Addition and Coupling Reactions of Zirconocene Cation Complexes that Contain a Pendant η^2-Formaldiminium Side Chain

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The pendant (η^2-formaldiminium)zirconocene cation complex **3** is generated by treatment of the (Cp–CMe$_2$NMe$_2$)CpZrMe$_2$ precursor **1** with B(C$_6$F$_5$)$_3$. The formation of **3** proceeds with C–H activation and methane evolution. Addition of the phosphanes PPh$_2$R (R = Ph, CH$_3$ and cyclopropyl) leads to the stable adducts **6a–c**, in which the Zr–CH$_2$–N three-membered ring structure of the (η^2-formaldiminium)Zr subunit is retained. The reactive complex **3** readily inserts benzophenone into the Zr–CH$_2$(N) linkage to yield the carbon–carbon coupling product **7**. α-Olefins also insert into the reactive Zr–C bond of **3**. Exposure of **3** to ethene at a low temperature (–50 °C) results in the formation of the labile metallacyclic mono-alkene-insertion product **8**, that is characterized spectroscopically. Styrene and 4-*tert*-butylstyrene undergo a clean [2,1]insertion into the Zr–C bond of **3** to selectively yield the isomerically pure mono-insertion products **9a** and **9b**, respectively, that exhibit their aryl substituents in the α-position adjacent to the zirconium center. In each case a single stereoisomer is formed that contains a σ-π-structured η^3-benzylic coordination of the chain end, exhibiting the *meso*-allyl position oriented *cis* to the substituted Cp ring at the resulting metallacyclic framework. Complex **9b** was characterized by X-ray crystal-structure analysis.

Introduction

Alkylzirconocene cations[1] are known to readily undergo alkene insertion;[2] this reaction is the basis for their action as active Ziegler polymerization catalysts.[3] However, they can also undergo C−H activation reactions if suitable reagents are brought in the vicinity of the $[Zr]^+-CH_3$ moiety.[4] Such behavior is observed when the amino-functionalized metallocene (Cp−CMe$_2$NMe$_2$)CpZr(CH$_3$)$_2$ (**1**)[5] is treated with the alkyl abstractor B(C$_6$F$_5$)$_3$ (Scheme 1).[6] The alkylzirconocene cation **2** which is generated in situ, is not stable under the reaction conditions but rapidly reacts further by proton abstraction from the pendant N−CH$_3$ group to form **3** with methane evolution. The product **3** probably contains a strong nitrogen−zirconium interaction and thus might be viewed as a η^2-formaldiminium complex. The three-membered ring structure is confirmed for the isonitrile adduct **4** by X-ray diffraction.[4] The Zr(η^2-CH$_2$=NR$_2^+$) moiety can also be recognized spectroscopically by a characteristically increased $^1J_{CH}$ coupling constant of the CH$_2$ group inside the three-membered metallacycle[7] [**4**: $^1J_{CH}$ = 153 Hz (N−CH$_2$−Zr), 138 Hz (N−CH$_3$); **3**: $^1J_{CH}$ = 152 Hz (N−CH$_2$−Zr), 139 Hz (N−CH$_3$)]. The ^{15}N-NMR chemical shift also seems to correspond to the coordinative situation at the pendant nitrogen functionality:[4,8] A ^{15}N-NMR resonance (in [D$_2$]dichloromethane) of $\delta = -338$ is observed for the starting material **1**, whereas markedly decreased ^{15}N-NMR shift values are observed for the (η^2-formaldiminium)zirconocene cations **3** [$\delta(^{15}N) = -358$] and **4** [$\delta(^{15}N) = -375$], respectively. We have studied the behavior of the reactive complex **3**[9] towards a variety of reagents, including phosphanes, organic carbonyl compounds, and alkenes. Representative examples of the reaction of the (η^2-formaldiminium)zirconium cation system with such reagents are described in this article.

Results and Discussion

The pendant (η^2-formaldiminium)Zr cation complex **3** was generated in situ by treatment of its immediate precursor **1** with B(C$_6$F$_5$)$_3$ in [D$_2$]dichloromethane at −50 °C.[4] The phosphanes PPh$_3$ (**5a**), P(Me)Ph$_2$ (**5b**), and P(cyclopropyl)Ph$_2$ (**5c**) were added to samples of this solution. The corresponding phosphane addition products[10] (**6a−c**, respectively) were formed instantaneously (Scheme 2). Upon addition of pentane and after warming to room temperature, they separated from the reaction mixture as dark-colored oils and were each isolated in a ca. 50% yield.

The cationic (triphenylphosphane)zirconium complex **6a** shows a ^{31}P-NMR resonance signal at δ = 31.2. The phosphane coordination results in a $^3J_{PH}$ coupling (1.5 Hz) of the Cp hydrogen atoms (Table 1).[11] The chiral metallocene complex exhibits two pairs of diastereotopic C$_5$H$_4$ NMR resonances at δ = 6.19, 5.93, 5.68, 4.58 (^{1}H) and δ = 113.0, 108.8, 107.2, 96.9 (^{13}C), as well as the signals of a pair of diastereotopic methyl groups [δ = 1.61, 1.01 (^{1}H); 25.3, 17.6 (^{13}C)] bonded to carbon atom C-4 (see Scheme 2), and the methylene hydrogen atoms at C-7 (see Table 1). All three complexes **6a−c** show ^{15}N-NMR resonance signals at δ ≈ −376. This is very characteristic for a bonding situation

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[+] NMR spectroscopy.

[++] X-ray crystal-structure analysis.

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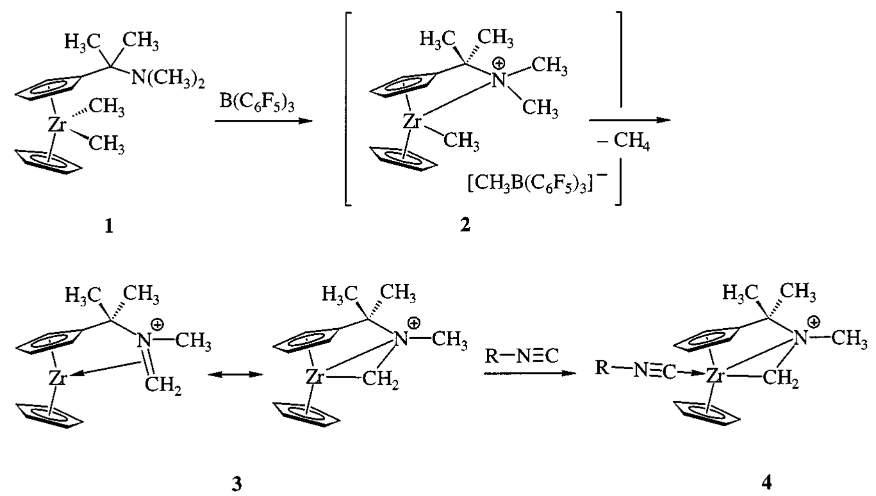
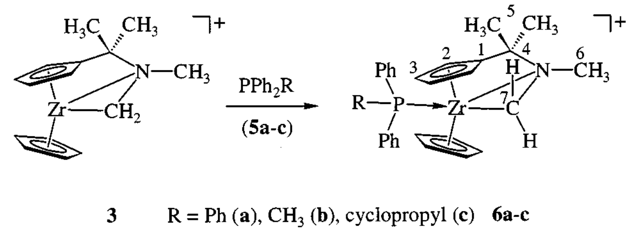


Scheme 1. Formation of **3** by a C−H abstraction route (complexes **3** and **4** with $[CH_3B(C_6F_5)_3]^-$ anion, R = $-C(CH_3)_3$)



Scheme 2. Formation of the phosphane adducts **6** (complexes **4** and **6** with $[CH_3B(C_6F_5)_3]^-$ anion)

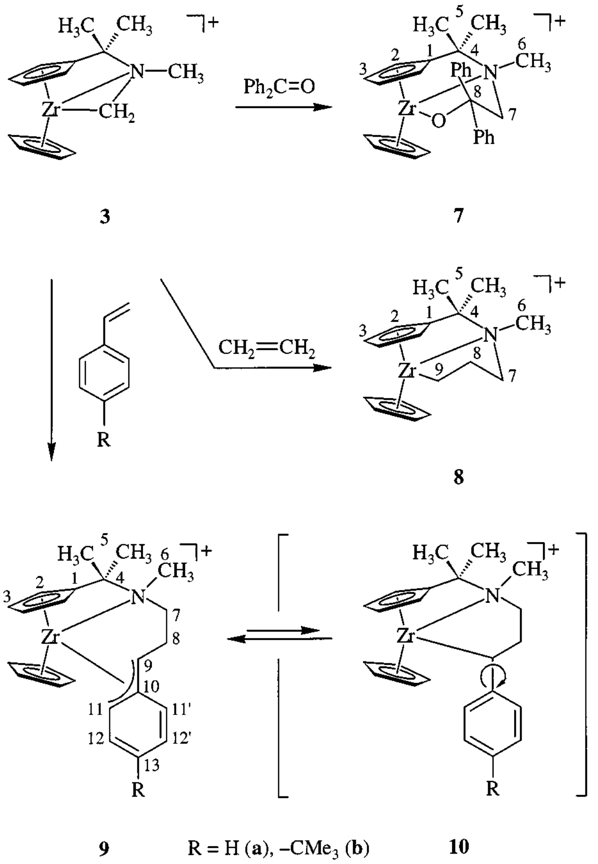
Table 1. Selected NMR data of the complexes **6** (in CD_2Cl_2 at ambient temperature)

Complex	**6a**	**6b**	**6c**
Cp (^1H)	5.88	5.94	6.02
($^3J_{PH}$)	(1.5 Hz)	(1.5 Hz)	(1.5 Hz)
(N)CH_2 (^1H)	1.89, 1.64	1.89, 1.43	1.79, 1.24
($^2J_{HH}$)	(9.4 Hz)	(9.5 Hz)	(m)
($^3J_{PH}$)	(4.8, 1.9 Hz)	(4.7, 2.0 Hz)	(m)
(N)CH_2 (^{13}C)	46.8	45.9	46.7
($^2J_{PC}$)	(15.5 Hz)	(15.7 Hz)	(15.8 Hz)
($^1J_{CH}$)	[a]	(155, 146 Hz)	[a]
(N)CH_3 (^{13}C)	44.5	44.7	44.6
($^1J_{CH}$)	[a]	(138 Hz)	[a]
(N)CH_3 (^{15}N)	−376	−377	−376

[a] Not determined.

where the forminium nitrogen atom retains a strong bonding contact with the central metal atom. The presence of a (Zr−N−CH_2) three-membered ring is further indicated by the rather large $^1J_{CH}$ coupling constants (155 and 146 Hz). They are much larger than the $^1J_{CH}$ value of the adjacent $N(CH_3)$ group (138 Hz). We thus conclude that phosphane addition to the zirconium atom in **3** does not lead to the opening of the (Zr−N−CH_2) three-membered ring structure of the cationic organometallic C−H activation product. The (η^2-formaldiminium)zirconocene unit is still intact in the complexes **6a**−**c**.

We then treated **3** with benzophenone.[12] As expected, a rapid reaction takes place. The spectra of the isolated product (57% yield) indicated that carbon−carbon coupling between the *N*-methylene group and the carbonyl carbon atom had taken place − i.e. the ketone inserts into the Zr−CH_2(N) σ bond of the starting material **3**, to yield the new cation complex **7**. The former carbonyl carbon atom (C-8 in Scheme 3) now shows a ^{13}C-NMR shift of δ = 81.0,[13] and the C-7 resonance signal is at δ = 66.8. Both values indicate that carbon−carbon coupling has taken place and that the three-membered ring was opened. The most remarkable feature of the new complex **7** is that it is chiral. This is evident from the NMR-spectroscopic obser-



Scheme 3. Insertion reactions of **3** (all complexes with $[CH_3B(C_6F_5)_3]^-$ anion)

vation of diastereotopic methyl groups at C-4 [δ = 1.65, 1.50 (^{1}H); 25.5, 22.5 (^{13}C)], diastereotopic hydrogen atoms at C-7 (δ = 3.90, 3.57), diastereotopic phenyl groups at C-8 and diastereotopic pairs of the C-2-H and C-3-H C_5H_4-methine moieties [δ = 6.45, 6.37, 6.23, 6.17 (^{1} H); 125.9, 107.5, 106.7, 104.9 (^{13}C)]. The chirality of **7** may result from the internal coordination of the nitrogen atom to the zirconium center, or from the internal ion pairing by $CH_3B(C_6F_5)_3^-$ anion coordination to the metal center. The available spectroscopic data [^{15}N-NMR resonance signals at δ = -339 in CD_2Cl_2, -344 in C_6D_6/[D_8]THF (1:1); $CH_3B(C_6F_5)_3^-$ resonance signals at δ = 0.40 (^{1}H NMR) and 9.4 (^{13}C NMR)] are inconclusive. Without an X-ray crystal-structure analysis it was not possible to decide, with conclusive certainty, between these two possibilities. Tentatively, we assigned complex **7** a structure with a weak intramolecular metal−nitrogen interaction.

Complex **3** readily inserts a variety of reactive α-olefins, such as ethene, propene, 1-butene or 1-decene at low temperature (−50 °C). In each case a single mono-insertion product was formed regioselectively[14,15] (regular [1,2]addition was observed[3] to give the β-alkyl-substituted products in the latter cases). However, all these products rapidly decomposed upon warming to 0 °C with the formation of as yet unidentified product mixtures. Due to this thermal instability these products could not be isolated, and we have limited ourselves to briefly describing the spectroscopic characterization of the ethene-mono-insertion product **8** (for further data see the Supporting Information).

The ethene-insertion product **8** was generated by treatment of **4** with gaseous C_2H_4 at −50 °C in [D_2]dichloromethane and directly characterized by NMR spectroscopy at a low temperature. The NMR spectra show that a C_3H_6 chain connects Zr and N in **8** [^{13}C: δ = 53.4 ($^1J_{CH}$ = 144 Hz, C-7), 14.3 (124 Hz, C-8), and 46.8 (132 Hz, C-9)]. The insertion product **8** is chiral {NMR signals of diastereotopic pairs of C_5H_4 methine groups at δ = 118.4, 117.1, 110.2, 106.9 (^{13}C) and 7.40, 6.44, 6.37, 6.33 (^{1} H); of methyl substituents at C-4 [δ = 1.48, 1.28 (^{1}H); 24.9, 20.9 (^{13}C)] and of hydrogen atoms at the connecting $-CH_2-CH_2-CH_2-$ chain} (see the Experimental Section for details). We assume that the chirality of the molecular framework of complex **8** is due to a (weak) intramolecular nitrogen−zirconium interaction. The corresponding ^{15}N-NMR resonance of **8** is found at δ = -349 (in [D_2]dichloromethane at 223 K).

We then treated the cation **3** with styrene and 4-*tert*-butylstyrene, respectively. The corresponding mono-insertion products **9a**, **9b** are rather stable and can be isolated as solid materials in 70−80% yield. Single crystals of the *p*-*tert*-butylstyrene insertion product **9b** could be obtained. Complex **9b** was characterized by an X-ray crystal-structure analysis (see Figure 1).

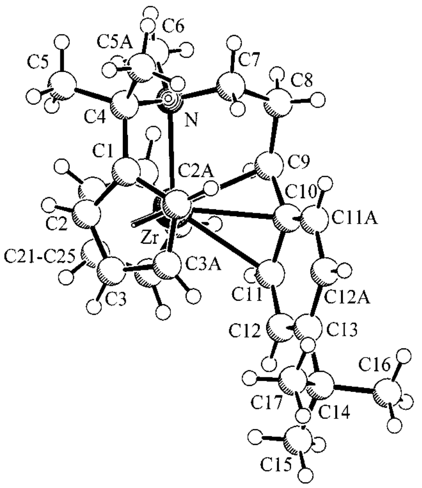


Figure 1. Molecular structure of complex **9b**; selected bond lengths [Å] and angles [°]: Zr−C1 2.461(4), Zr−C2 2.467(4), Zr−C2A 2.501(4), Zr−C3 2.541(4), Zr−C3A 2.560(4), Zr−N 2.498(3), Zr−C9 2.389(4), Zr−C10 2.604(4), Zr−C11 2.654(4), C1−C4 1.502(6), C4−N 1.554(6), N−C7 1.497(5), C7−C8 1.514(6), C8−C9 1.502(6), C9−C10 1.430(6), C10−C11 1.410(5), C10−C11A 1.424(5), C11−C12 1.405(6), C11A−C12A 1.351(6), C12−C13 1.374(6), C12A−C13 1.423(6); C1−C4−N 100.2(3), C4−N−C7 111.1(3), C4−N−Zr 98.4(2), Zr−N−C7 104.8(2), N−C7−C8 111.6(3), C7−C8−C9 111.3(4), C8−C9−Zr 115.8(3), C8−C9−C10 123.5(4), C9−C10−C11 117.6(4), C9−C10−C11A 126.3(4), C9−C10−Zr 65.3(2), C11−C10−Zr 76.4(2), C11A−C10−Zr 122.8(3), C10−C11−C12 121.8(4), C12−C11−Zr 125.4(3)

The solid-state structure of **9b** shows that a new carbon−carbon bond has been formed between the (N)−CH_2 methylene and the styrene $=CH_2$ group [C7−C8: 1.514(6) Å]. The adjacent alkyl-substituted benzyl subunit is η^3-coordinated to the zirconium center through the benzylic methine carbon atom and two of the arene carbon atoms, the *ipso*-C and one of the *ortho*-arene carbon atoms.[16] The corresponding C−C bond lengths inside the π-allyl moiety are 1.430(6) Å (C9−C10) and 1.410(5) Å (C10−C11). The (π-allyl)zirconocene unit is *syn*-substituted at C9 [angle C8−C9−C10 123.5(4)°]. As expected, the η^3-benzylic moiety is rather unsymmetrically bonded to the zirconium center[17] with Zr−C9 being much shorter [2.389(4) Å] than Zr−C10 [2.604(4) Å] and Zr−C11 [2.654(4) Å]. The partial π coordination of the arene ring in **9b** results in a slight bond alternation in the remaining framework [C11−C12 1.405(6) Å, C12−C13 1.374(6) Å, C13−C12A 1.423(6) Å, C12A−C11A 1.351(6) Å, C11A−C10 1.424(5) Å].

The Zr−N distance in **9b** is found at 2.498(3) Å. This is clearly within bonding distance,[18] but is substantially longer than that found in e.g. complex **4** [2.312(8) Å].[4] The nitrogen atom in **9b** is a distorted tetrahedron [bond angles C7−N−C4 111.1(3)°, C7−N−C6 107.4(3)°, C6−N−C4 113.9(3)°, Zr−N−C7 104.8(2)°, Zr−N−C6 120.7(3)°, and Zr−N−C4 98.4(2)°, sum of bond angles 656.3° vs. 656.8° of an ideal tetrahedron]. The formation of a small-ring Cp−CMe_2−N−Zr substructure introduces some strain into complex **9b**, which results in a slight distortion of the (η^5-C_5H_4R)Zr coordination [Zr−C(Cp) bond lengths ranging from 2.461(4)/2.467(4) Å through 2.501(4) Å to 2.541(4)/2.560(4) Å].

In principle, this general structural arrangement could have led to the formation of two stereoisomeric [2,1]insertion products[19] of the styrene reagents into the Zr−C(H$_2$) bond of **3**; however, in the crystal only the stereoisomer with the "tip" of the σ,π-benzyl unit pointing toward the substituted (η^5-C_5H_4)−CMe$_2$−(N) ring (*cis* isomer) is observed.

Only a single isomer of **9b** is seen by NMR spectroscopy in solution. Complex **9b** is also chiral in solution. The NMR spectrum shows two pairs of diastereotopic C_5H_4-methine groups (^{13}C-NMR resonances at δ = 124.8, 109.0, 106.9, 101.9; ^{1}H: δ = 5.96, 5.81, 4.66, 4.07), two diastereotopic methyl groups at C-4 [δ = 25.1, 22.5 (^{13}C); δ = 1.45, 1.33 (^{1}H)], and pairs of diastereotopic CH$_2$ hydrogen atoms at C-7 and C-8 (see the Experimental Section for details). The ^{15}N-NMR resonance of complex **9b** occurs at δ = −352. At low temperature (233 K), the four CH carbon resonances of the arene ring in **9b** are clearly distinguished [^{13}C: δ = 88.7 (C11), 124.0 (C11′), 133.6 (C12), 133.5 (C12′); ^{1}H: δ = 5.46 (11-H), 7.06 (11′-H), 7.30 (12-H), 7.73 (12′-H)]. The $^1J_{CH}$ coupling constant of the C-11-H unit is markedly smaller (150 Hz) than the related arene C-11′/C-12/C-12′-H $^1J_{CH}$ coupling constants, which are all in the typical arene 157−159 Hz range. The ^{13}C-NMR chemical shifts of the remaining carbon atoms of the (σ,π-allyl)Zr subunit of the substituted (η^3-benzyl)Zr moiety of **9b** are seen at δ = 135.6 (C-10) and 69.6 ($^1J_{CH}$ = 141 Hz, C-9). The 9-H ^{1}H-NMR signal is located at δ = 3.82.

Complex **9b** shows temperature-dependent NMR spectra of the arene methine signals originating from the substituted styrene reagent. Raising the temperature leads to the broadening of the 11-H/11′-H and 12-H/12′-H pairs of resonances and coalescence. We assume that this dynamic behavior is due to equilibration of the stable σ,π-coordinated η^3-arene complex **9b** with a reactive η^1-benzyl-type intermediate[16,20] (**10b**, see Scheme 3), which allows rapid rotation around the C(sp^2)−C(sp^3) σ bond on the NMR time scale, leading to the observed averaging of the pairs of CH resonances. From the 12-H/12′-H ^{1}H-NMR coalescence a Gibbs activation energy of $\Delta G^{\neq}$(278 K) = 10.7 ± 0.4 kcal mol^{-1} is obtained for this dynamic intramolecular equilibration process of complex **9b**.[21]

Styrene insertion into the Zr−C-7 bond of **3** proceeds analogously. Only the [2,1]insertion product is formed,[19] i.e. the regioisomer **9a** that features the arene substituent at the α-carbon atom adjacent to the metal center. This regiochemistry of the insertion reaction allows for the stabilization of the product by distorted η^3-benzylic arene coordination. This extra stabilization is likely to be the reason for the observed regiochemistry because there is evidence in the literature that rate-determining insertion in homogeneous metallocene Ziegler chemistry is preceded by a reversible alkene coordination/dissociation equilibrium,[22] which is a prerequisite of such a thermodynamic control of the regiochemistry. Styrene insertion also leads to a single stereoisomer **9a**. We again assume *cis* arrangement of the η^3-benzyl stereogenic unit with the substituted Cp ring.

Experimental Section

The reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. − ^{15}N-NMR spectra (60.7 MHz) were recorded with a Varian Unity Plus 600 NMR spectrometer by using a GHMBC pulse sequence ($^nJ(^{15}N,^1H)$ = 5 Hz, n = 3, 4). The ^{15}N chemical shift is given with respect to a 2% [^{15}N]benzamide/0.2% Cr(acac)$_3$ sample in DMSO [δ(^{15}N) = −279.3, relative to neat CH$_3$NO$_2$, δ(^{15}N) = 0; Ξ(^{15}N) = 10.1367 MHz]. (For additional general information see ref.[4]) The preparation of **3** was described by us previously.[4] Complex **1**[5] and B(C$_6$F$_5$)$_3$[6] were prepared as described in the literature.

Reaction of 3 with Triphenylphosphane. − Preparation of 6a: A cold solution (−50 °C) containing **1** (150 mg, 0.45 mmol) in 5 mL of dichloromethane was added to a solution of B(C$_6$F$_5$)$_3$ (228 mg, 0.45 mmol) in 5 mL of dichloromethane at −50 °C. The mixture was stirred for 30 min to generate **3**. Triphenylphosphane (117 mg, 0.45 mmol) was then added. The mixture was kept at −50 °C for 15 min and then warmed to room temperature. The product was precipitated as a dark brown oil by the dropwise addition of pentane (5 mL). The supernatant organic phase was decanted. The remaining oil was washed with pentane (5 mL). Pentane (7 mL) was then added and the product stirred overnight to give a solid, which was collected to yield 266 mg of **6a** (54%), m.p. 102 °C (dec. at 212 °C). − ^{1}H NMR ([D$_2$]dichloromethane, 599.99 MHz): δ = 7.59 (m, 3 H, Ph-*p*-H), 7.54 (m, 6 H, Ph-*m*-H), 7.36 (m, 6 H, Ph-*o*-H), 6.19, 5.93, 5.68, 4.58 (m, each 1 H, C$_5$H$_4$), 5.88 (d, $^3J_{PH}$ = 1.5 Hz, 5 H, Cp-H), 2.56 (s, 3 H, 6-H), 1.89 (dd, $^3J_{PH}$ = 4.8 Hz, $^2J_{HH}$ = 9.4 Hz, 1 H, 7-H), 1.64 (dd, $^3J_{PH}$ = 1.9 Hz, $^2J_{HH}$ = 9.4 Hz, 1 H, 7-H), 1.61, 1.01 (s, each 3 H, 5-H, 5-H), 0.50 [br s, 3 H, B(C$_6$F$_5$)$_3$-C*H*$_3$]. − ^{13}C NMR ([D$_2$]dichloromethane, 150.84 MHz): δ = 134.0 (d, $^2J_{PC}$ = 19.5 Hz, C-*o*-Ph), 131.7 (C-*p*-Ph), 129.7 (d, $^3J_{PC}$ = 9.0 Hz, C-*m*-Ph), 117.0 (C-1), 113.0, 108.8, 107.2, 96.9 (C$_5$H$_4$), 108.2 (C-Cp), 58.6 (C-4), 46.8 (d, $^2J_{PC}$ = 15.5 Hz, C-7), 44.5 (C-6), 25.3, 17.6 (C-5, C-5′); 148.6 [dm, $^1J_{CF}$ = 232 Hz, *o*-B(C$_6$F$_5$)$_3$], 137.8 [dm, $^1J_{CF}$ = 241 Hz, *p*-B(C$_6$F$_5$)$_3$], 136.8 [dm, $^1J_{CF}$ = 250 Hz, *m*-B(C$_6$F$_5$)$_3$], 128.5 [br, *ipso*-B(C$_6$F$_5$)$_3$], 10.0 [B(C$_6$F$_5$)$_3$-CH$_3$]; C-*ipso*-Ph resonance not observed. − ^{15}N,^{1}H GHMBC ([D$_2$]dichloromethane, 60.72/599.99 MHz, 223 K): δ = −376.3/1.61, −376.3/1.01 (N/5-H, N/5′-H). − ^{31}P NMR ([D$_2$]dichloromethane, 81.02 MHz): δ = 31.2. − $C_{52}H_{38}BF_{15}NPZr$ (1095): calcd. C 57.05, H 3.50, N 1.28; found C 56.10, H 3.75, N 1.15.

Reaction of 3 with Methyldiphenylphosphane. − Preparation of 6b: Analogously as described above a sample of **1** (150 mg, 0.45 mmol) (in 5 mL of dichloromethane) was treated at −36 °C with B(C$_6$F$_5$)$_3$ (228 mg, 0.45 mmol) (in 5 mL of dichloromethane), and with methyldiphenylphosphane (89 mg, 0.45 mmol) after 15 min. After workup, as described above, the yield was 237 mg (51%) of complex **6b**, m.p. 199 °C (dec.). − ^{1}H NMR ([D$_2$]dichloromethane, 599.99 MHz): δ = 7.59 (m, 1 H, Ph-*p*-H), 7.56 (m, 2 H, Ph-*m*-H), 7.51 (m, 1 H, Ph-*p*-H), 7.50 (m, 2 H, Ph-*m*-H), 7.35 (m, 2 H, Ph-*o*-H), 7.21 (m, 2 H, Ph-*o*-H), 6.17, 5.97, 5.80, 4.33 (m, each 1 H, C$_5$H$_4$), 5.94 (d, $^3J_{PH}$ = 1.7 Hz, 5 H, Cp−H), 2.52 (s, 3 H, 6-H), 2.05 (d, $^2J_{PH}$ = 6.6 Hz, 3 H, PC*H*$_3$), 1.89 (dd, $^2J_{HH}$ = 9.5 Hz, $^3J_{PH}$ = 4.7 Hz, 1 H, 7-H), 1.61, 1.01 (s, each 3 H, 5-H, 5′-H), 1.43 (dd, $^2J_{HH}$ = 9.5 Hz, $^3J_{PH}$ = 2.0 Hz, 1 H, 7-H′), 0.50 [br s, 3 H, B(C$_6$F$_5$)$_3$-C*H*$_3$]. − ^{13}C {GATED} NMR ([D$_2$]dichloromethane, 150.84 MHz): δ = 134.9 (d, $^1J_{PC}$ = 36.0 Hz, C-*ipso*-Ph), 133.4 [C-*ipso*-Ph (from GHMBC)], 133.0 (d, $^2J_{PC}$ = 11.2 Hz, C-*o*-Ph), 131.9 (C-*p*-Ph), 131.4 (d, $^2J_{PC}$ = 10.1 Hz, C-*o*-Ph), 131.2 (C-*p*-Ph), 129.8 (d, $^3J_{PC}$ = 9.2 Hz, C-*m*-Ph), 129.5 (d, $^3J_{PC}$ = 9.2 Hz, C-*m*-Ph), 112.6 (C-1), 108.3, 107.0, 106.5, 96.7 (C_5H_4), 107.5 (C-Cp), 58.7 (C-4), 45.9 (d, $^1J_{PC}$ = 15.7 Hz, $^1J_{CH}$ = 146 Hz, $^1J_{CH}$ = 155 Hz, C-7), 44.7 ($^1J_{CH}$ = 138 Hz, C-6), 25.3 ($^1J_{CH}$ = 128 Hz), 17.3 ($^1J_{CH}$ = 128 Hz) (C-5, C-5′), 15.0 ($^1J_{PC}$ = 24.0 Hz, $^1J_{CH}$ = 132 Hz, P*C*H_3); 148.6 [dm, $^1J_{CF}$ = 239 Hz, *o*-$B(C_6F_5)_3$], 137.8 [dm, $^1J_{CF}$ = 240 Hz, *p*-$B(C_6F_5)_3$], 136.8 [dm, $^1J_{CF}$ = 245 Hz, *m*-$B(C_6F_5)_3$], 10.5 [$B(C_6F_5)_3$-*C*H_3]; *ipso*-$B(C_6F_5)_3$ signal not observed. − $^{15}N,^1H$ GHMBC ([D_2]dichloromethane, 60.72/599.99 MHz): δ = −376.7/1.61, −376.7/ 1.01 (N/5-H, N/5-H′). − $C_{47}H_{36}BF_{15}NPZr$ (1033): calcd. C 54.66, H 3.51; found C 54.65, H 3.71.

Reaction of 3 with Cyclopropyl(diphenyl)phosphane. − Preparation of 6c: Complex **3** was generated analogously as described above by treatment of **1** (150 mg, 0.45 mmol) with $B(C_6F_5)_3$ (228 mg, 0.45 mmol) in 3 mL of dichloromethane at −36 °C. Cyclopropyl(diphenyl)phosphane (101 mg, 0.45 mmol) was added. The mixture was kept at −36 °C for 15 min and then warmed to room temperature. After workup, as described above, the yield was 243 mg (51%) of **6c**, m.p. 195 °C (decomp.). − ^1H NMR ([D_2]dichloromethane, 599.99 MHz): δ = 7.57 (m, 2 H, Ph-*p*-H), 7.53 (m, 4 H, Ph-*m*-H), 7.34 (m, 4 H, Ph-*o*-H), 6.11, 5.95, 5.86, 4.90 (m, each 1 H, C_5H_4), 6.02 (d, $^3J_{PH}$ = 1.4 Hz, 5 H, Cp−H), 2.47 (s, 3 H, 6-H), 1.79 (m, 1 H, 7-H), 1.61, 1.03 (s, each 3 H, 5-H, 5′-H), 1.43 (m, 1 H, PC*H*), 1.24 (m, 1 H, 7-H′), 1.14 (m, 2 H, P*c*C*H*$_2$), 0.50 [br s, 3 H, $B(C_6F_5)_3$-C*H*$_3$], 0.34 (m, 2 H, P*c*C*H*$_2$). − ^{13}C NMR ([D_2]dichloromethane, 150.84 MHz): δ = 133.5 (d, $^2J_{PC}$ = 10.9 Hz, C-*o*-Ph), 133.4 (d, $^2J_{PC}$ = 10.7 Hz, C-*o*-Ph), 131.8 (C-*p*-Ph), 131.6 (C-*p*-Ph), 129.5 (d, $^3J_{PC}$ = 9.0 Hz, C-*m*-Ph), 129.4 (d, $^3J_{PC}$ = 9.2 Hz, C-*m*-Ph), 112.4 (C-1), 107.9, 107.0, 106.8, 96.8 (C_5H_4), 107.5 (C-Cp), 58.7 (C-4), 46.7 (d, $^2J_{PC}$ = 15.8 Hz, C-7), 44.6 (C-6), 25.4, 17.0 (C-5, C-5′), 14.2 (s, P*C*H), 8.3 (d, $^1J_{PC}$ = 29.2 Hz, P*C*H), 5.7 (br, P*c*CH_2), 5.4 (d, $^2J_{PC}$ = 4.1 Hz, P*c*CH_2); 148.6 [dm, $^1J_{CF}$ = 239 Hz, *o*-$B(C_6F_5)_3$], 137.8 [dm, $^1J_{CF}$ = 240 Hz, *p*-$B(C_6F_5)_3$], 136.8 [dm, $^1J_{CF}$ = 245 Hz, *m*-$B(C_6F_5)_3$], 10.2 [$B(C_6F_5)_3$-CH_3]; *ipso*-$B(C_6F_5)_3$ and C-*ipso*-Ph signals not observed. − $^{15}N,^1H$ GHMBC ([D_2]dichloromethane, 60.72/599.99 MHz): δ = −376.2/1.61, −376.2/1.03 (N/5-H, N/5′-H). − $C_{49}H_{38}BF_{15}NPZr$ (1059): calcd. C 55.58, H 3.62, N 1.32; found C 55.70, H 3.50, N 1.31.

Reaction of 3 with Benzophenone. − Preparation of 7: A cold solution (−30 °C) containing **1** (150 mg, 0.45 mmol) in 3 mL of bromobenzene was treated with a solution of $B(C_6F_5)_3$ (228 mg, 0.45 mmol) in 6 mL of bromobenzene at −30 °C. The mixture was stirred for 15 min to generate **3**. Benzophenone (81 mg, 0.45 mmol) was then added. After 15 min at −30 °C, the red mixture was warmed to room temperature and the product was precipitated as a red oil by the addition of pentane (6 mL). The organic phase was decanted off. The residue was washed 4 times with pentane (3 mL each) and dried in vacuo to yield 265 mg (58%) of **7**, m.p. 213 °C (dec.). − ^1H NMR ([D_2]dichloromethane, 599.99 MHz, 223 K): δ = 7.71 (m, 2 H, Ph-*o*-H), 7.48 (m, 2 H, Ph-*m*-H), 7.35 (m, 1 H, Ph-*p*-H), 7.22 (m, 2 H, Ph-*o*-H), 7.11 (m, 3 H, Ph-*m*-H, Ph-*p*-H), 6.45, 6.37, 6.23, 6.17 (C_5H_4), 6.11 (s, 5 H, Cp-H), 3.90 (d, $^2J_{HH}$ = 13.8 Hz, 1 H, 7-H), 3.57 (d, $^2J_{HH}$ = 13.8 Hz, 1 H, 7-H), 2.41 (s, 3 H, 6-H), 1.65, 1.50 (s, each 3 H, 5-H, 5′-H), 0.40 [br s, 3 H, $B(C_6F_5)_3$-C*H*$_3$]. − ^{13}C NMR ([D_2]dichloromethane, 150.84 MHz, 223 K): δ = 147.0, 143.9 (each C-*ipso*-Ph), 128.3, 128.3 (each C-*m*-Ph), 127.3, 126.7 (C-*p*-Ph), 125.5, 124.4 (C-*o*-Ph), 125.9, 107.5, 106.7, 104.9 (C_5H_4), 125.0 (C1), 114.2 (C-Cp), 88.4 (C-8), 66.6 (C-7), 61.0 (C-4), 41.7 (C-6), 25.5, 22.5 (C-5, C-5′), 147.7 [dm, $^1J_{CF}$ = 241 Hz, *o*-$B(C_6F_5)_3$], 137.0 [dm, $^1J_{CF}$ = 250 Hz, *p*-$B(C_6F_5)_3$], 135.9 [dm, $^1J_{CF}$ = 247 Hz, *m*-$B(C_6F_5)_3$], 128.1 [br, *ipso*-$B(C_6F_5)_3$], 9.4 [$B(C_6F_5)_3$-C*H*$_3$]. − $^{15}N,^1H$ GHMBC ([D_2]dichloromethane, 60.72/599.99 MHz, 223 K): δ = −339.2/1.65, −339.2/1.50 (N/5-H, N/5-H). − $C_{47}H_{33}BF_{15}NOZr$ (1014.8): calcd. C 55.63, H 3.28, N 1.38; found C 55.52, H 3.47, N 1.46.

Treatment of 3 with Ethene. − Generation of 8: The insertion reaction was carried out as an NMR-spectroscopic experiment. A sample of **1** (11 mg, 29 μmol) was dissolved in 0.5 mL of [D_2]dichloromethane and this mixture was added at −50 °C to solid $B(C_6F_5)_3$ (15 mg, 29 μmol). The formation of **3** was monitored by NMR spectroscopy. Gaseous ethene (2 mL) was then introduced into the solution. The NMR-spectroscopic analysis at −50 °C revealed the clean formation of **8**. − ^1H NMR ([D_2]dichloromethane, 599.99 MHz, 223 K): δ = 7.40 (m, 1 H, 2′-H), 6.58 (s, 5 H, Cp-H), 6.44, 6.33 (m, each 1 H, 3-H, 3′-H), 6.37 (m, 1 H, 2-H), 3.38 (pt, 1 H, 7-H), 2.36 (m, 1 H, 9-H), 2.29 (m, 1 H, 7-H′), 2.27 (s, 3 H, 6-H), 2.02 (m, 1 H, 8-H), 1.75 (m, 1 H, 9-H′), 1.54 (m, 1 H, 8-H′), 1.48, 1.28 (s, each 3 H, 5-H, 5′-H), 0.39 [br s, 3 H, $(C_6F_5)_3$BC*H*$_3$]. − ^{13}C {GATED} NMR ([D_2]dichloromethane, 150.84 MHz, 223 K): δ = 121.8 (C-1), 118.4 ($^1J_{CH}$ = 177 Hz), 110.2 ($^1J_{CH}$ = 177 Hz) (C-3, C-3′), 117.1 ($^1J_{CH}$ = 175 Hz, C-2′), 115.2 ($^1J_{CH}$ = 175 Hz, C-Cp), 106.9 ($^1J_{CH}$ = 173 Hz, C-2), 63.1 (C-4), 53.4 ($^1J_{CH}$ = 144 Hz, C-7), 46.8 ($^1J_{CH}$ = 132 Hz, C-9), 41.2 ($^1J_{CH}$ = 139 Hz, C-6), 24.9 ($^1J_{CH}$ = 129 Hz), 20.9 ($^1J_{CH}$ = 129 Hz) (C-5, C-5′); 14.3 ($^1J_{CH}$ = 124 Hz, C-8), 147.7 [dm, $^1J_{CF}$ = 238 Hz, *o*-$B(C_6F_5)_3$], 137.0 [dm, $^1J_{CF}$ = 254 Hz, *p*-$B(C_6F_5)_3$], 135.9 [dm, $^1J_{CF}$ = 242 Hz, *m*-$B(C_6F_5)_3$], 127.8 [br, *ipso*-$B(C_6F_5)_3$], 9.5 [$B(C_6F_5)_3$-*C*H_3]. − $^{15}N,^1H$ GHMBC ([D_2]dichloromethane, 60.72/599.99 MHz, 223 K): δ = −348.9/1.48, −348.9/1.28 (N/5-H, N/5′-H).

Reaction of 3 with Styrene. − Preparation of 9a: A cold solution (−36 °C) containing **1** (150 mg, 0.45 mmol) in 3 mL of dichloromethane was added to solid $B(C_6F_5)_3$ (228 mg, 0.45 mmol). The mixture was stirred for 30 min to generate **3**. Styrene (47 mg, 0.45 mmol) was then added. After 45 min at −36 °C, the mixture was warmed to room temperature and the product was precipitated as a red oil by the dropwise addition of pentane (9 mL). The organic phase was carefully decanted. The remaining oil was washed with pentane (3 × 3 mL). Pentane (9 mL) was then added and the product stirred overnight to give a pale red solid, which was collected to yield 334 mg (79%) of **9a**, m.p. 211 °C (dec.). − ^1H NMR ([D_2]dichloromethane, 599.99 MHz): δ = 7.57 (m, 2 H, 12-H, 12′-H), 7.21 (t, $^3J_{HH}$ = 6.0 Hz, 13-H), 6.35 (s, 5 H, Cp-H), 5.97, 5.85, 4.71, 4.27 (m, each 1 H, C_5H_4), 3.92 (pd, 1 H, 9-H), 3.62 (m, 1 H, 7-H), 2.78 (m, 1 H, 8-H), 2.69 (m, 1 H, 7-H′), 2.42 (s, 3 H, 6-H), 2.35 (m, 1 H, 8-H′), 1.50, 1.39 (s, each 3 H, 5-H, 5-H′), 0.50 [br s, 3 H, $B(C_6F_5)_3$-C*H*$_3$]; remaining Ph-H signals not observed because of a dynamic process. − ^1H NMR ([D_2]dichloromethane, 599.99 MHz, 223 K): δ = 7.63 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, 12′-H), 7.42 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, 12-H), 7.15 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, 13-H), 7.07 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, 11′-H), 5.49 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, 11-H), 6.31 (s, 5 H, Cp-H), 5.95, 5.82, 4.62, 4.19 (m, each 1 H, C_5H_4), 3.87 (m, 1 H, 9-H), 3.54 (m, 1 H, 7-H), 2.72 (m, 1 H, 8-H), 2.64 (m, 1-H, 7-H′), 2.36 (s, 3 H, 6-H), 2.29 (m, 1 H, 8-H′), 1.45, 1.33 (s, each 3 H, 5-H, 5′-H), 0.39 [br s, 3 H, $B(C_6F_5)_3$-C*H*$_3$]. − ^{13}C {GATED} NMR ([D_2]dichloromethane, 150.84 MHz, 223 K): δ = 138.4 (C-10), 139.3 ($^1J_{CH}$ = 162 Hz, C-12), 134.7 ($^1J_{CH}$ = 160 Hz, C-12′), 125.9, 109.3, 106.2, 102.0 (C_5H_4), 124.1 ($^1J_{CH}$ = 162 Hz, C-13), 123.6 ($^1J_{CH}$ = 160 Hz, C-11′), 118.6 (C-1), 112.1 (C-Cp), 88.2 ($^1J_{CH}$ = 150 Hz, C-11), 70.0 ($^1J_{CH}$ = 145 Hz, C-9), 63.4 (C-7), 61.5 (C-4), 40.8 (C-6), 25.1, 22.6 (C-5, C-5′), 23.8 (C-8), 147.6 [dm, $^1J_{CF}$ = 240 Hz, *o*-$B(C_6F_5)_3$], 137.2 [dm, $^1J_{CF}$ = 259 Hz *p*-$B(C_6F_5)_3$], 135.8 [dm, $^1J_{CF}$ = 240 Hz, *m*-$B(C_6F_5)_3$], 127.8 [br, *ipso*-$B(C_6F_5)_3$], 9.5 [$B(C_6F_5)_3$-C*H*$_3$]. − $^{15}N,^1H$ GHMBC ([D_2]dichloromethane, 60.72/599.99 MHz): δ = −352.7/1.50,

−352.7/1.39 (N/5-H, N/5′-H). − Coalescence: 12-H and 12′-H: $\Delta G^{\neq} = 10.6 \pm 0.5$ kcal/mol ($T_C = 268$ K, $\Delta\nu = 126$ Hz; [D$_2$]dichloromethane). − $C_{42}H_{31}BF_{15}NZr$ (936.7): calcd. C 53.85, H 3.34, N 1.50; found C 54.00, H 3.28, N 1.23.

Reaction of 3 with 4-*tert*-Butylstyrene. − Preparation of 9b: Analogously as described above, complex **1** (150 mg, 0.45 mmol) was treated with $B(C_6F_5)_3$ (228 mg, 0.45 mmol) in dichloromethane (−36 °C) and after 15 min with 4-*tert*-butylstyrene (72 mg, 0.45 mmol). After 30 min at −36 °C, the mixture was warmed to room temperature. After workup as described above, the yield was 321 mg (72%) of complex **9b**. Single crystals of **9b** suitable for the X-ray crystal structure analysis were obtained by allowing diethyl ether vapor to diffuse into a solution of **9b** in dichloromethane at −36 °C; m.p. 124 °C. − ^{1}H NMR ([D$_2$]dichloromethane, 599.99 MHz): δ = 7.60 (br m, 2 H, 12′-H, 12-H), 6.34 (s, 5 H, Cp-H), 5.98, 5.83, 4.73, 4.16 (m, each 1 H, C_5H_4), 3.86 (pd, 1 H, 9-H), 3.62 (m, 1 H, 7-H), 2.77 (m, 1 H, 8-H), 2.67 (m, 1 H, 7-H′), 2.40 (s, 3 H, 6-H), 2.34 (m, 1 H, 8-H′), 1.50, 1.38 (s, each 3 H, 5-H, 5′-H), 1.34 (s, 9 H, 15-H), 0.50 [br s, 3 H, $B(C_6F_5)_3$-C*H*$_3$]; remaining Ph-H signals not observed because of a dynamic process. −^{1}H NMR ([D$_2$]dichloromethane, 599.99 MHz, 233 K): δ = 7.73 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, 12′-H), 7.30 (d, $^3J_{HH}$ = 8.7 Hz, 1 H, 12-H), 7.06 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, 11′-H), 6.31 (s, 5 H, Cp-H), 5.96, 5.81, 4.66, 4.07 (m, each 1 H, C_5H_4), 5.46 (d, $^3J_{HH}$ = 8.7 Hz, 1 H, 11-H), 3.82 (pd, 1 H, 9-H), 3.55 (m, 1 H, 7-H), 2.72 (m, 1 H, 8-H), 2.64 (m, 1 H, 7-H′), 2.35 (s, 3 H, 6-H), 2.28 (m, 1 H, 8-H′), 1.45, 1.33 (s, each 3 H, 5-H, 5′-H), 1.29 (s, 9 H, 15-H), 0.42 [br s, 3 H, $B(C_6F_5)_3$-C*H*$_3$]. − ^{13}C {GATED} NMR ([D$_2$]dichloromethane, 150.84 MHz, 233 K): δ = 147.6 (C-13), 135.6 (C-10), 133.6 ($^1J_{CH}$ = 159 Hz, C-12), 133.5 ($^1J_{CH}$ = 157 Hz, C-12′), 124.8 ($^1J_{CH}$ = 175 Hz), 109.0 ($^1J_{CH}$ = 174 Hz), 106.9 ($^1J_{CH}$ = 175 Hz), 101.9 ($^1J_{CH}$ = 173 Hz) (C_5H_4), 124.0 ($^1J_{CH}$ = 159 Hz, C-11′), 118.9 (C-1), 112.1 ($^1J_{CH}$ = 175 Hz, C-Cp), 88.7 ($^1J_{CH}$ = 150 Hz, C-11), 69.6 ($^1J_{CH}$ = 141 Hz, C-9), 63.6 ($^1J_{CH}$ = 136 Hz, C-7), 61.5 (C-4), 40.8 ($^1J_{CH}$ = 138 Hz, C-6), 34.4 (C-14), 30.6 ($^1J_{CH}$ = 126 Hz, C-15), 25.1 ($^1J_{CH}$ = 127 Hz), 22.5 ($^1J_{CH}$ = 128 Hz) (C-5, C-5′), 24.1 ($^1J_{CH}$ = 126 Hz, C-8), 148.6 [dm, $^1J_{CF}$ = 234 Hz, *o*-$B(C_6F_5)_3$], 137.8 [dm, $^1J_{CF}$ = 239 Hz, *p*-$B(C_6F_5)_3$], 136.8 [dm, $^1J_{CF}$ = 248 Hz, *m*-$B(C_6F_5)_3$], 128.7 [br, *ipso*-$B(C_6F_5)_3$], 9.9 [$B(C_6F_5)_3$-CH_3]. − ^{15}N,^{1}H GHMBC ([D$_2$]dichloromethane, 60.72/599.99 MHz): δ = −352.4/1.45, −352.4/1.33 (N/5-H, N/5′-H). − Coalescence: 12-H and 12′-H: $\Delta G^{\neq} = 10.7 \pm 0.5$ kcal/mol ($T_C = 278$ K, $\Delta\nu = 258$ Hz; [D$_2$]dichloromethane) − $C_{46}H_{39}BF_{15}NZr$ (992.8): calcd. C 55.65, H 3.96, N 1.41; found C 55.44, H 4.14, N 1.34. −

X-ray Crystal Structure Analysis of 9b: Empirical formula $C_{46}H_{39}BF_{15}NZr$, M = 992.8, yellow crystal 0.25 × 0.20 × 0.20 mm, a = 12.881(1) Å, b = 13.411(1) Å, c = 13.406(1) Å, α = 87.51(1)°, β = 63.99(1)°, γ = 86.67(1)°, V = 2077.4(3) Å^3, $\rho_{calcd.}$ = 1.587 g cm^{-3}, μ = 3.68 cm^{-1}, empirical absorption correction via ψ scan data ($0.914 \le T \le 0.930$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223 K, ω/2θ scans, 8809 reflections collected ($+h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.62 Å^{-1}, 8420 independent (R_{int} = 0.063) and 6020 observed reflections [$I \ge 2\,\sigma(I)$], 584 refined parameters, R = 0.053, wR^2 = 0.141, max. residual electron density 0.92 (−0.90) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. The data set was collected with a Nonius MACH3 diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection EXPRESS (Nonius B.V., **1994**); data reduction MolEN (K. Fair, Enraf Nonius B.V., **1990**); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**); graphics (with unsystematical numbering schemes) SCHAKAL (E. Keller, Universität Freiburg, **1997**). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-138759. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information Available: Additional spectroscopic details and characterization of additional reaction products of **3** with organic carbonyl compounds and alkenes. Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/eurjic or from the author.

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