Formation and Structural and Dynamic Features of Atropisomeric η^2-Iminoacyl Zirconium Complexes

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Received June 18, 2007

The $Cp_2ZrCl(\mu$-1,4-diphenylbutenyne)PX_2 complexes **7a** [$-P(C_6H_5)_2$] and **10** [$-P(C_6F_5)_2$] insert *tert*-butylisonitrile into the Zr−C(sp^2) σ bond to yield the N-inside η^2-iminoacyl zirconocene complexes **13a** and **13b**. X-ray crystal structure analysis of complexes **13a** and **13b** revealed the presence of a chiral atropisomeric structure with a torsion angle of 74.8(2)° (**13a**) and 72.9(6)° (**13b**), respectively, around the central iminoacyl/alkenyl C(sp^2)−C(sp^2) σ bond. In solution an analogous chiral structure is observed. The barrier of interconversion of the enantiomeric atropisomers of **13a** and **13b** was determined at $\Delta G^{\ddagger}$ (327K) = 14.9 ± 0.3 kcal mol^{-1} (**13a**) and $\Delta G^{\ddagger}$ (325K) = 14.8 ± 0.3 kcal mol^{-1} (**13b**) by temperature-dependent dynamic NMR spectroscopy. Reaction of **7a** and **10** with methyllithium followed by treatment with $B(C_6F_5)_3$ gave the corresponding cationic zirconocene complexes **12a** and **12b**. These complexes took up 2 mol equiv of *tert*-butylisonitrile to yield the cationic N-inside η^2-iminoacyl zirconocene systems **14a** and **14b** as isonitrile adducts. The cationic complexes **14a** and **14b** are also axially chiral. The barriers of enantiomerization ($\Delta G^{\ddagger}$ (288 K) = 13.1 ± 0.3 kcal mol^{-1} (**14a**), $\Delta G^{\ddagger}$ (293 K) = 13.4 ± 0.3 kcal mol^{-1} (**14b**)) were also determined by dynamic NMR spectroscopy.

Introduction

We have recently shown that bis(alkynyl)zirconocenes (**1**) rapidly react with a stoichiometric amount of the strong Lewis acid $B(C_6F_5)_3$ (**2**) to yield the zwitterionic diyne-bridged zirconocenium/borate betaine products (**3**).[1,2] Upon treatment with an isonitrile the systems **3** rapidly undergo further internal C−C coupling at room temperature or below to yield the unique functionalized methylenecyclopropene derivatives (**5**). Related chemistry is observed upon treatment of the compounds **3** with organonitrile reagents.[3−5] Thermodynamically, the endothermicity of the methylenecyclopropene formation is more than compensated by the energy gain associated with the newly formed C−C and Zr−N bonds. Kinetically, the situation is more complex. From a detailed theoretical analysis (DFT) it seems that the three-membered ring formation, which topologically requires insertion of the remaining −C≡C triple bond into the adjacent Zr−C(sp^2) σ bond, is triggered by nitrile (or isonitrile) addition to make a sufficiently kinetically favorable reaction pathway available.[6] From the respective DFT calculation formation of a reasonably stabilized local minimum intermediate (**4**) must be assumed[6] that surprisingly seems to contain a planar tetracoordinated carbon center (see Scheme 1).[7−9]

This posed the question of whether such unique methylenecyclopropene formation might occur specifically within the zwitterionic $Zr^+/-BR_3^-$ framework of **3** or if combinations of an electropositive group 4 metal with other types of electronically active peripheral substituents might be possible within this unique reaction scheme. We, therefore, developed a synthetic pathway to systems **7** which may be regarded as phosphine analogues of **3**.[10] Synthesis of **7** was straightforward: Treatment of the metallacyclocumulene **6**[11,12] with $ClPPh_2$ gave **7a**. The analogous reaction of **6** with PCl_3 led to formation of **7b** (see Scheme 2).[10]

We have now prepared a series of derivatives from the readily available precursors **7a**,**b** and investigated whether a related formation of stabilized methylenecyclopropene derivatives (**8**) would be observable under a variety of conditions. This actually

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† X-ray crystal structure analyses.

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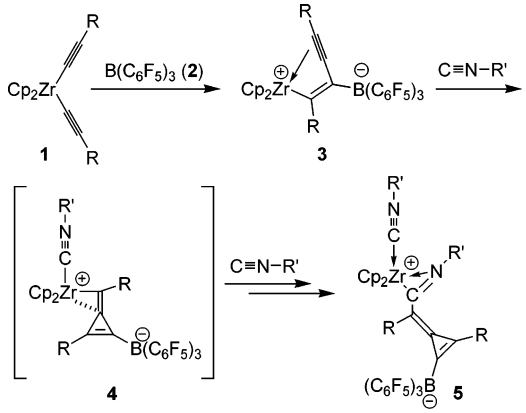
10.1021/om7005968 CCC: $37.00
Publication on Web 10/03/2007

Scheme 1



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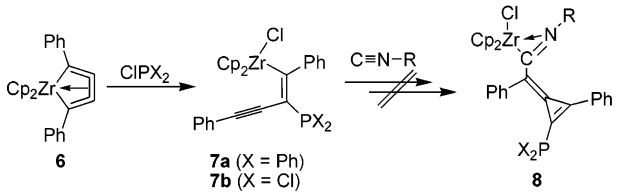


was never the case. However, isonitrile insertion into the Zr−C(sp^2) bond of some of the obtained systems resulted in formation of new sterically very encumbered η^2-iminoacyl zirconocene complexes that showed very remarkable structural and dynamic features. The synthetic pathways to these unique compounds and characterization of their remarkable properties will be described in this paper.

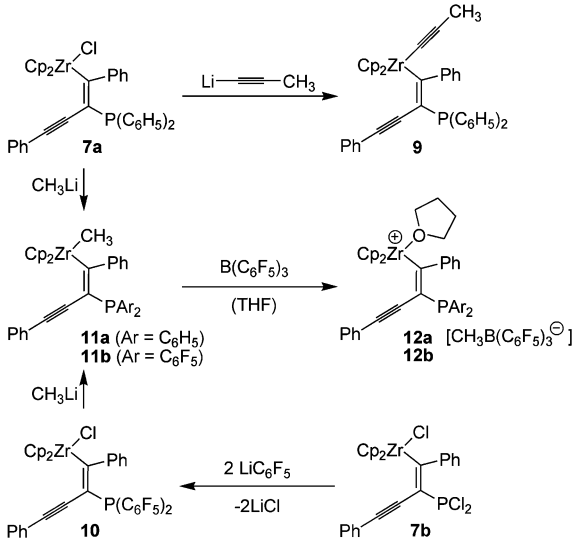
Results and Discussion

Formation of the Starting Materials and Structural Reference Systems. We prepared two series of complexes. Synthesis of one series started from **7a** (−PPh_2) and the other from **7b** (−PCl_2). Treatment of starting material **7a** with methyllithium in ether gave the corresponding Zr−CH_3 derivative **11a**. Its ^{1}H/^{13}C NMR spectra each exhibit a single Cp resonance at δ 6.21 (10H)/δ 110.8 and Zr−CH_3 resonances at δ −0.86 (3H)/δ 31.1. The C═C ^{13}C NMR resonances are very diagnostic: the C_α resonance occurs at δ 226.4 ($^2J_{PC}$ = 17.1 Hz), which is very characteristic for a sterically encumbered [Zr]−C(sp^2) situation. The adjacent C_β carbon NMR resonance is found at δ 126.4 ($^1J_{PC}$ = 29.0 Hz). The ^{13}C NMR signals of the C≡C unit were located at δ 94.4 and δ 92.7, respectively. We observed a single set of NMR resonances of the phenyl substituents of the −PPh_2 group [^{13}C δ 140.8 ($^1J_{PC}$ = 17.3, *i*-Ph), δ 133.9 ($^2J_{PC}$ = 19.7 Hz, *o*-Ph), δ 128.6 ($^3J_{PC}$ = 5.9 Hz, *m*-Ph), δ 128.4 (*p*-Ph)]. The ^{31}P NMR signal of complex **11a** is at δ −9.8.

Complex **7a** was reacted with propynyllithium to give the corresponding [Zr]−(σ-propynyl) complex **9** (ca. 50% isolated, see Scheme 3). Since this complex must be regarded as an important structural and spectroscopic reference (see below), it was characterized in some detail.

Single crystals suitable for the X-ray crystal structure analysis of **9** were obtained from diethyl ether. The compound features a bent metallocene framework that shows Zr−C(Cp) bond lengths in a rather narrow range between 2.471(2) and 2.531(2) Å. The angle between Zr−C41 (2.233(2) Å) and Zr−C2 (2.301(2) Å) amounts to 110.56(7)°. The σ-propynyl ligand is

Scheme 3



linear (C41−C42 1.201(3) Å, angles Zr−C41−C42 173.6(2)°, C41−C42−C43 177.8(2)°) as expected. The sterically encumbered tetrasubstituted σ-alkenyl ligand has the ═C(alkynyl)-PPh_2 end oriented toward the lateral sector of the bent metallocene wedge. It is only marginally rotated from the central σ-ligand plane (dihedral angle C41−Zr−C2−C3 173.8(2)°). In contrast, the phenyl substituent at the alkenyl α-carbon is rotated substantially out of the plane (θ C3−C2−C1−C11 104.2(2)°, C3−C2−C1−C15 −82.3(2)°). The C2−C3 bond is slightly elongated (1.351(2) Å), and the angles at the olefinic sp^2-carbon center C2 are markedly distorted [Zr−C2−C1 100.6(1)°, Zr−C2−C3 136.3(1)°, C1−C2−C3 123.0(2)° vs C2−C3−C4 122.0(2)°, C2−C3−P1 121.5(1)°, C4−C3−P1 116.5(1)°]. The phosphorus atom features a typical near to nonhybridized coordination sphere [bond lengths C3−P1: 1.843(2) Å, C31−P1 1.833(2) Å, C21−P1 1.826(2) Å, bond angles C3−P1−C21: 103.58(8)°, C3−P1−C31 99.82(8)°, C21−P1−C31 101.57(8)°]. Eventually, carbon atom C3 bears the linear phenylacetylide substituent (C3−C4 1.431(2) Å, C4−C5 1.198(3) Å, angles C3−C4−C5 174.1(2)°, C4−C5−C6 177.8(2)°).

Complex **9** behaves achiral in solution. It exhibits a single 10H intensity ^{1}H NMR Cp resonance at δ 6.17 (in d_6-benzene, ^{13}C Cp feature at δ 110.1). Also, the phenyl groups at the phosphorus center behave enantiotopic, i.e., they show a single set of resonances at δ 140.5 ($^1J_{PC}$ = 17.2 Hz, i), δ 133.8 ($^2J_{PC}$ = 19.5 Hz, o), δ 128.4 ($^3J_{PC}$ = 5.9 Hz, m), and δ 128.3 (*p*-Ph). The ^{13}C NMR features of the Zr−alkenyl unit are typical: δ 225.2 ($^2J_{PC}$ = 17.4 Hz, C_α), 127.0 ($^1J_{PC}$ = 29.3 Hz, C_β). The ^{31}P NMR resonance of complex **9** occurs at δ −8.3, and there is a $\tilde{\nu}$(C≡C) IR band at 2095 cm^{-1}.

Complex **11a** was used for metallocene cation generation. For this purpose it was treated with $B(C_6F_5)_3$[13] in d_8-THF to effect methyl anion equivalent abstraction.[14] The resulting THF-stabilized metallocene cation **12a** (with [CH_3−$B(C_6F_5)_3^-$] counteranion) was not isolated but only characterized in situ after generation in d_8-THF solution.[15,16] It features a single Cp

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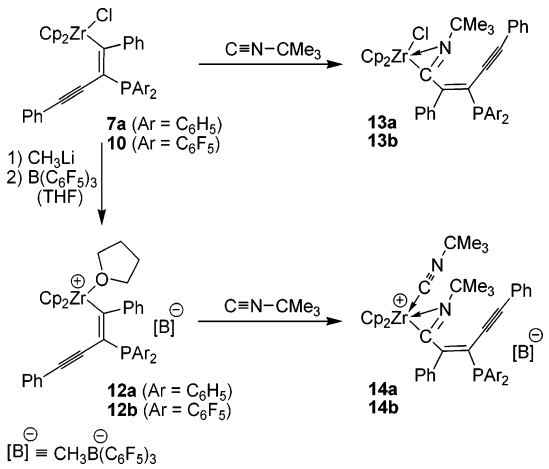
Scheme 4



resonance [^{1}H δ 6.68 (10H), ^{13}C δ 114.5] and typical [Zr]−alkenyl sp^2-C carbon resonances at δ 218.2 ($^2J_{PC}$ = 19.6 Hz, C$_\alpha$) and 132.8 ($^1J_{PC}$ = 30.3 Hz, C$_\beta$). Again, the system features an enantiotopic pair of phenyl groups at phosphorus [δ 139.4 ($^1J_{PC}$ = 15.7 Hz, i), 134.0 ($^2J_{PC}$ = 19.9 Hz, o), 129.0 ($^3J_{PC}$ = 6.4 Hz, m), and 130.3 (*p*-Ph)], indicating an achiral structure in solution.

A second series of compounds was synthesized starting from the corresponding −PCl$_2$-containing derivative **7b**. Reaction with 2 mol equiv of the in-situ-generated (***caution: explosive***!) reagent LiC$_6$F$_5$ proceeded very selectively. Only C$_6$F$_5$ addition to phosphorus was observed under the applied reaction conditions to give the product **10**, which was isolated in ca. 40% yield as a white solid (see Scheme 3). It features a single ^{1}H NMR Cp resonance at δ 6.49 (10H) in d_8-THF (^{13}C 113.8). The Zr−alkenyl ^{13}C NMR resonances occur at δ 227.7 ($^2J_{PC}$ = 20 Hz, C$_\alpha$) and 120.3 ($^1J_{PC}$ = 25.6 Hz, C$_\beta$). There is a single set of ^{19}F NMR signals of the pair of enantiotopic C$_6$F$_5$ substituents at phosphorus [δ −131.0 (o), −153.9 (p), −163.5 (m)].

Complex **10** was also characterized by X-ray diffraction. Its structure is similar to that of **9** (see above). The P−C bonds to the C$_6$F$_5$ ring system in **10** amount to 1.835(4) (P−C21) and 1.848(3) Å (P−C31), respectively (C21−P−C31 angle 105.2(2)°). The P−C3 bond (1.855(3) Å) is slightly longer, and the C2−C3 bond (1.346(5) Å) is marginally shorter than in the reference compound (**9**).[17]

Subsequent methylation at zirconium was carried out by treatment of complex **10** with a slight excess (1.3 mol equiv) of methyllithium in THF. The corresponding [Zr]−CH$_3$ product (**11b**) was isolated in ca. 50% yield. It shows the new [Zr]−CH$_3$ methyl resonances at δ −0.78 (^{1}H, 3H) and 33.0 (^{13}C), respectively. Complex **11b** shows a single ^{1}H NMR Cp resonance at δ 6.25 (10H; corresponding ^{13}C NMR signal at δ 111.2). In **11b** the enantiotopic C$_6$F$_5$ substituents at phosphorus show a single set of characteristic ^{19}F NMR resonances at δ −131.1 (o), −154.0 (p), and −163.5 (m). The complex features a ^{31}P NMR resonance at δ −48.8.

The corresponding cation system **12b** (with [CH$_3$−B(C$_6$F$_5$)$_3^-$] anion was generated by treatment of B(C$_6$F$_5$)$_3$ in d_8-THF solution (see Scheme 3). Again, this salt was not isolated but only characterized directly in solution [^{1}H δ 6.72 (s, 10H, Cp); ^{13}C δ 114.8 (Cp), 221.0 (Zr−C═); ^{19}F δ − 129.2 (o), − 150.7 (p), − 160.9 (m of P−C$_6$F$_5$); − 131.0 (o), − 165.0 (p), − 167.1 (m of MeBC$_6$F$_5$)$_3^-$]; ^{31}P δ − 43.8 (quin, $^3J_{PF}$ = 28 Hz).

Formation and Characterization of the η^2-Iminoacyl Zirconium Complexes. The neutral complexes **7a** and **10** were each treated with a slight excess of *tert*-butylisonitrile in toluene at ambient temperature. A clean monoinsertion of the CN−CMe$_3$ reagent into the Zr−C(sp^2) σ bond took place to yield the η^2-iminoacylzirconium complexes **13a** [−P(C$_6$H$_5$)$_2$] and **13b** [−P(C$_6$F$_5$)$_2$] that were isolated as yellow solids in ca. 80% yield.

Complexes **13a** and **13b** were characterized by X-ray diffraction (single crystals were obtained from diethyl ether). In the crystal both complexes (values for **13b** in square brackets) feature a bent metallocene backbone with Zr−C(Cp) bond lengths in a range between 2.480(3) [2.481(5)] and 2.539(3) [2.545(5)] Å. One important feature of the structure of **13a** is the presence of a η^2-iminoacyl ligand that is located in the σ-ligand plane. It is bonded in the N-inside fashion,[19,20] i.e., the iminoacyl nitrogen atom resides in a central position between the Zr−Cl (2.546(1) [2.539(1)] Å) and Zr−C1 (2.241(2) [2.248-(4)] Å) vectors (Zr−N1 2.233(2) [2.223(3)] Å, angles Cl−Zr−C1 117.3(1)° [117.5(1)°], C1−Zr−N1 32.9(1)° [32.9(1)°]). The C1−N1 bond length is in the C═N range (1.265(2) [1.266(5)] Å), and the iminoacyl nitrogen is planar tricoordinate (angles Zr−N1−C6 152.9(1)° [151.3(2)°], Zr−N1−C1 73.9(1)° [74.6(2)°], C1−N1−C6 133.0(2)° [134.0(3)°]). The adjacent iminoacyl carbon center C1 is also planar tricoordinate with the individual bond angles in the plane deviating substantially from the ideal sp^2-C values (N1−C1−Zr 73.2(1)° [72.5(2)°], C2−C1−Zr 148.9(1)° [149.3(3)°], N1−C1−C2 137.9(2)° [138.1(4)°]).

A remarkable structural feature of complexes **13** is the conformational orientation of the per-substituted alkenyl group that is attached at the iminoacyl carbon atom C1 (C1−C2 1.463(2) [1.465(5)] Å): it is strongly rotated out of the central η^2-iminoacyl plane (dihedral angles N1−C1−C2−C3 74.8(3)° [73.0(6)°], Zr−C1−C2−C3 −102.0(3)° [−102.7(6)°]) to create a chiral atropisomeric situation. Consequently, the C2−C21(aryl) vector is also located out of the central plane (dihedral angles N1−C1−C2−C21 −118.9(2)° [−118.0(5)°], C1−C2−C21−C22 −97.5(2)° [−79.8(5)°]). The alkenyl C2═C3 bond length (1.361(2) [1.350(5)] Å) and its bonding angles are in the normal range. The alkynyl substituent attached at C3 is close to linear (C4−C5 1.201(3) [1.192(5)] Å, angles C3−C4−C5 175.5(2)° [174.6(4)°], C4−C5−C51 179.2(2)° [176.3(4)]°). The geminal −PPh$_2$ substituent features a normal coordination geometry [C3−P 1.849(2) [1.844(4)] Å vs C31−P 1.832(2) [1.839(5)]

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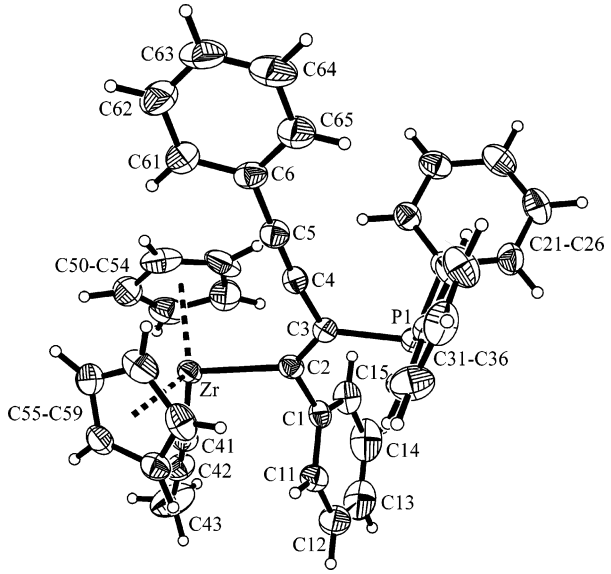


Figure 1. View of the molecular structure of complex **9**. Thermal ellipsoids are drawn at the 50% probability level.

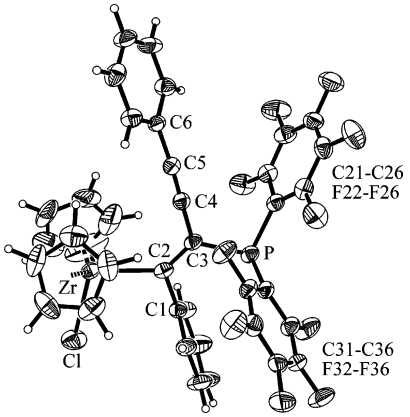


Figure 2. Projection of the molecular structure of complex **10**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr−C2 2.317(3), Zr−Cl 2.456(1), Zr−C(Cp) range 2.473(4)−2.524(4), C1−C2 1.498(4), C2−C3 1.346(5), C3−C4 1.433(4), C4−C5 1.195(4), C5−C6 1.443(4), C2−Zr−C1 103.2(1), C3−C2−C1 118.8(3), C3−C2−Zr 133.0(2), C1−C2−Zr 108.2(2), C2−C3−C4 121.7(3), C2−C3−P 118.7(2), C4−C3−P 119.5(3), C4−C5−C6 176.4(4), C5−C4−C3 178.9(4), C21−P−C31 105.2(2), C21−P−C3 101.4(2), C31−P−C3 102.2(1).

Å, C41−P 1.826(2) [1.844(4)] Å; bond angles at phosphorus C3−P−C41 103.0(1)° [99.7(2)°], C3−P−C31 101.1(1)° [107.5(2)°], C31−P−C41 102.3(1)° [100.0(2)°]].

Complex **13a** exhibits an analogous structure in solution. The presence of the η^2-iminoacyl group is indicated by a typical ^{13}C NMR *C*═N resonance at δ 223.4 ($^3J_{PC}$ = 2.0 Hz) [**13b** δ 222.8 ($^3J_{PC}$ = 2.9 Hz)]. The carbon NMR signals of the adjacent C═C double bond occur at δ 163.9 ($^2J_{PC}$ = 37.7 Hz, C2) and 110.2 ($^1J_{PC}$ = 24.1 Hz, C3) (tentative relative assignments) [**13b** δ 166.0 ($^2J_{PC}$ = 45.7 Hz) and 103.4 ($^1J_{PC}$ = 18 Hz)]. The carbon NMR resonances of the conjugated alkynyl substituent were located at δ 89.7 ($^2J_{PC}$ = 4.0 Hz) and 100.0, respectively [**13b** δ 86.9 ($^2J_{PC}$ = 4.5 Hz) and 99.1]. The ^{31}P NMR signal of complex **13a** is at δ −7.5 [**13b** δ −41.9].

Complexes **13** are chiral in solution. This becomes evident from the observation of the signals of a pair of diastereotopic Cp ligands of, e.g., **13a** in d_2-dichloromethane solution at 258 K: δ 6.02, 5.41 (each 5H)/δ 110.1, 109.5 (^{13}C) [**13b** (258 K) δ 6.06, 5.43 (each 5H Cp)/δ 110.2, 109.7]. The chirality of the complexes **13** is due to an element of axial chirality,[21] which most likely originates from the strong conformational distortion of the RN═C and C═C groups along their connecting C1−C2 σ-bond vector (see Figures 3 and 4 and Scheme 5). This results in formation of a pair of atropisomeric enantiomers whose interconversion is slow on the NMR time scale under the applied conditions at 300 K.

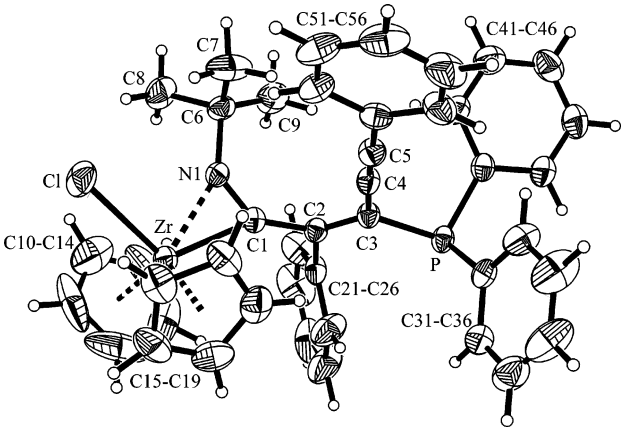


Figure 3. Molecular structure of complex **13a**. Thermal ellipsoids are drawn at the 50% probability level.

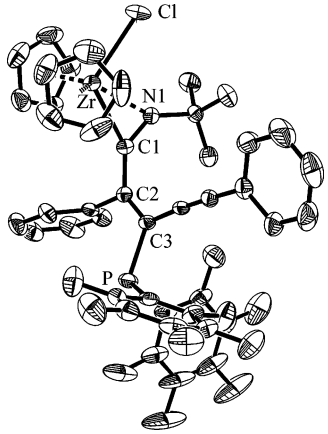
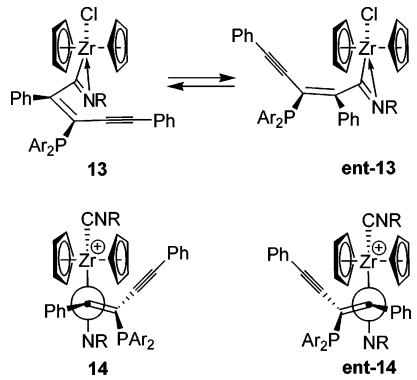


Figure 4. Projection of the structure of complex **13b** featuring the atropisomeric situation along the C1−C2 vector. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 5



This interpretation is strongly supported by the observed dynamic ^{1}H NMR spectra of the complexes **13** in d_8-toluene. Upon increasing the temperature from 300 to 355 K (at 200

(21) *Stereochemistry of Organic Compounds*; Eliel, E. L., Wilen, S. H., Mander, L. N., Eds.; Wiley: New York, 1994; Chapter 14.

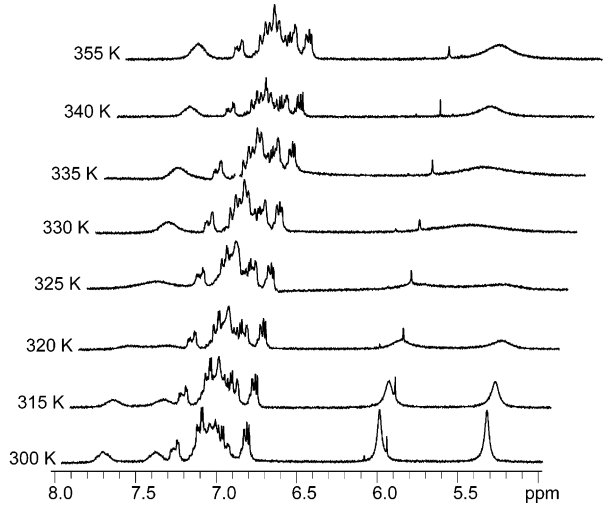


Figure 5. Temperature-dependent ^{1}H NMR spectra (200 MHz, d_8-toluene) featuring the thermally induced enantiomerization process of complex **13a**.

MHz see Figure 5), coalescence of the 1:1 intensity pair of ^{1}H NMR resonances at δ 5.98 and 5.32 to an averaged singlet of double intensity was observed. We also noticed a concurrent coalescence of a pair of phenyl resonances from the $-PPh_2$ substituent—the phenyl groups at phosphorus are also diastereotopic due to the presence of the element of axial chirality in complex **13a**. A similar ^{1}H NMR Cp coalescence behavior was observed for **13b**.

From the coalescence of the ^{1}H NMR Cp resonances we calculated an activation energy of the enantiomerization process (i.e., **13a**/**ent-13a**) of $\Delta G^{\ddagger}$(327 K) = 14.9 ± 0.3 kcal mol^{-1} and for **13b**/**ent-13b** of $\Delta G^{\ddagger}$(325 K) = 14.8 ± 0.3 kcal mol^{-1}.

Reaction of *tert*-butylisonitrile with salts **12a** and **12b** takes a similar course (see Scheme 4). The cations react with 2 mol equiv of the CN−R reagent to form **14a** and **14b**, respectively. In each case, 1 equiv of isonitrile has been inserted into the Zr−C(sp^2) bond of **12** to form the "N-inside" η^2-iminoacyl moiety [^{13}C NMR **14a** δ 216.5 ($^3J_{PC}$ = 1.6 Hz); **14b** δ 216.2 ($^3J_{PC}$ = 3.3 Hz)], the other is used to replace the coordinating THF ligand [κC−CNCMe$_3$ **14a** δ 145.9 (^{13}C); **14b** δ 145.4 (^{13}C), $\tilde{\nu}$ 2203 cm^{-1} (IR)]. The ^{13}C NMR resonances of the enyne substituent of **14a** were found at δ 161.2 ($^2J_{PC}$ = 38.2 Hz, C$_\alpha$), 113.0 ($^1J_{PC}$ = 26.1 Hz, C$_\beta$), 88.3 ($^2J_{PC}$ = 3.8 Hz, C$_\gamma$), and 100.9 (C$_\delta$) [**14b** δ 163.3 ($^2J_{PC}$ = 46.3 Hz, C$_\alpha$), 106.5 ($^1J_{PC}$ = 22.3 Hz, C$_\beta$), 85.5 ($^2J_{PC}$ = 3.9 Hz, C$_\gamma$), and 100.0 (C$_\delta$)].

The cationic η^2-iminoacyl complexes **14a** and **14b** are also chiral, again probably due to an element of axial chirality in this atropisomeric system. At low temperature in d_2-dichloromethane solution at 600 MHz complex **14b** features an equal intensity pair of ^{1}H NMR Cp signals at δ 5.98 and 5.33 (^{13}C NMR signals at δ106.9/106.4) that rapidly coalesce upon warming the sample. From the temperature-dependent ^{1}H NMR spectra a Gibbs activation energy of $\Delta G^{\ddagger}$ (293 K) = 13.4 ± 0.3 kcal mol^{-1} was calculated for the internal enantiomerization process of the cation **14b** [**14a** $\Delta G^{\ddagger}$ (288 K) = 13.1 ± 0.3 kcal mol^{-1}].

Chirality at the central moiety of the cation of **14b** implies that the $-C_6F_5$ substituents at the adjacent phosphorus center are prochiral and, consequently, diastereotopic. This is actually monitored in the ^{19}F NMR spectrum of **14b** at low temperature (see Figure 6). The ^{19}F NMR spectrum of **14b** (d_2-dichloromethane, 218 K) shows three prominent features of the [$CH_3B(C_6F_5)_3^-$] anion [δ −133.9 (o), −164.7 (p), −167.4 (m)]. The $-P(C_6F_5)_2$ moiety exhibits a double set of signals of the pairwise diastereotopic C_6F_5 substituents [δ −130.1 (o), −148.9 (p), −161.0 (m)/δ −131.9 (o), −151.3 (p), −160.7 (m)]. Increasing the monitoring temperature rapidly resulted in a pairwise coalescence of the ortho, para, and meta ^{19}F NMR signals of the $-P(C_6F_5)_2$ groups (see Figure 6), leaving the corresponding [$CH_3B(C_6F_5)_3^-$] anion ^{19}F NMR resonances unchanged.

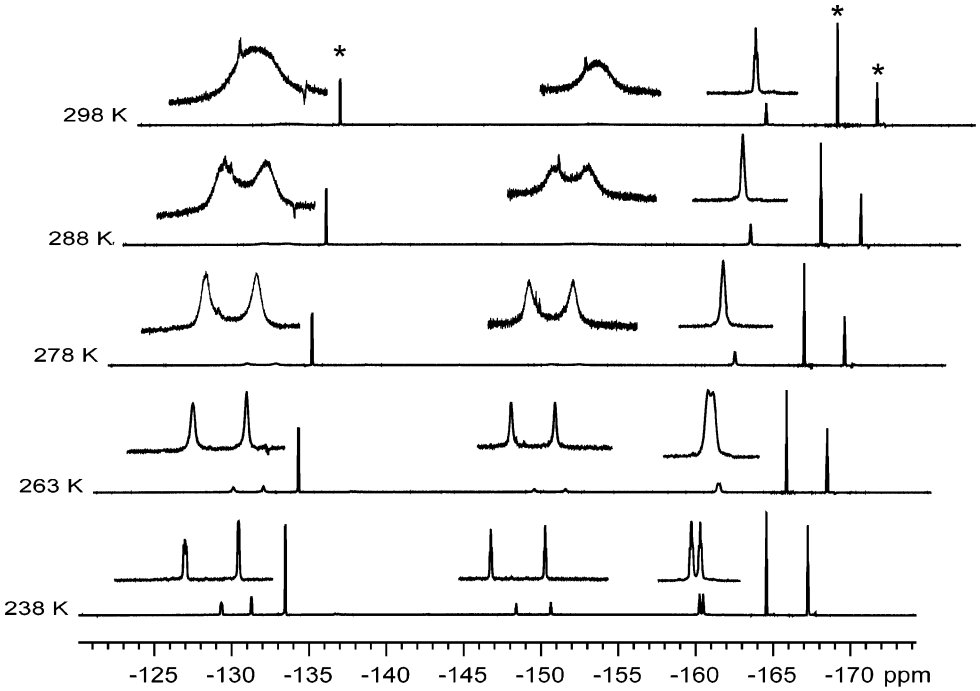


Figure 6. Temperature-dependent ^{19}F NMR spectra of the salt **14b** in d_2-dichloromethane (564 MHz) (asterisks (*) indicate largely temperature invariant signals belonging to the [$CH_3B(C_6F_5)_3^-$] anion).

Conclusions

None of the conjugated enyne Zr/P systems studied here showed any indication of a favorable ring-closure reaction to its methylenecyclopropene isomers neither upon electrophilic activation nor treatment with an organoisonitrile. This behavior of the Zr/enyne/P systems is in this respect quite contrary to that of their formally related Zr/enyne/B analogues which undergo this remarkable rearrangement readily when treated with a nitrile or an isonitrile.[4,5] It seems that the specific combination of the electrophilic group 4 metal center with the strongly Lewis acidic $-B(C_6F_5)_3$ substituent is very advantageous for this unusual intramolecular carbon−carbon coupling reaction (see Scheme 1).

The Zr/enyne/P systems investigated in this experimental study instead undergo the normal isonitrile insertion reaction into the reactive Zr−C(sp^2) σ bond to yield linearly conjugated η^2-iminoacyl zirconium complexes that bear a conjugated highly substituted enyne substituent at the electrophilic iminoacyl carbon atom. The η^2-iminoacyl moiety is found in the N-inside form at the front side of the bent metallocene wedge.

It is probably the large steric bulk of the substituents at the η^2-iminoacyl core that strongly forces the α,β-unsaturated iminoacyl system out of its usually favored planar conjugated situation into a bisected chiral atropisomeric conformation. Close inspection of the structural features of a pair of typical examples (**13**) of this class of compounds reveals that the rotational barrier is probably influenced to some degree by the combined steric bulk of all the substituents at the central C═C double bond as well as the proximal groups and substituents at the η^2-iminoacyl zirconocene core. Therefore, it is not unexpected that subtle changes of these groups have caused measurable differences in the activation barrier of the thermally induced automerization process of the respective organometallic atropisomers. Our study shows that sterically originated atropisomerism can be a major structural factor not only in purely organic systems, where it is important, e.g., in chiral ligand chemistry for asymmetric catalysis,[22] but also in the structural chemistry of organometallic systems in a more general sense.

Experimental Section

General Procedures. Reactions with organometallic compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. Compounds **7a** and **7b** were prepared analogously as described in the literature.[10]

The following instruments were used for physical characterization of the compounds. Melting points: DSC 2010 TA-instruments. Elemental analyses: Foss−Heraeus CHNO-Rapid. NMR: Bruker AC 200 P (^{1}H, 200 MHz; ^{11}B, 64 MHz; ^{31}P, 81 MHz), ARX 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz, ^{31}P, 121 MHz; ^{19}F, 282 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{31}P, 243 MHz; ^{19}F, 564 MHz). Assignments of the resonances are supported by 2D experiments and chemical shift calculations.

X-ray Crystal Structure Analyses. Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction Denzo (Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, *A59*, 228−234), and SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37. Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen: Göttingen, 1997), graphics XP (BrukerAXS, 2000).

Dynamic NMR Spectroscopy. For vt-low-temperature NMR a Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{31}P, 243 MHz; ^{19}F, 564 MHz) and for vt-high-temperature NMR a Bruker AC 200 P spectrometer (^{11}B, 64 MHz; ^{31}P, 81 MHz) were used. Activation energies were calculated from the coalescence temperature (T_c) and $\delta\nu$ of the respective resonances [$\Delta G^{\ddagger}(T_c) = RT_c(22.96 + \ln(T_c/\delta\nu))$].[23] Estimated errors (ca. 0.3 kcal mol^{-1}) were achieved from the accuracy range (ca. ±3 K) of the coalescence temperature determined from the spectra.

General Procedure for the Preparation of 9 and 11a. Complex **7a** was suspended in 100 mL of toluene and cooled to −78 °C. A solution of the respective organolithium reagent (1.1 equiv) in ether (for **11a**) or thf (for **9**) was added. The reaction mixture was stirred overnight while being allowed to warm to room temperature. Then the mixture was filtered over Celite, and the solvent was removed in vacuo until the product started to precipitate. To complete precipitation the reaction mixture was put in the freezer at −30 °C overnight. The product was isolated on a Schlenk frit, washed 3 times with 15 mL of pentane, and dried in vacuum.

Preparation of Complex 11a. A sample of 500 mg (0.78 mmol) of **7a** was treated with 0.53 mL (0.85 mmol) of a 1.6 M methyllithium solution in diethyl ether to yield 360 mg (74%) of a white solid, mp 194 °C (DSC, dec). Anal. Calcd for $C_{39}H_{33}PZr$ (623.88): C, 75.08; H, 5.33. Found: C, 74.61; H, 5.33. ^{1}H NMR (d_8-thf, 600 MHz, 298 K): δ = 7.44 (m, 4H, *o*-Ph^P); 7.31 (m, 4 H, *m*-Ph^P); 7.27 (m, 2H, *p*-Ph^P); 7.22 (m, 3H, *p*/*m*-Ph$^{C\equiv}$); 7.08 (m, 2H, *o*-Ph$^{C\equiv}$); 7.06 (m, 2H, *m*-Ph$^{C=}$); 7.01 (m, 1H, *p*-Ph$^{C=}$); 6.74 (m, 2H, *o*-Ph$^{C=}$); 6.21(s, 10H, Cp); −0.86 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (d_8-thf, 151 MHz, 298 K): δ = 226.4 (d, $^2J_{PC}$ = 17.1 Hz, Zr−C═); 140.84 (d, $^1J_{PC}$ = 17.3, *i*-Ph^P); 140.78 (d, $^3J_{PC}$ = 18.9 Hz, *i*-Ph$^{C=}$); 133.9 (d, $^2J_{PC}$ = 19.7 Hz, *o*-Ph^P); 131.7 (*o*-Ph$^{C\equiv}$); 129.0 (*m*-Ph$^{C\equiv}$); 128.6 (d, $^3J_{PC}$ = 5.9 Hz, *m*-Ph^P); 128.41 (*m*-Ph$^{C=}$); 128.37 (*p*-Ph^P); 128.1 (*p*-Ph$^{C\equiv}$); 128.0 (d, $^4J_{PC}$ = 1.7 Hz, *o*-Ph$^{C=}$); 126.4 (d, $^1J_{PC}$ = 29.0 Hz, ═C−P); 126.1 (*p*-Ph$^{C=}$); 125.2 (i-Ph$^{C\equiv}$); 110.8 (Cp); 94.4 (−C≡); 92.7 (≡C−Ph); 31.1 (CH_3). ^{31}P{^{1}H} NMR (d_8-thf, 81 MHz, 300 K): δ = −9.8 ($\nu_{1/2}$ = 2.5 Hz).

Preparation of Complex 9. A sample of 1.00 g (1.55 mmol) **7a** was treated with a solution of 78 mg (1.71 mmol) of propynyllithium in 10 mL of thf to give 560 mg (56%) of a white solid, mp 161 °C (DSC, dec). Anal. Calcd for $C_{41}H_{33}PZr$ (647.91): C, 76.01; H, 5.13. Found: C, 75.63; H, 4.89. ^{1}H NMR (d_6-benzene, 600 MHz, 298 K): δ = 7.72 (m, 4H, *o*-Ph^P); 7.21 (m, 2H, *o*-Ph$^{C\equiv}$); 7.14 (m, 6H, *m*-Ph^P, *m*-Ph$^{C=}$); 7.07 (m, 2H, *p*-Ph^P); 7.03 (m, 1H, *p*-Ph$^{C=}$); 7.02 (m, 2H, *m*-Ph$^{C\equiv}$); 6.95 (m, 1H, *p*-Ph$^{C\equiv}$); 6.87 (m, 2H, *o*-Ph$^{C=}$); 6.17 (s, 10H, Cp); 1.57 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (d_6-benzene, 151 MHz, 298 K): δ = 225.2 (d, $^2J_{PC}$ = 17.4 Hz, Zr−C═); 140.5 (d, $^1J_{PC}$ = 17.2 Hz, *i*-Ph^P); 137.5 (d, $^3J_{PC}$ = 18.5 Hz, *i*-Ph$^{C=}$); 133.8 (d, $^2J_{PC}$ = 19.5 Hz, *o*-Ph^P); 131.3 (*o*-Ph$^{C\equiv}$); 128.9 (d, $^4J_{PC}$ = 1.3 Hz, *o*-Ph$^{C=}$); 128.7 (*m*-Ph$^{C\equiv}$); 128.4 (d, $^3J_{PC}$ = 5.9 Hz, *m*-Ph^P); 128.3 (*p*-Ph^P); 128.2 (*m*-Ph$^{C=}$); 128.0, 118.8 (Zr−C≡C); 127.8 (*p*-Ph$^{C\equiv}$); 127.1 (*p*-Ph$^{C=}$); 127.0 (d, $^1J_{PC}$ = 29.3 Hz, ═C−P); 124.8 (*i*-Ph$^{C\equiv}$); 110.1 (Cp); 94.4 (−C≡); 92.9 (≡C−Ph); 6.3 (CH_3). ^{31}P{^{1}H} NMR (d_6-benzene, 81 MHz, 300K): δ = −8.3 ($\nu_{1/2}$ = 2.0 Hz). IR (KBr): $\tilde{\nu}$ = 2095 (m,$\nu_{C\equiv C}$).

X-ray Crystal Structure Analysis of 9. Formula $C_{41}H_{33}PZr$, M_w = 647.86, light yellow crystal 0.45 × 0.30 × 0.15 mm, a = 8.291(1) Å, b = 25.129(1) Å, c = 15.434(1) Å, β = 92.97(1)°, V = 3211.3(5) Å^3, ρ_{calcd} = 1.340 g cm^{-3}, μ = 0.420 mm^{-1}, empirical absorption correction (0.834 ≤ T ≤ 0.940), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 22 545 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 7862 independent (R_{int} = 0.035) and 6509 observed reflections [$I \geq 2\sigma(I)$], 389 refined parameters, R = 0.036, wR^2 = 0.092, max

(22) *Catalytic Asymmetric Synthesis*; Ojima, E., Ed.; Wiley, VCH: New York, 1993.

(23) *NMR Spektroskopie*; Günther, H., Ed.; Thieme: Stuttgart, 1992.

residual electron density 0.32 (−0.65) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Preparation of Complex 10. Brompentafluorbenzene (0.45 mL, 889 mg, 3.6 mmol) was dissolved in 80 mL of toluene and cooled to −78 °C. A 2.25 mL (3.6 mmol) amount of 1.6 M *n*-butyllithium solution in hexane was added, and the reaction mixture was stirred for 5 min at −78 °C **(Caution: LiC_6F_5 is a potentially explosive reagent)**. A solution of 1.01 g (1.8 mmol) of **7b** in 40 mL of toluene was added at −78 °C, and the mixture was stirred for 1 h at ambient temperature. The mixture was filtered over Celite, and the filtrate was evaporated to dryness in the oil-pump vacuum. The residue was suspended in 15 mL of pentane, isolated on a Schlenk frit, and dried in vacuo to yield 632 mg (43%) of a white solid, mp 229.1 °C (DSC). Anal. Calcd for $C_{38}H_{20}ClF_{10}PZr$ (824.2): C, 55.38; H, 2.45. Found: C, 55.42; H, 2.24. ^{1}H NMR (d_8-thf, 600 MHz, 253 K): δ = 7.37 (m, 3H, *m*,*p*-Ph$^{C\equiv}$); 7.32 (m, 2H, *o*-Ph$^{C\equiv}$); 7.14 (m, 2H, *m*-Ph$^{C=}$); 7.10 (m, 1H, *p*-Ph$^{C=}$); 6.93 (m, 2H, *o*-Ph$^{C=}$); 6.49 (s, 10H, Cp). ^{13}C NMR (d_8-thf, 151 MHz, 253 K): δ = 227.7 (d, $^2J_{PC}$ = 20 Hz, Zr−C═); 148.1 (d, $^1J_{FC}$ = 243 Hz, *m*-C_6F_5); 144.2 (d, $^3J_{PC}$ = 22.2 Hz, *i*-Ph$^{C=}$); 142.6 (d, $^1J_{FC}$ = 253, *p*-C_6F_5); 138.1 (d, $^1J_{FC}$ = 247 Hz, *o*-C_6F_5); 131.5 (*o*-Ph$^{C\equiv}$); 129.5 (*m*-Ph$^{C\equiv}$); 129.3 (*p*-Ph$^{C\equiv}$); 128.9 (*m*-Ph$^{C=}$); 127.4 (*o*-Ph$^{C=}$); 127.2 (*p*-Ph$^{C=}$); 123.7 (*i*-Ph$^{C\equiv}$); 120.3 (d, $^1J_{PC}$ = 25.6 Hz, ═C−P); 113.8 (Cp); 93.3 (≡C−Ph); 91.3 (−C≡); n.o. (*i*-C_6F_5). ^{19}F NMR (d_8-thf, 470 MHz, 298 K): δ = −131.0 (*o*-C_6F_5); −153.9 (*p*-C_6F_5); −163.5 (*m*-C_6F_5). ^{31}P{^{1}H} NMR (d_8-thf, 202 MHz, 298 K): δ = −48.5 (quin, $^3J_{PF}$ = 28 Hz). ^{31}P{^{1}H,^{19}F} NMR (d_8-thf, 202 MHz, 298K): δ = −48.5 (s, $\nu_{1/2}$ = 1.5 Hz).

X-ray Crystal Structure Analysis of 10. Formula $C_{38}H_{20}ClF_{10}PZr\cdot 1/2C_4H_8O$, M_w = 860.23, light yellow crystal 0.30 × 0.20 × 0.05 mm, a = 21.386(1) Å, b = 10.982(1) Å, c = 30.684(1) Å, β = 95.67(1)°, V = 7171.2(8) Å^3, ρ_{calcd} = 1.594 g cm^{-3}, μ= 0.508 mm^{-1}, empirical absorption correction (0.862 ≤ T ≤ 0.975), Z = 8, monoclinic, space group *C*2/*c* (No. 15), λ = 0.71073 Å, T = 198 K, ω and φ scans, 30 924 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.62 Å^{-1}, 7053 independent (R_{int} = 0.061) and 4938 observed reflections [$I \geq 2\sigma(I)$], 483 refined parameters, R = 0.049, wR^2 = 0.102, max residual electron density 0.44 (−0.36) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Preparation of Complex 11b. A sample of 600 mg (0.7 mmol) of **10** was dissolved in 20 mL of thf and cooled to −78 °C. A 2.5 mL (1.3 equiv, 21 mg) amount of a methyllithium solution in thf (c = 84 mg/10 mg) [solution was prepared from solid methyllithium stored in a glove box; solid methyllithium was obtained from commercially available 1.6 M methyllithium solution by removing the solvent in the oil-pump vacuum] was added at −78 °C. The mixture was stirred for 2 h at ambient temperature, the solvent was removed in vacuo, and the residue was dissolved in 30 mL of toluene. After filtration over Celite the filtrate was brought to dryness; the residue was suspended in 15 mL of pentane and isolated on a Schlenk frit. After drying in the oil-pump vacuum 337 mg (57%) of a white solid could be obtained, mp 150 °C (DSC). Anal. Calcd for $C_{39}H_{23}F_{10}PZr$ (803.79): C, 58.28; H, 2.88. Found: C, 57.75; H, 2.85. ^{1}H NMR (d_8-thf, 600 MHz, 298 K): δ = 7.34 (m, 3H, *m*,*p*-Ph$^{C\equiv}$); 7.30 (m, 2H, *o*-Ph$^{C\equiv}$); 7.12 (m, 2H, *m*-Ph$^{C=}$); 7.05 (m, 1H, *p*-Ph$^{C=}$); 6.77 (m, 2H, *o*-Ph$^{C=}$); 6.25 (s, 10H, Cp); −0.78 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (d_8-thf, 151 MHz, 298 K): δ = 230.6 (d, $^2J_{PC}$ = 18.6 Hz, Zr−C═); 148.3 (d, $^1J_{FC}$ = 248 Hz, *m*-C_6F_5); 142.6 (d, $^1J_{FC}$ = 254, *p*-C_6F_5); 141.2 (d, $^3J_{PC}$ = 22.9 Hz, *i*-Ph$^{C=}$); 138.2 (d, $^1J_{FC}$ = 251 Hz, *o*-C_6F_5); 131.5 (*o*-Ph$^{C\equiv}$); 129.4 (*m*-Ph$^{C\equiv}$); 129.0 (*p*-Ph$^{C\equiv}$); 128.9 (*m*-Ph$^{C=}$); 127.0 (d, $^3J_{PC}$ = 1.9 Hz, *o*-Ph$^{C=}$); 126.8 (*p*-Ph$^{C=}$); 124.2 (*i*-Ph$^{C\equiv}$); 118.1 (d, $^1J_{PC}$ = 27.5 Hz, ═C−P); 111.2 (Cp); 92.1 (≡C−Ph); 91.6 (−C≡); 33.0 (CH_3); n.o. (*i*-C_6F_5). ^{19}F NMR (d_8-thf, 564 MHz, 298 K): δ = −131.1 (*o*-C_6F_5); −154.0 (*p*-C_6F_5); −163.5 (*m*-C_6F_5). ^{31}P{^{1}H}NMR (d_6-benzene, 81 MHz, 300 K): δ = −48.8 (quin, $^3J_{PF}$ = 27 Hz).

General Procedure for Generation of Cations 12a and 12b. The respective neutral methylzirconium complexes (**11a**/**11b**) and tris(pentafluorophenyl)borane (1 equiv) were dissolved in 0.8 mL of d_8-thf, and the resulting cationic products were characterized by NMR spectroscopy.

Generation of Salt 12a. Reaction of 50 mg (0.08 mmol) of **11a** with 41 mg (0.08 mmol) of tris(pentafluorophenyl)borane gave a yellow solution. ^{1}H NMR (d_8-thf, 600 MHz, 298 K): δ = 7.49−7.39 (m, 7H, *p*-Ph$^{C=}$, *p*,*o*-Ph^{P}); 7.37−7.32 (m, 6H, *m*-Ph$^{C=}$, *m*-Ph^{P}); 7.28−7.22 (m, 5H, *p*,*m*-Ph$^{C\equiv}$, *o*-Ph$^{C=}$); 7.08 (m, 2H, *o*-Ph$^{C\equiv}$); 6.68 (s, 10H, Cp); 0.54 (br s, 3H, Me−B). ^{13}C{^{1}H} NMR (d_8-thf, 151 MHz, 298 K): δ = 218.2 (d, $^2J_{PC}$ = 19.6 Hz, Zr−C═); 149.2 (dm, $^1J_{FC}$ = 239 Hz, BC_6F_5); 139.4 (d, $^1J_{PC}$ = 15.7 Hz, *i*-Ph^{P}); 138.2 (dm, $^1J_{FC}$ = 244 Hz, BC_6F_5); 137.1 (dm, $^1J_{FC}$ = 248 Hz, BC_6F_5); 134.0 (d, $^3J_{PC}$ = 19.9 Hz, *o*-Ph^{P}); 133.6 (d, $^1J_{PC}$ = 18.2 Hz, *i*-Ph$^{C=}$); 132.8 (d, $^1J_{PC}$ = 30.3 Hz, ═C−P); 131.8 (*o*-Ph$^{C\equiv}$); 131.6 (d, $^4J_{PC}$ = 1.6 Hz, *o*-Ph$^{C=}$); 130.32 (*p*-Ph^{P}); 130.31(*p*-Ph$^{C=}$); 129.18, 129.15 (*m*-Ph$^{C\equiv}$, *m*-Ph$^{C=}$); 129.11 (*p*-Ph$^{C\equiv}$), 129.0 (d, $^3J_{PC}$ = 6.4 Hz, *m*-Ph^{P}); 123.9 (*i*-Ph$^{C\equiv}$); 114.5 (Cp); 96.6 (≡C−Ph); 92.9 (−C≡); 10.7 (br, Me−B). ^{19}F NMR (d_8-thf, 564 MHz, 300 K): δ = −132.8 (2F, *o*-BC_6F_5); −166.8 (1F, *p*-BC_6F_5); −168.9 (2F, *m*-BC_6F_5). ^{31}P{^{1}H} NMR (d_8-thf, 81 MHz, 300 K): δ = −3.3 ($\nu_{1/2}$ = 2.9 Hz) ^{11}B{^{1}H} NMR (d_8-thf, 96 MHz, 300 K): δ = −14.8 ($\nu_{1/2}$ = 43 Hz).

Generation of Salt 12b. Treatment of 50 mg (0.06 mmol) of **11b** with 31.8 mg (0.06 mmol) of tris(pentafluorophenyl)borane gave a yellow solution. ^{1}H NMR (d_8-thf, 600 MHz, 298 K): δ = 7.53 (m, 2H, *m*-Ph$^{C=}$); 7.47 (m, 1H, *p*-Ph$^{C=}$); 7.38 (m, 3H, *m*,*p*-Ph$^{C\equiv}$); 7.32 (m, 2H, *o*-Ph$^{C\equiv}$); 7.30 (m, 2H, *o*-Ph$^{C=}$); 6.72 (s, 10H, Cp); 0.51 (br s, 3H, Me−B). ^{13}C{^{1}H} NMR (d_8-thf, 151 MHz, 298 K): δ = 221.0 (Zr−C═); 149.1 (dm, $^1J_{FC}$ = 238 Hz, BC_6F_5); 148.2 (dm, $^1J_{FC}$ = 247 Hz, PC_6F_5); 142.9 (dm, $^1J_{FC}$ = 258 Hz, *p*-PC_6F_5); 138.2 (dm, PC_6F_5, *p*-BC_6F_5); 136.9 (dm, $^1J_{FC}$ = 248 Hz, BC_6F_5); 134.7 (*i*-Ph$^{C=}$); 131.5 (*o*-Ph$^{C\equiv}$); 130.8 (br, *p*,*m*-Ph$^{C=}$); 130.1 (*o*-Ph$^{C=}$); 129.6 (*m*-Ph$^{C\equiv}$); 129.5 (*p*-Ph$^{C\equiv}$); 122.6 (*i*-Ph$^{C\equiv}$); 114.8 (Cp); 109.6 (br, *i*-C_6F_5−P); 95.6 (≡C−Ph); 89.9 (−C≡); 10.9 (Me−B); n.o. (═C−P, *i*-C_6F_5); [each broad; assignment by 2D NMR experiments]. ^{19}F NMR (d_8-thf, 564 MHz, 398 K): δ = −129.2 (4F, *o*-PC_6F_5); −131.0 (6F, *o*-BC_6F_5); −150.7 (2F, *p*-PC_6F_5); −160.9 (4F, *m*-PC_6F_5); −165.0 (3F, *p*-BC_6F_5); −167.1 (6F, *m*-BC_6F_5). ^{31}P{^{1}H} NMR (d_8-thf, 122 MHz, 300K): δ = −43.8 (quin, $^3J_{PF}$ = 28 Hz). ^{11}B{^{1}H} NMR (d_8-thf, 96 MHz, 300 K): δ = −14.8 ($\nu_{1/2}$ = 250 Hz).

General Procedure for Preparation of Complexes 13a and 13b. The respective chlorozirconocene (**7a**/**10**) complex was dissolved/suspended in 100 mL of toluene. At ambient temperature a solution of *tert*-butylisonitrile (ca. 1.1 equiv) in 1 mL of toluene was added. The solution was stirred for 2 h at room temperature. The solvent was removed in vacuo, and the residue was suspended in 15 mL of pentane, isolated on a Schlenk frit, and dried in the oil-pump vacuum.

Preparation of Complex 13a. Reaction of 500 mg (0.78 mmol) of **7a** and 77 mg (0.92 mmol) of *tert*-butylisonitrile gave 490 mg (86%) of a yellow solid, mp 187.3 °C (DSC). Anal. Calcd for $C_{43}H_{39}ClNPZr$ (727.43): C, 71.00; H, 5.40; N, 1.93. Found: C, 70.54; H, 5.06; N, 1.87. ^{1}H NMR (d_2-dichloromethane, 600 MHz, 258 K): δ = 7.66 (m, 2H, *o*-Ph^{P}); 7.50 (m, 3H, *p*,*m*-Ph$^{C=}$); 7.44 (m, 2H, *m*-Ph^{P}), 7.43 (m, 1H, *p*-Ph^{P}); 7.33 (m, 1H, *p*-Ph$^{P'}$); 7.32 (m, 4H, *o*-Ph$^{C=}$, *m*-Ph$^{P'}$); 7.28 (m, 2H, *o*-Ph$^{P'}$); 7.23 (m, 1H, *p*-Ph$^{C\equiv}$); 7.19 (m, 2H, *m*-Ph$^{C\equiv}$); 6.90 (m, 2H, *o*-Ph$^{C\equiv}$); 6.02 (s, 5H, Cp); 5.41 (s, 5H, Cp′); 1.49 (s, 9H, *t*-Bu). ^{13}C NMR (d_2-dichloromethane, 151 MHz, 258 K): δ = 223.4 (d, $^3J_{PC}$ = 2.0 Hz, Zr−C═); 163.9 (d, $^2J_{PC}$ = 37.7 Hz, ═C−); 137.6 (d, J_{PC} = 11.6 Hz, *i*-Ph$^{P'}$); 136.9 (d, J_{PC} = 12.7 Hz, *i*-Ph^{P}); 136.0 (d, J_{PC} = 9.0 Hz, *i*-Ph$^{C=}$); 133.3 (d, $^2J_{PC}$ = 20.8 Hz, *o*-Ph$^{P'}$); 133.2 (d, $^2J_{PC}$ = 18.8 Hz, *o*-Ph^{P}); 131.1 (*o*-Ph$^{C\equiv}$); 129.4 (br, *o*-Ph$^{C=}$), 129.2 (*p*-Ph$^{C=}$); 128.9 (*p*-Ph^{P}); 128.8 (d, $^3J_{PC}$ = 6.3 Hz, *m*-Ph^{P}); 128.7 (*m*-

$Ph^{C=}$); 128.71 (*p*-$Ph^{P'}$); 128.5 (*p*-$Ph^{C\equiv}$); 128.4 (*m*-$Ph^{C\equiv}$); 128.3 (d, $^3J_{PC}$ = 6.3 Hz, *m*-$Ph^{P'}$); 122.7 (*i*-$Ph^{C\equiv}$); 110.2 (d, $^1J_{PC}$ = 24.1 Hz, =C−P); 110.1 (Cp); 109.5 (Cp′); 100.0 (≡C−Ph); 89.7 (d, $^2J_{PC}$ = 4.0 Hz, −C≡); 64.4, 28.2 (^{t}Bu) (tentative relative assignments for =C−, =C−P). ^{31}P NMR (d_6-benzene, 243 MHz, 300 K): δ = −7.5 ($\nu_{1/2}$ = 3.5 Hz). High-temperature NMR: ^{1}H NMR (d_8-toluene, 200 MHz) coalescence of the Cp resonances, T_c = 327 K, $\delta\nu$(300 K) = 134 Hz, $\Delta G^{\ddagger}$ = 14.9 ± 0.3 kcal/mol.

X-ray Crystal Structure Analysis of 13a. Formula $C_{43}H_{39}ClNPZr\cdot0.5C_7H_8$, M_w = 773.46, yellow crystal 0.45 × 0.30 × 0.15 mm, a = 8.412(1) Å, b = 11.119(1) Å, c = 22.698(1) Å, α = 81.52(1)°, β = 79.70(1)°, γ = 71.34(1)°, V = 1969.7(3) Å^3, ρ_{calcd} = 1.304 g cm^{-3}, μ = 0.420 mm^{-1}, empirical absorption correction (0.833 ≤ T ≤ 0.940), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 20 218 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 9348 independent (R_{int} = 0.044) and 8218 observed reflections [$I \geq 2\sigma$ ($\boldsymbol{I}$)], 463 refined parameters, R = 0.038, wR^2 = 0.103, max residual electron density 0.77 (−0.71) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Preparation of Complex 13b. Reaction of 500 mg (0.61 mmol) of **10** and 120 mg (1.4 mmol) of *tert*-butylisonitrile gave 431 mg (78%) of a yellow solid, mp 199 °C (DSC). Anal. Calcd for $C_{43}H_{29}ClF_{10}NPZr$ (907.34): C, 56.92; H, 3.22; N, 1.54. Found: C, 57.02; H, 3.23; N, 1.59. ^{1}H NMR (d_2-dichloromethane, 600 MHz, 258 K): δ = 7.56 (m, 3H, *m*,*p*-$Ph^{C=}$); 7.36 (br, 2H, *o*-$Ph^{C=}$); 7.30 (m, 3H, *m*,*p*-$Ph^{C=}$); 7.18 (m, 2H, *o*-$Ph^{C=}$); 6.06 (s, 5H, Cp); 5.43 (s, 5H, Cp′); 1.44 (s, 9H, *t*-Bu). ^{13}C NMR (d_2-dichloromethane, 150.8 MHz, 258 K): δ = 222.8 (d, $^3J_{PC}$ = 2.9 Hz, Zr−C=); 166.0 (d, $^2J_{PC}$ = 45.7 Hz, =C−); 147.7 (dm, $^1J_{FC}$ = 254.0 Hz), 146.8 (dm, $^1J_{FC}$ = 248 Hz) (C_6F_5); 142.4 (dm, $^1J_{FC}$ = 257 Hz), 141.8 (dm, $^1J_{FC}$ = 260 Hz) (*p*-C_6F_5); 137.4 (dm, $^1J_{FC}$ = 258 Hz, 2 × C_6F_5); 135.2 (d, $^3J_{PC}$ = 11.9 Hz, *i*-$Ph^{C=}$); 131.0 (*o*-$Ph^{C=}$); 130.1 (*p*-$Ph^{C=}$) 129.4 (*m*-$Ph^{C=}$); 129.2 (*p*-$Ph^{C\equiv}$); 128.9 (br, *o*-$Ph^{C=}$); 128.8 (*m*-$Ph^{C\equiv}$); 121.9 (*i*-$Ph^{C\equiv}$); 110.2 (Cp); 109.7 (Cp′); 108.2 (br, *i*-C_6F_5); 103.4 (d, $^1J_{PC}$ =18 Hz, =C−P); 99.1 (≡C−Ph); 86.9 (d, $^2J_{PC}$ = 4.5 Hz, −C≡); 64.7, 27.9 (^{t}Bu) (tentative relative assignments for =C−, =C−P). ^{19}F NMR (d_2-dichloromethane, 564 MHz, 258 K): δ = −129.4 (*o*-C_6F_5); −131.2 (*o*′-C_6F_5); −149.6 (*p*-C_6F_5); −151.5 (*p*′-C_6F_5); −160.8 (*m*-C_6F_5); −161.1 (*m*′-C_6F_5). ^{31}P{^{1}H} NMR (d_2-dichloromethane, 122 MHz, 300 K): δ = −41.9 (tt, each $^3J_{PF}$ = 20 Hz). High-temperature NMR: ^{1}H NMR (d_8-toluene, 200 MHz) coalescence of the Cp resonances, T_c = 325 K, $\delta\nu$(300 K) = 131 Hz, $\Delta G^{\ddagger}$ = 14.8 ± 0.3 kcal/mol.

X-ray Crystal Structure Analysis of 13b. Formula $C_{43}H_{29}ClF_{10}NPZr$, M_w = 907.31, yellow crystal 0.25 × 0.15 × 0.06 mm, a = 12.5348(2) Å, b = 17.3494(3) Å, c = 18.2500(3) Å, β = 103.452(1)°, V = 3859.96(11) Å^3, ρ_{calcd} = 1.561 g cm^{-3}, μ = 0.477 mm^{-1}, empirical absorption correction (0.890 ≤ T ≤ 0.972), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 26 540 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 9094 independent (R_{int} = 0.086) and 4445 observed reflections [$I \geq 2\sigma$ (I)], 517 refined parameters, R = 0.066, wR^2 = 0.135, max residual electron density 0.74 (−0.95) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Preparation of Salt 14a. A mixture of 173 mg (0.28 mmol) of **11a** and 142 mg (0.28 mmol) of tris(pentafluorophenyl)borane was dissolved in 5 mL of thf. The yellow solution was stirred for 1 min at room temperature; then a solution of 60 mg (0.72 mmol) of *tert*-butylisonitrile in 1 mL of thf was added, and the resulting yellow solution was stirred for 30 min at room temperature. The solvent was removed in vacuo, and the residue was dissolved in 2 mL of toluene. Pentane (1−2 mL) was added, and the product was deposited as a red oil. The supernatant liquid was removed via syringe; then the product was again dissolved in 1.5 mL of diethyl ether and precipitated by adding 1 mL of pentane. The overlaying solution was removed via syringe, and the product was dried in vacuum to yield 162 mg (44%) of a pale brown/yellow solid, mp 64 °C (DSC). Anal. Calcd for $C_{67}H_{51}BF_{15}N_2PZr$ (1302.14): C, 61.80; H, 3.95; N, 2.15. Found: C, 61.46; H, 3.84; N, 2.26. ^{1}H NMR (d_2-dichloromethane, 600 MHz, 218 K): δ = 7.66 (m, 2H, *o*-Ph^{P}); 7.54, 7.52 (m, 3H, *p*,*m*-$Ph^{C=}$); n.o. (*o*-$Ph^{C=}$); 7.49 (m, 2H, *m*-Ph^{P}); 7.47 (m, 1H, *p*-Ph^{P}); 7.35 (m, 1H, *p*-$Ph^{P'}$); 7.30 (m, 2H, *m*-$Ph^{P'}$); 7.24 (m, 1H, *p*-$Ph^{C=}$); 7.20 (m, 2H, *o*-$Ph^{P'}$); 7.18 (m, 2H, *m*-$Ph^{C=}$); 6.82 (m, 2H, *o*-$Ph^{C=}$); 5.93 (s, 5H, Cp); 5.32 (s, 5H, Cp′); 1.63 (s, 9H, ^{t}$Bu^{N\equiv C}$); 1.33 (s, 9H, (^{t}$Bu^{N=C}$); 0.41 (br, 3H, Me−B). ^{13}C{^{1}H} NMR (d_2-dichloromethane, 151 MHz, 218 K): δ = 216.5 (d, $^3J_{PC}$ = 1.6 Hz, Zr−C=); 161.2 (d, $^2J_{PC}$ = 38.2 Hz, =C); 147.7 (dm, $^1J_{FC}$ = 235 Hz, C_6F_5); 145.9 (C≡N); 137.0 (dm, $^1J_{FC}$ = 239 Hz, *p*-C_6F_5); 136.6 (d, $^1J_{PC}$ = 10.9 Hz, *i*-$Ph^{P'}$); 135.9 (dm, $^1J_{FC}$ = 242 Hz, C_6F_5); 135.5 (d, $^1J_{PC}$ = 11.8 Hz, *i*-Ph^{P}); 133.9 (d, J_{PC} = 9.0 Hz, *i*-$Ph^{C=}$); 133.1 (d, $^2J_{PC}$ = 20.2 Hz, *o*-$Ph^{P'}$); 132.7 (d, $^2J_{PC}$ = 19.2 Hz, *o*-Ph^{P}); 130.7 (*o*-$Ph^{C\equiv}$); 129.8 (*p*-$Ph^{C=}$); 129.0 (*p*-Ph^{P}); 128.9 (*m*-$Ph^{C=}$); 128.7 (*p*-$Ph^{P'}$); 128.7 (d, $^3J_{PC}$ = 7.0 Hz, *m*-Ph^{P}); 128.7 (*p*-$Ph^{C=}$); 128.3 (*m*-$Ph^{C=}$); 128.2 (br, *i*-C_6F_5); 128.1 (d, $^3J_{PC}$ = 6.6 Hz, *m*-$Ph^{P'}$); 121.5 (*i*-$Ph^{C=}$); 113.0 (d, $^1J_{PC}$ = 26.1 Hz, =C−P); 106.7 (Cp); 106.1 (Cp′); 100.9 (≡C−Ph); 88.3 (d, $^2J_{PC}$ = 3.8 Hz, −C≡); 60.2, 29.0 (^{t}$Bu^{C=N}$); 63.0, 27.2 (^{t}$Bu^{C=N}$); 9.6 (br, Me−B); n.o. (*o*-$Ph^{C=}$) (tentative relative assignments for =C−, =C−P). ^{31}P{^{1}H} NMR (d_2-dichloromethane, 122 MHz, 300 K): δ = −6.6 ($\nu_{1/2}$ = 11 Hz). ^{19}F NMR (d_2-dichloromethane, 564 MHz, 218 K): δ = −133.5 (*o*-C_6F_5); −164.2 (*p*-C_6F_5); 166.9 (*m*-C_6F_5). ^{11}B{^{1}H} NMR (d_2-dichloromethane, 96 MHz, 300 K): δ = −15.0 ($\nu_{1/2}$ = 31 Hz). IR (KBr): $\tilde{\nu}$ = 2202 (ν_{CN}). Low-temperature NMR: ^{1}H NMR (d_2- dichloromethane, 600 MHz) coalescence of the Cp resonances, T_c = 288 K, $\delta\nu$(218 K) = 361 Hz, $\Delta G^{\ddagger}$ = 13.1 ± 0.3 kcal/mol.

Preparation of Salt 14b. A 150 mg (0.19 mmol) amount of **11b** and 95.5 mg (0.19 mmol) of tris(pentafluorophenyl)borane were dissolved in 2 mL of toluene. The resulting deep red solution was stirred for 1 min at room temperature; then a solution of 33 mg (0.40 mmol) of *tert*-butylisonitrile in 1 mL of toluene was added, and the resulting yellow solution was stirred for 30 min at room temperature. Pentane (1 mL) was added, and the product was deposited as a red oil. The overlaying solution was removed with a syringe. The product was again dissolved in 1.5 mL of diethyl ether and precipitated by adding 1 mL of pentane. The overlaying solution was removed via syringe, and the product was dried in vacuum to yield 96 mg (0.06 mmol, 34%) of a pale brown/yellow solid, mp 154 °C (DSC, decom.). Anal. Calcd for $C_{67}H_{41}BF_{25}N_2PZr$ (1482.04): C, 54.30; H, 2.79; N, 1.89. Found: C, 54.19; H, 2.65; N, 1.67. ^{1}H NMR (d_2-dichloromethane, 600 MHz, 218 K): δ = 7.59, 7.06 (br m, 5H, *o*,*m*,*p*-$Ph^{C=}$); 7.32 (m, 1H, *p*-$Ph^{C\equiv}$); 7.28 (m, 2H, *m*-$Ph^{C\equiv}$); 7.15 (m, 2H, *o*-$Ph^{C\equiv}$); 5.98 (s, 5H, Cp); 5.33 (s, 5H, Cp′); 1.63 (s, 9H, ^{t}$Bu^{N\equiv C}$); 1.31 (s, 9H, ^{t}$Bu^{N=C}$); 0.45 (s, 3H, Me−B). ^{13}C{^{1}H} NMR (d_2-dichloromethane, 151 MHz, 218 K): δ = 216.2 (d, $^3J_{PC}$ = 3.3 Hz, Zr−C=); 163.3 (d, $^2J_{PC}$ = 46.3 Hz, =C−); 147.8 (dm, $^1J_{FC}$ = 240 Hz), 136.1 (dm, $^1J_{FC}$ = 246 Hz) (*o*,*m*-B−C_6F_5); 147.4 (dm, $^1J_{FC}$ = 248 Hz), 146.3 (dm, $^1J_{FC}$ = 248 Hz), 142.4 (dm, $^1J_{FC}$ = 255 Hz, *p*), 141.6 (dm, $^1J_{FC}$ = 255 Hz, *p*) (P−C_6F_5); 145.4 (C≡N); 137.4 (dm, $^1J_{FC}$ = 252 Hz), 2 × 137.1 (dm, $^1J_{FC}$ = 245 Hz) (C_6F_5); 133.3 (d, $^3J_{PC}$ = 11.4 Hz, *i*-$Ph^{C=}$); 130.7 (*o*-$Ph^{C=}$); 130.6, 129.5 (each br, $Ph^{C=}$); 129.4 (*p*-$Ph^{C=}$); 128.6 (*m*-$Ph^{C\equiv}$); 128.2 (br, *i*-B−C_6F_5); 120.8 (*i*-$Ph^{C=}$); 107.4 (br, *i*-C_6F_5−P); 106.9 (Cp); 106.5 (d, $^1J_{PC}$ = 22.3 Hz, =C−P); 106.4 (Cp′); 100.0 (≡C−Ph); 85.5 (d, $^2J_{PC}$ = 3.9 Hz, −C≡); 63.3, 27.0 (^{t}$Bu^{N\equiv C}$); 60.3, 29.0 (^{t}$Bu^{N\equiv C}$); 9.6 (br, Me−B); (tentative relative assignments for =C−, =C−P). ^{31}P{^{1}H} NMR (d_2-dichloromethane, 243 MHz, 300 K): δ = −42.7 (quin, $^3J_{PF}$ = 28 Hz). ^{19}F NMR (d_2-dichloromethane, 564 MHz, 218 K): δ = −130.1 (2F, *o*), −148.9 (1F, *p*), −161.0 (2F, *m*) (each m, P−C_6F_5); −131.9 (2F, *o*), −151.4 (1F, *p*), −160.7 (2F, *m*) (each m, P−C_6F_5); −133.9 (6F, *o*), −164.7 (3F, *p*), −167.4 (6F, *m*) (each m, B−C_6F_5). ^{11}B-{^{1}H} NMR (d_2-dichloromethane, 96 MHz, 300 K): δ = −15.0

($\nu_{1/2}$ = 30 Hz). IR (KBr): $\tilde{\nu}$ = 2204 (ν_{CN}). Low-temperature NMR: ^{1}H NMR (d_2- dichloromethane, 600 MHz) coalescence of the Cp resonances, T_c = 293 K, $\delta\nu$(218 K) = 386 Hz, $\Delta G^{\ddagger}$ = 13.4 ± 0.3 kcal/mol; ^{19}F NMR (d_2- dichloromethane, 564 MHz) coalescence of the *p*-$C_6F_5^P$ resonances, T_c = 298 K, $\delta\nu$(238 K) = 1263 Hz, $\Delta G^{\ddagger}$ = 13.6 kcal/mol.

Acknowledgment. Dedicated to Professor Herbert Mayr on the occasion of his 60th birthday. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank BASF for a generous gift of solvents.

Supporting Information Available: CIF files giving X-ray crystal data for the compounds reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7005968