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Reactions of (Diphenylphosphinomethyl)zirconocene Chloride with $B(C_6F_5)_3$: Competition between P/B and P/Zr^+ Frustrated Lewis Pair Reactions

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Supporting Information

ABSTRACT: The title complex $Cp_2ZrCl(CH_2PPh_2)$ reacts with $B(C_6F_5)_3$ under specific conditions by phosphinomethyl transfer to give the phosphane-stabilized salt $[Cp_2ZrCl^+][Ph_2PCH_2B(C_6F_5)_3^-]$. X-ray crystal structure analysis showed the P−Zr coordination. This salt is trapped by phenyl isocyanate in an in situ three-component reaction to yield the respective P/Zr^+ frustrated Lewis pair (FLP) addition product. In contrast, a mixture of $Cp_2ZrCl(CH_2PPh_2)/B(C_6F_5)_3$ and benzaldehyde under similar conditions gives the P/B FLP addition product. The $Cp_2ZrCl(CH_2PPh_2)/B(C_6F_5)_3$ system may form a P/B adduct $[Cp_2ZrCl(CH_2PPh_2)\cdot B(C_6F_5)_3]$ or a P/Zr^+ adduct $[Cp_2ZrCl\cdot PPh_2CH_2B(C_6F_5)_3]$. From the former it seems to show P/B FLP reaction and from the latter P/Zr^+ FLP behavior; the outcome is dependent on the specific reagent and reaction conditions chosen.

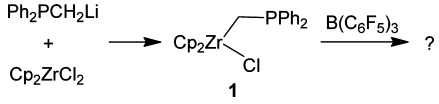
INTRODUCTION

Frustrated Lewis pair (FLP) chemistry has seen the development of a great variety of main-group element systems for small-molecule binding and activation.[1] Metal-free heterolytic dihydrogen splitting[2] by P/B or N/B systems (and a few others)[3] is a prominent example that has led to the development of FLP-catalyzed hydrogenation reactions of a variety of organic substrates.[4,5] Whereas most FLP systems contain Lewis acid/Lewis base components based on main-group elements, there has been a beginning development of using transition-metal-based Lewis acid components, most notably zirconocene-derived cations.[6,7] We here wish to describe first experiments that we have carried out in this direction using N. Shore's (diphenylphosphinomethyl)-zirconocene chloride complex **1**[8] in conjunction with $B(C_6F_5)_3$. This results in the interesting situation that **1** may just serve as a phosphane Lewis base (having a bulky organometallic substituent) to form a conventional P/B FLP with the tris(pentafluorophenyl)borane Lewis acid or undergo abstraction of the $Ph_2P-CH_2^-$ anion equivalent by the borane to then give a P/Zr^+ FLP (see Scheme 1). We shall see which pathway will be followed in this system.

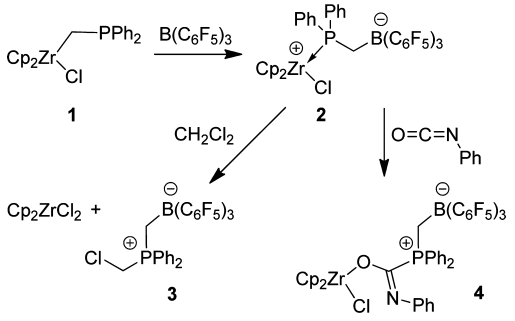
RESULTS AND DISCUSSION

FLP Trapping Reactions. We treated compound **1** with $B(C_6F_5)_3$ in dichloromethane solution for 3 days at ambient temperature. Workup then gave a mixture of Cp_2ZrCl_2 and the phosphonium borate product **3** (Scheme 2). We obtained single crystals that allowed us to identify and characterize compound **3** by X-ray diffraction (Figure 1). The analysis revealed that under these conditions the Ph_2PCH_2 group was transferred from the zirconocene to the borane, followed by trapping of the alleged product **2** by the CH_2Cl_2 solvent (Scheme 2).[7] Chloride abstraction by the cation gave zirconocene dichloride. The remaining $ClCH_2$ group was found bonded to the phosphorus atom of the respective $Ph_2P-CH_2-B(C_6F_5)_3$ anion. In the product **3** the boron and phosphorus atoms are bridged by a methylene group [B1−C1 1.673(5) Å, P1−C1 1.789(3) Å] and the phosphonium center bears the CH_2Cl group [P1−C2 1.811(4) Å, C2−Cl1 1.773(4) Å]. The central core of compound **3** shows a gauche conformation [B1−C1−P1−C2 −52.8(3)°].

Scheme 1. Synthesis of Compound 1



Scheme 2. Formation and Reactions of the P/Zr^+ FLP 2



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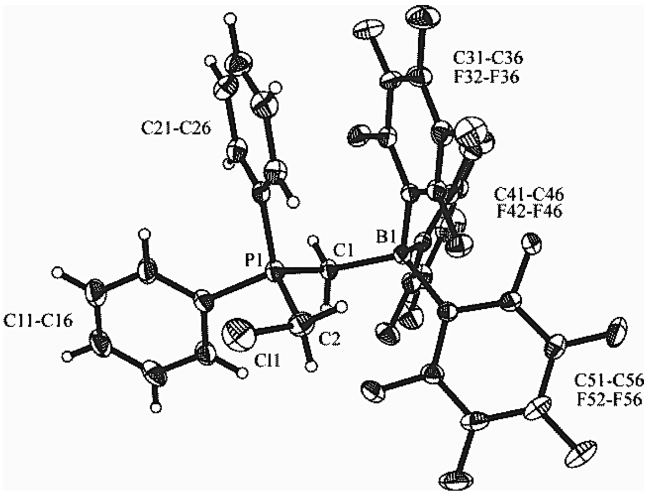


Figure 1. Molecular structure of the phosphonium borate zwitterion **3** (thermal ellipsoids are shown with 30% probability).

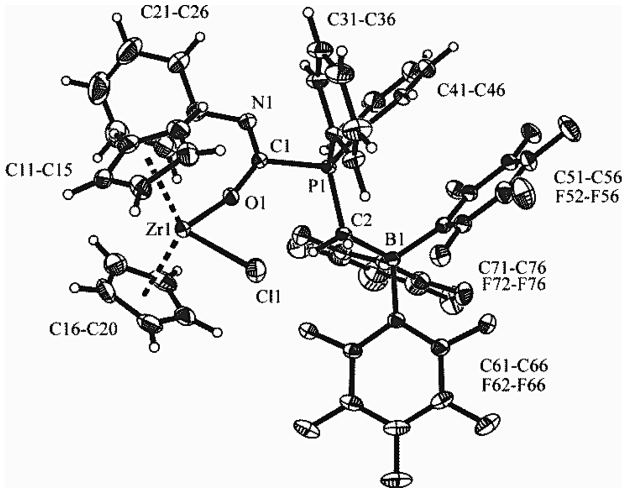


Figure 2. Molecular structure of compound **4** (thermal ellipsoids are shown with 30% probability).

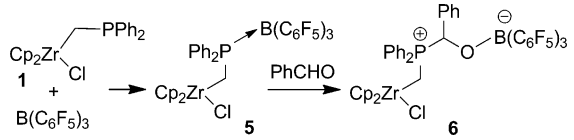
In solution we monitored the heteronuclear magnetic resonance signals of compound **3** [^{11}B: δ −15.7; ^{31}P: δ +34.3; ^{19}F: δ −131.9 (o), −160.5 (p), −164.9 (m)]. We observed the ^{1}H/^{13}C NMR signals of a pair of methylene groups. The [P]−CH_2−[B] group gives rise to an overlapping equal-intensity ^{1}H NMR doublet of 1:1:1:1 quartets at δ 3.05 ($^{2}J_{PH}$ = 16.9 Hz, $^{2}J_{BH}$ = 5.6 Hz; ^{13}C NMR resonance at δ 15.4). The [P]−CH_2Cl moiety gives rise to a ^{13}C NMR signal at δ 31.9 (d, $^{1}J_{PC}$ = 52.7 Hz) and a corresponding ^{1}H NMR signal at δ 4.36 ($^{2}J_{PH}$ = 5.0 Hz).

We were able to trap the P/Zr^{+} FLP **2** by a typical frustrated pair 1,2-addition reaction to the carbonyl group of phenyl isocyanate.[9] Treatment of an equimolar mixture of **1**, $B(C_6F_5)_3$, and O═C═NPh in dichloromethane/pentane gave the addition product **4** (Scheme 2) as a colorless crystalline precipitate that was isolated in >70% yield. In dichloromethane solution **4** shows a single sharp Cp ^{1}H NMR signal of the [Cp_2Zr] unit (δ 5.86, 10H; the corresponding ^{13}C NMR resonance is at δ 116.1) and the typical [P]−CH_2−[B] ^{1}H NMR signal at δ 3.08 (1H, doublet of 1:1:1:1 quartets, $^{2}J_{PH}$ = 18.4 Hz, $^{2}J_{BH}$ = 6.2 Hz; the corresponding ^{13}C, ^{11}B, and ^{31}P NMR signals are at δ 11.0, −15.8, and +23.9, respectively). The ^{13}C NMR signal of the O−C═N carbon was located at δ 157.6 ($^{1}J_{PC}$ = 144.7 Hz).

Product **4** was also characterized by X-ray diffraction (Figure 2), which confirmed that P/Zr^{+} FLP **2** underwent 1,2-addition to the carbonyl group. The zirconium atom added to the carbonyl oxygen atom of the isocyanate reagent [bond lengths Zr1−O1 2.042(2) Å, O1−C1 1.307(4) Å; angles Zr1−O1−C1 152.8(2)°, O1−Zr1−Cl1 95.7(1)°]. Carbon atom C1 is sp^{2}-hybridized and shows bond angles of N1−C1−O1 130.3(3)°, N1−C1−P1 116.6(3)°, and O1−C1−P1 112.9(2)°. The C1−N1 bond [1.273(4) Å] is in the typical C═N double-bond range. The phosphane added to C1 [P1−C1 1.852(3) Å]. The phosphorus atom also has the CH_2−$B(C_6F_5)_3$ unit bonded to it [bond lengths P1−C2 1.793(3) Å, C2−B1 1.666(5) Å; angle P1−C2−B1 123.9(2)°], which makes product **4** overall neutral.

These results indicate that we generated the P/Zr^{+} FLP **2** upon treatment of **1** with $B(C_6F_5)_3$. P/Zr^{+} FLP **2** was subsequently scavenged by, for example, phenyl isocyanate to yield product **4**. However, this seems not to be the only pathway that can be observed. We found a different reaction type to be favored when we treated the $Cp_2ZrCl(CH_2PPh_2)$/$B(C_6F_5)_3$ mixture with benzaldehyde under similar reaction conditions.[10] Treatment of **1** with $B(C_6F_5)_3$ and PhCHO in a 1:1:1 ratio for 2 days in CH_2Cl_2/pentane gave product **6** (Scheme 3), which was isolated as a white crystalline solid in ca. 75% yield.

Scheme 3. Formation of the P/B FLP 5 and Trapping of 5 to Give 6



X-ray crystal structure analysis of **6** (Figure 3) revealed that the phosphane of the intact $Cp_2ZrCl(CH_2PPh_2)$ moiety added

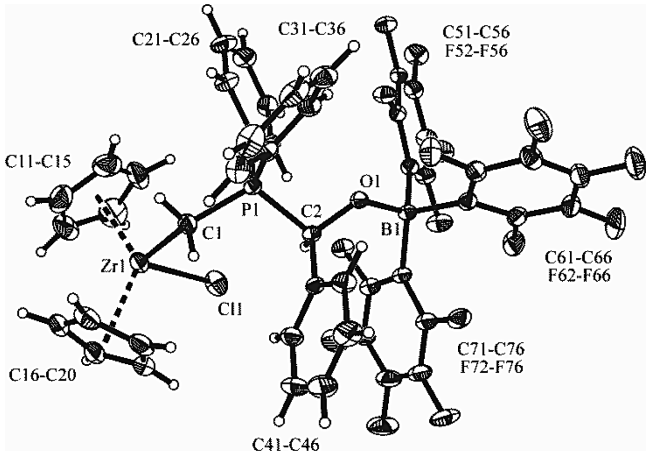


Figure 3. A view of the molecular structure of complex **6** (thermal ellipsoids are shown with 30% probability).

to the benzaldehyde carbonyl carbon atom [bond lengths P1−C2 1.859(2) Å, C2−O1 1.399(3) Å; angle P1−C2−O1 104.7(1)°] and the $B(C_6F_5)_3$ Lewis acid added to the carbonyl oxygen atom [bond length O1−B1 1.484(3) Å; angle C2−O1−B1 122.3(2)°; P1−C2−O1−B1 dihedral angle −154.7(2)].

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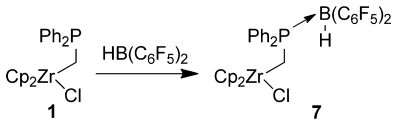
The $Cp_2ZrCl(CH_2PPh_2)$ unit in **6** shows the following bonding parameters: bond lengths Zr1−Cl1 2.426(1) Å, Zr1−C1 2.357(2) Å, C1−P1 1.774(2) Å; angles Cl1−Zr1−C1 98.0(1)°, Zr1−C1−P1 129.3(1)°. It should be noted that Shore's complex **1**[8] shows similar data (e.g., Zr−Cl 2.45 Å, Zr−CH_2 2.28 Å, Cl−Zr−CH_2 90.4°, Zr−C−P 130.1°).

Complex **6** shows a ^{31}P NMR resonance at δ 37.3 and a ^{11}B NMR signal at δ −2.2. The hydrogen atoms of the [Zr]−CH_2−[P] methylene group are diastereotopic. Their ^1H NMR signals occur at δ 1.64 ($^2J_{PH}$ = 21.3 Hz) and 1.39 ($^2J_{PH}$ = 18.8 Hz, $^2J_{HH}$ = 13.0 Hz). The corresponding ^{13}C NMR resonance is at δ 10.8 ($^1J_{PC}$ = 30.5 Hz). The former aldehyde carbonyl carbon atom gives rise to a ^{13}C NMR signal at δ 78.1 ($^1J_{PC}$ = 68.7 Hz). The corresponding ^1H NMR resonance occurs at δ 5.55 ($^2J_{PH}$ = 5.5 Hz).

We also treated the P/B FLP **5** with phenyl isocyanate. However, in this case we observed the addition product **4** derived from the rearranged P/Zr^+ FLP **2** (for details, see the Supporting Information).

Identification and Characterization of the P/B and P/Zr^+ FLP Isomers. It looks as if there are two different frustrated Lewis pairs operative in the $Cp_2ZrCl(CH_2PPh_2)$/$B(C_6F_5)_3$ system, namely, the P/B system [**5** ⇄ **1** + $B(C_6F_5)_3$] and the P/Zr^+ system **2** (see Schemes 2 to 4). Possibly, these

Scheme 4. Formation of the P/B Lewis pair 7



interconverte under the specific conditions that we applied in our trapping experiments. In order to get some more direct information about the species involved, we reacted **1** with electrophilic boranes under various reaction conditions.

We tried but could not get crystals of the phosphane/$B(C_6F_5)_3$ adduct **5**. However, a related P/B adduct, **7**, was obtained as colorless crystals (ca. 71% isolated yield) from the reaction mixture of **1** with Piers' borane [$HB(C_6F_5)_2$][11] in CH_2Cl_2/pentane after several days at room temperature (Scheme 4).

In the crystal structure of compound **7** (Figure 4), we found that the $HB(C_6F_5)_2$ unit is bonded to the phosphane of the $Cp_2ZrCl(CH_2PPh_2)$ unit [bond lengths P1−B1 1.972(4) Å, C1−P1 1.789(3) Å; angle C1−P1−B1 109.2(2)°]. The remaining bonding parameters of the metallocene unit are as follows: C1−Zr1 2.365(3) Å, Zr1−Cl1 2.423(1) Å, C1−Zr1−Cl1 104.9(1)°. Both the phosphorus and boron atoms show pseudotetrahedral coordination geometries ($\sum P1^{CCC}$ = 318.7°, $\sum B1^{PCC}$ = 339.9°). The complex shows a conformation in the solid state that is characterized by Cl1−Zr1−C1−P1 and Zr1−C1−P1−B1 dihedral angles of −21.7(2)° and 64.0(2)°, respectively.

The **1**/$HB(C_6F_5)_2$ adduct **7** is characterized by a ^{31}P NMR signal at δ 18.4 and an ^{11}B NMR resonance at δ −23.6. It features $^1J_{PB} \approx {}^1J_{BH}$ coupling constants of ca. 77 Hz. The [B]H resonance was located in the ^1H NMR spectrum as a broad signal at δ 4.08. The [Zr]−CH_2−[P] ^1H NMR resonance of **7** was found at δ 1.58 ($^2J_{PH}$ = 16.0 Hz); the corresponding ^{13}C resonance is at δ 27.6 ($^1J_{PC}$ = 22.6 Hz).

We generated the $Cp_2ZrCl(CH_2PPh_2)\cdot B(C_6F_5)_3$ adduct **5** in situ and characterized it by NMR spectroscopy.[12] The

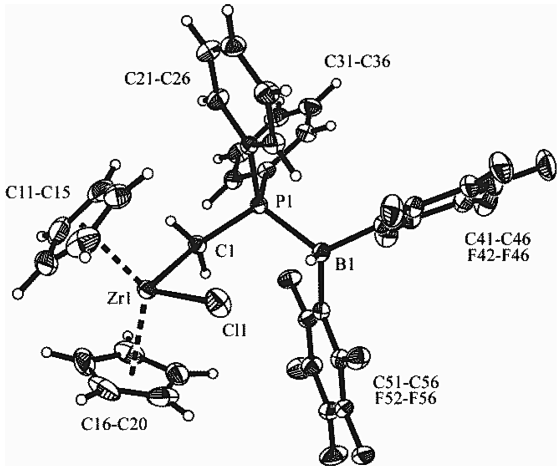


Figure 4. A projection of the molecular structure of complex **7** (thermal ellipsoids are shown with 30% probability).

zirconium complex **1** was mixed with $B(C_6F_5)_3$ in CD_2Cl_2 solution in a 1:1 molar ratio. The NMR spectra were measured after ca. 30 min reaction time at r.t. Adduct **5** shows ^{31}P and ^{11}B heteronuclear magnetic resonance signals at δ 31.5 (**1**: −2.2) and δ −8.4. The ^{19}F NMR resonances of **5** are as expected for tetracoordinate boron. The [Zr]−CH_2−[P] methylene ^1H NMR resonance of **5** was located at δ 1.24. It features a $^2J_{PH}$ coupling constant of 14.3 Hz. The ^{13}C NMR CH_2 resonance of **5** is at δ 25.3 ($^1J_{PC} \approx$ 24 Hz). The corresponding NMR data of the starting material (i.e., Shore's complex **1**) are quite different, namely, δ^1H 1.71 ($^2J_{PH}$ = 3.2 Hz), $\delta^{13}C$ 46.5 ($^1J_{PC}$= 43.5 Hz). The $^1H/^{13}C$ NMR Cp signals of **1** are at δ 6.19/113.8, and the corresponding signals of adduct **5** were monitored at δ 6.02/114.6 (all data were measured in CD_2Cl_2 solution).

We were eventually able to isolate the new P/Zr^+ FLP **2** by adjusting the reaction conditions. The reaction between **1** and $B(C_6F_5)_3$ (1:1) was carried out in C_6D_6 for 4 days at r.t. Then the solution was covered with pentane, and the resulting product **2** slowly crystallized. It was isolated from the reaction mixture as a white crystalline solid in ca. 49% yield.

In bromobenzene solution, the P/Zr^+ FLP **2** shows a ^1H NMR Cp resonance at δ 5.98 that features a coupling constant of J_{PH} = 1.2 Hz. The [P]−CH_2−[B] ^1H NMR signal occurs at δ 2.93 (broad; the corresponding ^{13}C NMR resonance is at δ 21.9). Compound **2** shows a ^{31}P NMR signal at δ 32.8 and a ^{11}B NMR resonance at δ −13.5.

Single crystals of the P/Zr^+ FLP **2** were obtained from a two-layer toluene/cyclopentane mixture. The X-ray crystal structure analysis of **2** (Figure 5) confirmed the abstraction of the −CH_2PPh_2 σ ligand from zirconium by the $B(C_6F_5)_3$ Lewis acid. The remaining Cp_2ZrCl^+ cation has the resulting Ph_2P−CH_2−$B(C_6F_5)_3^-$ borate anion coordinated to the metal center via the phosphane donor [bond lengths P1−Zr1 2.783(1) Å, Zr1−Cl1 2.405(1) Å; angle P1−Zr1−Cl1 90.3(1)°]. The new ligand has the following characteristic bonding features: bond lengths P1−C1 1.831(3) Å, C1−B1 1.671(5) Å; angle P1−C1−B1 130.6(2)°. Complex **2** features a conformation that is characterized by Cl1−Zr1−P1−C1 and Zr1−P1−C1−B1 dihedral angles of 49.5(1)° and −179.8(3)°, respectively.

The in situ generated P/Zr^+ FLP **2** was reacted with phenyl isocyanate to give the 1,2-P/Zr^+ adduct **4**. Compound **2** was also treated with benzaldehyde. This gave a major product different from **6** (Scheme 3). We assume that it was probably

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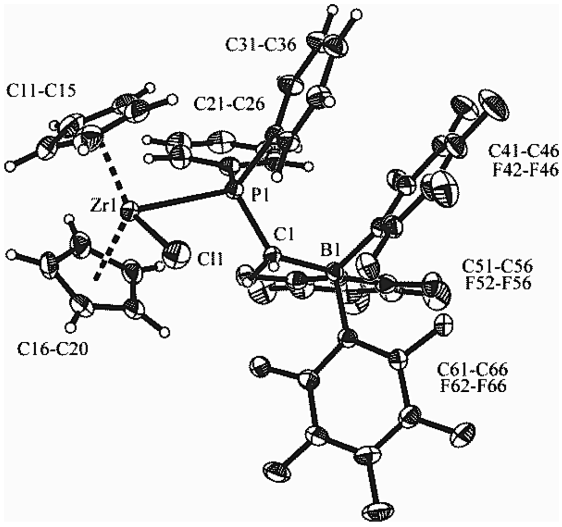

Figure 5. Molecular structure of complex **2** (thermal ellipsoids are shown with 30% probability).

formed by 1,2-carbonyl addition of the P/Zr^+ FLP; however, we could not isolate it in a pure form (for details, see the Supporting Information).

CONCLUSIONS

Dimethylzirconocenes react with $B(C_6F_5)_3$ by rapid methyl anion equivalent abstraction to yield the salt $[Cp_2ZrCH_3^+][H_3CB(C_6F_5)_3^-]$, usually isolated as a tight ion pair or in ligand-stabilized form.[13,14] Variants of this reaction have been of great importance in homogeneous Ziegler–Natta olefin polymerization catalysis.[15] Alkyl anion abstraction from an alkylzirconocene halide is much more difficult because the resulting cation would be much less stabilized.[16] In our case, phosphane coordination is probably a decisive factor to see the Ph_2PCH_2- transfer reaction from zirconocene to borane proceed at all in the competition with simple phosphane/borane coordination of the starting material.

Under the various reaction conditions utilized in this study, we therefore have a competing situation between the formation of the adduct **5** and the product **2**. Both probably represent the FLP resting stages of the respective active (i.e., dissociated) forms[17] of the P/B and P/Zr^+ systems. The transfer product **2** cleanly reacts in an FLP manner, giving for example the phenyl isocyanate addition product. The P/B form can, however, apparently be chemically addressed under very similar reaction conditions. The respective product of P/B 1,2-addition to benzaldehyde is an example. It is likely that the systems **2** and **5** (and their respective dissociated forms) interconverte (maybe slowly) under the here-applied typical reaction conditions. It will require a much more detailed study to unveil these rather complicated equilibrating processes and to learn how they can be controlled a priori, but the outcome of the here-described reaction teaches us that metal-free and metal-containing FLPs in a system like the one described here, where such a choice exists, can actively compete for added substrates. This is an interesting new facet of frustrated Lewis pair chemistry.

EXPERIMENTAL SECTION

General Procedures. All experiments were carried out under a dry argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. NMR spectra were recorded on VNMRS 500 MHz (Agilent), DD2 600 MHz (Agilent), Bruker AV400, and Bruker DPX300 spectrometers. Chemical shifts are given in parts per million relative to solvents [^{1}H and ^{13}C, $\delta(SiMe_4) = 0$] or an external standard [$\delta(BF_3{\cdot}OEt_2) = 0$ for ^{11}B NMR, $\delta(CFCl_3) = 0$ for ^{19}F NMR]. Elemental analysis data were recorded on a Foss-Heraeus CHNO-Rapid analyzer. For X-ray crystal structure analysis, data sets were collected with a Nonius KappaCCD diffractometer. The following programs were used: data collection, COLLECT;[18] data reduction, Denzo-SMN;[19] absorption correction, Denzo;[20] structure solution, SHELXS-97;[21] structure refinement, SHELXL-97;[22] and graphics, XP.[23] Thermal ellipsoids are shown with 30% probability; R values are given for observed reflections, and wR_2 values are given for all reflections. Exceptions and special features: For compounds **2** and **6**, one unidentified disordered solvent molecule was found in the asymmetric unit. The program SQUEEZE[24] was therefore used to remove mathematically the effect of the disordered unidentified solvent molecule. A cyclopentane group disordered over two positions was found in the asymmetric unit of compound **4**. Several restraints (SAME, SIMU, and SADI) were used in order to improve the refinement stability. In compound **7**, the hydrogen on the B1 atom was refined freely. For details of the X-ray crystal structure analyses, see the Supporting Information.

Preparation of Complex 2. Complex **1** (18.2 mg, 40 μmol) and $B(C_6F_5)_3$ (20.5 mg, 40 μmol) were mixed in C_6D_6 (1 mL). After 4 days of standing at room temperature, the reaction mixture was covered with pentane (3 mL). Complex **2** was obtained as a white crystalline solid (18.8 mg, 49% yield). Crystals suitable for single-crystal X-ray structure analysis were obtained from a two-layer procedure using a toluene solution of **2** and cyclopentane at room temperature. Anal. Calcd for $C_{41}H_{22}BClF_{15}PZr{\cdot}C_5H_{12}$: C, 53.11; H, 3.29. Found: C, 52.74; H, 2.75. ^{1}H NMR (500 MHz, C_6D_5Br, 299 K): δ 7.17 (m, 1H, *p*-Ph), 7.15 (m, 2H, *o*-Ph)*, 7.12 (m, 2H, *m*-Ph)*, 5.98 (d, $^3J_{PH}$ = 1.2 Hz, 5H, Cp), 2.93 (br, 1H, CH_2P) [resonances marked with * are from the ghsqc experiment]. $^{13}C\{^1H\}$ NMR (126 MHz): δ 148.2 (dm, $^1J_{FC} \approx$ 241 Hz, C_6F_5), 138.5 (dm, $^1J_{FC} \approx$ 245 Hz, C_6F_5), 136.5 (dm, $^1J_{FC} \approx$ 250 Hz, C_6F_5), 133.3 (d, $^2J_{PC}$ = 10.3 Hz, *o*-Ph), 130.8 (*p*-Ph)*, 128.7 (d, $^1J_{PC}$ = 39.3 Hz, *i*-Ph)^t, 128.4 (d, $^3J_{PC}$ = 9.9 Hz, *m*-Ph), n.o. (*i*-C_6F_5), 115.6 (Cp), 21.9 (br, CH_2P)^t, [^{t} tentatively assigned, * from the ghsqc experiment]. $^{31}P\{^1H\}$ NMR (202 MHz): δ 32.8 (m). ^{19}F NMR (470 MHz): δ −130.0 (br, 2F, *o*-C_6F_5), −160.5 (t, $^3J_{FF}$ = 19.9 Hz, 1F, *p*-C_6F_5), −164.0 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.5]. $^{11}B\{^1H\}$ NMR (160 MHz): δ −13.5 ($\nu_{1/2} \approx$ 30 Hz).

Preparation of Compound 3 (Activation of CH_2Cl_2). Complex **1** (73.0 mg, 160 μmol) and $B(C_6F_5)_3$ (82.0 mg, 160 μmol) were mixed in CH_2Cl_2 (2 mL). After the reaction mixture was stored at room temperature for 3 days, pentane (3 mL) was added to cover the reaction mixture. A white crystalline solid (105.0 mg) was obtained within 2 days. It was collected and analyzed as a mixture of Cp_2ZrCl_2 and complex **3** [61:39 (^{1}H)]. Several crystals were suitable for the single-crystal X-ray structure analysis of compound **3**.

Data for Cp_2ZrCl_2: ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ 6.49 (s, Cp). $^{13}C\{^1H\}$ NMR (126 MHz): δ 116.5 (Cp).

Data for complex **3**: ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ 7.75 (m, 1H, *p*-Ph), 7.58 (m, 2H, *m*-Ph), 7.50 (m, 2H, *o*-Ph), 4.36 (d, $^2J_{PH}$ = 5.0 Hz, 1H, $ClCH_2$), 3.05 (dq (1:1:1:1), $^2J_{PH}$ = 16.9 Hz, $^2J_{BH}$ = 5.6 Hz, 1H, BCH_2). $^{13}C\{^1H\}$ NMR (126 MHz): δ 148.4 (dm, $^1J_{FC} \approx$ 235 Hz, C_6F_5), 139.4 (dm, $^1J_{FC} \approx$ 249 Hz, C_6F_5), 137.3 (dm, $^1J_{FC} \approx$ 242 Hz, C_6F_5), 134.7 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Ph), 132.9 (d, $^2J_{PC}$ = 9.2 Hz, *o*-Ph), 130.0 (d, $^3J_{PC}$ = 12.3 Hz, *m*-Ph), 122.5 (br, *i*-C_6F_5), 119.6 (d, $^1J_{PC}$ = 86.0 Hz, *i*-Ph), 31.9 (br d, $^1J_{PC}$ = 52.7 Hz, $ClCH_2$), 15.4 (m, BCH_2). $^{31}P\{^1H\}$ NMR (202 MHz): δ 34.3 ($\nu_{1/2} \approx$ 6 Hz). ^{19}F NMR (470 MHz): δ −131.9 (m, 2F, *o*-C_6F_5), −160.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), −164.9 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 4.4]. $^{11}B\{^1H\}$ NMR (160 MHz): δ −15.7 ($\nu_{1/2} \approx$ 20 Hz).

Preparation of Complex 4. (**Caution**: many isocyanates are toxic and must be handled with due care.) Complex **1** (18.2 mg, 40 μmol) and $B(C_6F_5)_3$ (20.5 mg, 40 μmol) were mixed in CH_2Cl_2 (1 mL). After the mixture was stored at room temperature for 5 min, PhNCO (4.8 mg, 40 μmol) was added. Subsequently, the reaction mixture was covered with pentane (3 mL). After 2 days, complex **4** was obtained as

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a white crystalline solid (31.0 mg, 71% yield). Crystals suitable for single-crystal X-ray structure analysis were obtained from a two-layer procedure using a CH_2Cl_2 solution of **4** and cyclopentane at room temperature. Anal. Calcd for $C_{48}H_{27}BClF_{15}NOPZr$: C, 53.03; H, 2.50; N, 1.29. Found: C, 52.73; H, 2.64; N, 1.12. ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ 7.69 (m, 2H, *p*-Ph^P), 7.64 (m, 4H, *o*-Ph^P), 7.51 (m, 4H, *m*-Ph^P), 7.50 (m, 2H, *m*-Ph^N), 7.27 (m, 1H, *p*-Ph^N), 6.97 (m, 2H, *o*-Ph^N), 5.86 (s, 10H, Cp), 3.08 (dq (1:1:1:1), $^2J_{PH}$ = 18.4 Hz, $^2J_{BH}$ = 6.2 Hz, 2H, BCH_2). ^{13}C{^{1}H} NMR (151 MHz): δ 157.6 (d, $^1J_{PC}$ = 144.7 Hz, N═C), 148.5 (dm, $^1J_{FC} \approx$ 238 Hz, C_6F_5), 146.4 (d, $^3J_{PC}$ = 18.6 Hz, *i*-Ph^N), 139.1 (dm, $^1J_{FC} \approx$ 247 Hz, C_6F_5), 137.1 (dm, $^1J_{FC} \approx$ 255 Hz, C_6F_5), 134.2 (d, $^2J_{PC}$ = 9.4 Hz, *o*-Ph^P), 134.1 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Ph^P), 129.6 (*m*-Ph^N), 129.4 (d, $^3J_{PC}$ = 12.0 Hz, *m*-Ph^P), 125.1 (*p*-Ph^N), 123.6 (br, *i*-C_6F_5), 121.5 (*o*-Ph^N), 121.2 (d, $^1J_{PC}$ = 79.9 Hz, *i*-Ph^P), 116.1 (Cp), 11.0 (br m, BCH_2). ^{31}P{^{1}H} NMR (243 MHz): δ 23.9 ($\nu_{1/2} \approx$ 13 Hz). ^{19}F NMR (564 MHz): δ −131.8 (m, 2F, *o*-C_6F_5), −161.7 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −166.1 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 4.4]. ^{11}B{^{1}H} NMR (192 MHz): δ −15.8 ($\nu_{1/2} \approx$ 15 Hz).

Generation of Complex 5 (NMR Scale). Complex **1** (18.2 mg, 40 μmol) and $B(C_6F_5)_3$ (20.5 mg, 40 μmol) were mixed in CD_2Cl_2 (0.6 mL). Then the reaction mixture was transferred to an NMR tube, and after 30 min the reaction solution was characterized by NMR experiments. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ 7.52 (m, 1H, *p*-Ph), 7.45 (m, 2H, *o*-Ph), 7.37 (m, 2H, *m*-Ph), 6.02 (s, 5H, Cp), 1.24 (d, $^2J_{PH}$ = 14.3 Hz, 1H, CH_2P). ^{13}C{^{1}H} NMR (126 MHz): δ 148.9 (dm, $^1J_{FC} \approx$ 242 Hz, *o*-C_6F_5), 140.0 (dm, $^1J_{FC} \approx$ 256 Hz, *p*-C_6F_5), 137.4 (dm, $^1J_{FC} \approx$ 248 Hz, *m*-C_6F_5), 134.0 (d, $^2J_{PC}$ = 7.5 Hz, *o*-Ph), 131.7 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Ph), 128.7 (d, $^1J_{PC} \approx$ 51 Hz, *i*-Ph)*, 128.4 (d, $^3J_{PC}$ = 9.9 Hz, *m*-Ph), 117.5 (br, *i*-C_6F_5), 114.6 (Cp), 25.3 (dm, $^1J_{PC} \approx$ 24 Hz, CH_2P) [* from the ghmbc experiment]. ^{31}P{^{1}H} NMR (202 MHz): δ 31.5 ($\nu_{1/2} \approx$ 160 Hz). ^{19}F NMR (470 MHz): δ −126.7 (br m, 2F, *o*-C_6F_5), −158.0 (br m, 1F, *p*-C_6F_5), −165.2 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 7.2]. ^{11}B{^{1}H} NMR (160 MHz): δ −8.4 ($\nu_{1/2} \approx$ 200 Hz).

Preparation of Complex 6. Following the procedure described for the preparation of compund **4**, reaction of complex **1** (18.2 mg, 40 μmol), $B(C_6F_5)_3$ (20.5 mg, 40 μmol), and PhCHO (4.2 mg, 40 μmol) gave compound **6** as a white crystalline solid (32.0 mg, 75% yield). Crystals suitable for single-crystal X-ray structure analysis were obtained from a two-layer procedure using a CH_2Cl_2 solution of **6** and pentane at −35 °C. Anal. Calcd for $C_{48}H_{28}BClF_{15}OPZr$: C, 53.67; H, 2.63. Found: C, 53.12; H, 2.50. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ 7.76 (m, 1H, *p*-PhP^A), 7.73 (m, 2H, *o*-PhP^A), 7.61 (m, 1H, *p*-PhP^B), 7.54 (m, 2H, *m*-PhP^A), 7.38 (m, 2H, *m*-PhP^B), 7.32 (m, 1H, *o*-PhP^B), 7.09 (m, 1H, *p*-Ph), 6.97 (m, 2H, m-Ph), 6.68 (br m, 2H, *o*-Ph), 6.30, 6.05 (each s, each 5H, Cp), 5.55 (d, $^2J_{PH}$ = 5.5 Hz, 1H, CH), 1.64 (dd, $^2J_{PH}$ = 21.3 Hz, $^2J_{HH}$ = 13.0 Hz, 1H, CH_2), 1.39 (dd, $^2J_{PH}$ = 18.8 Hz, $^2J_{HH}$ = 13.0 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (126 MHz): δ 148.2 (dm, $^1J_{FC} \approx$ 234 Hz, C_6F_5), 139.0 (dm, $^1J_{FC} \approx$ 261 Hz, C_6F_5), 137.0 (dm, $^1J_{FC} \approx$ 250 Hz, C_6F_5), 136.8 (*i*-Ph), 134.9 (d, $^2J_{PC}$ = 8.1 Hz, *o*-PhP^A), 134.2 (d, $^4J_{PC}$ = 2.9 Hz, *p*-PhP^A), 133.9 (d, $^4J_{PC}$ = 2.9 Hz, *p*-PhP^B), 133.7 (d, $^2J_{PC}$ = 8.1 Hz, *o*-PhP^B), 129.3 (d, $^3J_{PC}$ = 11.5 Hz, *m*-PhP^B), 129.1 (d, $^3J_{PC}$ = 11.5 Hz, *m*-PhP^A), 128.5 (d, *J* = 3.5 Hz, *p*-Ph), 127.8 (d, $^4J_{PC}$ = 2.7 Hz, *m*-Ph), 127.6 (d, $^3J_{PC}$ = 5.3 Hz, *o*-Ph), 123.2 (br, *i*-C_6F_5), 122.4 (d, $^1J_{PC}$ = 80.0 Hz, *i*-PhP^B), 121.7 (d, $^1J_{PC}$ = 79.1 Hz, *i*-PhP^A), 115.5, 114.8 (Cp), 78.1 (d, $^1J_{PC}$ = 68.7 Hz, CH), 10.8 (d, $^1J_{PC}$ = 30.5 Hz, CH_2). ^{31}P{^{1}H} NMR (202 MHz): δ 37.3 ($\nu_{1/2} \approx$ 16 Hz). ^{19}F NMR (470 MHz): δ −131.5 (m, 2F, *o*-C_6F_5), −162.3 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −166.6 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 4.3]. ^{11}B{^{1}H} NMR (160 MHz): δ −2.2 ($\nu_{1/2} \approx$ 90 Hz).

Preparation of Complex 7. Complex **1** (27.4 mg, 60 μmol) and $HB(C_6F_5)_2$ (20.8 mg, 60 μmol) were mixed in CH_2Cl_2 (2 mL). Then the reaction mixture was covered with pentane (3 mL). After several days, complex **7** was obtained as colorless crystals (38.0 mg, 71% yield), some of which were suitable for single-crystal X-ray structure analysis of compound **7**. Anal. Calcd for $C_{36}H_{23}BClF_{10}PZr{\cdot}CH_2Cl_2$: C, 49.44; H, 2.80. Found: C, 49.98; H, 2.83. ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ 7.55 (m, 2H, *p*-Ph), 7.49 (m, 4H, *o*-Ph), 7.44 (m, 4H, *m*-Ph), 6.07 (s, 10H, Cp), 4.08 (br, 1H, BH), 1.58 (d, $^2J_{PH}$ = 16.0 Hz, 2H, CH_2). ^{13}C{^{1}H} NMR (151 MHz): δ 148.5 (dm, $^1J_{FC} \approx$ 239 Hz, C_6F_5), 139.8 (dm, $^1J_{FC} \approx$ 248 Hz, C_6F_5), 137.4 (dm, $^1J_{FC} \approx$ 250 Hz, C_6F_5), 133.4 (d, $^2J_{PC}$ = 8.1 Hz, *o*-Ph), 131.7 (d, $^1J_{PC}$ = 59.3 Hz, *i*-Ph), 131.6 (d, $^4J_{PC}$ = 2.6 Hz, *p*-Ph), 128.7 (d, $^3J_{PC}$ = 9.9 Hz, *m*-Ph), 117.5 (br, *i*-C_6F_5), 114.5 (Cp), 27.6 (d, $^1J_{PC}$ = 22.6 Hz, CH_2). ^{31}P{^{1}H} NMR (243 MHz): δ 18.4 (m). ^{19}F NMR (564 MHz): δ −128.3 (m, 2F, *o*-C_6F_5), −159.3 (t, $^3J_{FF}$ = 19.9 Hz, 1F, *p*-C_6F_5), −164.8 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 5.5]. ^{11}B{^{1}H} NMR (192 MHz): δ −23.6 (d, $^1J_{PB} \approx$ 77 Hz). ^{11}B NMR: δ −23.6 (t, $^1J_{PB} \approx {}^1J_{BH} \approx$ 77 Hz).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and physical characterization of the new compounds, crystallographic data, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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†C.G.D. performed the X-ray crystal structure analyses.

Notes

The authors declare no competing financial interest.

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