Internally Phosphine-Stabilized Zirconocene Cations Employing Substituted ((Diarylphosphino)methyl)cyclopentadienyl Ligand Systems

Boris E. Bosch, Gerhard Erker,* Roland Fröhlich, and Oliver Meyer

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

The dimethylzirconocene complex [(Cp−CMe$_2$−PAr$_2$)$_2$ZrMe$_2$], **2a** (Ar = *p*-tolyl), was treated with 1 molar equiv of B(C$_6$F$_5$)$_3$ to yield the salt [(Cp−CMe$_2$−PAr$_2$)$_2$ZrMe$^+$MeB(C$_6$F$_5$)$_3^-$], **3a**. The X-ray crystal structure analysis of **3a** shows that both −PAr$_2$ units are intramolecularly coordinated to zirconium in a close to C_2-symmetric arrangement with the [Zr]−CH$_3$ group placed in the central position in the bent metallocene σ-ligand plane. Treatment of **2a** with 2 equiv of B(C$_6$F$_5$)$_3$ generates the highly reactive dication system [(Cp−CMe$_2$−PAr$_2$)$_2$Zr^{2+}] (**4** with two MeB(C$_6$F$_5$)$_3^-$ anions). The highly electrophilic cation **4** abstracts chloride from, e.g., dichloromethane solvent to yield [(Cp−CMe$_2$−PAr$_2$)$_2$Zr-Cl$^+$] (**5**, with MeB(C$_6$F$_5$)$_3^-$ anion). The same cation (**5′**, with ClB(C$_6$F$_5$)$_3^-$ anion) was obtained from the reaction of [(Cp−CMe$_2$−PAr$_2$)$_2$ZrCl$_2$] (**1a**) with B(C$_6$F$_5$)$_3$. The C_2-symmetric, internally −PAr$_2$-stabilized dication adds acetonitrile or 2,6-dimethylphenyl isocyanide to give the respective C_2-symmetric donor-ligand adducts in which the −PAr$_2$ coordination to zirconium is retained. The complexes **3a** ($\Delta G^{\ddagger}_{enant}$ (300 K) = 14.0 ± 0.5 kcal/mol) and **5** ($\Delta G^{\ddagger}_{enant}$ (360 K) = 17.5 ± 0.5 kcal/mol) show dynamic NMR spectra due to an intramolecular enantiomerization process proceeding with a rate-determining cleavage of the Zr−P linkages. Complex **5** was also characterized by an X-ray crystal structure analysis.

Introduction

The chemistry of zirconocene cation systems has become of great interest recently. The donor-ligand-free Cp$_2$ZrR$^+$ species and especially the olefin complexes of the related modified *ansa*-metallocene cations probably serve as essential intermediates in homogeneous metallocene Ziegler catalysis.[1] Also, the donor-ligand-stabilized systems Cp$_2$ZrR(L)$^+$ or Cp$_2$ZrR(L)$_2^+$ are of importance.[2] Early examples have paved the way toward an understanding of group 4 metallocene cation chemistry related to homogeneous Ziegler catalysis,[3] and postulated single steps of catalytic cycles could be studied in detail using such stabilized metallocene cations as suitable model systems.[4] Also, the metal-

locene cation serves as an activating organometallic Lewis acid in these adducts that may lead to novel stoichiometric reactions.[5]

Donor ligands used to stabilize the Cp$_2$ZrR$^+$ moiety in these adduct systems are often nitriles or cyclic ethers.[2,3] Phosphorus-containing systems are quite rare in this metallocene cation chemistry.[6] After we had gained some experience with internal amine stabilization of alkylzirconocene cation-type systems, making use of substituted ((dimethylamino)methyl)cyclopentadienyl

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) Reviews: Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. Aulbach, M.; Küber, F. *Chem. Unserer Zeit* **1994**, *28*, 197. Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem.* **1995**, *107*, 1255; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255 and references cited in these articles.

(2) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. Jordan, R. F.; Guram, A. S. *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson G., Eds.; Pergamon: New York, 1995; Vol. 4, pp 589−625.

(3) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539. Eshuis, J. J. W.; Tan, Y. Y.; Renkema, J.; Teuben, J. H. *J. Mol. Catal.* **1990**, *62*, 277. Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268. Alelyunas, Y. W.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406. Amorose, D. M.; Lee, R. P.; Petersen, J. L. *Organometallics* **1991**, *10*, 2191. Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362.

(4) (a) Temme, B.; Karl, J.; Erker, G. *Chem. Eur. J.* **1996**, *2*, 919. Karl, J.; Erker, G. *J. Mol. Catal.*, in press. Karl, J.; Erker, G. *Chem. Ber.*, in press. (b) Pellechia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473. Pellechia, C.; Grassi, A.; Immirzi, A. *J. Am. Chem. Soc.* **1993**, *115*, 1160. Pellechia, C.; Immirzi, A.; Pappalardo, D.; Peluso, A. *Organometallics* **1994**, *13*, 3773. Pellechia, C.; Grassi, A.; Zambelli, A. *Organometallics* **1994**, *13*, 298. Immirzi, A.; Zambelli, A. *J. Organomet. Chem.* **1994**, *479*, C9. (c) Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1976**, 841. Yoshikawa, S.; Kiji, J.; Furukawa, J. *J. Macromol. Chem.* **1977**, *178*, 1077. Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480. Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Florence, L. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053. Ishikawa, M.; Ohskita, J.; Ito, Y.; Minato, A. *J. Organomet. Chem.* **1988**, *346*, C58. Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980. Guram, A. S.; Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 1833. Horton, A. D.; Orpen, A. G. *Angew. Chem.* **1992**, *104*, 912; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 876; *Organometallics* **1992**, *11*, 8. Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185. Röttger, D.; Erker, G.; Fröhlich, R.; Kotila, S. *Chem. Ber.* **1996**, *129*, 5.

(5) Jordan, R. F.; La Pointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. Berg, F. J.; Petersen, J. L. *Organometallics* **1989**, *8*, 2461. Jordan, R. F.; Guram, A. S. *Organometallics* **1990**, *9*, 2116. Guram, A. S.; Jordan, R. F. *Organometallics* **1991**, *10*, 3470. Guram, A. S.; Guo, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 4902. Guo, Z.; Swenson, D. C.; Guram, A. S.; Jordan, R. F. *Organometallics* **1994**, *13*, 766.
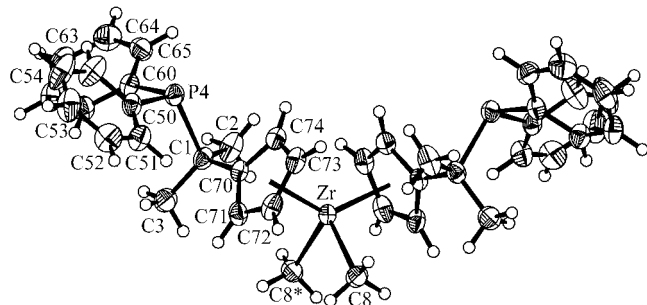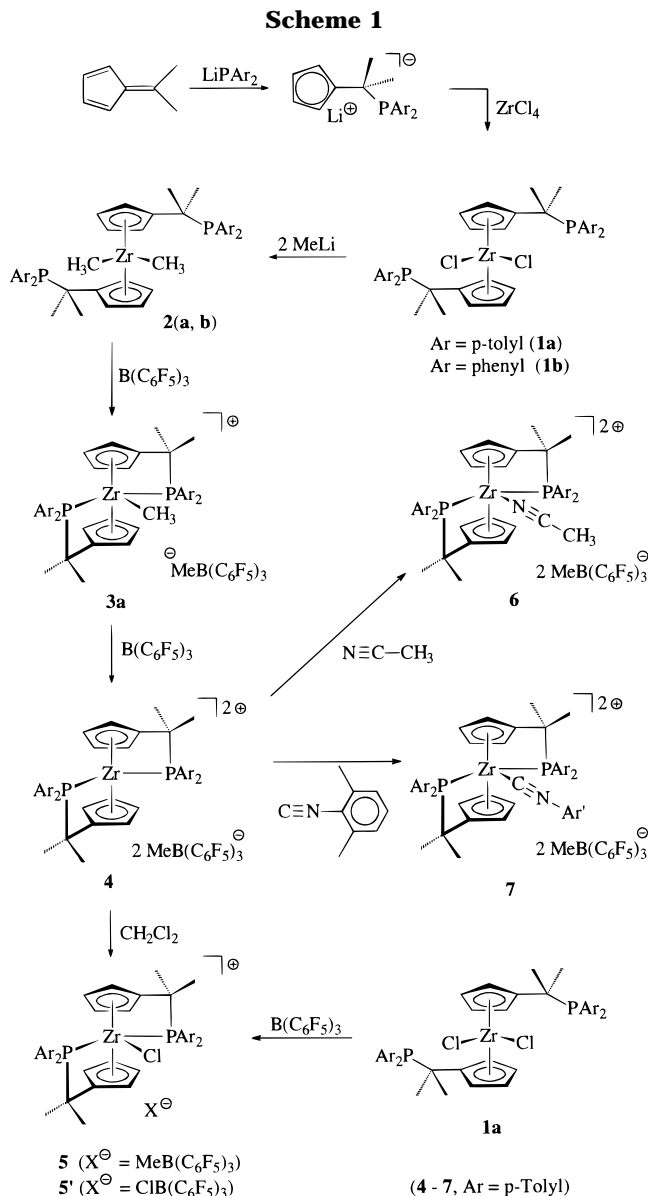
Figure 1. View of the molecular geometry of **2b**. Selected bond lengths (Å) and angles (deg): Zr−C8 2.277(3), Zr−C$_{Cp}$ 2.544(3), C70−C1 1.524(4), C1−C2 1.542(4), C1−C3 1.521(4), C1−P4 1.904(3), P4−C50 1.840(3), P4−C60 1.844-(3); C8−Zr−C8* 92.2(2), C2−C1−C3 109.9(3), C2−C1−P4 103.2(2), C2−C1−C70 111.2(2), C3−C1−P4 114.6(2), C3−C1−C70 111.5(3), P4−C1−C70 106.0(2), C1−P4−C50 107.85(14), C1−P4−C60 102.38(13), C50−P4−C60 100.84-(13).

ligand systems,[7] we developed synthetic entries into related ((diarylphosphino)methyl)cyclopentadienyl-derived zirconocenes suited for conversion into the respective internally phosphine-stabilized zirconocene cation systems.[8] This has led to the development of straightforward synthetic routes to novel mono- and dicationic phosphine-stabilized zirconocene systems, some of which constitute very interesting new organometallic Lewis acid systems.[9] This synthetic development along with a chemical and structural characterization of a variety of key examples is described in this article.

Results and Discussion

The synthesis of the [1-methyl-1-((diarylphosphino)-ethyl)]cyclopentadienyl ligand systems used in this study was carried out by means of the fulvene route.[10] 6,6-Dimethylfulvene was treated with lithiodiarylphosphide (Ar = *p*-tolyl or phenyl), Scheme 1. The resulting ligand system was then treated with 0.5 molar equiv of ZrCl$_4$ to yield the metallocene complexes **1a** (Ar = *p*-tolyl) and **1b** (Ar = phenyl), as was previously described by us.[8] The complexes **1a,b** were each subsequently treated with 2 molar equiv of methyllithium to furnish the dimethylzirconocene complexes **2a** (Ar = *p*-tolyl) and **2b** (Ar = phenyl), respectively. Out of each

(6) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041. Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289. Razavi, A.; Thewalt, U. *J. Organomet. Chem.* **1993**, *445*, 111. Alelyunas, Y. W.; Guo, Z.; LaPointe, R. E.; Jordan, R. F. *Organometallics* **1993**, *12*, 544. Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424.
(7) Bertuleit, A.; Fritze, C.; Erker, G.; Fröhlich, R. *Organometallics* **1997**, *16*, 2891. and references cited therein. See also (reviews): Jutzi, P.; Dahlhaus, J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *87*, 73. Jutzi, P.; Dahlhaus, J. *Coord. Chem. Rev.* **1994**, *137*, 179. Okuda, J. *Comm. Inorg. Chem.* **1994**, *16*, 185. Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175.
(8) Bosch, B.; Erker, G.; Fröhlich, R. *Inorg. Chim. Acta*, in press.
(9) For the use of specific organometallic Lewis acids in organic catalysis see e.g.: Erker, G.; Schamberger, J.; van der Zeijden, A. A. H.; Dehnicke, S.; Krüger, C.; Goddard, R.; Nolte, M. *J. Organomet. Chem.* **1993**, *459*, 107 and references cited therein.
(10) Ziegler, K.; Schäfer, W. *Justus Liebigs Ann. Chem.* **1934**, *511*, 101. Ziegler, K.; Gellert, H.-G.; Martin, H.; Nagel, K.; Schneider, J. *Justus Liebigs Ann. Chem.* **1954**, *589*, 91. Sullivan, M. F.; Little, W. F. *J. Organomet. Chem.* **1967**, *8*, 277. Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978**, *148*, 43. Brickhouse, M. D.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 2706. Okuda, J. *Chem. Ber.* **1989**, *122*, 1075. Squires, R. R. *Acc. Chem. Res.* **1992**, *25*, 461. Clark, T. J.; Killian, C. M.; Luthra, S.; Nile, T. A. *J. Organomet. Chem.* **1993**, *462*, 247.

Scheme 1

series of these starting materials, one representative example was crystallized and characterized by an X-ray crystal structure analysis. The molecular structures of the metallocene dichloride (**1b**) and dimethyl (**2b**) complexes are very similar. Therefore, the structural data of **1b** are provided in the Supporting Information. A view of the molecular geometry of **2b** is given in Figure 1. Figure 1 shows that the bonding parameters around the pseudotetrahedrally coordinated zirconium atom in **2b** are unexceptional[11] (Zr−C8 = 2.277(3) Å, C8−Zr−C8* = 92.2(2)°, D1−Zr−D1* = 132.0°, D1 and D2 denote the centroids of the two Cp ring systems). The conformational properties of the metallocene system **2b** are noteworthy though. In the crystal, **2b** is C_2-symmetric. The system shows a rotameric structure where both −CMe$_2$−PPh$_2$ substituents at the Cp rings are oriented in opposite lateral sectors at the bent metallocene wedge. The (Cp−CMe$_2$PPh$_2$)$_2$ZrMe$_2$ complex **2b**, thus, exhibits a bis(lateral):anti-metallocene

(11) Bochmann, M. *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 4, p 273. Ryan, E. J. *Ibid.* p 483. Hey-Hawkins, E. *Ibid.* p 501. Gambarotta, S.; Jubb, J.; Song, J.; Richeson, D. *Ibid.*, p. 543. Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986.

conformation.[12] One of the methyl groups at C1, namely C^3H_3, is oriented close to the Cp-ligand plane (dihedral angle θ C3−C1−C70−C71 = −3.9(4)°), whereas the phosphorus atom P4 and the remaining C^2H_3 group are located out of this plane (θ P4−C1−C70−C71 121.5(3)°, C2−C1−C70−C71 = −127.0(3)°).

The [Cp−CMe$_2$−P(p-tolyl)$_2$]$_2$Zr(CH$_3$)$_2$ complex **2a** was used as a starting material for generating the metal-locene cation complexes. Complex **2a** was therefore treated with 1 molar equiv of tris(pentafluorophenyl)-borane in toluene.[13] The [(Cp−CMe$_2$−P(p-tolyl)$_2$)$_2$Zr-(CH$_3$)$^+$ CH$_3$B(C$_6$F$_5$)$_3^-$] salt **3a** was formed instantaneously and isolated in >90% yield. In dichloromethane-d_2, it exhibits a C_2-symmetric structure in solution, as apparent from the NMR spectra at low temperature (^{1}H/^{13}C NMR (600/150 MHz at 253 K) δ 6.44, 6.40, 6.26, 5.94/111.9, 106.92, 106.79, 97.8 (Cp−); δ 1.82, 1.28/30.3, 25.5 (C(*CH$_3$*)$_2$); δ 2.37 (12H)/21.38, 21.15 (p-tolyl-*CH$_3$*), δ −0.39/17.3 (Zr−*CH$_3$*)). The ^{1}H NMR signal of the Zr−C*H$_3$* group is split as a binominal triplet due to coupling with the two symmetry-equivalent phosphorus nuclei ($^3J_{PH}$ = 15 Hz), as is the corresponding ^{13}C NMR resonance ($^2J_{PC}$ = 10.5 Hz). The C(C*H$_3$*)$_2$ methyl-group ^{1}H NMR resonances also show coupling to two ^{31}P nuclei (as part of an A$_3$A$_3'$XX'-type system[14]). The cation complex **3a** exhibits a single ^{31}P NMR resonance as expected, but with a very unusual chemical shift of δ −22.0 (for comparison, the corresponding ^{31}P NMR resonance of the starting material **2a** occurs at δ +31.2). This enormous shifting of the ^{31}P NMR resonance of the system upon cation formation and establishing the phosphine-to-metal coordination was not expected per se. It may be explained by either a very pronounced Δ_R-effect[15] or by assuming that the phosphorus of the −P(aryl)$_2$ moiety has entered the magnetically deshielding anisotropy cone of the adjacent Cp-ring system in the unusual overall coordination geometry that has resulted from the formation of the internally phosphine-coordinated cationic metallocene system (further structural evidence on this point is given below).

Complex **3a** exhibits dynamic NMR spectra. Raising the monitoring temperature of the ^{1}H NMR experiment (at 200 MHz) above 280 K results in a broadening of the C$_5$*H$_4$* resonances and the C(CH$_3$)$_2$ signals. Eventually, the δ 6.44/5.94 (273 K) pair of resonances reaches coalescence (T_c = 300 K), as does the 6.39/6.24 pair (T_c = 295 K) and the δ 1.82/1.31 pair of methyl signals (T_c = 300 K). The dynamic process that leads to a symmetry exchange of these pairs of signals must be described as an intramolecular enantiomerization process of **3a**. Its Gibbs activation energy was estimated

Scheme 2

3 (R = Me), **5** (R = Cl)

ent-**3** (R =Me)
ent-**5** (R = Cl)

8

at $\Delta G^{\ddagger}$ (300 K) = 14.0 ± 0.5 kcal/mol from the temperature-dependent dynamic ^{1}H NMR spectra described above.[16] The dynamic symmetrization process requires a "left/right-exchange" of the phosphorus ligands bonded to zirconium in the σ-ligand plane of **3a**. Due to the specific stereoelectronic features of the bent metallocene unit,[17] this requires (reversible) rupture of *both* zirconium−phosphorus bonds (see Scheme 2). The magnitude of the activation barrier is, thus, determined by a process leading to the unsaturated intermediate **8** that is devoid of any stabilization by coordination of electron-donating −PAr$_2$ ligands. Qualitatively, the activation barrier of this dynamic automerization process of **3a**, thus, provides a measure of the stabilization energy that a very electrophilic "naked" [Zr]−CH$_3$ cation gains by (intramolecularly) coordinating two R−PAr$_2$ donor ligands to it. The diphenylphosphino-substituted derivative **3b** shows an analogous dynamic behavior. From the temperature-dependent ^{1}H NMR spectra, an almost identical $\Delta G^{\ddagger}_{enant}$ = 14.1 ± 0.5 kcal/mol was obtained.

Complex **3a** was characterized by an X-ray crystal structure analysis. In the crystal, the CH$_3$B(C$_6$F$_5$)$_3^-$ anion is independent of the **3a** cation. The structural parameters of the anion are unexceptional.[13] The cation shows a pseudopenta-coordinated zirconium atom with two substituted Cp ligands, a methyl group, and both −P(p-tolyl)$_2$ moieties bonded to the metal center. This leads to a (noncrystallographic) very close to C_2-symmetric molecular geometry of the **3a** cation. The D1−Zr−D2 angle is 137.2° (D1 and D2 denote the centroids of the two Cp ligands). The Zr−C10 bond length is 2.350(4) Å.[18] The C^{10}H$_3$ group is bonded to zirconium in the front of the bent metallocene wedge in the central position of the σ-ligand plane. The phosphorus atoms P1 and P11 are bonded to Zr laterally adjacent to the Zr−CH$_3$ vector (Zr−P1 = 2.8370(14) Å, Zr−P11 = 2.8447(14) Å, P1−Zr−C10 = 77.55(10)°, P11−Zr−C10 = 77.31(10)°, P1−Zr−P11 = 154.78(4)°). Both P atoms
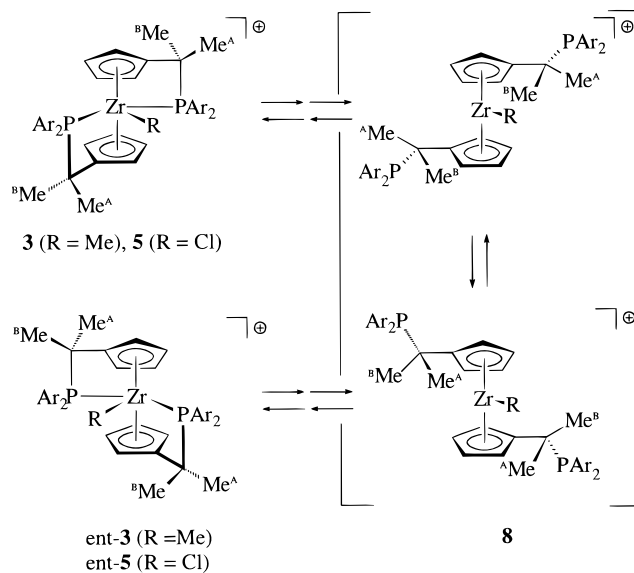
(12) For leading references on the conformational features of group 4 bent metallocene complex chemistry, see, e.g.: Krüger, C.; Nolte, M.; Erker, G.; Thiele, S. *Z. Naturforsch.* **1992**, *47b*, 995. Erker, G.; Temme, B. *J. Am. Chem. Soc.* **1992**, *114*, 4004. Krüger, C.; Lutz, F.; Nolte, M.; Erker, G.; Aulbach, M. *J. Organomet. Chem.* **1993**, *452*, 79. Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590. Fritze, C.; Knickmeier, M.; Erker, G.; Zaegel, F.; Gautheron, B.; Meunier, P.; Paquette, L. A. *Organometallics* **1995**, *14*, 5446. Knickmeier, M.; Erker, G.; Fox, T. *J. Am. Chem. Soc.* **1996**, *118*, 9623 and references cited therein.

(13) For leading references on this method of generating group 4 bent metallocene cation complexes, see: Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015 and references cited therein.

(14) Leoni, P.; Marchetti, F.; Paoletti, M. *Organometallics* **1997**, *16*, 2146.

(15) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435. Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(16) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228. Green, M. L. H.; Wong, L.-L.; Seela, A. *Organometallics* **1992**, *11*, 2660 and references cited therein.

(17) Brintzinger, H. H.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 1105. Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.
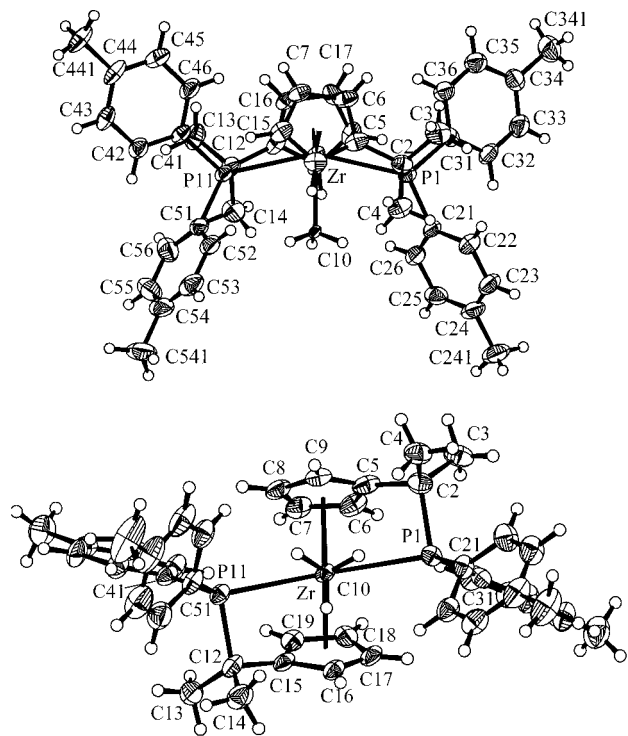
Figure 2. Two projections of the molecular structure of **3a** (cation only) in the crystal. Selected bond lengths (Å) and angles (deg): Zr−C10 2.350(4), Zr−C_{Cp} 2.512(5), Zr−P1 2.8370(14), Zr−P11 2.8447(14), P1−C2 1.894(5), P11−C12 1.892(5), P1−C21 1.809(5), P11−C51 1.808(5), P1−C31 1.850(5), P11−C41 1.835(5), C2−C3 1.540(7), C12−C13 1.543(7), C2−C4 1.538(7), C12−C14 1.529(7), C2−C5 1.518(7), C12−C15 1.516(7); C10−Zr−P1 77.55(10), C10−Zr−P11 77.31(10), P1−Zr−P11 154.78(4), Zr−P1−C2 89.0-(2), Zr−P11−C12 89.2(2), Zr−P1−C21 125.7(2), Zr−P11−C51 123.8(2), Zr−P1−C31 120.0(2), Zr−P11−C41 120.7(2), P1−C2−C3 114.9(4), P11−C12−C13 113.7(3), P1−C2−C4 111.8(4), P11−C12−C14 113.5(4), P1−C2−C5 99.5(3), P11−C12−C15 98.9(3).

are located markedly outside the bent metallocene σ-ligand plane (i.e., C_2-symmetrically above and below, see Figure 2). The angle between the D1−Zr−D2 and P1−Zr−P11 planes is 80.6°. This deviation from an electronically favored arrangement of the P1,Zr,P11 unit in the Cp−Zr−Cp bisecting major plane of the bent metallocene unit is enforced geometrically by the attachment of the −PAr_2 groups at the Cp ligands by the CMe_2 linkages (C2−P1 = 1.894(5) Å, C12−P11 = 1.892-(5) Å, C5−C2−P1 = 99.5(3)°, C2−P1−Zr = 89.0(2)°, C15−C12−P11 = 98.9(3)°, C12−P11−Zr = 89.2(2)°). This geometric arrangement brings each phosphorus atom rather close to one Cp edge (C5···P1 = 2.615 Å, C15···P11 = 2.600 Å). The methyl groups at C2 (and C12) are in a markedly different environment. The C^4H_3 group points toward the front side of the bent metallocene wedge, whereas the C^3H_3 substituent is oriented toward a hind lateral sector. The relative orientation of the aryl groups at the phosphorus atoms
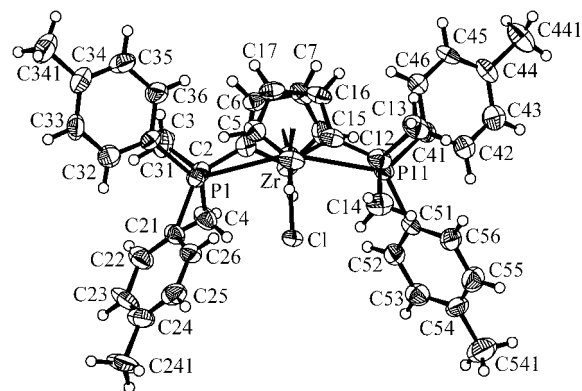
(18) Atwood, J. L.; Barker, G. K.; Holton, J.; Hunter, W. E.; Lappert, M. F.; Pearce, R. *J. Am. Chem. Soc.* **1977**, *99*, 6645. Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1593. Atwood, J. L.; Hunter, W. E.; Hrncir, D. C.; Bynum, V.; Penttila, R. A. *Organometallics* **1983**, *2*, 750. Krüger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *4*, 215. See also: Orpen, G. A.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

Figure 3. View of the molecular geometry of **5** ($CH_3B(C_6F_5)_3^-$ anion not depicted). Selected bond lengths (Å) and angles (deg): Zr−Cl 2.453(2), Zr−C_{Cp} 2.499(7), Zr−P1 2.846(2), Zr−P11 2.846(2), P1−C2 1.885(7), P11−C12 1.891(7), P1−C21 1.798(7), P11−C51 1.814(7), P1−C31 1.833(7), P11−C41 1.827(7), C2−C3 1.534(10), C12−C13 1.536(10), C2−C4 1.549(10), C12−C14 1.529(9), C2−C5 1.516(10), C12−C15 1.532(10); Cl−Zr−P1 77.83(6), Cl−Zr−P11 78.03(6), P1−Zr−P11 155.81(6), Zr−P1−C2 88.3(2), Zr−P11−C12 88.8(2), Zr−P1−C21 124.6(2), Zr−P11−C51 122.6(3), Zr−P1−C31 120.8(2), Zr−P11−C41 121.9(2), P1−C2−C3 115.3(6), P11−C12−C13 113.9(5), P1−C2−C4 111.7-(5), P11−C12−C14 112.5(5), P1−C2−C5 99.5(4), P11−C12−C15 98.3(4).

(P1, P11) is similar; this leads to some lateral shielding of the central Zr−CH_3 group by the bulky substituents at phosphorus (see Figure 2).

Next, we tried to generate the internally phosphane-stabilized dication **4** (Ar = *p*-tolyl, see Scheme 1).[19] In the first series of experiments, we treated the dimethylzirconocene complex **2a** (Ar = *p*-tolyl) with 2 molar equiv of $B(C_6F_5)_3$ in dichloromethane. The reaction rapidly goes to completion when carried out at room temperature. A single reaction product was obtained almost quantitatively. Recrystallization from dichloromethane/pentane gave single crystals suited for the X-ray crystal structure analysis. This revealed that instead of the expected dication complex [(Cp−CMe_2-$PAr_2)_2Zr^{2+}$·2 $MeB(C_6F_5)_3^-$] (**4**, see below) the [(Cp−$CMe_3PAr_2)_2Zr−Cl^+MeB(C_6F_5)_3^-$] salt **5** had been formed and isolated in excellent yield. The structure of the chloro-containing monocation **5** (see Figure 3) is very similar to the methyl-containing cation **3a** (see above). The overall molecular arrangement is again close to C_2-symmetric with two −P(*p*-tolyl)$_2$ ligands internally coordinating to zirconium as close to the σ-ligand plane of the bent metallocene wedge as the rigid system allows. The Zr−Cl vector is located in the central position in the σ-ligand plane (Zr−Cl = 2.453(2) Å, Zr−P1 = 2.846(2) Å, Zr−P11 = 2.846(2) Å, D1−Zr−D2 = 134.9°, P1−Zr−Cl = 77.83(6)°, P11−Zr−Cl = 78.03(6)°, P1−Zr−P11 = 155.81(6)°, C2−P1−Zr = 88.3(2)°, C12−P11−Zr = 88.8(2)°).

Complex **5** exhibits the very characteristic NMR spectra of the chiral C_2-symmetric cation at ambient

(19) (a) Zirconium: Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1987**, *26*, 383. Billinger, P. N.; Claire, P. P. K.; Collins, H.; Willey, G. R. *Inorg. Chim. Acta* **1988**, *149*, 63. Thewalt, U.; Lasser, W. *J. Organomet. Chem.* **1984**, *276*, 341. Lasser, W.; Thewalt, U. *J. Organomet. Chem.* **1986**, *311*, 69. (b) Titanium: Thewalt, U.; Klein, H.-P. *J. Organomet. Chem.* **1980**, *194*, 297. Thewalt, U.; Berhalter, K. *J. Organomet. Chem.* **1986**, *302*, 193. Honold, B.; Thewalt, U. *J. Organomet. Chem.* **1986**, *316*, 291. Berhalter, K.; Thewalt, U. *J. Organomet. Chem.* **1987**, *332*, 123.

temperature (^{13}C NMR (CD$_2$Cl$_2$, 150 MHz) δ 116.3, 112.8, 108.4, 100.9 (Cp), 29.8, 26.4 (C(CH$_3$)$_2$), 21.7, 21.4 (tolyl−CH$_3$); ^{1}H NMR (C$_6$D$_5$Br, 200 MHz, 303 K) δ 6.23, 6.22, 6.01, 5.86 (Cp), 1.49, 1.32 (C(CH$_3$)$_2$). The ^{31}P NMR resonance of **5** is at δ −33.0 ppm (in CD$_2$Cl$_2$).

Complex **5** shows a dynamic NMR behavior at higher temperatures similar to that previously observed for **3a**. The ^{1}H NMR spectrum of **5** in bromobenzene-d_5 shows a broadening of the lines at temperatures above ca. 340 K (200 MHz) with subsequent coalescence of the former δ 6.23/6.01 (T_c = 363 K) and δ 6.22/5.86 (T_c = 370 K) pairs of Cp resonances as well as the former δ 1.49/1.32 ^{1}H NMR C(CH$_3$)$_2$ resonance pair (T_c = 358 K). The enantiomerization process of **5** is analogous to that observed and described for **3** (see above and Scheme 2) and is also likely to proceed through a nondonor-ligand-stabilized intermediate (**8**), however, in the case of the [Zr]−Cl$^+$ complex this should be even further destabilized due to the presence of the electron-withdrawing σ-chloride ligand at zirconium instead of −CH$_3$. Thus, the **5** → **8** transition should have a higher activation barrier compared to the corresponding **3** → **8** reaction, which it has. The Gibbs activation energy of the thermally induced intramolecular **5** ⇌ ent-**5** automerization process was derived at $\Delta G^{\ddagger}_{ent}$ (360 K) = 17.5 ± 0.5 kcal/mol from the dynamic ^{1}H NMR spectra.[16]

The cation **5** was prepared independently. We have treated the substituted zirconocene dichloride **1a** (Ar = *p*-tolyl) directly with 1 molar equiv of the Lewis acid B(C$_6$F$_5$)$_3$ in dichloromethane. At ambient temperature one chloride is rapidly removed from zirconium with formation of the [(Cp−CMe$_2$−P(*p*-tolyl)$_2$)$_2$Zr−Cl$^+$ClB-(C$_6$F$_5$)$_3^-$] salt **5′**. The ClB(C$_6$F$_5$)$_3^-$ anion was identified by LDI-TOF-MS (m/z = 547) in the negative ion mode and by an X-ray crystal structure analysis (B−Cl2 = 1.907(8) Å; for details of this structure, see the Supporting Information). The NMR spectra of the independently prepared compound **5′** are very similar to those of **5** (for details, see the Experimental Section).

It is very likely that the chloride-containing complex [(Cp−CMe$_2$−PAr$_2$)$_2$Zr-Cl$^+$CH$_3$B(C$_6$F$_5$)$_3^-$] **5** was formed in the reaction between **2a** and 2 equiv of B(C$_6$F$_5$)$_3$ via the reactive [(Cp−CMe$_2$−PAr$_2$)$_2$Zr^{2+}·2CH$_3$B(C$_6$F$_5$)$_3^-$] dication intermediate **4**, which is not stable under the applied reaction conditions. It must be assumed that the ultimately obtained reaction products originate from **4**, which is converted to **5** by a subsequent chloride abstraction reaction from the halocarbon solvent.

This was shown to be true, although the organic stoichiometric reaction product could not be identified. The reaction of **2a** with 2 equiv of B(C$_6$F$_5$)$_3$ in CD$_2$Cl$_2$ was carried out at variable temperatures under direct ^{1}H and ^{31}P NMR control. The reaction was started at 213 K, a temperature where the formation of the monocation **3a** is very rapid. After 30 min at 213 K, a mixture containing **3a** (65%), **5** (9%), and the new complex **4** (i.e., the donor-ligand-stabilized dication, 26%) was obtained. Slowly raising the temperature resulted in a predominant conversion of **3a** to **4** (by means of intermolecular CH$_3$ abstraction by the B(C$_6$F$_5$)$_3$ reagent) without very much subsequent chloride abstraction. At 228 K after a total reaction time of 60 min, a **3a**:**5**:**4** ratio of 27:11:62 was obtained, and at 253 K after a total reaction time of 125 min, the primary product **3a** was no longer observed, the **5**:**4** ratio was

now 20:80. Raising the temperature further then led to an increased consumption of the dication **4** with formation of **5**. The characteristic NMR data of **4** were obtained from a ca. 1:1 mixture of **4** and **5** at 275 K in dichloromethane-d_2 (δ 2.39, 2.29 (*p*-tolyl CH$_3$); δ 1.93, 1.59 (C(CH$_3$)$_2$)). The ^{31}P NMR resonance of **4** (CD$_2$Cl$_2$) is at δ −48.5 ppm. Complex **4** was also obtained as an insoluble oil by treatment of **2a** with ca. 2 molar equiv of B(C$_6$F$_5$)$_3$ in toluene (see Experimental Section). Since **4** is insoluble in the aromatic hydrocarbon solvent, the product was spectroscopically characterized using CD$_2$-Cl$_2$ or C$_6$D$_5$Br solutions (see above).

We have characterized the dication **4** by its reaction with external donor ligands. The resulting [(Cp−CMe$_2$−PAr$_2$)$_2$Zr−L^{2+}·2 CH$_3$B(C$_6$F$_5$)$_3^-$] complexes are more stable than the very electrophilic dication **4** and, thus, are easier to handle and isolate.[20]

The reaction between **3a**, B(C$_6$F$_5$)$_3$ (2 molar equiv), and acetonitrile was carried out in toluene. The reaction rapidly turns heterogeneous, and the reaction product (**6**, see Scheme 1) separates as an oil. The isolated (89% yield) complex [(Cp−CMe$_2$−PAr$_2$)$_2$Zr-(N≡C−CH$_3$)$^{2+}$·2 CH$_3$B(C$_6$F$_5$)$_3^-$] (**6**) is stable in dichloromethane. It shows the typical NMR spectra of a C_2-symmetric cationic species in solution (^{1}H/^{13}C NMR δ 6.73, 6.46, 6.38, 6.20/117.1, 108.5, 107.9, 101.2 (Cp); δ 2.43, 2.41/21.53, 21.42 (CH$_3$ of *p*-tolyl), 1.78, 1.44/29.4, 26.3 (C(CH$_3$)$_2$)). The ^{1}H NMR resonance of the coordinated acetonitrile ligand appears at δ 1.32 as a triplet due to coupling with the two adjacent symmetry-equivalent ^{31}P NMR nuclei ($^5J_{PH}$ = 3.3 Hz). The coordinated −C≡N ^{13}C NMR resonance is at δ 141.5 ppm, and the corresponding acetonitrile methyl ^{13}C NMR signal is at δ 2.92. Complex **6** exhibits a ^{31}P NMR resonance at δ −44.7 ppm. The typical IR bands of the coordinated acetonitrile ligand are found at 2307 (combination) and 2273 cm^{-1} (C≡N) (free acetonitrile shows the corresponding IR bands at $\tilde{\nu} \approx$ 2290 and 2255 cm^{-1}).[20,21]

We have also trapped the in-situ-generated metallocene dication **4** by addition of 2,6-dimethylphenyl isocyanide (reaction carried out in toluene). The [(Cp−CMe$_2$−PAr$_2$)$_2$Zr(C≡N-Ar′)$^{2+}$·2CH$_3$B(C$_6$F$_5$)$_3^-$] salt **7** (see Scheme 1) was isolated in ca. 80% yield. It again exhibits the typical NMR spectra of a C_2-symmetric adduct (for details see the Experimental Section). The $\tilde{\nu}$ (C≡N−R) IR band of **7** was monitored at $\tilde{\nu}$ = 2170 cm^{-1} (free C≡N−C$_6$H$_3$Me$_2$ 2122 cm^{-1}).

Conclusions

This study shows that phosphine stabilization of the very electrophilic zirconium center in the mono- and dicationic bent metallocene complexes can become very pronounced and dominant if the P-donor ligands become attached to the Cp rings by suitable linkages and, thus, can coordinate intramolecularly. In this manner, even the very electrophilic 16-electron dication **4** has attained a moderate stability, although it apparently is so electrophilic that it rapidly starts to abstract chloride

(20) See, for a comparison: Brackemeyer, T.; Erker, G.; Fröhlich, R. *Organometallics* **1997**, *16*, 531. Brackemeyer, T.; Erker, G.; Fröhlich, R.; Prigge, J.; Peuchert, U. *Chem. Ber.* **1997**, *130*, 899.
(21) Bruce, M. R. M.; Tyler, D. R. *Organometallics* **1985**, *4*, 528. Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718.

from the solvent at or above ca. −20 °C to cleanly form the C_2-symmetric chloride containing 18-electron monocation **5**. Similarly, there is an apparently large thermodynamic driving force of **4** to add neutral donor ligands (nitrile, isonitrile) to give the respective very stable 18-electron complexes (**6**,**7**) which have the third donor ligand bonded at zirconium in the central position in the σ-ligand plane. This study shows that the selected synthetic route (**1** → **2** → **3** → **4**, see Scheme 1) is suited and easy to use for generating the reactive chiral internally donor-ligand-stabilized metallocene dication system **4**.[22] Whether this rather electrophilic dication system can be used as a catalyst or a stoichiometric reagent in organic transformations and whether its inherent chirality can be utilized in such reactions is currently being studied in our laboratory.

Experimental Section

All compounds described are air and moisture sensitive. They were prepared and handled in an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents) were dried and distilled under argon prior to use. NMR spectra were recorded on a Bruker AC 200 P (^{1}H, 200 MHz; ^{31}P, 81 MHz, H_3PO_4 external standard; ^{13}C, 50.3 MHz) or a Varian Unity plus (^{1}H, 600 MHz; ^{13}C, 150 MHz) NMR spectrometer. IR spectroscopy: Nicolet 5 DXC FT-IR spectrometer (KBr). Elemental analyses: Foss Heraeus CHNO-Rapid. DSC: Dupont 2910 DSC (STA instruments). X-ray crystal structure analyses: Enraf-Nonius MACH 3 diffractometer (programs used, SHELX 86, SHELX 93, DIAMOND, and SCHAKAL). The complexes **1a** and **1b** were prepared as recently described by us.[8] $B(C_6F_5)_3$ was prepared according to a literature procedure.[23]

X-ray Crystal Structure Analysis of 1b. Formula $C_{40}H_{40}Cl_2P_2Zr$; $M = 744.78$; $0.20 \times 0.20 \times 0.10$ mm; $a = 31.058(6)$ Å, $b = 6.537(1)$ Å, $c = 18.167(4)$ Å, $\beta = 108.57(2)°$, $V = 3496.2-(12)$ Å^3, $\rho_{calc} = 1.415$ g cm^{-3}, $\mu = 5.87$ cm^{-1}, empirical absorption correction via φ scan data ($0.925 \leq C \leq 0.998$), $Z = 4$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 0.710\,73$ Å, $T = 223$ K, ω scans, 3660 reflections collected ($\pm h, +k, -l$), [(sin $\theta)/\lambda] = 0.62$ Å^{-1}, 3528 independent and 2112 observed reflections [$I \geq 2\,\sigma(I)$], 207 refined parameters, R1 = 0.048, wR2 = 0.106, max (min) residual electron density 0.76 (−1.15) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Bis[[1-methyl-1-(di-*p*-tolylphosphino)ethyl]cyclopentadienyl]dimethylzirconium (2a). 1a (16.0 g, 20 mmol) was suspended in 150 mL of diethyl ether, and 24 mL (40 mmol) of methyllithium (1.68 M in Et$_2$O) was added at −78 °C. The suspension was allowed to warm to room temperature overnight. Celite filtration and washings of the filter pad with 100 mL of diethyl ether produced a red solution. The solvent was evaporated, the residue taken up in 60 mL of pentane, and the product collected on a Schlenk frit, washed with two 20 mL portions of pentane, and dried in vacuo. Yield: 8.61 g, 57%. Mp 112 °C. Anal. Calcd for $C_{46}H_{54}P_2Zr$ (760.1): C, 72.69; H, 7.16. Found: C, 70.25; H, 7.21. IR (KBr): $\tilde{\nu}$ 3080, 3069, 3022, 3013, 2971, 2960, 2911, 2864, 1598, 1558, 1498 (vs), 1474, 1446, 1409, 1397, 1377, 1358, 1307, 1261, 1187, 1120 (vs), 1089, 1038, 1020, 932, 874, 862, 853, 810 (br, vs), 716, 710, 699, 662, 649, 623, 611 cm^{-1}. ^{1}H NMR (benzene-d_6, 200.1 MHz): δ 7.47 (m, 8H, *o*-tol-H), 6.99 (m, 8H, *m*-tol-H), 5.73 (s, 8H, C$_5$H$_4$), 2.08 (s, 12H, *p*-tol-CH$_3$), 1.42 (d, $^3J_{PH}$ = 13.6 Hz, 12H, CMe$_2$), -0.03 (s, 6H, Zr−CH$_3$). ^{13}C NMR (benzene-d_6, 50.3 MHz): δ 138.8 (*p*-tol), 135.7 ($^2J_{PC}$ = 21 Hz, *o*-tol), 135.0 ($^2J_{PC}$ = 7 Hz, C1 of Cp), 133.4 ($^1J_{PC}$ = 21 Hz, ipso

C of tol), 128.9 ($^3J_{PC}$ = 7 Hz, *m*-tol), 110.3 ($^3J_{PC}$ = 5 Hz, C2 of Cp), 109.6 (Cp), 37.9 ($^1J_{PC}$ = 21 Hz, CMe$_2$), 32.3 (Zr−CH$_3$), 26.4 ($^2J_{PC}$ = 18 Hz, C(CH$_3$)$_2$), 21.2 (tol-CH$_3$). ^{31}P NMR (benzene-d_6, 81.0 MHz): δ 31.2.

Bis[[1-methyl-1-(diphenylphosphino)ethyl]cyclopentadienyl]dimethylzirconium (2b). To a suspension of 3.11 g (4.17 mmol) of bis[[1-methyl-1-(diphenylphosphino)ethyl]cyclopentadienyl]dichlorozirconium (**1b**) in 80 mL of pentane was added 5.0 mL of methyllithium (1.68 M in diethyl ether, 8.4 mmol) at −78 °C. A yellow suspension was obtained after stirring overnight. Subsequently, the solvent was evaporated into a cold trap, and the residue was taken up in 150 mL of toluene and filtered through a 2 cm bed of Celite. The toluene was evaporated, and the crude product **2b** was washed with two 20 mL portions of pentane, leaving 2.35 g (80%) of **2b** as a white solid. A sample of **2b** was dissolved in a 3:1 mixture of toluene and pentane. Cooling this mixture to −20 °C yielded white crystals suitable for the X-ray diffraction analysis. Mp 178 °C. Anal. Calcd for $C_{42}H_{46}P_2Zr$ (704.0): C, 71.66; H, 6.59. Found: C, 70.17; H, 6.47. IR (KBr): $\tilde{\nu}$ = 3075, 3058, 2971, 2964, 2932, 2915, 2868, 1583 (s), 1481, 1461, 1435 (s), 1429 (s), 1412, 1377, 1358, 1223, 1091, 1068, 1051, 1039, 1025, 1000, 931, 875, 865, 854, 810 (vs), 747, 739 (s), 698 (s) cm^{-1}. ^{1}H NMR (benzene-d_6, 200.1 MHz): δ 7.53−7.44 (m, 8H, *o*-Ph), 7.19−7.14 (m, 12H, *p,m*-Ph), 5.73 (s, 8H, C$_5$H$_4$), 1.39 (d, $^3J_{PH}$ = 13.5 Hz, 12H, CMe$_2$), −0.07 (s, 6H, Zr−CH$_3$). ^{13}C NMR (APT, benzene-d_6, 50.3 MHz): δ 136.7 ($^1J_{PC}$ = 23 Hz, ipso C of Ph), 135.5 ($^2J_{PC}$ = 20 Hz, *o*-Ph), 129.0 (*p*-Ph), 128.2 ($^3J_{PC}$ = 7 Hz, *m*-Ph), 110.2 ($^3J_{PC}$ = 6 Hz, C2 of Cp), 109.6 (Cp), 37.9 ($^1J_{PC}$ = 21 Hz, CMe$_3$), 32.3 (Zr−CH$_3$), 26.3 ($^2J_{PC}$ = 18 Hz, C(CH$_3$)$_2$); C1 of Cp not observed. ^{31}P NMR (benzene-d_6, 81.0 MHz): δ 32.5.

X-ray Crystal Structure Analysis of 2b. Formula $C_{42}H_{46}P_2Zr$; $M = 703.95$; $0.50 \times 0.30 \times 0.20$ mm; $a = 31.554-(3)$ Å; $b = 7.028(1)$ Å; $c = 16.735(2)$ Å, $\beta = 105.72(1)°$, $V = 3572.4(7)$ Å^3, $\rho_{calc} = 1.309$ g cm^{-3}, $\mu = 4.26$ cm^{-1}, empirical absorption correction via φ scan data ($0.962 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 0.710\,73$ Å, $T = 223$ K, ω scans, 3771 reflections collected ($\pm h, -k, -l$), [(sin $\theta)/\lambda] = 0.62$ Å^{-1}, 3636 independent and 2622 observed reflections [$I \geq 2\,\sigma(I)$], 207 refined parameters, R1 = 0.039, wR2 = 0.083, max (min) residual electron density 0.41 (−0.32) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Methylbis{[[1-methyl-1-(di-*p*-tolylphosphino)ethyl]-η^5-cyclopentadienyl]-κ^2-*P,P*}zirconium(IV) Methyltris(pentafluorophenyl)borate (3a). 2a (760 mg, 1.0 mmol) and 512 mg (1.0 mmol) of $B(C_6F_5)_3$ were mixed as solids and suspended in 25 mL of toluene. The orange suspension was stirred for 1 h, and the mixture was concentrated in vacuo to 2 mL. Pentane (20 mL) was added, and the mixture was stirred for 1 h. The pale yellow product was isolated on a Schlenk frit, washed with two 10 mL portions of pentane, and dried in vacuo to yield 1.15 g (91%) of the pale yellow monocation complex **3a**. It was possible to grow large crystals of **3a** by layering a dichloromethane solution with an equal amount of pentane at −20 °C. Single crystals suitable for the X-ray diffraction analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **3a** at 4 °C. Mp 160 °C (dec). Anal. Calcd for $C_{64}H_{54}BF_{15}P_2Zr$ (1272.08): C, 60.43; H, 4.28. Found: C, 59.26; H, 4.09. IR (KBr): $\tilde{\nu}$ = 3028, 2994, 2974, 2956, 2923, 2869, 1641 (B(C$_6$F$_5$)$_3$), 1600, 1510, 1498, 1458 (br, vs), 1265 (B(C$_6$F$_5$)$_3$), 1190, 1117, 1088, 1081, 994, 975, 965, 947, 934, 838, 822, 800, 658 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 200.1 MHz, 253 K): δ 7.27 (m, 16H, *p*-tol-H), 6.43 (m, 4H, C$_5$H$_4$), 6.27, 5.94 (each m, each 2H, C$_5$H$_4$), 2.36 (s, 12H, tol-CH$_3$), 1.81 (m, 6H, CMe$_2$), 1.28 (m, 6H, CMe$_2$), 0.43 (br s, 3H, [B]−CH$_3$), −0.42 (t, $^3J_{PH}$ = 15.1 Hz, 3H, Zr−CH$_3$). ^{13}C NMR (dichloromethane-d_2, 150 MHz, 253 K): δ 148.1 ($^1J_{FC}$ = 228 Hz, *o*-C$_6$F$_5$), 142.05, 141.92 (each *p*-tol), 137.4 ($^1J_{FC}$ = 235 Hz, *p*-C$_6$F$_5$), 137.1 (ipso-C of Cp), 136.3 (C$_6$F$_5$), 135.38 (*o*-tol), 134.43 (*o*-tol), 130.1 (*m*-tol), 129.9 (*m*-tol), 125.8 (ipso-C of tol), 121.7 (ipso-C of tol), 111.9, 106.92, 106.79, 97.8 (Cp), 34.9 (CMe$_2$),

(22) For a structurally related neutral system, see: Christoffers, J.; Bergman, R. G. *Angew. Chem.* **1995**, *107*, 2423; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2266.

(23) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

30.3, 25.5 (C(CH₃)₂), 21.38, 21.15 (tol-CH₃) 17.3 (t, $^2J_{PC}$ = 10.5 Hz, Zr–CH₃), 9.8 (br, H₃C[B]). ³¹P NMR (dichloromethane-d_2, 81.0 MHz): δ −22.0. ¹¹B NMR (dichloromethane-d_2, 64.2 MHz): δ −15.

X-ray Crystal Structure Analysis of 3a. Formula $C_{64}H_{54}$-BF₁₅P₂Zr; *M* = 1272.04; 0.40 × 0.25 × 0.10 mm; *a* = 14.139(2) Å, *b* = 14.976(2) Å, *c* = 16.145(2) Å, α = 113.62(1)°, β = 109.24-(1)°, γ = 95.84(1)°, *V* = 2847.2(7) Å³, ρ_{calc} = 1.484 g cm⁻³, μ = 3.40 cm⁻¹, empirical absorption correction via φ scan data (0.918 ≤ *C* ≤ 0.999), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, *T* = 223 K, ω/2θ scans, 10 412 reflections collected (±*h*, ±*k*, −*l*), [(sin θ)/λ] = 0.59 Å⁻¹, 10 024 independent and 6956 observed reflections [*I* ≥ 2 σ(*I*)], 758 refined parameters, R1 = 0.063, wR2 = 0.182, max (min) residual electron density 0.99 (−1.25) e Å⁻³, hydrogens calculated and refined as riding atoms.

Methylbis{[[1-methyl-1-(diphenylphosphino)ethyl]-η⁵-cyclopentadienyl]-κ²-P,P′}zirconium(IV) Methyltris(pentafluorophenyl)borate (3b). In a similar procedure, the analogous cationic system with Ar = Ph was obtained, starting from 211 mg (0.3 mmol) of **2b** and 154 mg (0.3 mmol) of B(C₆F₅)₃. Yield of **3b**: 350 mg (95%). Large colorless crystals were grown by diffusion of pentane into a dichloromethane solution of **3a** at −20 °C. Mp 201 °C (dec). Anal. Calcd for C₆₀H₄₆BF₁₅P₂Zr (1215.97): C, 59.27; H, 3.81. Found: C, 59.30; H, 3.81. IR (KBr): ṽ 3121, 3064, 2996, 2964, 2941, 2929, 2903, 2844, 1641, 1511, 1458 (br, vs), 1436, 1265, 1096 (br, vs), 995, 978, 965, 949, 935, 828, 802, 743, 707, 696, 659, 640 cm⁻¹. ¹H NMR (dichloromethane-d_2, 200.1 MHz, 243 K): δ 7.7−7.2 (m, 20H, Ph), 6.47 (m, 4H, C₅H₄), 6.33, 5.97 (each m, each 2H, C₅H₄), 1.86 (m, 6H, CMe₂), 1.29 (m, 6H, CMe₂), 0.45 (br s, 3H, [B]−CH₃), −0.39 (t, $^3J_{PH}$ = 15.1 Hz, 3H, Zr−CH₃). ¹³C NMR (dichloromethane-d_2, 50.3 MHz, 238 K): δ 147.8 ($^1J_{FC}$ = 229 Hz, o-C₆F₅), 137.3 ($^1J_{FC}$ = 230 Hz, p-C₆F₅), 136.9 (ipso-C of Cp), 136.0 ($^1J_{FC}$ = 250 Hz, m-C₆F₅), 135.3 (o-Ph), 134.5 (o-Ph), 131.13, 131.05 (p-Ph), 129.3 (m-Ph), 129.0 (m-Ph), 124.9 (ipso-C of Ph), 111.5, 106.9 (double intensity), 97.7 (Cp), 34.8 (CMe₂), 30.3, 25.2 (C(CH₃)₂), 17.3 (t, $^2J_{PC}$ = 10 Hz, Zr−CH₃), 9.7 (br, [B]−CH₃); one ipso-C of Ph not observed. ³¹P NMR (dichloromethane-d_2, 81.0 MHz): δ −22.3.

Chlorobis{[[1-methyl-1-(di-p-tolylphosphino)ethyl]-η⁵-cyclopentadienyl]-κ²-P,P′}zirconium(IV) Methyltris(pentafluorophenyl)borate (5). A solution of 408 mg (0.80 mmol) of B(C₆F₅)₃ in 20 mL of dichloromethane was added to a solution of 304 mg (0.43 mmol) of **2a** in 20 mL of dichloromethane at 0 °C. A yellow solution was formed immediately. Removal of the solvent and washing of the product with pentane and drying in vacuo yielded 670 mg of crude **5**. Mp. 222 °C (dec). By layering a dichloromethane solution of **5** with pentane at −20 °C, big crystals covered with some oily product could be isolated. Repetition of the crystallization process and washing of the so-formed crystals with cold dichloromethane yielded crystals suitable for an X-ray-diffraction analysis. IR (KBr): ṽ 3029, 2993, 2973, 2957, 2924, 2864, 1641, 1598, 1510, 1498, 1459 (br, vs), 1411, 1398, 1384, 1370, 1311, 1295, 1266, 1191, 1088, 1081 993, 976, 965, 947, 935, 830, 802, 766, 757, 736, 707, 659, 631, 607 cm⁻¹. ¹H NMR (dichloromethane-d_2, 200.1 MHz): δ 7.5−7.2 (m, 16H, tol-H), 6.5−6.4 (m, 8H, C₅H₄), 6.22 (m, 4H, C₅H₄), 6.12 (m, 4H, C₅H₄), 2.41 (s, 12H, tol-CH₃), 1.75 (m, 6H, CMe₂), 1.55 (m, 6H, CMe₂), 0.50 (br s, 6H, [B]−CH₃). ¹³C NMR (dichloromethane-d_2, 150 MHz): δ 148.7 ($^1J_{FC}$ = 221 Hz, o-C₆F₅), 142.88, 142.33 (each ipso-C of p-tol), 139.5 (br s, C1 of Cp), 137.9 (p-C₆F₅), 136.8 ($^1J_{FC}$ = 249 Hz, m-C₆F₅), 136.89 (o-tol), 134.2 (o-tol), 130.7 (m-tol), 129.9 (m-tol), 129.2 (br, ipso-C of H₃CB(C₆F₅)₃⁻), 126.3 (ipso-C of tol), 122.1 (ipso-C of tol), 116.3, 112.7, 108.3, 100.8 (Cp), 35.73 (CMe₂), 29.75, 26.38 (C(CH₃)₂), 21.70, 21.35 (CH₃) 10.6 ([B]−CH₃). ³¹P NMR (dichloromethane-d_2, 81.0 MHz): δ −33.0. ¹¹B NMR: δ −15. LDI-TOF MS (negative): *m/z* = 527 (H₃CB(C₆F₅)₃⁻). Anal. Calcd for C₆₃H₅₁BClF₁₅P₂Zr (1292.50): C, 58.54; H, 3.98. Found: C, 57.41; H, 3.97.

X-ray Crystal Structure Analysis of 5. Formula $C_{63}H_{51}$-BClF₁₅P₂Zr; *M* = 1292.46; 0.40 × 0.30 × 0.30 mm; *a* = 14.165-(3) Å, *b* = 14.950(2) Å, *c* = 16.165(3) Å, α = 113.94(2)°, β = 109.62(2)°, γ = 95.48(2)°, *V* = 2838.3(9) Å³, ρ_{calc} = 1.512 g cm⁻³, μ = 3.88 cm⁻¹, empirical absorption correction via φ scan data (0.907 ≤ *C* ≤ 0.999), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, *T* = 223 K, ω/2φ scans, 10 438 reflections collected (−*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.59 Å⁻¹, 9994 independent and 6378 observed reflections [*I* ≥ 2 σ(*I*)], 753 refined parameters, R1 = 0.065, wR2 = 0.168, max (min) residual electron density 1.13 (−0.93) e Å⁻³, hydrogens calculated and refined as riding atoms.

Chlorobis{[[1-methyl-1-(di-p-tolylphosphino)ethyl]-η⁵-cyclopentadienyl]-κ²-P,P′}zirconium(IV) Chlorotris(pentafluorophenyl)borate (5′). **1a** (200 mg, 0.25 mmol) and 1 equiv of B(C₆F₅)₃ (128 mg, 0.25 mmol) were mixed and then dissolved in 20 mL of dichloromethane at room temperature. The yellow solution was stirred for 15 min. The solvent was then removed in vacuo and the residue was washed with two 5 mL portions of pentane and dried in vacuo to yield 290 mg (88%) of **5′** as an off-white solid. Crystalline material was obtained by layering a dichloromethane solution of **5′** with an equal amount of pentane at −20 °C. Mp 99 °C (dec). IR (KBr): ṽ 3032, 2966, 2925, 2871, 1644, 1599, 1515, 1464 (br, vs), 1399, 1381, 1374, 1280, 1263, 1194, 1095 (br, s), 979 (br, s), 825, 806 (s), 772, 765, 668 cm⁻¹. ¹H NMR (dichloromethane-d_2, 200.1 MHz): δ 7.50, 7.33, 7.14 (each m, 16H, tol-H), 6.42 (2 m), 6.26, 6.21 (each m, each 2H, C₅H₄), 2.41 (s, 12H, tol-CH₃), 1.75 (m, 6H, CMe₂), 1.51 (m, 6H, CMe₂). ¹³C NMR (dichloromethane-d_2, 150 MHz): δ 148.5 ($^1J_{FC}$ = 232 Hz, o-C₆F₅), 142.77, 142.27 (each ipso-C of p-tol), (m,p-C₆F₅ could not unambiguously be assigned), 139.3 (br s, C1 of Cp), 136.9 (o-tol), 134.2 (o-tol), 130.6 (m-tol), 129.8 (m-tol), 126.2 (ipso-C of tol), 122.2 (ipso-C of tol), 116.2, 112.6, 108.7, 101.1 (Cp), 35.7 (CMe₃), 29.7, 26.4 (C(CH₃)₂), 21.7, 21.3 (each tol-CH₃). ³¹P NMR (dichloromethane-d_2, 81.0 MHz): δ −33.0. ¹¹B NMR: δ −3. LDI-TOF (negative): *m/z* = 547 (ClB(C₆F₅)₃⁻). Anal. Calcd for C₆₂H₄₈BCl₂F₁₅P₂Zr (1312.92): C, 56.72; H, 3.68. Found: C, 54.29; H, 3.44.

X-ray Crystal Structure Analysis of 5′. Formula $C_{62}H_{48}$-BCl₂F₁₅P₂Zr; *M* = 1312.87; 0.15 × 0.10 × 0.05 mm; *a* = 14.157-(4) Å, *b* = 14.964(5) Å, *c* = 16.122(4) Å, α = 114.37(2)°, β = 109.69(3)°, γ = 95.51(2)°, *V* = 2817.0(14) Å³, ρ_{calc} = 1.548 g cm⁻³, μ = 4.38 cm⁻¹, empirical absorption correction via φ scan data (0.924 ≤ *C* ≤ 0.999), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, *T* = 223 K, ω scans, 9230 reflections collected (±*h*, +*k*, ±*l*), [(sin θ)/λ] = 0.57 Å⁻¹, 8846 independent and 4148 observed reflections [*I* ≥ 2 σ(*I*)], 756 refined parameters, R1 = 0.057, wR2 = 0.109, max (min) residual electron density 1.05 (−0.48) e Å⁻³, hydrogens calculated and refined as riding atoms.

Low-Temperature Study on the Demethylation−Chlorination Process in Dichloromethane. **2a** (15.2 mg) and B(C₆F₅)₃ (20.4 mg) were dissolved separately in dichloromethane-d_2, and the B(C₆F₅)₃ solution was cannula-transferred to the **2a** solution at −78 °C. The first NMR spectrum was obtained at a temperature of −50 °C after keeping the solution for 30 min at −78 °C. ³¹P NMR (dichloromethane-d_2, 81.0 MHz): δ −22.0 (**3a**), −33 (**5**), −48 (**4**). The following **3a:5:4** ratios were observed by ³¹P NMR spectroscopy subsequently after keeping the same sample for the time indicated at the temperatures noted: *T* = 213 K (30 min), 65:9:26; 223 K (45 min), 51:9:40; 228 K (60 min), 27:11:62; 228 K (90 min), 11:15:74; 238 K (105 min), 9:18:73; 253 K (125 min), 0:20:80; 275 K (170 min) and 295 K (5 min) 0:48:52; ambient temperature (225 min) and 295 K (30 min) 0:100:0.

Formation of the Dication 4. Toluene (20 mL) was vacuum-condensed from potassium/sodium alloy onto a mixture of 400 mg (0.57 mmol) of **2a** and 512 mg (1.00 mmol) of B(C₆F₅)₃ in a Schlenk tube. A red oily product formed as the reaction mixture was warmed to room temperature. After 15 min at this temperature, the toluene was decanted inside the

glovebox and the remaining red oil was washed twice with 10 mL portions of pentane and then dried in vacuo yielding 850 mg (93%) of **4** as an orange solid. The product is insoluble in toluene and slightly soluble in bromobenzene and was identified by low-temperature NMR in dichloromethane-d_2 and its dichloromethane-stable acetonitrile adduct (**6**), which could also be synthesized on a preparative scale. ^{1}H NMR of **4** (275 K, dichloromethane-d_2 (spectra were recorded using a 1:1 mixture of **4** and **5**)): 7.6−7.0 (m, 16H, tol-H), 6.85 (m, 4H, C$_5$H$_4$), 6.49 (m, 4H, C$_5$H$_4$), 2.39 (s, 6H, tol-CH$_3$), 2.29 (s, 6H, tol-CH$_3$), 1.93 (m, 6H, CMe$_2$), 1.59 (m, CMe$_2$), 0.45 ([B]−CH$_3$). ^{31}P NMR (dichloromethane-d_2, 81.0 MHz, 275 K): δ −48.5. ^{31}P NMR (bromobenzene-d_5, 81.0 MHz): δ −48.3. Anal. Calcd for C$_{82}$H$_{54}$B$_2$F$_{30}$P$_2$Zr (1784.06); C, 55.21; H, 3.05. Found: C, 55.18; H, 3.44.

Preparation of Acetonitrilobis{[[1-methyl-1-(di-*p*-tolylphosphino)ethyl]-η^5-cyclopentadienyl]-κ^2-*P,P'*}-zirconium(IV) Bis(methyltris(pentafluorophenyl)borate) 6. (a) Homogeneously in CH$_2$Cl$_2$: To a solution of 152 mg (0.2 mmol) of **2a** in 5 mL of dichloromethane was added a solution of 204 mg of B(C$_6$F$_5$)$_3$ (0.4 mmol) in 20 mL of dichloromethane at −78 °C. The solution turned bright yellow within minutes. The temperature was raised to −50 °C within 1 h. The reaction mixture was stirred for additional 90 min at temperatures around −40 °C. At this temperature, 10.4 μL (0.2 mmol) of acetonitrile was added and the mixture kept overnight at −20 °C. The solvent was removed in vacuo, yielding 350 mg of a 70:30 mixture of the acetonitrile adduct **6** and the chlorocation **5**. (b) Heterogeneously from toluene: A Schlenk flask was charged with 234 mg (0.3 mmol) of **2a** and 308 mg (0.6 mmol) of B(C$_6$F$_5$)$_3$, and then 10 mL of toluene was added at room temperature in the glovebox. The mixture immediately turned orange with the dication **4** precipitating as a red oil. After 30 min, 16 μL (0.3 mmol) of acetonitrile was added and the reaction mixture stirred for additional 15 min. The toluene solvent was decanted from the oily product. Washing with 5 mL of toluene and then 5 mL of pentane and drying in vacuo for 24 h led to the formation of a yellow solid product. Yield of **6**: 490 mg (89%). Mp 192 °C (dec). IR (KBr): $\tilde{\nu}$ 3122, 2962, 2927, 2867, 2307 (ν(C≡N), comb.), 2273 (ν(C≡N)), 1641, 1599, 1511 (vs), 1458 (br, vs), 1400, 1382, 1267, 1194, 1087 (br, vs), 995, 979, 966, 952, 934, 835, 805, 660 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 600 MHz): 7.38 (m, 12H, o,*m*-tol-H), 7.18 (m, 4H, *o*-tol-H), 6.73, 6.46, 6.38, 6.20 (each m, each 2H, C$_5$H$_4$), 2.43, 2.41 (each s, each 6H, tol-CH$_3$), 1.78 (m, 6H, CMe$_2$), 1.44 (m, 6H, CMe$_2$), 1.32 (t, $^5J_{PH}$ = 3.3 Hz, 3H, Zr-NC-CH$_3$), 0.50 (br, [B]−CH$_3$). ^{13}C NMR (dichloromethane-d_2, 150 MHz): δ 148.7 ($^1J_{FC}$ = 240 Hz, *o*-C$_6$F$_5$), 145.1, 144.6 (each s, ipso-C of *p*-tol), 141.5 (s, C≡N), 137.8 ($^1J_{FC}$ = 242 Hz, *p*-C$_6$F$_5$), 137.8 (C1 of Cp), 136.7 ($^1J_{FC}$ = 245 Hz, *m*-C$_6$F$_5$), 135.5 (*o*-tol), 134.4 (*o*-tol), 131.5 (2*m*-tol), 122.5 (ipso-C of tol), 119.6 (ipso-C of tol), 117.1, 108.5, 107.9, 101.2 (Cp), 36.0 (CMe$_2$), 29.4, 26.3 (C(CH$_3$)$_2$), 21.53, 21.42 (tol-CH$_3$), 10.5 ([B]−CH$_3$), 2.92 (s, CH$_3$CN). GHSQC-NMR^{24} (dichloromethane-d_2): δ 135.5/7.38, 134.4/7.18, (each *o*-tol); 131.5/7.38 (*m*-tol); 117.1/6.73, 108.5/6.46, 107.9/6.20, 101.2/6.38, (each C$_5$H$_4$); 29.4/1.44, 26.33/1.78 (CMe$_2$); 21.53, 21.42/2.43, 2.41 (each tol-CH$_3$); 10.5/0.50 ([B]−CH$_3$); 1.32/2.92 (CH$_3$CN). GHMBC-NMR^{24} (dichloromethane-d_2): δ 145.1 (*p*-tol)/7.38 (o,*m*-tol-H), 2.43, 2.41 (tol-CH$_3$); 144.6 (*p*-tol)/7.18 (o-tol-H), 2.43, 2.41 (tol-CH$_3$); 141.5 (C≡N)/1.32 (CH$_3$CN); 137.8 (C1 of Cp)/6.44, 6.38 (C$_5$H$_4$), 1.78, 1.44 (CMe$_2$); 135.5 (*o*-tol)/7.38 (o,*m*-tol-H); 134.4 (*o*-tol)/7.18 (o-tol-H); 131.5 (2-*m*-tol)/7.38 (o,*m*-tol-H), 2.43, 2.41 (tol-CH$_3$); 122.5 (ipso-C of tol)/7.38 (o,*m*-tol-H); 119.6 (ipso-C of tol)/7.38 (o,*m*-tol-H); 117.1/6.38, 108.5/6.20, 107.9/6.46, 6.38, 101.2/6.20 (each C$_5$H$_4$/C$_5$H$_4$); 36.0 (CMe$_2$)/1.78, 1.44 (C(CH$_3$)$_2$); 29.4 (C(CH$_3$)$_2$)/1.78 (C(CH$_3$)$_2$); 26.3 (C(CH$_3$)$_2$)/1.44 (C(CH$_3$)$_2$); 21.5, 21.4 (tol-CH$_3$)/7.38 (o,*m*-tol-H), 2.43, 2.41 (tol-CH$_3$). ^{31}P NMR (dichloromethane-d_2, 81.0 MHz): δ −44.7. Anal. Calcd for

C$_{84}$H$_{57}$NB$_2$F$_{30}$P$_2$Zr (1825.11): C, 55.28; H, 3.15; N, 0.77. Found: C, 55.40; H, 3.53; N, 0.70.

((2,6-Dimethylphenyl)isonitrilo)bis{[[1-methyl-1-(di-*p*-tolylphosphino)ethyl]-η^5-cyclopentadienyl]-κ^2-*P,P'*}-zirconium(IV) Bis(methyltris(pentafluorophenyl)borate) (7). Formation of the dication **4** in toluene from 234 mg (0.3 mmol) of **2a** and 308 mg (0.6 mmol) of B(C$_6$F$_5$)$_3$ followed by addition of 39 mg (0.30 mmol) of (2,6-dimethylphenyl)isonitrile, dissolved in 3 mL of toluene, resulted in the formation of adduct **7** as a red oil. The solvent was decanted, and the product was worked-up as described above. Yield: 470 mg (0.24 mmol, 81%). Mp 168 °C (dec). IR (KBr): $\tilde{\nu}$ 3123, 2964, 2927, 2871, 2170 (C≡N−R), 1641, 1599, 1511 (vs), 1458 (br, vs), 1400, 1382, 1267, 1087 (br, vs), 995, 979, 966, 952, 934, 833, 805, 660 cm^{-1}. ^{1}H NMR (dichloromethane-d_2, 600 MHz): 7.37, 7.32, 7.07−7.03 (each m, 19H, tol-H, isonitrile-H), 6.54, 6.46, 6.44, 6.38 (m, each 2H, each C$_5$H$_4$), 2.42 (s, 6H, tol-CH$_3$), 2.06 (s, 6H, CH$_3$ of isonitrile), 2.02 (s, 6H, tol-CH$_3$), 1.97 (m, 6H, CMe$_2$), 1.42 (m, 6H, CMe$_2$), 0.51 (br, 6H, [B]−CH$_3$). ^{13}C NMR (dichloromethane-d_2, 150 MHz): δ 148.6 ($^1J_{FC}$ = 235 Hz, *o*-C$_6$F$_5$), 144.71, 144.57 (*p*-tol), 137.9 ($^1J_{FC}$ = 242 Hz, *p*-C$_6$F$_5$), 136.7 ($^1J_{FC}$ = 238 Hz, *m*-C$_6$F$_5$), 136.4 (C1 of Cp), 135.5 (C2/C6 of isonitrile), 134.45 (*o*-tol), 134.19 (*o*-tol), 133.1 (CN-Ph tentatively), 131.4 (*m*-tol), 130.9 (*m*-tol), 129.3 (*m*-CH of isonitrile), 123.3 (ipso-C of tol), 122.8 (C1 of isonitrile), 120.7 (ipso-C of tol), 117.7, 107.3, 101.6, 100.3 (Cp), 36.0 (CMe$_2$), 28.9, 27.1 (C(CH$_3$)$_2$), 21.4, 21.2 (tol-CH$_3$), 19.2 (CH$_3$ of isonitrile), 10.5 (br, [B]−CH$_3$); *p*-CH of isonitrile not observed, probably hidden by *o*-tol-CH at 134.5 ppm. GHSQC-NMR^{24} (dichloromethane-d_2): δ 134.5/7.32 (*o*-tol), 134.2/7.07 (*o*-tol), 131.4/7.37 (*m*-tol), 130.9/7.03 (*m*-tol), 129.3/7.07 (*m*-CH of isonitrile) 117.6/6.46, 107.3/6.54, 101.6/6.38, 100.3/6.44 (each C$_5$H$_4$), 28.9/1.42, 27.1/1.97 (C(CH$_3$)$_2$), 21.4/2.42, 21.2/2.02 (tol-CH$_3$), 19.2/2.06 (CH$_3$ of isonitrile), 10.5/0.51 ([B]−CH$_3$). GHMBC-NMR^{24} (dichloromethane-d_2): δ 144.71, 144.57 (*p*-tol)/7.32, 7.07−7.03 (o,*m*-tol-H), 2.42, 2.02 (tol-CH$_3$), 136.4 (C1 of Cp)/6.54, 6.46, 6.44, 6.38 (C$_5$H$_4$), 1.97, 1.42 (C(CH$_3$)$_2$), 135.5 (C2/C6 of isonitrile)/7.32 (CH of isonitrile), 2.06 (CH$_3$ of isonitrile), 134.5, 134.2 (*o*-tol)/7.37, 7.32, 7.07−7.03 (o,*m*-tol-H), 131.4, 130.9 (*m*-tol)/7.37, 7.03 (o,*m*-tol-H), 2.42, 2.02 (tol-CH$_3$), 129.3 (CH of isonitrile)/7.07 (CH of isonitrile), 2.06 (CH$_3$ of isonitrile), 123.3 (ipso-C of tol)/7.37 (*m*-tol-H), 1.97, 1.42 (C(CH$_3$)$_2$), 122.8 (C1 of isonitrile)/7.07 (*m*-CH of isonitrile), 120.7 (ipso-C of tol)/7.03 (*m*-tol-H), 1.42 (C(CH$_3$)$_2$), (117.7/6.44, 6.38), (107.3/6.44, 6.38), (101.6/6.54, 6.44), (100.3/6.38) (each C$_5$H$_4$/C$_5$H$_4$), 36.0 (CMe$_2$)/1.97, 1.42 (C(CH$_3$)$_2$), 28.9 (C(CH$_3$)$_2$)/1.97 (C(CH$_3$)$_2$), 27.08 (C(CH$_3$)$_2$)/1.42 (C(CH$_3$)$_2$), 21.4, 21.2 (tol-CH$_3$)/7.37, 7.07−7.03 (o,*m*-tol-H), 2.42, 2.02 (tol-CH$_3$), 19.2 (CH$_3$ of isonitrile)/2.06 (CH$_3$ of isonitrile). ^{31}P NMR (dichloromethane-d_2, 81.0 MHz): δ −51.7. Anal. Calcd for C$_{91}$H$_{63}$-NB$_2$F$_{30}$P$_2$Zr (1915.24): C, 57.07; H, 3.32; N, 0.73. Found: C, 56.70; H, 3.59; N, 0.80.

Supporting Information Available: Details about the X-ray crystal structures; including ORTEP diagrams and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **1b**, **2b**, **3a**, **5**, and **5′** (52 pages). Ordering information is given on any current masthead page.

(24) Braun, S.; Kalinowski, H.; Berger, S. In *100 and More Basic NMR Experiments*; VCH: Weinheim, 1996; and references cited therein.