butadiene)zirconocene. The reaction takes only ca. 7 h to go to completion. The metallacyclic 1:1 addition product **8d** was

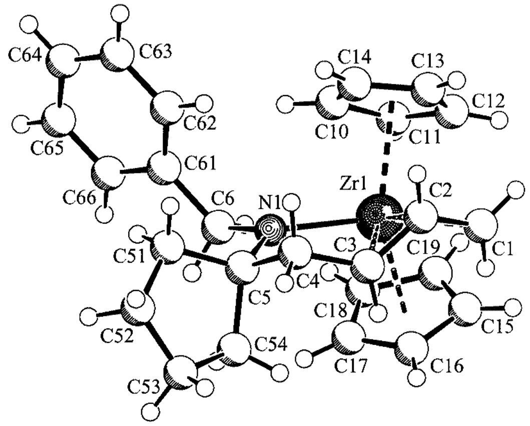


Figure 3. Molecular structure of complex **8c**; selected bond lengths [Å] and angles [°]: Zr1−N1 2.178(3), Zr1−C1 2.473(4), Zr1−C2 2.491(4), Zr1−C3 2.635(4), C1−C2 1.406(6), C2−C3 1.373(5), C3−C4 1.476(5), C4−C5 1.534(5), C5−N1 1.487(5), N1−C6 1.476(5); N1−Zr1−C1 123.3(1), N1−Zr1−C2 91.4(1), N1−Zr1−C3 67.2(1), C1−Zr1−C2 32.9(1), C1−Zr1−C3 57.1(1), C2−Zr1−C3 30.9(1), Zr1−N1−C5 128.5(2), Zr−N1−C6 115.0(2), Zr1−C1−C2 74.3(2), C1−C2−Zr1 72.8(2), C3−C2−Zr1 80.3(2), C2−C3−Zr1 68.8(2), C4−C3−Zr1 108.8(2), C1−C2−C3 123.2(4), C2−C3−C4 125.7(4), C3−C4−C5 110.0(3), C4−C5−N1 105.2(3), C5−N1−C6 111.8(3); C1−C2−C3−C4 −160.5(4)

isolated in 74% yield as a pale yellow solid. The ^{1}H NMR spectrum of **8d** (in CD_2Cl_2) shows a large separation of the signals of the diastereotopic Cp ligands ($\delta = 5.85$ and 5.26 ppm). The typical π-allyl resonances of **8d** are listed in Tables 1 and 2. The broad NH ^{1}H NMR resonance of **8d** is found at $\delta = 1.71$ ppm (in CD_2Cl_2). Figure 4 shows a typical ^{1}H NMR spectrum of complex **8d**.

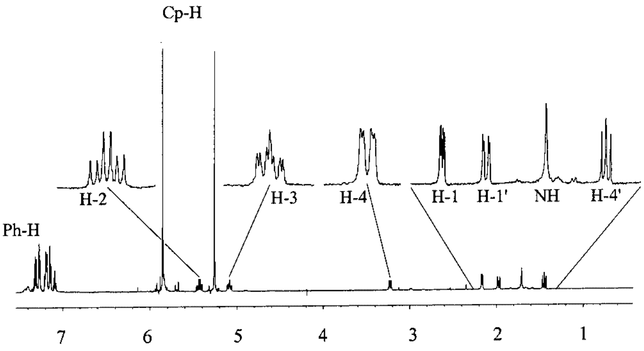
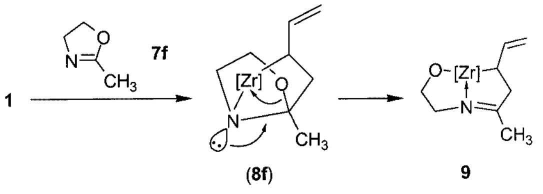


Figure 4. ^{1}H NMR spectrum of **8d** (CD_2Cl_2, 600 MHz, 298 K, δ in ppm)

Addition of the cyclic imine Δ^1-2-methylpyrroline (**7e**) to **1** at room temperature gave **8e** (single diastereomer, 60% isolated, for characterization see Tables 1 and 2, and the Exp. Sect.). The complexes **8c**−**e** were also characterized by ^{15}N NMR spectroscopy.[14] They showed ^{15}N NMR resonances at $\delta = -279$ (**8c**), $\delta = -254$ (**8d**), and $\delta = -249$ ppm (**8e**) (external reference: nitromethane, $\delta = 0$ ppm). These values are in a range that is typical for trigonal-planar nitrogen derivatives[15] including zirconocene-bound amido ligands.[16]

Reaction of 2-Methyl-2-oxazoline with (Butadiene)zirconocene

The reaction of **1** with the oxazoline reagent **7f** takes place slowly at room temperature in toluene solution (see Scheme 4). Workup after 20 h of reaction time gave the product **9** in ca. 80% yield, which was different from the expected simple addition product **8f**. Single crystals were obtained from toluene solution that allowed **9** to be structurally characterized by X-ray diffraction. The result of the X-ray crystal structure analysis (see Figure 5) revealed that the oxazoline heterocycle had been opened in the course of the reaction, and that a thermodynamically favorable zirconium−oxygen bond had been formed. Related ring-opened products have previously been obtained by Rosenthal et al. in the reaction of a [η^2-bis(trimethylsilyl)acetylene]zirconocene complex with thiazoles or benzoxazole.[17]



Scheme 4

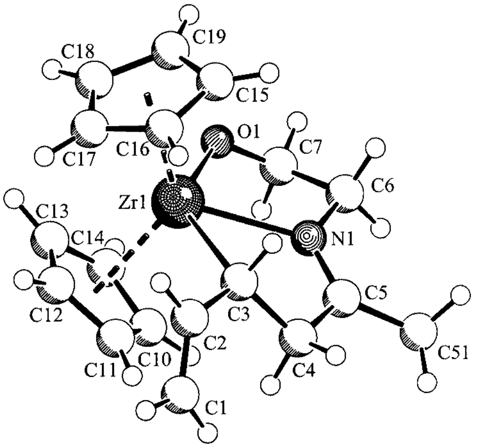


Figure 5. Molecular structure of complex **9**; selected bond lengths [Å] and angles [°]: Zr1−O1 2.094(2), Zr1−N1 2.378(2), Zr1−C3 2.448(2), C1−C2 1.336(4), C2−C3 1.470(3), C3−C4 1.517(3), C4−C5 1.491(4), C5−N1 1.279(3), N1−C6 1.467(3), C6−C7 1.492(4), C7−O1 1.365(3); O1−Zr1−N1 69.8(1), O1−Zr1−C3 135.2(1), N1−Zr1−C3 66.2(1), C7−O1−Zr1 123.4(2), Zr1−N1−C5 122.9(2), Zr−N1−C6 114.6(2), C2−C3−Zr1 118.8(2), C4−C3−Zr1 110.5(2), C1−C2−C3 128.3(3), C2−C3−C4 114.0(2), C3−C4−C5 110.6(2), C4−C5−N1 115.9(2), C5−N1−C6 121.8(2), N1−C6−C7 106.2(2), C6−C7−O1 111.2(2); C1−C2−C3−C4 −13.3(4)

In the reaction a metallabicyclic framework has been formed. The structural core is made up of an eight-membered ring comprising the zirconium atom, the $-O-CH_2-CH_2-N{=}C(CH_3)-$ core of the oxazoline reagent, and two butadiene carbon atoms. The metallabicyclic structure is formed from building up a close transannular zirconium−nitrogen contact. In **9** the Zr−O bond length is 2.094(2) Å, which is rather long and indicates the absence of a significant O→Zr π-interaction.[18] Consequently, the Zr−O−C7 bond angle is in the "normal" range at 123.4(2)°.

The N−C5 bond length is 1.279(3) Å, which clearly indicates the presence of an imine-type N=C double bond.[19] Consequently, the remaining lone pair on the N atom is used to coordinate to the zirconium atom [Zr−N: 2.378(2) Å]. The coordination geometry at the nitrogen atom in **9** is trigonal-planar (sum of bonding angles: 359.3°) as is the adjacent sp^2-hybridized carbon atom C5 (360°). The lateral Zr−C σ-bond length is 2.448(2) Å. The σ-ligand angle at the five-coordinate zirconium atom in **9** is rather large [O−Zr−C3: 135.2(1)°]. It is divided almost equally by the central N−Zr dative bond [O−Zr−N: 69.8(1)°; N−Zr−C3: 66.2(1)°]. The remaining vinyl group at C3 does not interact with the zirconium atom. It is pointing away from the metal center and is rotated out of the σ-plane [dihedral angle C4−C3−C2−C1: −13.3(4)°]. Consequently, a typical $C(sp^3)-C(sp^2)$ σ-bond length is observed for C2−C3 [1.470(3) Å]. The C1−C2 length [1.336(4) Å] denotes the presence of a C=C double bond.[19]

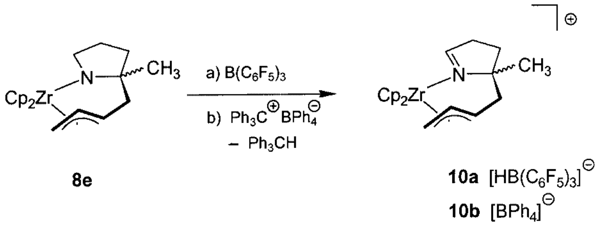
The ^{13}C NMR spectrum of complex **9** shows a typical imine carbon resonance of the N=C unit at δ = 187.2 ppm and a corresponding ^{15}N NMR signal at δ = −105.6.[14] The C4 ^{13}C NMR resonance of **9** is observed at δ = 48.8 ppm with a $^1J_{CH}$ coupling constant of 121 Hz, similar to the C3 resonance (δ = 52.6 ppm, $^1J_{CH}$ = 125 Hz). The C1 (δ = 97.5 ppm, $^1J_{CH}$ = 157 Hz and 151 Hz) and C2 (δ = 147.9 ppm, $^1J_{CH}$ = 144 Hz) signals indicate the presence of a σ-allyl group [^1H NMR signals at δ = 6.23 (2-H), 4.36, and 4.19 (1-H/1-H′) ppm]. Complex **9** exhibits a pair of equal-intensity ^1H NMR signals for the diastereotopic Cp ligands at δ = 5.95 and 5.70 ppm.

It is conceivable that the reaction of **1** with the oxazoline **7f** initially takes the usual course, and the addition product **8f**, that already contains the essential newly formed carbon−carbon bond, is actually formed. The applied reaction conditions probably favor thermodynamically controlled product formation. A subsequent β-oxygen elimination pathway that transforms **8f** to the more stable product **9** is viable (see Scheme 4).

Reactions of the Complexes 8 with Electrophiles

The reaction of alkylzirconocene complexes with activator Lewis acids, such as $B(C_6F_5)_3$[19,20] or the salt $[Ph_3C^+][B(C_6H_5)_4^-]$,[21] mostly proceeds with abstraction of an alkyl anion equivalent from the metal center with formation of a metallocene-derived cation.[22] Such cations often serve as very active homogeneous Ziegler−Natta catalysts for α-olefin polymerization.[23] In this context we were interested to learn about the favored reaction pathways that might be followed upon treatment of the heteroatom-functionalized metallacycles **8** with such electrophilic reagents.

We first reacted the bicyclic (butadiene)zirconocene/imine addition product **8e** with tris(pentafluorophenyl)borane (Scheme 5). The starting materials were dissolved in dichloromethane at 0 °C, and their reaction was then allowed to go to completion over 1 h at room temperature. The resulting product **10a** was isolated as an amorphous solid in greater than 80% yield. The NMR spectroscopic analysis showed that the $B(C_6F_5)_3$ electrophile had not attacked the Zr−allyl group (see Table 1). Instead, the borane had selectively abstracted a hydride from the C8 methylene group adjacent to the nitrogen atom, with formation of a κ*N*-coordinated imine.[24] The ^{11}B NMR spectrum of the salt shows a characteristic doublet (δ = −24.9 ppm, $^1J_{BH}$ = 85 Hz) of the $[HB(C_6F_5)_3^-]$ anion. In addition, the typical $^1H/^{13}C$ NMR spectroscopic features of the metal−imine moiety are observed at δ = 7.42 (8-H) and 183.5 ppm (C8), which were shifted drastically from the respective resonances of the starting material [**8e**: δ = 3.22, 2.90 (8-H); δ = 56.0 ppm (C8)].



Scheme 5

An even more pronounced $\Delta\delta^{15}N$ value was observed upon transforming the neutral starting material **8e** ($\delta^{15}N$ = −249 ppm) to the salt **10a** ($\delta^{15}N$ = −89 ppm). Figure 6 shows the characteristic appearance of the ^1H NMR spectrum of complex **10a** in [D$_5$]bromobenzene (the $HBAr_3^-$ ^1H NMR resonance was not observed).

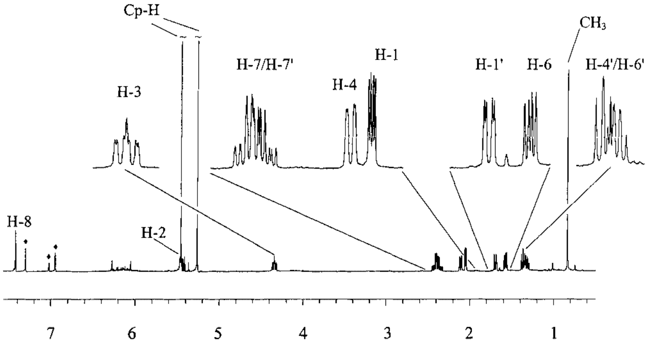
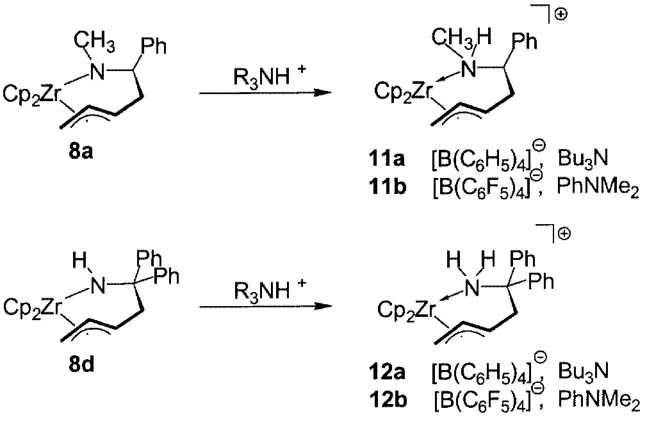


Figure 6. ^1H NMR spectrum of **10a** in [D$_5$]bromobenzene (600 MHz, 298 K, δ in ppm, black diamonds = solvent peaks)

Treatment of **8e** with trityl tetraphenylborate proceeded similarly. Hydride abstraction[25] from C8 takes place cleanly with formation of triphenylmethane and the organometallic salt **10b**.

We then treated the complexes **8a** and **8d** with both the ammonium Brønsted acids $[Bu_3NH^+][B(C_6H_5)_4^-]$ and $[PhNMe_2H^+][B(C_6F_5)_4^-]$.[26,27] Again, the Zr(π-allyl) moiety proved to be inert to electrophilic attack. Instead, in both cases it is the amido nitrogen atom that picks up the proton. We isolated the respective salts **11** and **12** [with

BPh_4^- (**a**) or $B(C_6F_5)_4^-$ (**b**) anions, respectively, see Scheme 6]. Both systems show the typical ^1H and ^{13}C NMR spectroscopic features of the remaining substituted (η^3-allyl)zirconocene moiety (see Tables 1 and 2). Protonation at the nitrogen atom has resulted in characteristic ^1H NMR spectroscopic features of **11b**, such as the $N-CH_3$ doublet at δ = 2.27 ppm and the characteristic triplet of doublets of 5-H at δ = 4.09 ppm (see Figure 7).



Scheme 6

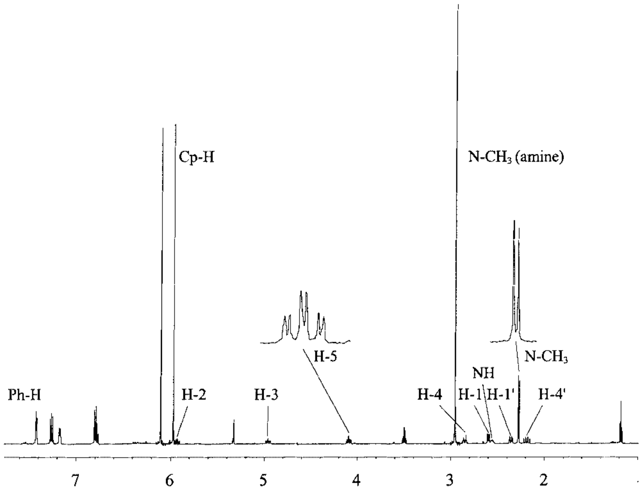


Figure 7. ^1H NMR spectrum of the salt **11b** [with $B(C_6F_5)_4^-$ anion]; the sample contains ca. 1 mol-equiv. of *N,N*-dimethylaniline (δ in ppm)

All the isolated samples of the complexes **11** and **12** contained ca. 1 mol-equiv. of the respective tertiary amine base, which could not readily be removed during the workup procedure. This has led us to assume an equilibrium of intra- and intermolecular amine coordination to the strongly electrophilic group-4 transition metal in these systems. For simplicity, the structures with intramolecular amine coordination to the zirconocene cation moiety are drawn in Scheme 6, although this has not been strictly proven.

We have employed the complexes **10a**, **11b**, and **12b** {all with $[HB(C_6F_5)_3^-]$ or $[B(C_6F_5)_4^-]$ anions} in polymerization experiments. Ethene polymerization was carried out with these systems in toluene solution (200 mL) at room temperature (2 bar of ethylene). The solution contained 0.5 mL of triisobutylaluminum as a "scrubbing agent" to prevent hydrolysis of the very sensitive homogeneous Ziegler−Natta catalyst systems at the very low concentrations that were used. The organometallic single component catalyst systems were injected as bromobenzene/toluene solutions to the pre-equilibrated reaction mixtures. All three systems turned out to be catalysts with moderate activity in the ethene polymerization experiments. Linear polyethylenes were obtained in all three cases (see Table 3).

Table 3. Ethene polymerization with the metallocene cation complexes **10**, **11**, and **12**

[a]	Catalyst [mg]	PE [g]	Activity[b]	M.p. [°C]
10a	15.0	2.24	65	129
11b	15.0	2.74	110	129
12b	15.0	4.30	177	131

[a] In 200 mL of toluene/0.5 mL of Bu_3Al, 1 h, room temperature, 2 bar of ethene. [b] Catalyst activities in kg(polymer)/[mol(cat.)·h·bar(ethene)].

We conclude that the (butadiene)zirconocene reagent is just reactive enough to add to the organic imines. It seems that in these cases the limit of the reactivity of these organometallic reagents is approached, since a subsequent carbon−carbon coupling at the other former diene terminus could not be achieved in these reactions. The nitrogen lone pair of the resulting metal amides does not seem to be substantially involved in bonding to the zirconocene unit.[26] This becomes apparent from the structural data of the complexes characterized here, which all feature relatively long Zr−N bonds. It also shows up in the reactions of these (π-allyl)zirconacycles: protonation occurs at the rather basic Zr−N bond, but not at the allyl carbanion equivalent, and hydride abstraction α to the nitrogen atom is also a favorable reaction of the systems **8**. Overall, this provides interesting selectivity features. We will explore whether the resulting cationic systems **10**, **11**, **12** can be used in selective stoichiometric carbon−carbon coupling reactions with functionalized unsaturated organic reagents. The observed moderate ethene polymerization activity of these systems allows us to believe that this can be achieved.

Experimental Section

General: Reactions with organometallic compounds were carried out under argon using Schlenk-type glassware or a glove-box. Solvents were dried and distilled under argon before use. NMR spectroscopic experiments were carried out with a Varian Unity plus 600 or a Bruker AC 200 NMR spectrometer. The NMR assignments were usually secured by carrying out a series of 2D NMR spectroscopy experiments.[29] For details see the Supporting Information. The following instruments were used for additional physical characterization: IR spectroscopy: Nicolet 5DXC FT-IR spectrometer; melting points: DSC 2010 (TA instruments); elemental analyses:

Foss Heraeus CHN-O-Rapid. (Butadiene)zirconocene (**1**)[3] and tris(pentafluorophenyl)borane[20] were prepared according to literature procedures. Commercially available imines [imine of benzophenone, Δ^1-2-methylpyrroline, benzylidene(methyl)amine, benzyl(benzylidene)amine] were distilled under argon prior to use. The other imines used in this study were prepared by condensation reactions of the respective carbonyl compound with the amine using 4 Å molecular sieves. The molecular sieves were activated by heating them to approx. 600 °C in vacuo, prior to use. The aldehyde or ketone (50.0 mmol) and the amine (50.0 mmol) were dissolved in dry toluene (150 mL) and stirred overnight with the activated molecular sieves at ambient temperature under argon. The molecular sieves were filtered off and the solvent removed in vacuo. The remaining crude imine was then purified by distillation and kept at 7 °C under argon.

Reaction of (Butadiene)zirconocene with Benzylidene(methyl)amine. Formation of 8a: Benzylidene(methyl)amine (**7a**, 0.24 g, 2.00 mmol) was added to a solution of (butadiene)zirconocene (**1**) (0.55 g, 2.00 mmol) in toluene (150 mL). After stirring at room temperature for 40 h the mixture was filtered and the solvent evaporated in vacuo. The crude residue was then treated with pentane (40 mL) to precipitate the insertion product (**8a**) as a yellow amorphous solid. The product was collected by filtration, washed with pentane (20 mL) and dried in vacuo. Yield: 0.60 g (75%). M.p. 194 °C. IR (KBr): $\tilde{\nu}$ = 3088 w, 2897 w, 2840 m, 2754 s, 1450 m, 1004 s, 999 s, 979 s, 877 m, 804 vs, 763 s, 703 s cm^{-1}. ^1H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 7.25 (pt, 2 H, ph-H_{meta}), 7.14 (pt, 1 H, ph-H_{para}), 7.12 (pd, 2 H, ph-H_{ortho}), 5.87 (s, 5 H, cp-H), 5.8 (m, 1 H, 2-H), 5.82 (s, 5 H, cp-H), 5.04 (m, 1 H, 3-H), 4.60 (dd, $^3J_{H,H}$ = 11.5, $^3J_{H,H}$ = 4.5 Hz, 1 H, 5-H), 2.41 (m, 1 H, 4-H), 2.24 (s, 3 H, 6-H), 2.19 (dd, $^3J_{H,H}$ = 8.0, $^2J_{H,H}$ = 2.5 Hz, 1 H, 1-H), 1.89 (dd, $^3J_{H,H}$ = 14.5, $^2J_{H,H}$ = 2.5 Hz, 1 H, 1′-H), 1.72 (m, 1 H, 4′-H) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 148.1 (ph-C_{ipso}), 128.3 (ph-C_{meta}), 127.2 (ph-C_{ortho}), 126.4 (ph-C_{para}), 124.7 (C-2), 110.5 (C-3), 108.4 (cp-C), 106.6 (cp-C), 96.4 (C-5), 46.6 (C-4), 45.6 (C-6), 42.9 (C-1) ppm.

X-ray Crystal Structure Analysis of 8a: Crystals were obtained by slow concentration of a dichloromethane solution. Formula $C_{22}H_{25}NZr$, M = 394.65, green-yellow crystal 0.35 × 0.10 × 0.05 mm, a = 20.995(1), c = 8.039(1) Å, V = 3543.5(5) $Å^3$, $\rho_{calcd.}$ = 1.480 $g\cdot cm^{-3}$, μ = 6.23 cm^{-1}, empirical absorption correction (0.812 ≤ T ≤ 0.970), Z = 8, tetragonal, space group $I\bar{4}$ (no. 82), λ = 0.71073 Å, T = 198 K, ω and φ scans, 6355 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.65 $Å^{-1}$, 3654 independent (R_{int} = 0.032) and 3400 observed reflections [$I \geq 2\sigma(I)$], 218 refined parameters, R = 0.028, wR^2 = 0.054, Flack parameter −0.02(4), max. residual electron density 0.27 (−0.25) $e\cdot Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Reaction of (Butadiene)zirconocene with Benzyl(benzylidene)amine. Formation of 8b: Benzyl(benzylidene)amine (**7b**, 1.97 g, 10.0 mmol) was added to a solution of (butadiene)zirconocene (**1**) (2.26 g, 10.0 mmol) in toluene (200 mL). After stirring for 60 h, the mixture was filtered and the solvent evaporated in vacuo. The crude residue was then treated with pentane (150 mL) to precipitate the insertion product as a yellow powder. The product was collected by filtration, washed twice with pentane (50 mL) and dried in vacuo. Yield: 2.12 g (45%). M.p. 114 °C. IR (KBr): $\tilde{\nu}$ = 3078 w, 3024 w, 2892 m, 2831 m, 2796 m, 2767 m, 1598 m, 1570 s, 1489 s, 1450 s, 1344 s, 1261 s, 1190 m, 1024 vs, 875 m, 811 vs, 740 vs, 702 s cm^{-1}. ^1H NMR (599.9 MHz, CD_2Cl_2, 253 K): δ = 7.34 (pt, 2 H, ph-$H_{meta/B}$), 7.24 (pt, 2 H, ph-$H_{meta/A}$), 7.1 (m, 4 H, ph-$H_{para/A}$, ph-$H_{para/B}$, ph-$H_{ortho/B}$), 7.01 (pd, 2 H, ph-$H_{ortho/A}$), 6.06 (m, 1 H, 2-H), 5.83 (s, 5 H, cp-H), 5.80 (s, 5 H, cp-H), 5.67 (m, 1 H, 3-H), 4.91 (m, 1 H, 5-H), 4.24 (d, $^2J_{H,H}$ = 17.2 Hz, 1 H, 6-H), 3.48 (d, $^2J_{H,H}$ = 17.2 Hz, 1 H, 6′-H), 2.39−2.28 (m, 3 H, 4-H/4′-H/1-H), 1.88 (m, 1 H, 1′-H) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 253 K): δ = 146.9 (ph-$C_{ipso/A}$), 142.4 (ph-$C_{ipso/B}$), 128.1 (ph-$C_{meta/B}$), 127.9 (ph-$C_{meta/A}$), 127.6 (ph-$C_{ortho/A}$), 127.5 (ph-$C_{ortho/B}$), 126.9 (C-2), 126.2 (ph-$C_{para/A}$), 125.7 (ph-$C_{para/B}$), 112.7 (C-3), 108.4 (cp-C), 106.7 (cp-C), 88.4 (C-5), 60.0 (C-6), 44.0 (C-1), 40.9 (C-4) ppm. $C_{28}H_{29}NZr$ (470.7): calcd. C 71.44, H 6.21, N 2.98; found C 71.21, H 6.32, N 2.66.

X-ray Crystal Structure Analysis of 8b: Crystals were obtained from a saturated toluene solution. Formula $C_{28}H_{29}NZr$, M = 470.74, yellow crystal 0.15 × 0.15 × 0.05 mm, a = 11.516(1), b = 17.227(1), c = 22.510(1) Å, V = 4465.7(5) $Å^3$, $\rho_{calcd.}$ = 1.400 $g\cdot cm^{-3}$, μ = 5.07 cm^{-1}, empirical absorption correction (0.928 ≤ T ≤ 0.975), Z = 8, orthorhombic, space group $P2_12_12_1$ (no. 19), λ = 0.71073 Å, T = 198 K, ω and φ scans, 37107 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 $Å^{-1}$, 10611 independent (R_{int} = 0.077) and 7135 observed reflections [$I \geq 2\sigma(I)$], 541 refined parameters, R = 0.050, wR^2 = 0.080, Flack parameter 0.01(4), max. residual electron density 0.33 (−0.51) $e\cdot Å^{-3}$, hydrogen atoms calculated and refined as riding atoms, two almost identical independent molecules in the asymmetric unit, being enantiomers of each other.

Reaction of (Butadiene)zirconocene with Benzyl(cyclopentylidene)amine. Formation of 8c: Benzyl(cyclopentylidene)amine (**7c**, 0.87 g, 5.0 mmol) was added to a solution of (butadiene)zirconocene (**1**) (1.38 g, 5.0 mmol) in toluene (120 mL). After stirring for 16 h, the mixture was filtered and the solvent was evaporated in vacuo. The crude residue was then treated with pentane (100 mL) to precipitate the insertion product **8c** as a yellow powder. The product was collected by filtration, washed with pentane (50 mL) and dried in vacuo. Yield: 1.82 g (81%). M.p. 130 °C. IR (KBr): $\tilde{\nu}$ = 3072 w, 2951 m, 2863 m, 2792 w, 1575 w, 1446 m, 1087 m, 1017 s, 803 vs, 736 s cm^{-1}. ^1H NMR (599.9 MHz, CD_2Cl_2, 273 K): δ = 7.34 (pd, 2 H, ph-H_{ortho}), 7.29 (pt, 2 H, ph-H_{meta}), 7.15 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, ph-H_{para}), 5.83 (ddd, $^3J_{H,H}$ = 14.5, $^3J_{H,H}$ = 14.5, $^3J_{H,H}$ = 7.2 Hz, 1 H, 2-H), 5.81 (s, 5 H, cp-H), 5.66 (s, 5 H, cp-H), 4.87 (ddd, $^3J_{H,H}$ = 14.5, $^3J_{H,H}$ = 11.5, $^3J_{H,H}$ = 3.5 Hz, 1 H, 3-H), 4.41 (d, $^2J_{H,H}$ = 18.5 Hz, 1 H, 8-H), 3.91 (d, $^2J_{H,H}$ = 18.5 Hz, 1 H, 8′-H), 2.44 (dd, $^3J_{H,H}$ = 3.5, $^2J_{H,H}$ = 11.5 Hz, 1 H, 4-H), 2.22 (dd, $^3J_{H,H}$ = 7.2, $^2J_{H,H}$ = 2.5 Hz, 1 H, 1-H), 1.88 (dd, $^3J_{H,H}$ = 14.5, $^2J_{H,H}$ = 2.5 Hz, 1 H, 1′-H), 1.81−1.73 (m, 1 H, 6-H_a), 1.68 (m, 1 H, 4′-H), 1.65−1.50 (m, 3 H, 6-H_b/7-H_{a+b}), 1.45−1.27 (m, 2 H, 7′-H_{a+b}), 1.09−0.93 (m, 2 H, 6′-H_{a+b}) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 273 K): δ = 148.6 (ph-C_{ipso}), 127.5 (ph-C_{meta}), 127.2 (ph-C_{ortho}), 125.3 (C-2), 124.8 (ph-C_{para}), 109.4 (C-3), 108.1 (cp-C), 106.2 (cp-C), 97.2 (C-5), 55.8 (C-8), 44.9 (C-1), 44.0 (C-4), 40.7 (C-6′), 29.6 (C-6), 23.5 (C-7′), 21.1 (C-7) ppm. (^1H-^{15}N)-GHMBC (599.9 MHz/60.0 MHz, CD_2Cl_2, 273 K): δ^1H/$\delta^{15}N$ = 4.41, 3.91/−279.5 ppm. $C_{26}H_{31}NZr$ (448.7): calcd. C 69.59, H 6.96, N 3.12; found C 67.94, H 6.62, N 2.50.

X-ray Crystal Structure Analysis of 8c: Single crystals were obtained from a saturated toluene solution. Formula $C_{26}H_{31}NZr$, M = 448.74, light yellow crystal 0.15 × 0.10 × 0.03 mm, a = 8.206(1), b = 25.367(1), c = 20.260(1) Å, β = 90.84(1)°, V = 4216.9(6) $Å^3$, $\rho_{calcd.}$ = 1.414 $g\cdot cm^{-3}$, μ = 5.33 cm^{-1}, empirical absorption correction (0.924 ≤ T ≤ 0.984), Z = 8, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 42299 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 $Å^{-1}$, 9977 independent (R_{int} = 0.124) and 5583 observed reflections [$I \geq 2\sigma(I)$], 505 refined parameters, R = 0.060, wR^2 = 0.086, max.

residual electron density 0.57 (−0.77) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms, two almost identical independent molecules in the asymmetric unit.

Reaction of (Butadiene)zirconocene with the Imine of Benzophenone. Formation of 8d: Imine **7d** (0.91 g, 5.0 mmol) of benzophenone was added to a solution of (butadiene)zirconocene (**1**) (1.38 g, 5.0 mmol) in toluene (150 mL). After stirring for 7 h, the solvent was evaporated in vacuo and the crude residue was treated with pentane (100 mL) to precipitate the insertion product **8d** as a light-yellow powder. The product was collected by filtration, washed with pentane (50 mL) and dried in vacuo. Yield: 1.69 g (74%). M.p. 129 °C. IR (KBr): ṽ = 3052 s, 2936 m, 2912 s, 2849 m, 1643 s, 1604 s, 1576 s, 1493, 1450 s, 1228 m, 1173 s, 1064 s, 1020 s, 800 vs, 712 s, 611 s cm^{-1}. ^{1}H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 7.47−7.06 (m, 10 H, ph-H), 5.85 (s, 5 H, cp-H), 5.43 (ddd, $^{3}J_{H,H}$ = 14.8, $^{3}J_{H,H}$ = 14.8, $^{3}J_{H,H}$ = 8.1 Hz, 1 H, 2-H), 5.26 (s, 5 H, cp-H), 5.08 (ddd, $^{3}J_{H,H}$ = 14.8, $^{3}J_{H,H}$ = 11.2, $^{3}J_{H,H}$ = 3.8 Hz, 1 H, 3-H), 3.22 (dd, $^{3}J_{H,H}$ = 3.8, $^{2}J_{H,H}$ = 12.7 Hz, 1 H, 4-H), 2.16 (dd, $^{3}J_{H,H}$ = 8.1, $^{2}J_{H,H}$ = 3.2 Hz, 1 H, 1-H), 1.97 (dd, $^{3}J_{H,H}$ = 14.8, $^{2}J_{H,H}$ = 3.2 Hz, 1 H, 1′-H), 1.71 (br, 1 H, NH), 1.45 (dd, $^{3}J_{H,H}$ = 11.2, $^{2}J_{H,H}$ = 12.7 Hz, 1 H, 4′-H) ppm. $^{13}C\{^{1}H\}$ NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 155.4, 151.6, 128.2, 127.8, 127.5, 126.1, 125.7, 125.6 (ph-C), 124.8 (C-2), 114.2 (C-3), 108.6, 106.3 (cp-C), 97.3 (C-5), 47.6 (C-4), 41.2 (C-1). (^{1}H-^{15}N)-GHMBC (599.9 MHz/60.0 MHz, CD_2Cl_2, 273 K): δ^{1}H/δ^{15}N = 1.71/−254.3 (d, $^{1}J_{HN}$ = 62 Hz) ppm. $C_{27}H_{27}NZr$ (456.74): calcd. C 71.00, H 5.96, N 3.07; found C 71.14, H 5.93, N 2.93.

Reaction of (Butadiene)zirconocene with Δ^{1}-2-Methylpyrroline. Formation of 8e: Δ^{1}-2-Methylpyrroline (**7e**, 0.84 g, 10.0 mmol) was added to a solution of (butadiene)zirconocene (**1**) (2.76 g, 10.0 mmol) in toluene (200 mL). After stirring for 16 h, the mixture was filtered and the solvent evaporated in vacuo. The residue was washed with three portions of pentane (3 × 50 mL). The filtrate was concentrated in vacuo until precipitation of the product occurred, and then stored at −18 °C overnight. The resulting product was collected by filtration and washed with cold pentane (20 mL). Subsequent concentration of the mother liquor and crystallization gave a combined yield of 2.15 g (60%) of the insertion product **8e**. M.p. 70 °C. IR (KBr): ṽ = 3088 w, 2951 m, 2863 m, 1628 w, 1441 w, 1015 s, 797 vs, 740 vs cm^{-1}. ^{1}H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 5.79 (s, 5 H, cp-H), 5.71 (s, 5 H, cp-H), 5.68 (ddd, $^{3}J_{H,H}$ = 14.5, $^{3}J_{H,H}$ = 14.5, $^{3}J_{H,H}$ = 7.7 Hz, 1 H, 2-H), 5.22 (ddd, $^{3}J_{H,H}$ = 14.5, $^{3}J_{H,H}$ = 11.5, $^{3}J_{H,H}$ = 3.5 Hz, 1 H, 3-H), 3.22 (m, 1 H, 8-H), 2.90 (m, 1 H, 8′-H), 2.27 (dd, $^{3}J_{H,H}$ = 3.5, $^{2}J_{H,H}$ = 11.5 Hz, 1 H, 4-H), 2.12 (dd, $^{3}J_{H,H}$ = 7.7, $^{2}J_{H,H}$ = 3.2 Hz, 1 H, 1-H), 1.83 (dd, $^{3}J_{H,H}$ = 14.5, $^{2}J_{H,H}$ = 3.2 Hz, 1 H, 1′-H), 1.68−1.61 (m, 2 H, 7-H/7′-H), 1.53 (m, 1 H, 6-H), 1.35 (m, 1 H, 4′-H), 1.26 (m, 1 H, 6′-H), 1.06 (s, 3 H, 9-H) ppm. $^{13}C\{^{1}H\}$ NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 125.2 (C-2), 117.4 (C-3), 109.2 (cp-C), 107.7 (cp-C), 98.9 (C-5), 56.0 (C-8), 49.1 (C-4), 42.9 (C-6), 41.7 (C-1), 28.0 (C-7), 24.1 (C-9, s, $^{1}J_{CH}$ = 124 Hz) ppm. (^{1}H-^{15}N)-GHMBC (599.9 MHz/60.0 MHz, CD_2Cl_2, 273 K): δ^{1}H/δ^{15}N = 3.22, 2.90/−249.3 ppm. $C_{19}H_{25}NZr$ (358.64): calcd. C 63.63, H 7.03, N 3.91; found C 62.42, H 6.80, N 3.56.

Reaction of (Butadiene)zirconocene with 2-Methyl-2-oxazoline. Formation of 9: 2-Methyl-2-oxazoline (**7f**, 171 mg, 2.00 mmol) was added to a solution of butadiene(zirconocene) (**1**) (551 mg, 2.00 mmol) in toluene (50 mL). After stirring for 17 h, the mixture was filtered and the solvent evaporated in vacuo. The crude residue was then treated with pentane (20 mL) to precipitate the insertion product as a light brown powder. The product was collected by filtration, washed twice with pentane (10 mL) and dried in vacuo. Yield: 613 mg (85%). IR (KBr): ṽ = 3060 m, 2826 m, 2673 w, 1654 s, 1589 s, 1448 w, 1368 w, 1106 s, 1015 s, 821 s, 795 vs, 765 m cm^{-1}. ^{1}H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 6.23 (ddd, $^{3}J_{H,H}$ = 10.5, $^{3}J_{H,H}$ = 16.9, $^{3}J_{H,H}$ = 5.4 Hz, 1 H, 2-H), 5.95 (s, 5 H, cp-H), 5.70 (s, 5 H, cp-H), 4.36 (ddd, $^{3}J_{H,H}$ = 10.5, $^{2}J_{H,H}$ = 2.2, $^{4}J_{H,H}$ = 2.1 Hz, 1 H, 1-H), 4.19 (ddd, $^{3}J_{H,H}$ = 16.9, $^{2}J_{H,H}$ = 2.2, $^{4}J_{H,H}$ = 2.1 Hz, 1 H, 1′-H), 3.90 (ddd, $^{3}J_{H,H}$ = 5.7, $^{3}J_{H,H}$ = 5.8, $^{2}J_{H,H}$ = 9.8 Hz, 1 H, 7-H), 3.71 (ddd, $^{3}J_{H,H}$ = 5.4, $^{3}J_{H,H}$ = 6.6, $^{2}J_{H,H}$ = 9.8 Hz, 1 H, 7′-H), 3.28 (m, 1 H, 6-H), 3.11 (m, 1 H, 6′-H), 2.95 (m, 1 H, 4-H), 2.80 (m, 1 H, 4′-H), 2.53 (m, 1 H, 3-H), 2.03 (s, 3 H, 8-H) ppm. $^{13}C\{^{1}H\}$ NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 187.2 (C-5, s), 147.9 (C-2, d, $^{1}J_{CH}$ = 144 Hz), 111.0 (cp-C, d, $^{1}J_{CH}$ = 171 Hz), 110.6 (cp-C, d, $^{1}J_{CH}$ = 171 Hz), 97.5 (C-1, dd, $^{1}J_{CH}$ = 151, $^{1}J_{CH}$ = 157 Hz), 69.0 (C-7, t, $^{1}J_{CH}$ = 139 Hz), 56.4 (C-6, t, $^{1}J_{CH}$ = 137 Hz), 52.6 (C-3, d, $^{1}J_{CH}$ = 125 Hz), 48.8 (C-4, t, $^{1}J_{CH}$ = 121 Hz), 20.2 (C-8, q, $^{1}J_{CH}$ = 128 Hz) ppm. (^{1}H-^{15}N)-GHMBC (599.9 MHz/60.0 MHz, CD_2Cl_2, 273 K): δ^{1}H/δ^{15}N = 3.28, 3.11/−105.6 ppm. $C_{18}H_{23}NOZr$ (360.61): calcd. C 59.95, H 6.43, N 3.88; found C 58.74, H 6.53, N 3.48.

X-ray Crystal Structure Analysis of 9: Single crystals were obtained from a saturated toluene solution. Formula $C_{18}H_{23}NOZr$, M = 360.59, light yellow crystal 0.15 × 0.15 × 0.10 mm, a = 10.486(1), b = 13.273(1), c = 11.591(1) Å, β = 94.73(1)°, V = 1607.7(2) Å^{3}, $\rho_{calcd.}$ = 1.490 g·cm^{-3}, μ = 6.83 cm^{-1}, empirical absorption correction (0.905 ≤ T ≤ 0.935), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 13970 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 3845 independent (R_{int} = 0.048) and 3039 observed reflections [$I \geq 2\sigma(I)$], 191 refined parameters, R = 0.033, wR^2 = 0.072, max. residual electron density 0.63 (−0.61) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Data sets were collected with a Nonius Kappa CCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., **1998**), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33−37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**), graphics SCHAKAL (E. Keller, Universität Freiburg, **1997**). CCDC-183380 to -183383 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Reaction of 8e with Tris(pentafluorophenyl)borane. Formation of 10a: Compound **8e** (0.36 g, 1.0 mmol) was treated with tris(pentafluorophenyl)borane (0.51 g, 1.0 mmol) in dichloromethane (20 mL) at 0 °C for 1 h. Evaporation of the solvent yielded a semisolid material, which was suspended in pentane (30 mL) and stirred for 2 d at ambient temperature to precipitate the reaction product. Filtration gave 0.77 g (88%) of complex **10a**. M.p. 244 °C (decomp.). IR (KBr): ṽ = 3124 w, 2973 m, 2368 m, 1643 m, 1511 s, 1461 vs, 1272 m, 1103 s, 968 s, 821 s cm^{-1}. ^{1}H NMR (599.9 MHz, C_6D_5Br, 298 K): δ = 7.42 (s, 1 H, 8-H), 5.45 (s, 5 H, cp-H), 5.44 (ddd, $^{3}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 14.5, $^{3}J_{H,H}$ = 7.8 Hz, 1 H, 2-H), 5.26 (s, 5 H, cp-H), 4.34 (ddd, $^{3}J_{H,H}$ = 15.2, $^{3}J_{H,H}$ = 11.9, $^{3}J_{H,H}$ = 2.9 Hz, 1 H, 3-H), 2.46-2.32 (m, 2 H, 7-H, 7′-H), 2.11 (dd, $^{3}J_{H,H}$ = 2.9, $^{2}J_{H,H}$ = 13.0 Hz, 1 H, 4-H), 2.05 (dd, $^{3}J_{H,H}$ = 7.8, $^{2}J_{H,H}$ = 3.7 Hz, 1 H, 1-H), 1.70 (dd, $^{3}J_{H,H}$ = 14.5, $^{2}J_{H,H}$ = 3.7 Hz, 1 H, 1′-

H), 1.58 (m, 1 H, 6-H), 1.37−1.30 (m, 2 H, 4′-H, 6′-H), 0.84 (s, 3 H, 9-H) ppm. The $H-B(C_6F_5)_3^-$ resonance was not observed. $^{13}C\{^1H\}$ NMR (150.8 MHz, C_6D_5Br, 298 K): δ = 183.5 (C-8, d, $^1J_{CH}$ = 181 Hz), 127.6 (C-2), 107.9 (cp-C), 107.3 (cp-C), 102.0 (C-3), 98.8 (C-5), 45.2 (C-1), 43.1 (C-4), 38.1 (C-7), 36.9 (C-6), 23.4 (C-9) ppm. ^{11}B NMR (64.2 MHz, C_6D_5Br, 298 K): δ = −24.9 (d, $^1J_{BH}$ = 85 Hz) ppm. (^1H-^{15}N)-GHMBC (599.9 MHz/60.0 MHz, CD_2Cl_2, 273 K): δ^1H/δ^{15}N = 7.42/−88.8 ppm. HRMS (EI): calcd. for $C_{19}H_{24}NZr^+$ 356.0956, found 356.0965.

Reaction of Complex 8e with Trityl Tetraphenylborate. Formation of 10b: A sample of **8e** (0.36 g, 1.00 mmol) was treated with trityl tetraphenylborate (0.57 g, 1.00 mmol) in dichloromethane (20 mL) at −78 °C. The mixture was then warmed to ambient temperature and stirred overnight. Evaporation of the solvent yielded a white, solid material, which was suspended in pentane (30 mL) and stirred for 17 h at ambient temperature to precipitate the product and to dissolve triphenylmethane. Filtration and washing with pentane yielded 0.58 g (85%) of complex **10b**. M.p. 215 °C (decomp.). ^1H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 7.45−7.40 (m, 8 H, ph-H_{borate}), 7.23 (m, 1 H, 8-H), 7.08 (pt, 8 H, ph-H_{borate}), 6.93 (pt, 4 H, ph-H_{borate}), 5.93 (m, 1 H, 2-H), 5.88 (s, 5 H, cp-H), 5.62 (s, 5 H, cp-H), 4.89 (ddd, $^3J_{H,H}$ = 2.8, $^3J_{H,H}$ = 11.5, $^3J_{H,H}$ = 14.9 Hz, 1 H, 3-H), 2.59−2.53 (m, 3 H, 4-H, 7-H, 7′-H), 2.47 (dd, $^3J_{H,H}$ = 7.7, $^2J_{H,H}$ = 3.6 Hz, 1 H, 1-H), 2.14 (dd, $^3J_{H,H}$ = 14.1, $^2J_{H,H}$ = 3.6 Hz, 1 H, 1′-H), 1.99 (m, 1 H, 6-H), 1.78 (dd, $^3J_{H,H}$ = 11.5, $^2J_{H,H}$ = 13.0 Hz, 1 H, 4′-H), 1.65 (m, 1 H, 6′-H), 1.25 (s, 3 H, 9-H) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 184.6 (C-8), 164.5 (q, ph-$C_{ipso/borate}$, $^1J_{BC}$ = 49.5 Hz), 136.2 (ph-$C_{ortho/borate}$), 128.2 (C-2), 126.3 (q, ph-$C_{meta/borate}$, $^3J_{BC}$ = 2.8 Hz), 122.4 (ph-$C_{para/borate}$), 108.6 (cp-C), 108.0 (cp-C), 102.6 (C-3), 99.6 (C-5), 46.1 (C-1), 44.0 (C-4), 38.9 (C-7), 37.7 (C-6), 24.4 (C-9) ppm. HRMS (EI): calcd. for $C_{19}H_{24}NZr^+$ 356.0956, found 356.0987.

Reaction of 8a with Tri(*n*-butyl)ammonium Tetraphenylborate. Formation of 11a: A sample of **8a** (0.39 g, 1.00 mmol) was treated with tri(*n*-butyl)ammonium tetraphenylborate (0.51 g, 1.00 mmol) in diethyl ether (20 mL) at −78 °C. The mixture was then warmed to ambient temperature and stirred overnight. Evaporation of the solvent yielded a white solid, which was suspended in pentane (30 mL) and stirred for 17 h at ambient temperature. Filtration gave 0.79 g (88%) of complex **11a**. M.p. 204 °C. ^1H NMR (599.9 MHz, C_6D_6/[D_8]THF ≈ 4:1, 298 K): δ = 7.39−7.33 (m, 3 H, ph-H), 7.31−7.27 (m, 8 H, ph-H_{borate}), 7.27−7.24 (m, 2 H, ph-H), 6.86 (pt, 8 H, ph-H_{borate}), 6.72 (pt, 4 H, ph-H_{borate}), 6.04 (s, 5 H, cp-H), 5.93 (s, 5 H, cp-H), 5.90 (dt, $^3J_{H,H}$ = 14.5, $^3J_{H,H}$ = 8.2 Hz, 1 H, 2-H), 4.92 (ddd, $^3J_{H,H}$ = 14.5, $^3J_{H,H}$ = 11.2, $^3J_{H,H}$ = 3.5 Hz, 1 H, 3-H), 4.11 (m, 1 H, 5-H), 2.89 (m, 1 H, NH), 2.64 (m, 1 H, 4-H), 2.47 (dd, $^3J_{H,H}$ = 8.2, $^2J_{H,H}$ = 3.2 Hz, 1 H, 1-H), 2.43 (br, 6 H, α-H_{amine}) 2.27−2.24 (m, 1 H, 1′-H), 2.20 (m, 1 H, 4′-H), 2.15 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, 6-H), 1.40 (m, $^3J_{H,H}$ = 7.4 Hz, 6 H, β-H_{amine}), 1.31 (m, $^3J_{H,H}$ = 7.4 Hz, 6 H, γ-H_{amine}), 0.90 (t, $^3J_{H,H}$ = 7.4 Hz, 9 H, δ-H_{amine}) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, [D_6]benzene/[D_8]THF ≈ 4:1, 298 K): δ = 165.2 (q, $C_{ipso/borate}$, $^1J_{BC}$ = 50.2 Hz), 139.0 (ph-C), 137.2 ($C_{ortho/borate}$), 129.8, 128.2, 127.9 (ph-C), 128.9 (C-2), 125.8 (q, $C_{meta/borate}$, $^3J_{BC}$ = 2.5 Hz), 121.9 ($C_{para/borate}$), 110.3 (cp-C), 109.8 (cp-C), 103.6 (C-3), 82.5 (C-5), 54.6 (α-C_{amine}), 47.6 (C-1), 41.6 (C-4), 39.6 (C-6), 29.6 (β-C_{amine}, only visible in the 50 MHz spectrum), 21.2 (γ-C_{amine}), 14.3 (δ-C_{amine}) ppm. HRMS (EI): calcd. for $C_{22}H_{26}NZr^+$ 394.1112, found 394.1147.

Reaction of Complex 8a with *N*,*N*-Dimethylammonium Tetrakis(pentafluorophenyl)borate. Formation of 11b: A mixture of **8a** (395 mg, 1.00 mmol) and *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate (800 mg, 1.00 mmol) was dissolved in diethyl ether (50 mL) at −78 °C. The mixture was then warmed to ambient temperature and stirred overnight. Evaporation of the solvent yielded a white solid, which was suspended in pentane (30 mL) and stirred for 17 h at ambient temperature to precipitate the product. Filtration gave 0.88 g (74%) of complex **11b**. M.p. 267 °C (decomp.). ^1H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 7.42 (m, 3 H, ph-H), 7.26 (m, 2 H, ph-H_{amine}), 7.17 (m, 2 H, ph-H), 6.78 (m, 3 H, ph-H_{amine}), 6.10 (s, 5 H, cp-H), 5.96 (s, 5 H, cp-H), 5.92 (m, 1 H, 2-H), 4.95 (ddd, $^3J_{H,H}$ = 15.3, $^3J_{H,H}$ = 11.3, $^3J_{H,H}$ = 3.6 Hz, 1 H, 3-H), 4.09 (dt, $^3J_{H,H}$ = 3.6, $^3J_{H,H}$ = 12.1 Hz, 1 H, 5-H), 2.95 [s, 6 H, $N(CH_3)_{amine}$], 2.85 (dt, $^3J_{H,H}$ = 3.6, $^2J_{H,H}$ = 14.5 Hz, 1 H, 4-H), 2.59 (dd, $^3J_{H,H}$ = 8.1, $^2J_{H,H}$ = 3.6 Hz, 1 H, 1-H), 2.55 (m, 1 H, NH), 2.35 (dd, $^3J_{H,H}$ = 14.3, $^2J_{H,H}$ = 3.6 Hz, 1 H, 1′-H), 2.27 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, N-CH_3), 2.18 (ddd, $^3J_{H,H}$ = 15.3, $^3J_{H,H}$ = 12.1, $^2J_{H,H}$ = 14.5 Hz, 1 H, 4′-H) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 150.5 ($C_{ipso/amine}$), 148.6 (dm, $C_{ortho/borate}$, $^1J_{C,F}$ = 241 Hz), 138.6 (dm, $C_{para/borate}$, $^1J_{C,F}$ = 247 Hz), 137.3 (ph-C_{ipso}), 136.7 (dm, $C_{meta/borate}$, $^1J_{C,F}$ = 245 Hz), 130.1 (ph-C), 130.0 (ph-C), 129.5 ($C_{meta/amine}$), 128.6 (C-2), 126.4 (ph-C), 124.7 ($C_{ipso/borate}$), 118.0 ($C_{para/amine}$), 113.4 ($C_{ortho/amine}$), 109.5 (cp-C), 108.9 (cp-C), 102.4 (C-3), 83.1 (C-5), 47.8 (C-1), 41.7 (C-4), 41.2 [$N(CH_3)_{amine}$], 39.6 (N-CH_3) ppm. HRMS (EI): calcd. for $C_{22}H_{26}NZr^+$ 394.1112, found 394.1099.

Reaction of Complex 8d with Tri(*n*-butyl)ammonium Tetraphenylborate. Formation of 12a: A sample of complex **8d** (457 mg, 1.00 mmol) and tri(*n*-butyl)ammonium tetraphenylborate (0.51 g, 1.00 mmol) was suspended in diethyl ether (20 mL) at −78 °C. The mixture was then warmed to ambient temperature and stirred overnight. Evaporation of the solvent yielded a white solid, which was stirred in pentane (30 mL) for 17 h at ambient temperature. Filtration gave 0.71 g (74%) of complex **12a**. M.p. 247 °C (decomp.). Due to rapid decomposition of compound **12a** in solution only ^1H and ^1H/^1H-correlation NMR spectra were recorded. ^1H NMR (599.9 MHz, C_6D_6/[D_8]THF = 2:1, 298 K): δ = 7.72 (m, 8 H, Ph-H_{borate}), 7.25 (m, 1 H, Ph-H), 7.23 (m, 1 H, Ph-H), 7.19 (pt, 8 H, Ph-H_{borate}), 7.17 (m, 4 H, Ph-H), 7.09 (pt, 2 H, Ph-H), 7.03 (pt, 4 H, Ph-H_{borate}), 6.90 (pd, 2 H, Ph-H), 5.46 (ddd, $^3J_{H,H}$ = 14.2, $^3J_{H,H}$ = 15.1, $^3J_{H,H}$ = 8.0 Hz, 1 H, H-2), 5.39 (s, 5 H, Cp-H), 5.09 (s, 5 H, Cp-H), 4.63 (m, 1 H, H-3), 3.69 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, NH), 3.27 (d, $^2J_{H,H}$ = 14.5 Hz, 1 H, H-4), 3.01 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, NH′), 2.17 (dd, $^3J_{H,H}$ = 8.0, $^2J_{H,H}$ = 3.3 Hz, 1 H, H-1), 2.10 (br, 6 H, α-H_{amine}) 1.93 (dd, $^3J_{H,H}$ = 14.2, $^2J_{H,H}$ = 3.3 Hz, 1 H, H-1′), 1.86 (dd, $^3J_{H,H}$ = 11.9, $^2J_{H,H}$ = 14.5, 1 H, H-4′), 1.02 (br, 6 H, γ-H_{amine}), 0.98 (br, 6 H, β-H_{amine}), 0.90 (br, 9 H, δ-H_{amine}) ppm.

Reaction of Complex 8d with *N*,*N*-Dimethylanilinium Tetrakis(pentafluorophenyl)borate. Formation of 12b: A mixture of compound **8d** (457 mg, 1.00 mmol) and *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate (800 mg, 1.00 mmol) was suspended in diethyl ether (50 mL) at −78 °C. The mixture was then warmed to ambient temperature and stirred overnight. Evaporation of the solvent yielded a white solid, which was suspended in pentane (30 mL) and stirred for 17 h at ambient temperature. Filtration gave 1.02 g (81%) of complex **12d**. M.p. 288 °C (decomp.). ^1H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 7.60 (m, 2 H, Ph-H_{meta}), 7.52 (m, 1 H, Ph-H_{para}), 7.43 (m, 2 H, Ph-H_{ortho}), 7.38 (m, 2 H, Ph-H_{meta}), 7.32 (m, 1 H, Ph-H_{para}), 7.26 (m, 2 H, Ph-H_{amine}), 7.03 (m, 2 H, Ph-H_{ortho}), 6.81 (m, 3 H, Ph-H_{amine}), 5.98 (m, 1 H, H-2), 5.96, 5.54 (s, each 5 H, Cp-H), 5.13 (ddd, $^3J_{H,H}$ = 14.9, $^3J_{H,H}$ = 11.9, $^3J_{H,H}$ = 2.8 Hz, 1 H, H-3), 3.76 (dd, $^3J_{H,H}$ = 14.9, $^2J_{H,H}$ = 15.6 Hz, 1 H, H-4), 3.57, 3.30 (d, $^2J_{H,H}$ = 12.5 Hz, each 1 H, NH, and NH′), 2.95 [s, 6 H, $N(CH_3)_{amine}$], 2.60 (dd, $^3J_{H,H}$ = 8.2, $^2J_{H,H}$ =

3.7 Hz, 1 H, H-1), 2.38 (dd, $^3J_{H,H}$ = 14.2, $^2J_{H,H}$ = 3.7 Hz, 1 H, H-1′), 2.31 (dd, $^3J_{H,H}$ = 11.9, $^2J_{H,H}$ = 15.6 Hz, 1 H, H-4′) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 149.9 (C, Ph-$C_{ipso/amine}$), 148.6 (CF, dm, Ph-$C_{ortho/borate}$, $^1J_{C,F}$ = 242 Hz), 146.4, 140.1 (C, Ph-C_{ipso}), 138.7 (CF, dm, Ph-$C_{para/borate}$, $^1J_{C,F}$ = 242 Hz), 136.7 (CF, dm, Ph-$C_{meta/borate}$, $^1J_{C,F}$ = 248 Hz), 130.5 (CH, Ph-C), 130.3 (CH, C-2), 129.9, 129.7 (CH, Ph-C), 129.6 (CH, Ph-$C_{meta/amine}$), 128.7, 126.8, 124.2 (CH, Ph-C), 124.0 (C, br, Ph-$C_{ipso/borate}$), 118.7 (CH, Ph-$C_{para/amine}$), 113.8 (CH, Ph-$C_{ortho/amine}$), 108.7, 108.4 (CH, Cp-C), 102.1 (CH, C-3), 85.9 (C, C-5), 46.6 (CH_2, C-1), 44.6 (CH_2, C-4), 41.6 [CH_3, $N(CH_3)_{amine}$] ppm. HRMS (EI): calcd. for $C_{27}H_{28}NZr^+$ 456.1269, found 456.1231.

Polymerization Experiments: The polymerization experiments were carried out in a thermostatted 1-L Büchi glass autoclave. The reaction mixtures contained toluene (200 mL) and triisobutylaluminum (0.5 mL) as the scavenger. The stirred (700 rpm) solution was saturated with ethylene at 2 bar for 45 min before the polymerization reactions were started by injection of the group-4 metal catalyst precursors, dissolved in 3−7 mL of a toluene/bromobenzene mixture. The polymerization reactions were stopped after 1 h by the addition of ca. 20 mL of a 1:1 mixture of 1 N aqueous HCl in methanol after the pressure had been released and the excess ethylene vented. The mixture was stirred for an additional 30 min. The polymer formed was collected by filtration, washed with aqueous HCl and water and dried in vacuo at an elevated temperature. Further information is provided in Table 3.

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