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Reactions of a Cationic Geminal Zr^+/P Pair with Small Molecules

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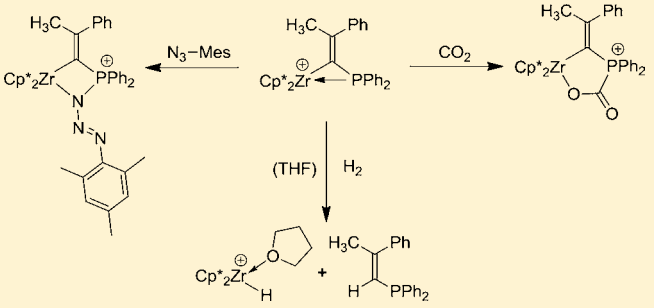
Supporting Information

ABSTRACT: The metallocene cation complex $[Cp^*_2ZrCH_3]^+[B(C_6F_5)_4]^-$ inserts the phosphino-substituted alkyne Ph−C≡C−PPh_2 into the [Zr]-CH_3 bond to form the internally phosphane-stabilized cation $[Cp^*_2Zr-C(=CMePh)PPh_2]^+$ (**10**). Complex **10** adds alkyl isocyanides as well as pivalonitrile at a lateral site at the bent metallocene wedge with retention of the Zr−P bond. Complex **10** acts as a reactive frustrated Lewis pair toward heterocumulenes, undergoing Zr^+/P addition reactions to the carbonyl groups of an alkyl isocyanate and of carbon dioxide to form the respective five-membered metallaheterocyclic adducts **13** and **14**. With mesityl azide complex **10** undergoes a Zr^+/P FLP N,N-addition reaction at the terminal azide nitrogen atom to form the four-membered FLP cycloadduct **15**. The Zr^+/P FLP is a reactive hydrogen activator. In a stoichiometric reaction it generates a hydridozirconocene cation that subsequently serves as a hydrogenation catalyst for various olefinic or acetylenic substrates. The Zr^+/P pair **10** undergoes selective 1,4-addition reactions to conjugated enones and to a conjugated ynone to give the corresponding seven-membered metallacyclic Zr^+/P FLP addition products. Many compounds of this study were characterized by X-ray diffraction.



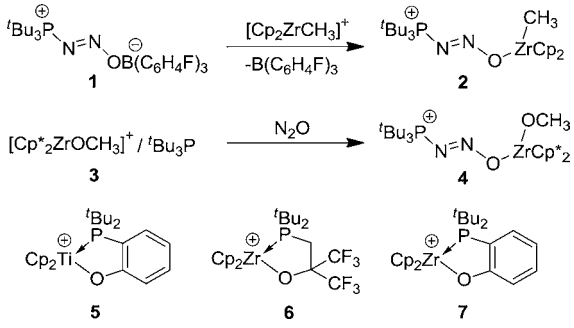
INTRODUCTION

Frustrated Lewis Pair (FLP) chemistry has developed at an impressive pace in recent years.[1] The phosphane/borane systems[2] (and to a lesser extent amine/borane[3] or carbon based Lewis base/borane[4] combinations) have had a substantial impact on the metal-free activation and/or binding of small molecules. While the Lewis base in FLPs has varied considerably, most FLPs have involved boron Lewis acids; especially $RB(C_6F_5)_2$ derivatives[5] have been used in the advancement of FLP chemistry. There have been attempts to use Lewis acid components other than the strongly electrophilic C_6F_5 containing boranes. Some progress has been made in using aluminum based Lewis acids.[6] There have been cases of carbon based systems,[4] and quite recently some strongly electrophilic halophosphonium cation systems have successfully been tested.[7]

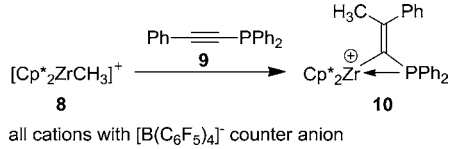
It is probably natural to return to systems that contain transition metals.[8] D. Stephan et al. have exchanged the borane component for $[Cp_2ZrCH_3]^+$ in a P/B FLP adduct of N_2O. They have also used the intermolecular Zr^+/P pair **3** for trapping N_2O (see Scheme 1).[9] In a beautiful series of papers, D. F. Wass et al. have described various intramolecular FLPs based on the group 4 bent metallocene cations (and a pending phosphane base). Some of these systems were shown to bind, e.g., CO_2, or to activate dihydrogen.[10] Scheme 1 shows typical examples of this FLP type (**5** to **7**).

We had recently prepared the Zr^+/P system **10** by an insertion reaction of the diphenylphosphino-substituted alkyne **9** into the [Zr]-CH_3 bond of $[Cp^*_2Zr\text{-}CH_3]^+$ cation **8** (see Scheme 2).[11] The product **10** contains an unsaturated electrophilic zirconium center.[12] This posed the question whether **10** might be able to serve as a new Zr^+/P FLP despite its apparently strong coordinative P−Zr interaction. The first results of our investigation about the FLP features of the Zr^+/P system **10** will be described and discussed in this account.

Scheme 1



Scheme 2



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RESULTS AND DISCUSSION

Reactions with Typical Donor Ligands Leading to "Normal" Coordination Behavior. We first reacted the zirconium complex **10** with two active alkyl isonitriles. Both *t*-butyl and *n*-butyl isocyanide coordinated to the electrophilic zirconium center of the cationic complex **10**. Both products **11a** and **11b** were isolated from the reaction mixtures in good yields (>70%). Both compounds were characterized by X-ray diffraction (see Figures 1 and 2). Isonitrile coordination to zirconium in both cases occurred at the available lateral site in the bent metallocene σ-ligand plane[13] proximal to the Zr−P vector.

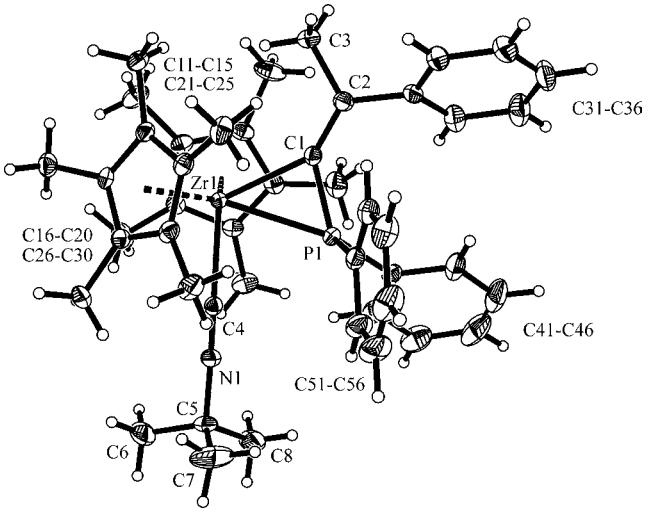


Figure 1. Molecular structure of the ^{t}BuNC adduct **11a** (only the cation is shown).

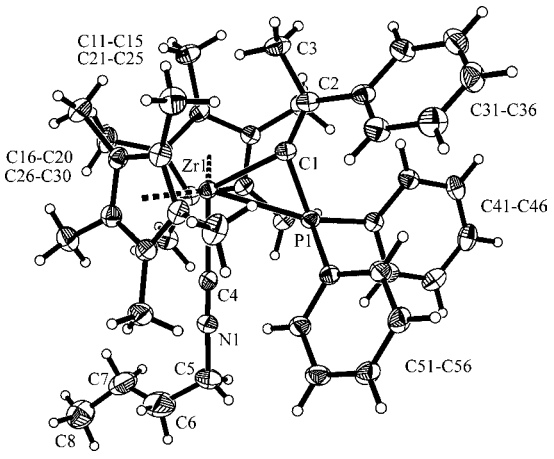


Figure 2. View of the molecular structure of adduct **11b** (only the cation is shown).

Upon coordination of the isocyanide ligands to the Zr center of **10** to form **11a** and **11b**, respectively (see Table 1), the principal coordination geometry of the ene-phosphino ligand is retained. Isonitrile coordination has resulted in a shifting of the respective ^{31}P NMR resonance of **11a** and **11b** to negative values as compared to **10** (see Table 2). We conclude that the addition of the isonitriles to Zr^{+}/P complex **10** occurs readily. In the coordination compounds the metal−phosphane bond is retained.

Table 1. Selected Structural Data of the Zr^{+}/P Cation 10 and Its Isonitrile Adducts 11a and 11b[a]

comp (lig)	**10** (−)[b]	**11a** (^{t}BuNC)	**11b** (^{n}BuNC)
Zr1−C1	2.290(3)	2.358(4)	2.350(3)
Zr1−C4	-	2.317(4)	2.331(3)
Zr1−P1	2.667(1)	2.704(1)	2.683(1)
C1−P1	1.804(3)	1.775(4)	1.771(3)
C1−C2	1.344(4)	1.349(6)	1.353(4)
C1−Zr1−P1	41.8(1)	40.3(1)	40.5(1)
C1−Zr1−C4	-	118.3(1)	120.2(1)
Zr1−P1−C1	57.9(1)	59.3(1)	59.6(1)
Zr1−C4−N1	-	178.5(4)	178.6(3)
C4−N1−C5	-	178.3(4)	176.2(4)

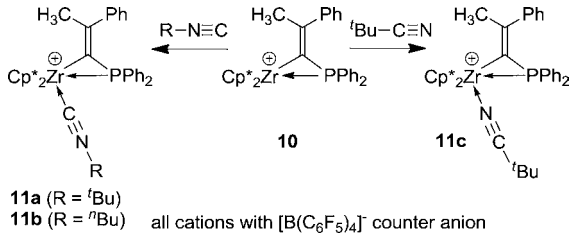
[a]Bond lengths in Å, angles in deg. [b]Ref 11.

Table 2. Selected NMR Data of the Complexes 10, 11a, and 11b[a]

comp (lig)	**10** (−)[b]	**11a** (^{t}BuNC)	**11b** (^{n}BuNC)
δ ^{31}P	17.6	−76.5	−76.1
δ ^{13}C1 ($^{1}J_{PC}$)	186.2(103.7)	156.3(119.8)	156.3(119.6)
δ ^{13}C2 ($^{2}J_{PC}$)	170.6(17.3)	169.4(17.2)	169.2(17.5)
δ ^{13}C≡N	-	n.o.	159.9(br)

[a]Chemical shifts: rel. TMS [δ ^{13}C(TMS) = 0, δ ^{13}C(CD_2Cl_2) = 53.8], rel. external H_3PO_4 (80%, δ ^{31}P = 0), coupling constants in Hz. [b]Ref 11.

Scheme 3



We have also added pivalonitrile to the zirconium center of complex **10** and obtained the Me_3C−C≡N adduct **11c** (69% isolated). It features the IR (C≡N) band at 2261 cm^{-1}. The ^{13}C NMR nitrile resonance was observed at δ 141.4 and the ^{31}P NMR signal was located at δ −64.8.

Compound **11c** was also characterized by X-ray diffraction. It shows the typical bonding parameters of the Zr−C[P]= CMePh unit [Zr1−C1 2.353(4) Å, C1−C2 1.349(6) Å, C1−P1 1.786(4) Å]. Addition of the nitrile donor ligand to the electrophilic zirconium center [Zr1−N1 2.296(4) Å, N1−C4 1.132 (5) Å, angle Zr1−N1−C4 177.7 (3)°] in **11c** has also left the adjacent Zr1−P1 bond almost unaffected [Zr1−P1: 2.711(1) Å] (see Figure 3).

We conclude that the cation **10** first appears to add a variety of common donor ligands to the vacant lateral coordination site adjacent to the inherent phosphane donor by making use of its available empty valence orbital. This additional coordination to the d^0-metal center has apparently no pronounced influence on the remaining ligands in the metallocene σ-ligand plane. The coordinatively saturated complexes **11** show very similar structural parameters as compared to their common unsaturated precursor **10**. The Zr^{+}/P linkage is not much affected.

FLP-Reminiscent Reaction Behavior of Complex 10 toward Unsaturated Small Organic Molecules. The situation changed markedly when we reacted the Zr^{+}/P

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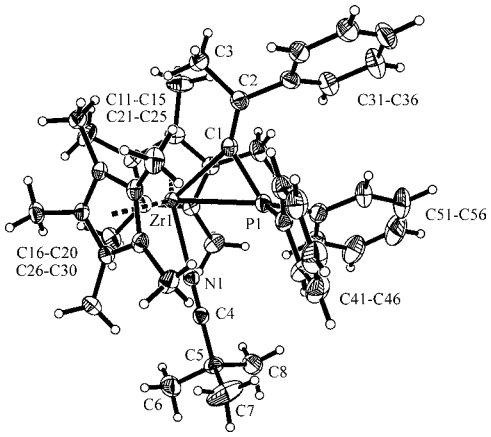


Figure 3. Molecular structure of complex **11c** (only the cation is depicted).

complex **10** with a variety of other unsaturated reagents. We first treated **10** with N_2O. This resulted in oxidation of the phosphane and consequently to cleavage of the Zr−P linkage with formation of a new zirconium−oxygen bond. The X-ray crystal structure analysis of the product **12** (see Figure 4)

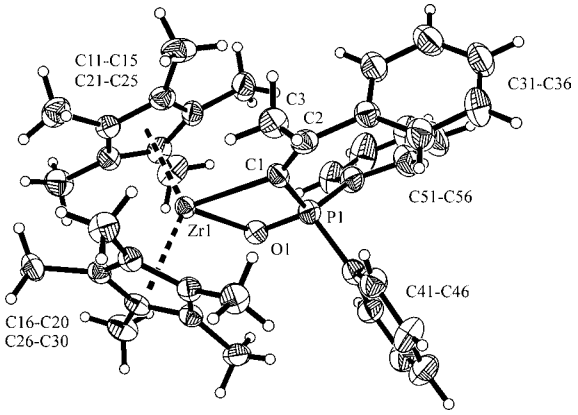


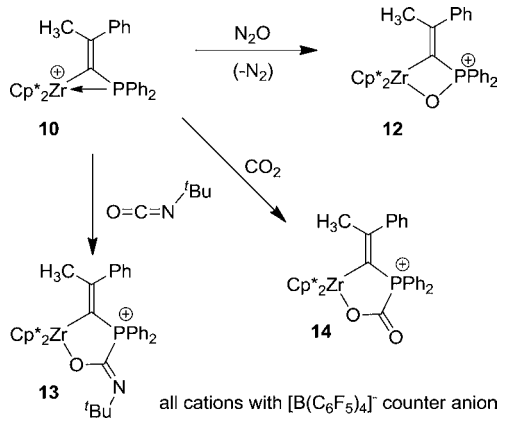
Figure 4. View of the molecular structure of compound **12** (only the cation is shown).

showed the newly formed central four-membered metallaheterocyclic core structure of **12** with bond lengths of 2.399 (6) Å (Zr1−C1), 1.772(7) Å (C1−P1), 1.543(5) Å (P1−O1), and 2.168(5) Å (O1−Zr1) (C1−C2:1.325(9) Å). In solution, compound **12** shows a ^{31}P NMR signal at δ 17.4.

Complex **10** was then reacted with the heterocumulenes *t*-butyl isocyanate and with CO_2, respectively. In both cases insertion into the Zr−P linkage was observed, forming the products **13** and **14** which at least formally resemble typical Zr^+/P FLP addition products to the π-systems of these reagents. The reaction of **10** with *tert*-butyl isocyanate was carried out in dichloromethane/pentane for 3 d at room temperature. Workup gave the product **13** as a yellow solid in close to 80% yield. It was characterized by C, H, N elemental analysis, by spectroscopy, and by X-ray diffraction.

The X-ray crystal structure analysis revealed that the carbonyl group of the isocyanate reagent had added across the Zr−P bond of the starting material **10**.[14] The product **13** contains a new Zr−O bond (2.075(3) Å) and the phosphane has added to the sp-carbon atom of the isocyanate (P1−C4 1.848(5) Å). The molecule contains a central metallaheterocyclic core (Zr1−

Scheme 4



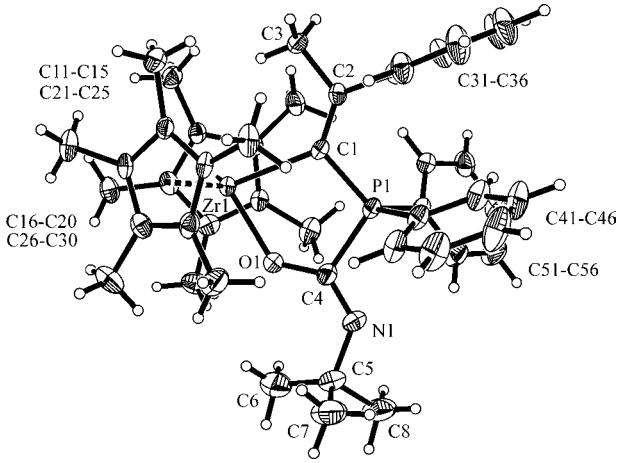


Figure 5. Molecular structure of the isocyanate addition product **13** (only the cation is depicted).

C1 2.393(5) Å, C1−P1 1.801(4) Å, O1−C4 1.325(6) Å). To this core the exocyclic =C double bond is attached via C1 (C1−C2 1.351(7) Å) and the =N^{t}Bu unit at C4 (C4−N1 1.257(6) Å, angle C4−N1−C5 127.4(5)°). The phosphorus atom inside the five-membered ring is a tetra-substituted phosphonium center. The zirconocene unit shows the typical bonding features of a group 4 bent metallocene unit (σ-ligand angle C1−Zr1−O1 79.55(14)°).

In solution, complex **13** exhibits a typical borate ^{11}B NMR signal at δ −16.7. The cation shows a ^{31}P NMR signal with a phosphonium like chemical shift at δ 33.7. The heterocyclic core of the molecule features ^{13}C NMR signals at δ 151.3 (−O−C=N; $^1J_{PC}$ = 158.5 Hz) and δ 158.5 (=C[Zr], $^1J_{PC}$ = 18.5 Hz). The signal of the exocyclic carbon of this C=C double bond shows up at δ 174.5 ($^2J_{PC}$ = 6.4 Hz) and we have found a single sharp ^{1}H NMR resonance of the ten methyl groups of the Cp*$_2$Zr bent metallocene unit.

Complex **10** also showed a frustrated Lewis pair-like behavior toward carbon dioxide.[15] It reacted rapidly with CO_2 under mild conditions (0 °C to r.t.) to give the Zr^+/P addition product **14** to the carbonyl functionality of carbon dioxide. The product **14** was isolated as a yellow solid in 77% yield. Single crystals suited for the X-ray crystal structure analysis were obtained from dichloromethane/cyclopentane at low temperature (−35 °C). The structure shows that the electrophilic zirconium Lewis acid center of **10** has added to a former carbonyl oxygen atom of the CO_2 molecule; the Zr−P linkage

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of **10** was opened during the reaction and the attached phosphane Lewis base had attacked the CO_2 carbonyl carbon atom. In the resulting five-membered heterocyclic core of **14** we have found typical bond length of 2.097(2) Å (Zr1−O1), 2.402(3) Å (Zr1−C1), and 1.789(3) Å (P1−C1). The newly formed P1−C4 bond length is markedly longer at 1.887(3) Å and the internal C4−O1 bond length is 1.290(4) Å. The remaining carbonyl group at C4 is shorter (C4−O2: 1.197(4) Å), as expected. The remaining bonding features of the cationic metallocene/phosphonium system **14** are unexceptional (see Figure 6).

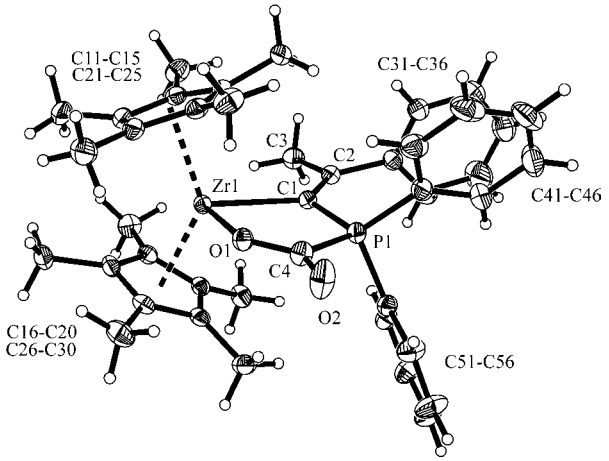
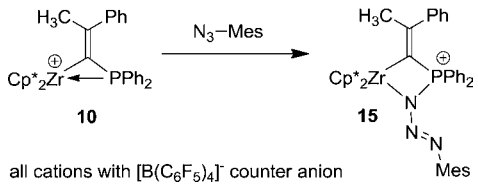


Figure 6. View of the molecular structure of the CO_2 addition product **14** (only the cation is depicted).

The CO_2 addition product **14** features a strong IR (C═O) band at 1699 cm^{-1}. The carbonyl carbon ^{13}C NMR resonance was found at δ 165.5 with a coupling constant of $^1J_{PC}$ = 125.1 Hz. Compound **14** shows a phosphonium ^{31}P NMR signal at δ 27.6. The ^{13}C NMR signals of the exocyclic C═C double bond occur at δ 155.7 ($^1J_{PC}$ = 27.0 Hz, ═C[Zr]) and δ 175.8 ($^2J_{PC}$ = 7.2 Hz), respectively.

Scheme 5



Compound **10** reacts in a typical Zr^+/P FLP fashion with mesityl azide. Mes-N_3 reacts rapidly even at low temperature (−35 °C) with the zirconium cation complex **10**. We isolated the product as a red crystalline solid in 70% yield. Complex **15** was characterized by C, H, N elemental analysis, by spectroscopy, and by X-ray diffraction (single crystals were obtained from dichloromethane/cyclopentane at −35 °C). The structure of **15** revealed that the Zr−P bond of the starting material **10** had opened and the cationic Zr^+ Lewis acid and the adjacent phosphane Lewis base had both added to the terminal mesityl azide nitrogen atom.[14b,16,17] That resulted in the formation of a four-membered metallaheterocyclic structure. The "kite-shaped" Zr, C, P, N core of complex **15** features two long Zr1−C1 (2.368(3) Å) and Zr1−N1 (2.247(2) Å) bonds (angle C1−Zr1−N1 65.6(1)°) and two short P1−C1

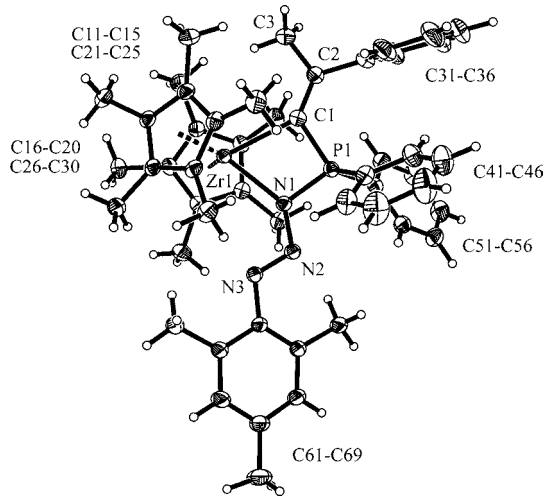


Figure 7. Molecular structure of the mesitylazide adduct **15** (only the cation is shown).

(1.789(3) Å) and P1−N1 (1.654(2) Å) linkages (angles Zr1−N1−P1 105.2(1)°, Zr1−C1−P1 96.3(1)°, C1−P1−N1 93.0(1)°). There is an exocyclic C═C bond terminated at C1 (C1−C2 1.347(4) Å). The N_3-mesityl unit is trans-configurated at the N2−N3 double bond (1.262(3) Å) and it shows bond alternation (N1−N2 1.386 (3) Å).

In solution, complex **15** shows the typical $^1H/^{13}C$ NMR features of the Cp^*_2Zr subunit and the endocyclic PPh_2 building block (^{31}P: δ 12.3). The ^{13}C NMR signals of the exocyclic C═C double bond occur at δ 158.8 ($^1J_{PC}$ = 8.0 Hz) and δ 172.2 ($^2J_{PC}$ = 2.3 Hz), respectively.

Reactions with Dihydrogen. Since the cationic complex **10** showed some frustrated Lewis pair-like behavior toward the heterocumulenes and the azide reagent, it was tempting to learn whether the Zr^+/P pair could heterolytically split dihydrogen similar to many main group element FLPs,[18] although some of the resulting reactions would be anticipated to show complications due to the known, sometimes high reactivity of an ensuing cationic zirconium hydride product.[19]

We first reacted the cationic zirconocene/phosphane complex **10** with dihydrogen in dichloromethane solution. A solution of **10** in CH_2Cl_2 was exposed to a hydrogen atmosphere (1.5 bar) for 2 h at room temperature. Covering with pentane eventually gave a crystalline solid formed from the two-phase system that was recovered in *ca.* 50% yield. The obtained single crystals were composed of a 1:1 mixture of $Cp^*_2ZrCl_2$ (**19**) and the phosphonium salt **20**. In the crystal (see Figure 8) one observes the separate bent metallocene molecule **19** and the cation and $[B(C_6F_5)_4]^-$ anion of the salt **20**. The cation of **20** features a tetracoordinated phosphonium phosphorus center that has two phenyl groups and the Z−CH═CPh(CH_3) substituent bonded to it. The fourth ligand at P1 is a $-CH_2Cl$ group.

We dissolved the solid in CD_2Cl_2 and monitored the typical $^1H/^{13}C$ NMR spectra of the $Cp^*_2ZrCl_2$ bent metallocene dichloride, the typical $^{11}B/^{19}F$ NMR signals of the $[B(C_6F_5)_4]^-$ anion and the characteristic signals of the newly formed phosphonium cation **20** (see Scheme 6). Its ^1H NMR spectrum shows a doublet of quartets of the newly attached proton at the olefinic carbon atom at δ 6.30 ($^2J_{PH}$ = 21.8 Hz, $^4J_{HH}$ = 1.4 Hz); ^{13}C: δ 102.0 ($^1J_{PC}$ = 90.8 Hz) and a doublet of the $-CH_2Cl$ group attached at phosphorus [δ 4.03, $^2J_{PH}$ = 5.8 Hz, ^{13}C: δ

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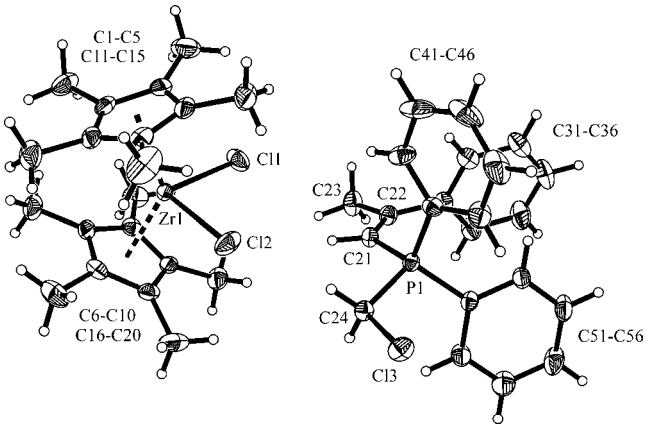
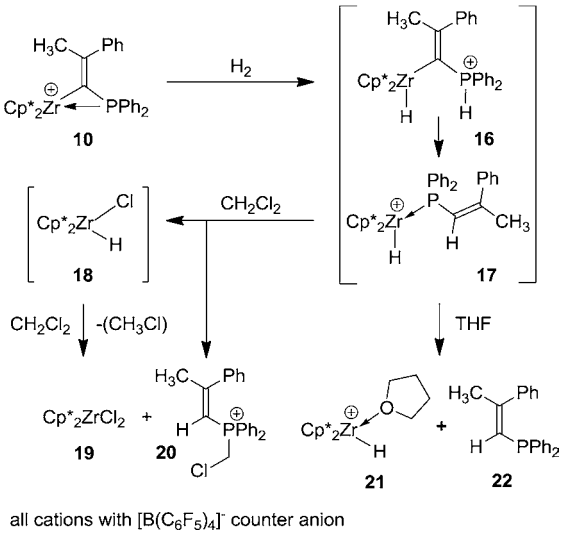


Figure 8. Molecular geometry of the **19**/**20** mixture in the crystal (only the cation is shown).

Scheme 6



35.3 ($^1J_{PC}$ = 61.4 Hz)]. The ^{31}P NMR signal of **20** occurs at δ 14.1.

Apparently the Zr$^+$/P cation **10** is quite reactive toward dihydrogen. We assume that **10** rapidly splits dihydrogen heterolytically to generate the hydridozirconium/phosphonium system **16**. Having a Brønsted acidic phosphonium salt geminally attached to a zirconium−carbon σ-ligand is apparently not a stable situation.[20] We assume fast protonolytic cleavage of the Zr−C(sp^2) σ-bond occurring to possibly generate **17**. In dichloromethane solution, the highly reactive metallocene cation may abstract a chloride anion from the solvent with the aid of the phosphane nucleophile. This should produce the phosphonium salt **20** which we have observed and Cp*$_2$Zr(H)Cl. It is known that hydridozirconocenes may react with dichloromethane.[21] Consequently, **17** in situ generated in this sequence could have been converted to the observed Cp*$_2$ZrCl$_2$ product **19** (either directly or via **18**) (plus methylchloride that was probably lost under our reaction conditions).[22]

This tentative description of the reaction course taken upon treatment of **10** with H$_2$ was supported by an experiment where **10** was treated with dihydrogen in d_6-benzene solution in the presence of a small quantity of THF. Again, complex **10** reacted rapidly with H$_2$ (1.5 bar, 10 min) under these mild reaction conditions. Workup with pentane after the short reaction time gave yellow crystals of a zirconium containing salt **21** that was characterized by X-ray diffraction. The crystal contains a metallocene cation to which 1 equiv of THF is coordinated (Zr1−O1 2.240(3) Å). The remaining adjacent σ-ligand site at the cationic bent metallocene unit is to *ca.* 25% occupied by chloride (which we assume to originate from some small residual amount of CH_2Cl_2 from the preparation).[23] The remaining 75% of that site seem to be occupied by hydride (see Figure 9). We also found the independent $[B(C_6F_5)_4]^-$ counteranion in the crystal.

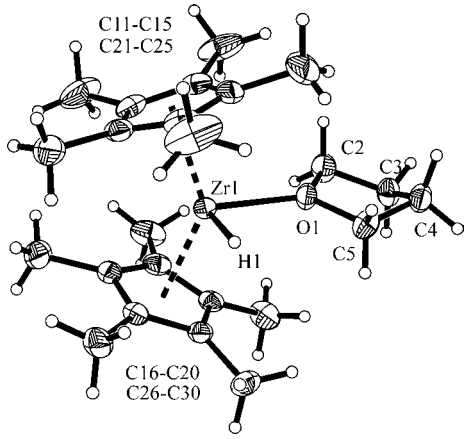


Figure 9. View of the molecular structure of the (hydrido)-zirconocene(THF) cationic product **21** (the σ-ligand site is *ca.* 25% occupied by chloride).

In the ^{1}H NMR spectrum of compound **21** in C_6D_5Br we observed the signals of the THF ligand at δ 3.14 and 1.54 and the large sharp signal of the ten methyl groups at the Cp*-rings (δ 1.66) plus a singlet at δ 7.73 (1H rel. intensity) that we associate with the formal [Zr]$^+$-H hydride.[24]

The stoichiometric alkenylphosphane coproduct **22** was recovered from the organic solution (admixed with a small metallocene amount). Compound **22** shows a typical ^{1}H NMR dd at δ 2.05 ($^4J_{HH}$ = 1.4 Hz, $^4J_{PH}$ = 0.7 Hz) of the methyl substituent and a dq ($^2J_{PH}$ = 3.9 Hz, $^4J_{HH}$ = 1.4 Hz) of the olefinic proton at δ 6.32. The ^{31}P NMR resonance of compound **22** is at δ −25.0.

The origin of the newly introduced hydrogen atoms from dihydrogen were confirmed by carrying out the reaction under analogous conditions with D$_2$. The ^{2}H NMR spectrum showed the [Zr]-D resonance at *ca.* 7.70 (in bromobenzene) and the olefinic D-[C](PPh$_2$)= resonance at δ 6.34.

We investigated whether the **10**/H$_2$ system might be also suited for hydrogen transfer. In a first experiment we exposed a styrene solution in C_6D_5Br containing 1 mol % of the Zr$^+$/P complex **10** (and 10 mol % of ferrocene as an internal standard) briefly to an atmosphere of dihydrogen at 1.5 bar. The reaction was stopped after 10 min and the composition of the solution monitored by ^{1}H NMR spectroscopy to reveal a 57% conversion of the olefin to ethylbenzene under these mild conditions (Table 3, entry 1). After optimizing the reaction conditions, we found that the hydrogenation reaction can be completed with 1 mol % of **10** in 30 min (Table 3, entry 2). Even with a very small amount of **10** (0.5 mol %) the reaction still gave 63% conversion in 1 h and 86% conversion in 3.5 h (Table 3, entries 3 and 4), respectively. A few other olefins and

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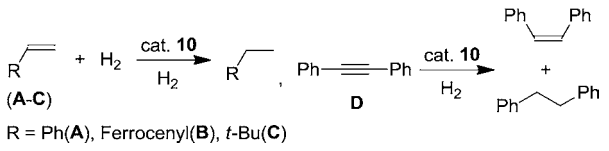
Table 3. Hydrogenation of Alkenes and an Alkyne Catalyzed by Complex 10[a]



entry	substrate	[cat.]/[sub.] (%)	time (min)	conversion[b] (%)
1	**A**	1.0	10	57
2	**A**	1.0	30	93[c]
3	**A**	0.5	60	63[d]
4	**A**	0.5	210	86
5	**B**	1.0	120	99(77)[e]
6	**C**	1.0	60	94
7	**D**	1.0	30	73(13:1)[f]
8	**D**	1.0	90	97(7:1)[f]

[a]Room temperature, 1.5 bar H_2, C_6D_5Br as the solvent, substrate (0.5 mmol). [b]NMR yield determined relative to ferrocene internal standard. [c]Ca. 0.3% 2,4-diphenyl-1-butene. [d]Ca. 0.5% 2,4-diphenyl-1-butene. [e]Yield of isolated product. [f]Mol ratio of *cis*-stilbene/1,2-diphenylethane.

an alkyne were hydrogenated with the **10**/H_2 system as well. Vinylferrocene was quantitatively converted to ethylferrocene under our typical hydrogenation conditions (1 mol % **10**, C_6D_5Br solution, 1.5 bar H_2, r.t.). The product was isolated in 77% yield. Treatment with D_2 gave (1,2-dideuteroethyl)-ferrocene instead. *t*-Butylethene gave 2,2-dimethylbutane and tolane gave a mixture of *cis*-stilbene (major) and 1,2-diphenylethane (minor product, see Table 3 and the Supporting Information for details).

It is conceivable that some conventional Ziegler–Natta catalyst generated from **10** under these conditions is responsible for the styrene hydrogenation activity. Therefore, we carried out a number of control and reference experiments using either $[Cp^*_2ZrMe]^+$ $[B(C_6F_5)_4]^-$[25] or $[Cp^*_2ZrH]^+$[26] (the latter in situ generated under various conditions) with or without added phosphanes for the styrene hydrogenation reaction. In several of these examples we found minute amounts of additional products derived from styrene dimerization pathways, namely, 1,3-diphenylbutane or 2,4-diphenyl-1-butene (for details see the Supporting Information). However, we regard these observed differences as probably too small to draw any solid mechanistic conclusion from them at this time.

FLP-Like Reactions of Complex 10 with Conjugated Enones and Ynones. Some intramolecular frustrated Lewis pairs show a high tendency to undergo kinetically controlled selective 1,4-addition reactions to conjugated enynes[27] and ynones.[28] If the Zr^+/P system **10** could show a similar behavior, this might serve as an indication for **10** featuring some FLP characteristics. We, therefore, reacted the geminal Zr^+/P pair **10** with selected conjugated enones and ynones.

Complex **10** reacted with the enone **24a** at room temperature to give the 1,4-addition product **25a** cleanly. The product was isolated in 69% yield. It was characterized by X-ray diffraction using single crystals that were grown from a dichloromethane solution layered with cyclopentane. The addition product features a seven-membered metallacyclic core structure that has the former carbonyl oxygen atom bonded to zirconium (Zr1–O1 1.985(2) Å). This oxygen atom is now part of an endocyclic zirconium enolate structure (O1–C6 1.342(4) Å, C6–C5 1.335(4) Å, C5–C4 1.507(4) Å). The enolate is part of the seven-membered ring, it is consequently *Z*-configurated (dihedral angle O1–C6–C5–C4 −4.2(5)°). It has the pair of phenyl substituents attached at carbon atoms C6 and C4, which has formed the new bond to phosphorus (P1–C4 1.882(3) Å), thereby closing the metallacycle (P1–C1 1.818(3) Å, C1–C2 1.353(4) Å, C1–Zr1 2.487(3) Å) (see Figure.10).

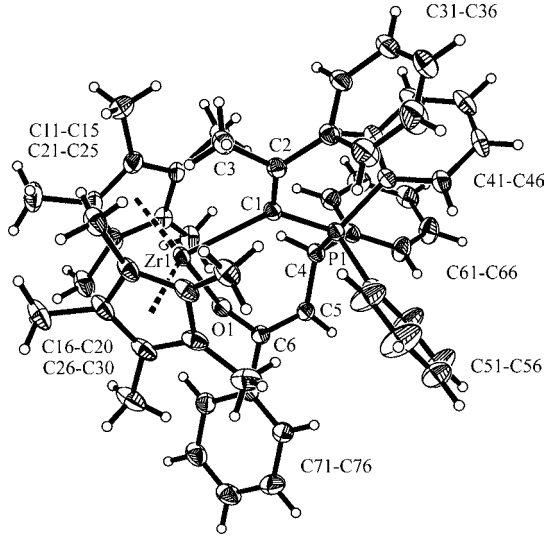


Figure 10. Molecular structure of the Zr^+/P 1,4-addition product **25a** (only the cation is depicted).

The Zr^+/P system **10** also undergoes an analogous 1,4-addition reaction to the conjugated enone **24b** (R = Ph) to yield the seven-membered metallacycle **25b** (isolated in 77% yield). Complex **25b** has also been characterized by X-ray diffraction; its structural features are similar to those of complex **25a**. A view of the structure is provided with the Supporting Information. In solution, compound **25b** features a ^{31}P NMR signal at δ 26.6 [**25a**: δ 22.1; ^{13}C NMR of the [Zr]–O–C(Ph)=CH unit: δ 160.6 ($^3J_{PC}$ = 7.5 Hz), δ 100.7 ($^2J_{PC}$ = 9.7 Hz), corresponding =CH– ^1H NMR signal at δ 4.56 ($^3J_{PH}$ = 6.1 Hz)].

Complex **10** also undergoes a 1,4-addition reaction to the ynone **26**. The corresponding seven-membered metallacyclic Zr-enolate product (**27**) was isolated in 55% yield. It was characterized by X-ray diffraction (see Figure 11). The structure confirms the selective Zr^+/P 1,4-addition reaction (Zr1–O1 2.313(2) Å, P1–C4 1.806(3) Å). The enolate shows coordination of the central =C= carbon atom to the zirconium atom. (C4–C5 1.330(4) Å, C5–C6 1.413(4) Å, C6–O1 1.276(3) Å, C5–Zr1 2.382(3) Å, angles P1–C4–C5 109.9(2)°, C4–C5–C6 135.2(2)°, C5–C6–O1 112.2(2)°, dihedral angles C7–C4–C6–C61 48.1°, P1–C4–C6–O1 64.9°) (see Scheme 7). The Zr1–C1 bond (2.509(2) Å) in the resonance hybrid **27**/**27′** is rather long (C1–C2 1.357(3) Å, C1–P1 1.808(3) Å).

■ CONCLUSIONS

Frustrated Lewis pair chemistry at the beginning seemed to be rather simple: neutralizing adduct formation between the Lewis acid and base components was hindered by steric bulk. This resulted in situations of coexistent free Lewis acids and Lewis bases in solution that could then either react independently or

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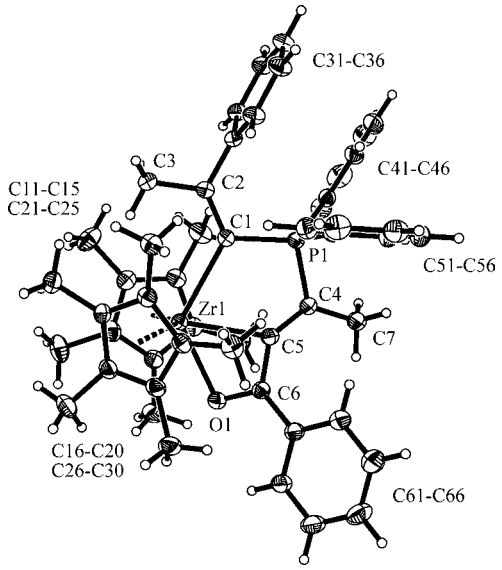
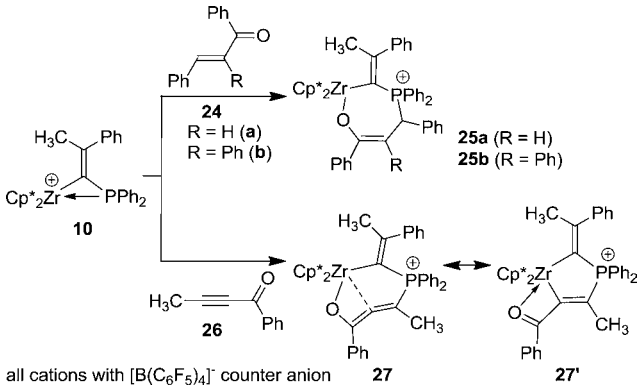


Figure 11. Molecular structure of the compound **27** (only the cation is shown).

Scheme 7



jointly with added substrates. These cooperative reactions opened pathways to unprecedented chemical behavior and new reactions, the most prominent being the metal-free splitting and activation of dihydrogen and the utilization of that feature for developing novel metal-free catalytic hydrogenation processes for a variety of specific substrates.[1,29] In addition, we have seen more and more addition and activation reactions by FLPs that have led to new exciting chemical developments.

With its rapid development taking place FLP chemistry has not remained that simple and, consequently, the FLP concept has not remained that simplistic. A great number of cases have been disclosed where Lewis acids and bases do show some interaction, especially in the many intramolecular FLP examples,[3c,30] but nevertheless have served as very potent frustrated Lewis pair systems in active small molecule addition and/or activation. We have even encountered examples where strong but apparently reversible Lewis acid/Lewis base adduct formation precedes FLP reactions.[31] More and more, we discover dichotomies in chemical behavior of FLP systems, and our organometallic Zr^+/P system described here seems to be a prominent example. Complex **10** is a coordinatively unsaturated group 4 metallocene system and in many cases it just acts as such. It adds isonitriles or a nitrile without affecting the adjacent Zr−P linkage;[13] no FLP behavior is visible in these reactions of **10**. The reactions of **10** with dihydrogen seem to be different. Here we assume FLP-like behavior of the frustrated Zr^+ Lewis acid/phosphane Lewis base pair that eventually leads to heterolytic splitting of dihydrogen and its subsequent follow-up reactions. In some such sequences eventually $[Cp^*_2ZrH]^+$ (or a stabilized form thereof)[26] is formed, a species that then is probably responsible for the observed catalytic hydrogenation reactions. That means that the initiation of these reaction sequences is to be regarded as typical FLP chemistry; its subsequent chemistry including the catalytic hydrogenation reactions may not (although we have found some phosphane influence on the catalytic hydrogenation reaction).

The scale is tipped completely to the FLP reactivity side in the reactions of the Zr^+/P pair **10** with carbon dioxide, with the isocyanate, and with mesityl azide, which gives rise to the formation of typical FLP addition products analogous to what has been observed for, e.g., many B/P pairs.[14,15,32] The FLP behavior of **10** is found similarly pronounced in the reactions with conjugated enones and ynones which give similar products, as they are observed in typical main group element FLPs with such substrates.[28] Our study shows that FLP chemistry is rapidly expanding also to organometallic chemistry, but that at the same time the reaction behavior of such systems is becoming more diverse and complex.

EXPERIMENTAL SECTION

Preparation of complex 11a. *Caution: Isocyanides Are Toxic and Must Handled with Due Care.* ^{t}BuNC (1.1 mg, 13.6 μmol) was added to a solution of complex **10** (19.2 mg, 13.6 μmol) in CH_2Cl_2 (1 mL). The color of the reaction mixture became pale yellow immediately. Then it was covered with cyclopentane (3 mL). After several days, complex **11a** was obtained as a pale yellow crystalline solid (15.0 mg, 74% yield). Crystals suitable for X-ray single crystal analysis were grown from a two-layer procedure using CH_2Cl_2/cyclopentane at −35 °C. Elemental Analysis: calcd. for $C_{70}H_{57}BF_{20}NPZr \cdot CH_2Cl_2$: C, 56.47; H, 3.94; N, 0.93. Found: C, 56.27; H, 3.88; N, 1.31. IR (KBr): 2178 (s, N≡C) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.41 (m, 2H, *o*-Ph), 7.35 (m, 3H, *m*,*p*-Ph), 7.32 (m, 2H, *p*-Ph_2P), 7.21 (m, 4H, *m*-Ph_2P), 7.14 (m, 4H, *o*-Ph_2P), 2.58 (s, 3H, Me), 1.79 (s, 30H, C_5Me_5), 1.77 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 169.4 (d, $^2J_{PC}$ = 17.2 Hz, C═), 156.3 (d, $^1J_{PC}$ = 119.8 Hz, ═CZr), 148.5 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 147.4 (d, $^3J_{PC}$ = 8.5 Hz, *i*-Ph), 138.7 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 136.6 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 135.4 (d, $^2J_{PC}$ = 12.4 Hz, *o*-Ph_2P), 132.1 (d, $^1J_{PC}$ = 22.4 Hz, *i*-Ph_2P), 130.6 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Ph_2P), 128.7 (*m*-Ph), 128.43 (d, $^3J_{PC}$ = 10.3 Hz, *m*-Ph_2P), 128.39 (*p*-Ph), 128.3 (d, $^4J_{PC}$ = 0.7 Hz, *o*-Ph), 118.0 (C_5Me_5), 60.1 (^{t}Bu), 34.6 (d, $^3J_{PC}$ = 23.4 Hz, Me), 30.7 (d, *J* = 1.7 Hz, ^{t}Bu), 12.4 (C_5Me_5), n.o. (CN, *i*-C_6F_5). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = −76.5 ($\nu_{1/2}$ ~ 8 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (m, 2F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 25 Hz).

X-ray Crystal Structure Analysis of Complex 11a. Formula $C_{70}H_{57}BF_{20}NPZr \cdot CH_2Cl_2$, *M* = 1510.09, colorless crystal, 0.45 × 0.15 × 0.04 mm^3, *a* = 10.8271(2), *b* = 17.5768(3), *c* = 18.7712(3) Å, α = 110.892(1), β = 100.261(1), γ = 92.846(1)°, *V* = 3259.05(10) $Å^3$, ρ_{calc} = 1.539 gcm^{-3}, μ = 0.377 mm^{-1}, empirical absorption correction (0.848 ≤ *T* ≤ 0.985), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, *T* = 223(2) K, ω and φ scans, 29611 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 $Å^{-1}$, 15649 independent (R_{int} = 0.056) and 12463 observed reflections [$I > 2\sigma(I)$], 898 refined parameters, *R* = 0.078, wR^2 = 0.197, max. (min.) residual electron density 1.23 (−0.95) e.$Å^{-3}$, hydrogen atoms were calculated and refined as riding atoms.

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Preparation of Complex 11b. Following the procedure described for the preparation of **11a**: reaction of complex **10** (25.5 mg, 18.1 μmol) with ^{n}BuNC (1.5 mg, 18.1 μmol) gave **11b** as a pale yellow crystalline solid (20.5 mg, 80% yield). Elemental Analysis: calcd. for $C_{70}H_{57}BF_{20}NPZr \cdot CH_2Cl_2 \cdot C_5H_{10}$: C, 57.76; H, 4.40; N, 0.89. Found: C, 57.48; H, 4.17; N, 1.07. IR (KBr): 2191 (s, N≡C) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.44 (m, 2H, *o*-Ph), 7.35 (m, 3H, *m,p*-Ph), 7.33 (m, 2H, *p*-Ph_2P), 7.22 (m, 4H, *m*-Ph_2P), 7.13 (m, 4H, *o*-Ph_2P), 4.07 (m, 2H, NCH_2), 2.59 (s, 3H, Me), 1.99 (m, 2H, $^{Bu}CH_2$), 1.77 (s, 30H, C_5Me_5), 1.60 (m, 2H, CH_2CH_3), 1.04 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $^{Bu}CH_3$). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 169.2 (d, $^2J_{PC}$ = 17.5 Hz, C═), 159.9 (br, NC)[i], 156.3 (d, $^1J_{PC}$ = 119.6 Hz, ═CZr), 148.6 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 147.3 (d, $^3J_{PC}$ = 8.3 Hz, *i*-Ph), 138.6 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 136.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 135.2 (d, $^2J_{PC}$ = 12.2 Hz, *o*-Ph_2P), 131.9 (d, $^1J_{PC}$ = 22.5 Hz, *i*-Ph_2P), 130.6 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Ph_2P), 128.7 (*m*-Ph), 128.6 (d, $^3J_{PC}$ = 10.4 Hz, *m*-Ph_2P), 128.4 (*p*-Ph), 128.2 (d, $^4J_{PC}$ = 1.0 Hz, *o*-Ph), 118.0 (C_5Me_5), 124.3 (br, *i*-C_6F_5), 45.6 (NCH_2), 34.6 (d, $^3J_{PC}$ = 23.4 Hz, Me), 31.3 ($^{Bu}CH_2$), 20.5 (CH_2CH_3), 13.3 ($^{Bu}CH_3$), 12.3 (C_5Me_5). [[i] from the ghmbc experiment]. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = −76.1 ($\nu_{1/2}$ ~ 8 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br, 2F, *o*-C_6F_5), −163.8 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (m, 2F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 25 Hz).

X-ray Crystal Structure Analysis of Complex 11b. Formula $C_{70}H_{57}BF_{20}NPZr \cdot C_5H_{10}$, *M* = 1495.30, colorless crystal, 0.28 × 0.18 × 0.12 mm^3, *a* = 14.2433(1), *b* = 32.5730(3), *c* = 15.0069(2) Å, β = 103.477(1) °, *V* = 6770.69(12) Å^3, ρ_{calc} = 1.467 gcm^{-3}, μ = 0.286 mm^{-1}, empirical absorption correction (0.924 ≤ *T* ≤ 0.966), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, *T* = 223(2) K, ω and φ scans, 44278 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 11597 independent (R_{int} = 0.054) and 9833 observed reflections [$I > 2\sigma(I)$], 960 refined parameters, *R* = 0.047, wR^2 = 0.108, max. (min.) residual electron density 0.43 (−0.39) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 11c. Following the procedure described for the preparation of **11a**: reaction of complex **10** (30.7 mg, 21.7 μmol) with ^{t}BuCN (1.8 mg, 21.7 μmol) gave **11c** as a pale yellow crystalline solid (22.5 mg, 69% yield). Crystals suitable for X-ray single crystal analysis were grown from a two layer procedure using CH_2Cl_2/cyclopentane at −35 °C. Elemental Analysis: calcd. for $C_{70}H_{57}BF_{20}NPZr \cdot CH_2Cl_2$: C, 56.47; H, 3.94; N, 0.93. Found: C, 55.10; H, 3.79; N, 0.60. IR (KBr): 2261 (m, N≡C) cm^{-1}. ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.40 (m, 2H, *o*-Ph), 7.34 (m, 3H, *m,p*-Ph), 7.31 (m, 2H, *p*-Ph_2P), 7.20 (m, 4H, *m*-Ph_2P), 7.09 (m, 4H, *o*-Ph_2P), 2.47 (s, 3H, Me), 1.79 (s, 30H, C_5Me_5), 1.65 (br, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 168.6 (d, $^2J_{PC}$ = 15.2 Hz, C═), 163.1 (d, $^1J_{PC}$ = 119.0 Hz, ═CZr), 148.5 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 147.3 (d, $^3J_{PC}$ = 9.1 Hz, *i*-Ph), 141.4 (br, CN), 138.7 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 136.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 135.4 (d, $^2J_{PC}$ = 12.6 Hz, *o*-Ph_2P), 132.9 (d, $^1J_{PC}$ = 18.8 Hz, *i*-Ph_2P), 130.4 (d, $^4J_{PC}$ = 2.6 Hz, *p*-Ph_2P), 128.7 (*m*-Ph), 128.40 (d, $^3J_{PC}$ = 10.6 Hz, *m*-Ph_2P), 128.36 (d, $^4J_{PC}$ = 0.8 Hz, *o*-Ph), 128.3 (*p*-Ph), 124.5 (br, *i*-C_6F_5), 119.7 (C_5Me_5), 34.6 (d, $^3J_{PC}$ = 22.4 Hz, Me), 30.6 (^{t}Bu), 28.3 (^{t}Bu), 12.5 (C_5Me_5). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = −64.8 ($\nu_{1/2}$ ~ 3 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.2 (br, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (m, 2F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 30 Hz).

X-ray Crystal Structure Analysis of Complex 11c. Formula $C_{70}H_{57}BF_{20}NPZr \cdot CH_2Cl_2$, *M* = 1510.09, pale yellow crystal, 0.33 × 0.04 × 0.03 mm^3, *a* = 10.8445(2), *b* = 17.5706(3), *c* = 18.7237(3) Å, α = 110.727(1), β = 100.205(1), γ = 92.786(7)°, *V* = 3259.9(1) Å^3, ρ_{calc} = 1.538 gcm^{-3}, μ = 0.377 mm^{-1}, empirical absorption correction (0.885 ≤ *T* ≤ 0.988), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, *T* = 223(2) K, ω and φ scans, 31273 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.62 Å^{-1}, 15923 independent (R_{int} = 0.048) and 12431 observed reflections [$I > 2\sigma(I)$], 916 refined parameters, *R* = 0.075, wR^2 = 0.171, max. (min.) residual electron density 2.21 (−0.84) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Preparation of Complex 12. A solution of complex **10** (22.4 mg, 15.8 μmol) in 1 mL of CH_2Cl_2 was degassed and N_2O (1.5 bar) was introduced to the evacuated reaction flask for 10 min. The reaction mixture was then covered with cyclopentane (4 mL) to give yellow crystals of **12** (12.8 mg, 59% yield). Crystals suitable for X-ray single crystal analysis were grown from a two layer procedure using CH_2Cl_2/cyclopentane at −35 °C. Elemental Analysis: calcd. for $C_{65}H_{48}BF_{20}OPZr$: C, 57.49; H, 3.56. Found: C, 56.47; H, 4.14. IR (KBr): 1643 (m), 1594 (w), 1514 (s), 1464 (s), 980 (s) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.52 (m, 2H, *p*-Ph_2P), 7.41 (m, 2H, *o*-Ph), 7.38 (m, 3H, *m,p*-Ph), 7.36 (m, 4H, *m*-Ph_2P), 7.30 (m, 4H, *o*-Ph_2P), 2.18 (d, $^4J_{PH}$ = 0.96 Hz, 3H, Me), 1.96 (s, 30H, C_5Me_5). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 169.4 (d, $^2J_{PC}$ = 3.2 Hz, C═)[t], 156.7 (d, $^1J_{PC}$ = 9.6 Hz, ═CZr)[t], 148.5 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 145.2 (d, $^3J_{PC}$ = 15.6 Hz, *i*-Ph)[t], 138.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 136.7 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 133.3 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Ph_2P), 132.7 (d, $^2J_{PC}$ = 12.2 Hz, *o*-Ph_2P), 131.8 (d, $^1J_{PC}$ = 86.4 Hz, *i*-Ph_2P)[t], 129.3 (*m*-Ph), 129.2 (*p*-Ph)[t], 128.7 (d, $^3J_{PC}$ = 13.2 Hz, *m*-Ph_2P), 127.9 (d, $^4J_{PC}$ = 1.6 Hz, *o*-Ph), 127.4 (C_5Me_5), 124.7 (br, *i*-C_6F_5), 35.2 (d, $^3J_{PC}$ = 34.6 Hz, Me), 12.4 (C_5Me_5), [[t] tentative assignment]. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = 17.4 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br, 2F, *o*-C_6F_5), −163.8 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (m, 2F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 25 Hz).

X-ray Crystal Structure Analysis of Complex 12. Formula $C_{65}H_{48}BF_{20}OPZr \cdot C_5H_{10}$, *M* = 1428.16, yellow crystal, 0.20 × 0.12 × 0.03 mm^3, *a* = 10.6759(2), *b* = 15.4536(3), *c* = 19.3351(5) Å, α = 84.321(1), β = 82.779(2), γ = 83.515(2)°, *V* = 3132.73(12) Å^3, ρ_{calc} = 1.514 gcm^{-3}, μ = 0.306 mm^{-1}, empirical absorption correction (0.941 ≤ *T* ≤ 0.990), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, *T* = 223(2) K, ω and φ scans, 32038 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.59 Å^{-1}, 10726 independent (R_{int} = 0.052) and 8666 observed reflections [$I > 2\sigma(I)$], 904 refined parameters, *R* = 0.087, wR^2 = 0.242, max. (min.) residual electron density 2.92 (−0.69) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 13. *Caution: Isocyanates Are Toxic and Must Handled with Due Care.* ^{t}BuNCO (1.4 mg, 14.2 μmol) was added to a solution of complex **10** (20.0 mg, 14.2 μmol) in CH_2Cl_2 (1 mL), and then the reaction mixture was covered with pentane (3 mL). After several days a beige oil was formed. The solvent was decanted and the obtained residue was stirred in pentane (5 mL). The obtained precipitate was collected and then washed with pentane (3*2 mL) to give complex **13** as a yellow solid (16.0 mg, 79% yield). Crystals suitable for X-ray single crystal analysis were grown from a two layer procedure using CH_2Cl_2/cyclopentane at −35 °C. Elemental Analysis: calcd. for $C_{70}H_{57}BF_{20}NOPZr$: C, 58.34; H, 3.99; N, 0.97. Found: C, 58.57; H, 4.28; N, 1.01. IR (KBr): 1641 (s, C═N) cm^{-1}. ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.60 (m, 2H, *p*-Ph_2P), 7.47 (m, 4H, *o*-Ph_2P), 7.40 (m, 4H, *m*-Ph_2P), 7.09 (m, 1H, *p*-Ph), 6.93 (m, 2H, *m*-Ph), 6.79 (m, 2H, *o*-Ph), 2.02 (s, 30H, C_5Me_5), 1.71 (s, 3H, Me), 1.26 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 174.5 (d, $^2J_{PC}$ = 6.4 Hz, C═), 158.5 (d, $^1J_{PC}$ = 18.5 Hz, ═CZr), 151.3 (d, $^1J_{PC}$ = 158.5 Hz, C═N), 148.5 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 143.2 (d, $^3J_{PC}$ = 14.7 Hz, *i*-Ph), 138.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 136.7 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 134.2 (d, $^2J_{PC}$ = 9.8 Hz, *o*-Ph_2P), 133.5 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Ph_2P), 129.0 (d, $^3J_{PC}$ = 11.9 Hz, *m*-Ph_2P), 128.7 (*m*-Ph), 128.2 (*p*-Ph), 127.5 (d, $^4J_{PC}$ = 1.3 Hz, *o*-Ph), 127.1 (d, $^1J_{PC}$ = 68.8 Hz, *i*-Ph_2P), 126.5 (C_5Me_5), 123.9 (br, *i*-C_6F_5), 57.1 (d, $^3J_{PC}$ = 18.3 Hz, ^{t}Bu), 37.7 (d, $^3J_{PC}$ = 31.7 Hz, Me), 30.9 (^{t}Bu), 12.7 (C_5Me_5).[[t] tentatively assigned]. ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = 33.7 ($\nu_{1/2}$ ~ 5 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (m, 2F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 20 Hz).

X-ray Crystal Structure Analysis of Complex 13. Formula $C_{70}H_{57}BF_{20}NOPZr \cdot CH_2Cl_2$, *M* = 1526.09, yellow crystal, 0.33 × 0.10 × 0.03 mm^3, *a* = 10.7932(3), *b* = 18.4658(5), *c* = 19.7558(6) Å, α =

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105.168(1), β = 99.567(1), γ = 92.603(2)°, V = 3731.02(18) Å^3, ρ_{calc} = 1.358 gcm^{-3}, μ = 0.331 mm^{-1}, empirical absorption correction (0.898 ≤ T ≤ 0.990), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 33362 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 12817 independent (R_{int} = 0.064) and 10366 observed reflections [$I > 2\sigma(I)$], 925 refined parameters, R = 0.077, wR^2 = 0.197, max. (min.) residual electron density 0.81 (−0.62) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Preparation of Complex 14. A solution of complex **10** (37.0 mg, 26.2 μmol) in CH_2Cl_2 (1 mL) was degassed and CO_2 (1 bar) was introduced to the evacuated reaction flask at 0 °C for 5 min. After warming to room temperature, the reaction mixture was covered with pentane (3 mL) to eventually gave complex **14** as a yellow solid (28.0 mg, 77% yield). Crystals suitable for X-ray single crystal analysis were grown from a two layer procedure using CH_2Cl_2/cyclopentane at −35 °C. Elemental Analysis: calcd. for $C_{66}H_{48}BF_{20}O_2PZr$: C, 57.19; H, 3.49. Found: C, 57.25; H, 3.36. IR (KBr): 1699 (s, C═O) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.66 (m, 2H, p-Ph_2P), 7.47 (m, 4H, m-Ph_2P), 7.39 (m, 4H, o-Ph_2P), 7.17 (m, 1H, p-Ph), 7.01 (m, 2H, m-Ph), 6.88 (m, 2H, o-Ph), 2.01 (s, 30H, C_5Me_5), 1.71 (d, $^4J_{PH}$ = 0.6 Hz, 3H, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 175.8 (d, $^2J_{PC}$ = 7.2 Hz, C═), 165.5 (d, $^1J_{PC}$ = 125.1 Hz, (O)CO), 155.7 (d, $^1J_{PC}$ = 27.0 Hz, ═CZr), 148.5 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 142.9 (d, $^3J_{PC}$ = 15.1 Hz, i-Ph), 138.6 (dm, $^1J_{FC}$ ~ 230 Hz, C_6F_5), 136.6 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 134.4 (d, $^4J_{PC}$ = 3.1 Hz, p-Ph_2P), 133.9 (d, $^2J_{PC}$ = 9.9 Hz, o-Ph_2P), 129.7 (d, $^3J_{PC}$ = 11.9 Hz, m-Ph_2P), 129.0 (m-Ph), 128.9 (p-Ph), 127.5 (C_5Me_5), 127.3 (d, $^4J_{PC}$ = 1.7 Hz, o-Ph), 124.8 (d, $^1J_{PC}$ = 65.1 Hz, i-Ph_2P), n.o. (i-C_6F_5), 37.3 (d, $^3J_{PC}$ = 32.9 Hz, Me), 12.5 (C_5Me_5). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = 27.6 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br, 2F, o-C_6F_5), −163.8 (t, $^3J_{FF}$ = 20.3 Hz, 1F, p-C_6F_5), −167.7 (m, 2F, m-C_6F_5). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 25 Hz).

X-ray Crystal Structure Analysis of Complex 14. Formula $C_{66}H_{48}BF_{20}O_2PZr$, M = 1386.04, yellow crystal, 0.25 × 0.13 × 0.02 mm^3, a = 10.6552(2), b = 16.3512(2), c = 18.5198(3) Å, α = 91.707(1), β = 91.971(1), γ = 104.075(1)°, V = 3125.47(9) Å^3, ρ_{calc} = 1.473 gcm^{-3}, μ = 0.305 mm^{-1}, empirical absorption correction (0.927 ≤ T ≤ 0.993), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 29120 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 10788 independent (R_{int} = 0.040) and 9535 observed reflections [$I > 2\sigma(I)$], 831 refined parameters, R = 0.046, wR^2 = 0.122, max. (min.) residual electron density 0.43 (−0.35) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Preparation of Complex 15. $MesN_3$ (2.1 mg, 13.3 μmol) was added to a solution of complex **10** (18.8 mg, 13.3 μmol) in CH_2Cl_2 (1 mL) at *ca.* −35 °C. The color of the reaction mixture became red immediately. The reaction solution was covered with cyclopentane (3 mL) and stored in the fridge (*ca.* −35 °C) for several days. Complex **15** was obtained as a red crystalline solid (14.6 mg, 70% yield). Crystals suitable for X-ray single crystal analysis were grown from a two layer procedure using CH_2Cl_2/cyclopentane at −35 °C. Elemental Analysis: calcd. for $C_{74}H_{59}BF_{20}N_3PZr$: C, 59.12; H, 3.96; N, 2.80. Found: C, 58.03; H, 4.19; N, 2.49. IR (KBr): 1609 (w, N═N) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.61 (m, 2H, p-Ph_2P), 7.39 (m, 4H, m-Ph_2P), 7.32 (m, 4H, o-Ph_2P), 7.28 (m, 1H, p-Ph), 7.19 (m, 2H, m-Ph), 7.09 (m, 2H, o-Ph), 6.81 (m, 2H, m-Mes), 2.22 (s, 3H, $CH_3^{p\text{-Mes}}$), 2.10 (s, 30H, C_5Me_5), 2.05 (s, 6H, $CH_3^{o\text{-Mes}}$), 2.03 (s, 3H, Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 172.2 (d, $^2J_{PC}$ = 2.3 Hz, C═), 158.8 (d, $^1J_{PC}$ = 8.0 Hz, ═CZr), 148.5 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 144.5 (i-Mes), 144.4 (d, $^3J_{PC}$ = 15.8 Hz, i-Ph), 138.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 138.0 (p-Mes), 136.7 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 135.2 (d, $^2J_{PC}$ = 10.7 Hz, o-Ph_2P), 134.0 (d, $^4J_{PC}$ = 3.0 Hz, p-Ph_2P), 131.8 (o-Mes), 130.7 (m-Mes), 129.2 (m-Ph), 128.71 (d, $^3J_{PC}$ = 11.1 Hz, m-Ph_2P), 128.66 (p-Ph), 128.6 (C_5Me_5), 128.3 (d, $^1J_{PC}$ = 71.0 Hz, i-Ph_2P), 127.7 (d, $^4J_{PC}$ = 1.6 Hz, o-Ph), 124.7 (br, i-C_6F_5), 36.4 (d, $^3J_{PC}$ = 35.5 Hz, Me), 21.1 ($CH_3^{o\text{-Mes}}$), 20.8 ($CH_3^{p\text{-Mes}}$), 13.1 (C_5Me_5). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = 12.3 ($\nu_{1/2}$ ~ 3 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br, 2F, o-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, p-C_6F_5), −167.7 (m, 2F, m-C_6F_5). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 20 Hz).

X-ray Crystal Structure Analysis of Complex 15. Formula $C_{74}H_{59}BF_{20}N_3PZr \cdot C_5H_{10}$, M = 1573.37, yellow-orange crystal, 0.28 × 0.17 × 0.08 mm^3, a = 40.5492(6), b = 14.9195(2), c = 24.7606(4) Å, β = 99.432(1)°, V = 14777.0(4) Å^3, ρ_{calc} = 1.414 gcm^{-3}, μ = 0.267 mm^{-1}, empirical absorption correction (0.929 ≤ T ≤ 0.979), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 47775 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.67 Å^{-1}, 12838 independent (R_{int} = 0.041) and 10528 observed reflections [$I > 2\sigma(I)$], 960 refined parameters, R = 0.047, wR^2 = 0.123, max. (min.) residual electron density 0.39 (−0.36) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of Complex 10 with H_2 (D_2) (in CH_2Cl_2). A solution of complex **10** (28.2 mg, 20.0 μmol) in CH_2Cl_2 (2 mL) was degassed and H_2 (1.5 bar) was introduced to the evacuated reaction flask for 2 h. Then the reaction mixture was covered with pentane (4 mL) to give a white crystalline solid (16 mg, 55% yield **19**/**20**) (suitable for X-ray crystal structure analysis). The solid was identified as a mixture of $Cp^*_2ZrCl_2$ (**19**) and compound **20** (ratio: 1:6, ^{1}H NMR) in CD_2Cl_2. *Data of $Cp^*_2ZrCl_2$ (**19**):* ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 1.97 (s, 30H, C_5Me_5). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 124.2 (C_5Me_5), 12.1 (C_5Me_5). *Data of complex **20**:* ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.81 (m, 2H, p-Ph_2P), 7.62 (m, 4H, m-Ph_2P), 7.54 (m, 4H, o-Ph_2P), 7.26 (m, 1H, p-Ph), 7.10 (m, 2H, m-Ph), 6.84 (m, 2H, o-Ph), 6.30 (dq, $^2J_{PH}$ = 21.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, ═CH), 4.03 (d, $^2J_{PH}$ = 5.8 Hz, 2H, $ClCH_2$), 2.58 (dd, $^4J_{HH}$ = 1.4 Hz, $^4J_{PH}$ = 1.0 Hz, 3H, Me). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 176.7 (d, $^2J_{PC}$ = 1.6 Hz, C═), 148.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 138.5 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 138.2 (d, $^3J_{PC}$ = 7.2 Hz, i-Ph), 136.5 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 136.3 (d, $^4J_{PC}$ = 3.1 Hz, p-Ph_2P), 133.4 (d, $^2J_{PC}$ = 10.2 Hz, o-Ph_2P), 130.87 (d, $^3J_{PC}$ = 13.1 Hz, m-Ph_2P), 130.86 (p-Ph), 129.4 (m-Ph), 126.5 (d, $^4J_{PC}$ = 1.5 Hz, o-Ph), 124.4 (br, i-C_6F_5), 116.8 (d, $^1J_{PC}$ = 89.8 Hz, i-Ph_2P), 102.0 (d, $^1J_{PC}$ = 90.8 Hz, ═CH), 35.3 (d, $^1J_{PC}$ = 61.4 Hz, $ClCH_2$), 30.9 (d, $^3J_{PC}$ = 17.2 Hz, Me). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = 14.1 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br, 2F, o-C_6F_5), −163.8 (t, $^3J_{FF}$ = 20.3 Hz, 1F, p-C_6F_5), −167.6 (m, 2F, m-C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 20 Hz).

Under similar conditions as described above the reaction between complex **10** and D_2 gave **19** and **20**-D (ratio ca. 1:8, ^{1}H NMR). *Data of complex **20-D**:* ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.82 (m, 2H, p-Ph_2P), 7.64 (m, 4H, m-Ph_2P), 7.54 (m, 4H, o-Ph_2P), 7.27 (m, 1H, p-Ph), 7.11 (m, 2H, m-Ph), 6.84 (m, 2H, o-Ph), 4.03 (d, $^2J_{PH}$ = 5.8 Hz, 2H, $ClCH_2$), 2.59 (d, $^4J_{PH}$ = 1.0 Hz, 3H, Me). ^{2}H NMR (77 MHz, CH_2Cl_2, 299 K): δ = 6.33 (br, ═CD).

X-ray Crystal Structure Analysis of Compound 19/20. Formula $C_{20}H_{30}Cl_2Zr \cdot C_{46}H_{21}BF_{20}ClP$, M = 1463.42, yellow crystal, 0.45 × 0.20 × 0.12 mm^3, a = 13.9278(5), b = 15.0219(4), c = 16.8483(7) Å, α = 70.762(2), β = 78.877(2), γ = 70.199(2)°, V = 3118.27(19) Å^3, ρ_{calc} = 1.559 gcm^{-3}, μ = 0.432 mm^{-1}, empirical absorption correction (0.829 ≤ T ≤ 0.949), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 23638 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.59 Å^{-1}, 10412 independent (R_{int} = 0.037) and 9545 observed reflections [$I > 2\sigma(I)$], 840 refined parameters, R = 0.041, wR^2 = 0.103, max. (min.) residual electron density 0.49 (−0.48) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Reaction of Complex 10 with H_2 (D_2) (in C_6D_6).[23] A solution of complex **10** (20.5 mg, 14.5 μmol) in 1 mL of C_6D_6 (3 drops of THF was added) was degassed and H_2 (1.5 bar) was introduced to the evacuated reaction flask for 10 min. The reaction mixture was then covered with pentane (4 mL) to give yellow crystals of **21** (12.0 mg, 52% yield of **21**/**21**-Cl) (see X-ray crystal structure analysis: the σ-ligand site is *ca.* 25% occupied by chloride [$Cp^*_2Zr(THF)Cl$][B-(C_6F_5)$_4$] (**21**-Cl) probably resulted from traces of CH_2Cl_2 in the starting material **10**). The volatiles of the mother liquid were removed *in vacuo* to get **22** (*ca.* 6 mg, 83% yield) admixed with **21** and **21**-Cl (85: 10: 5). *Data of Complex **21** (**21**: **21**-Cl = 70: 30, ^{1}H NMR):* ^{1}H NMR (600 MHz, C_6D_5Br, 299 K): δ = 7.73 (s, 1H, ZrH), 3.15 (br,

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4H, $CH_2^{\alpha\text{-THF}}$), 1.66 (s, 30H, C_5Me_5), 1.54 (br, 4H, $CH_2^{\beta\text{-THF}}$). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_5Br, 299 K): δ = 148.6 (dm, $^1J_{FC} \sim 240$ Hz, C_6F_5), 138.4 (dm, $^1J_{FC} \sim 245$ Hz, C_6F_5), 136.5 (dm, $^1J_{FC} \sim 245$ Hz, C_6F_5), 124.7 (br, *i*-C_6F_5), 123.4 (C_5Me_5), 70.9 (br, $CH_2^{\alpha\text{-THF}}$), 24.3 (br, $CH_2^{\beta\text{-THF}}$), 11.3 (C_5Me_5). ^{19}F NMR (564 MHz, C_6D_5Br, 299 K): δ = −131.5 (br, 2F, *o*-C_6F_5), −161.8 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*-C_6F_5), −165.7 (m, 2F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (192 MHz, C_6D_5Br, 299 K): δ = −16.0 ($\nu_{1/2} \sim 20$ Hz). *Data of Compound* **22** *(***22***: 21: 21-Cl = 85: 10: 5, ^1H NMR):* ^1H NMR (600 MHz, C_6D_6, 299 K): δ = 7.46 (m, 4H, *o*-Ph_2P), 7.28 (m, 2H, *o*-Ph), 7.09 (m, 2H, *m*-Ph), 7.08 (m, 4H, *m*-Ph_2P), 7.05 (m, 1H, *p*-Ph), 7.04 (m, 2H, *p*-Ph_2P), 6.32 (dq, $^2J_{PH}$ = 3.9 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, =CH), 2.05 (dd, $^4J_{HH}$ = 1.4 Hz, $^4J_{PH}$ = 0.7 Hz, 3H, Me). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 299 K): δ = 154.4 (d, $^2J_{PC}$ = 25.7 Hz, C=), 141.9 (d, $^3J_{PC}$ = 6.7 Hz, *i*-Ph), 141.3 (d, $^1J_{PC}$ = 11.9 Hz, *i*-Ph_2P), 133.0 (d, $^3J_{PC}$ = 19.0 Hz, *o*-Ph_2P), 128.7 (d, $^3J_{PC}$ = 6.2 Hz, *m*-Ph_2P), 128.4 (d, $^4J_{PC}$ = 4.7 Hz, *o*-Ph), 128.3 (*p*-Ph_2P), 128.1 (*m*-Ph), 127.9 (*p*-Ph), 126.4 (d, $^1J_{PC}$ = 11.6 Hz, =CH), 27.6 (d, $^3J_{PC}$ = 6.0 Hz, Me). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6, 299 K): δ = −25.0 ($\nu_{1/2} \sim 2$ Hz).

Under similar conditions as described above the reaction between complex **10** and D_2 gave **21**-D and **22**-D. *Data of complex* ***21***-D (***21***-D: ***21***-Cl = 84: 16, ^1H NMR): ^1H NMR (500 MHz, C_6D_5Br, 299 K): δ = 3.15 (br, 4H, $CH_2^{\alpha\text{-THF}}$), 1.66 (s, 30H, C_5Me_5), 1.54 (br, 4H, $CH_2^{\beta\text{-THF}}$). ^2H NMR (77 MHz, C_6H_5Br, 299 K): δ = 7.70 (s, ZrD). *Data of* **22***-D*: ^1H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.39 (m, 4H, *o*-Ph_2P), 7.34 −7.30 (m, 9H, Ph), 7.26 (m, 2H, *p*-Ph_2P), 2.33 (d $^4J_{PH}$ = 0.6 Hz, 3H, Me). ^2H NMR (77 MHz, CH_2Cl_2, 299 K): δ = 6.34 (br, =CD).

X-ray Crystal Structure Analysis of Compound 21. Formula $C_{48}H_{38.75}BCl_{0.25}F_{20}OZr$, M = 1122.43, yellow crystal, 0.23 × 0.05 × 0.03 mm^3, a = 10.8133(2), b = 14.3998(2), c = 15.2987(4) Å, α = 77.974(1), β = 86.094(1), γ = 83.647(1)°, V = 2313.07(8) Å^3, ρ_{calc} = 1.612 gcm^{-3}, μ = 0.370 mm^{-1}, empirical absorption correction (0.919 ≤ T ≤ 0.989), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 21051 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.67 Å^{-1}, 8023 independent (R_{int} = 0.043) and 6815 observed reflections [$I > 2\sigma(I)$], 663 refined parameters, R = 0.055, wR^2 = 0.115, max. (min.) residual electron density 0.34 (−0.43) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms. *Comment:* the σ-ligand site is *ca.* 25% occupied by chloride; the remaining 75% of that site seem to be occupied by hydride.

General Procedure of the Catalytic Hydrogenation. Compound **10**, substrate (0.5 mmol), and ferrocene (9.3 mg, 50 μmol) as standard compound were dissolved in C_6D_5Br (1 mL). Then the reaction mixture was frozen and evacuated, then H_2 (1.5 bar, r.t.) was introduced for the respective reaction time. Subsequently the reaction solution was transferred to an NMR tube and monitored by ^1H NMR. The NMR yield was determined relative to ferrocene as internal standard.

Preparation of Complex 25a. A solution of complex **10** (19.5 mg, 13.8 μmol) in 0.5 mL of CH_2Cl_2 was added to a CH_2Cl_2 solution (0.5 mL) of *trans*-chalcone (2.9 mg, 13.8 μmol) at room temperature, and then the reaction mixture was covered with cyclopentane (3 mL) to eventually gave complex **25a** as a yellow crystalline solid (14.8 mg, 69% yield). Crystals suitable for X-ray single crystal analysis were grown from a two layer procedure using CH_2Cl_2/cyclopentane at room temperature. Elemental Analysis: calcd. for $C_{80}H_{60}BF_{20}OPZr \cdot CH_2Cl_2$: C, 59.49; H, 3.82. Found: C, 59.33; H, 3.78. IR (KBr): 1644 (s), 1622 (m), 1512 (s), 1465 (s), 979 (s) cm^{-1}. ^1H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 8.40 (2H, *o*), 7.92 (1H, *p*), 7.89 (2H, *m*) (each m, Ph_2P), 7.30 (3H, *m,p*), 7.21 (2H, *o*) (each m, Ph^O), 6.96 (3H, *m,p*), 6.91 (2H, *o*) (each m, Ph^{CH}), 6.94 (2H, *m*), 6.69 (1H, *p*), n.o. (very br, 2H, *o*) (each br m, Ph_2P')^t, n.o. (very br, 4H, *o,m*), 6.81 (br m, 1H, *p*) (Ph)^t, 5.26 (dd, $^2J_{PH}$ = 19.6 Hz, $^3J_{HH}$ = 6.2 Hz, 1H, C*H*Ph), 4.56 (dd, $^3J_{PH}$ = 6.1 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, HC=), 2.29 (s, 15H, C_5Me_5), 1.83 (br, 3H, Me), 1.68 (s, 15H, C_5Me_5'), [^{t} tentative assignment]. $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 171.4 (d, $^2J_{PC}$ = 8.0 Hz, C=), 160.6 (d, $^3J_{PC}$ = 7.5 Hz, OC=), 155.7 (d, $^1J_{PC}$ = 37.2 Hz, =CZr), 144.4 (d, $^3J_{PC}$ = 17.2 Hz, *i*), 127.3 (*p*), n.o. (*o,m*) (Ph)^t, 140.0 (d, $^4J_{PC}$ = 3.2 Hz, *i*), 129.0 (*p*), 128.6 (*m*), 126.7 (*o*) (Ph^O), 138.9 (d, $^2J_{PC}$ = 2.6 Hz, *i*), 129.9 (*o*), 129.2 (*m*), 127.3 (*p*) (Ph^{CH}), 136.0 (d, $^2J_{PC}$ = 7.2 Hz, *o*), 134.5 (d, $^4J_{PC}$ = 3.3 Hz, *p*), 129.8 (d, $^3J_{PC}$ = 4.2 Hz, *m*), 121.8 (d, $^1J_{PC}$ = 77.5 Hz, *i*) (Ph_2P), 131.5 (d, $^3J_{PC}$ = 3.3 Hz, *m*), 128.2 (br, *p*), n.o. (*i, o*) (Ph_2P')^t, 125.3 (C_5Me_5'), 125.0 (C_5Me_5), 100.7 (d, $^2J_{PC}$ = 9.7 Hz, HC=), 46.3 (d, $^1J_{PC}$ = 50.6 Hz, CHPh), 38.9 (d, $^3J_{PC}$ = 36.7 Hz, Me), 13.4 (C_5Me_5), 12.6 (C_5Me_5'), [C_6F_5 not listed; ^{t} tentative assignment]. $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = 22.1 ($\nu_{1/2} \sim 2$ Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.2 (br, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (m, 2F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2} \sim 25$ Hz).

X-ray Crystal Structure Analysis of Complex 25a. Formula $C_{80}H_{60}BF_{20}OPZr \cdot C_5H_{10}$, M = 1620.41, yellow crystal, 0.33 × 0.10 × 0.07 mm^3, a = 13.9073(2), b = 14.3933(2), c = 19.6665(3) Å, α = 72.517(1), β = 85.337(1), γ = 77.455(1)°, V = 3664.64(9) Å^3, ρ_{calc} = 1.468 gcm^{-3}, μ = 0.271 mm^{-1}, empirical absorption correction (0.915 ≤ T ≤ 0.981), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 33878 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.59 Å^{-1}, 12687 independent (R_{int} = 0.045) and 10908 observed reflections [$I > 2\sigma(I)$], 1039 refined parameters, R = 0.052, wR^2 = 0.121, max. (min.) residual electron density 0.46 (−0.42) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 25b. Following the procedure described for the preparation of **25a**: reaction of complex **10** (21.7 mg, 15.4 μmol) with 1,2,3-triphenylprop-2-en-1-one (4.4 mg, 15.4 μmol) gave **25b** as a pale yellow crystalline solid (20.2 mg, 77% yield). Crystals suitable for X-ray single crystal analysis were grown from a two layer procedure using CH_2Cl_2/cyclopentane at −35 °C. Elemental Analysis: calcd. for $C_{86}H_{64}BF_{20}OPZr \cdot C_5H_{10}$: C, 64.42; H, 4.40. Found: C, 64.48; H, 5.03. IR (KBr): 1643 (m), 1588 (w), 1513 (s), 1464 (s), 979 (s) cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 8.39 (2H, *o*), 8.07 (1H, *p*), 8.00 (2H, *m*) (each m, Ph), 7.59, 7.19, 6.77, 6.18, 5.68 (each br m, each 1H, Ph), 7.05 (3H, *m,p*), 6.94 (2H, *o*) (each m, Ph), 6.86 (br), 6.81 (m, 1H), 6.53 (m), 6.52 (m), 5.78 (br) (each 1H, Ph), 6.85, 6.74, 6.45, 6.42, 5.87 (each m, each 1H, Ph), n.o. (br, 3H), 6.62 (1H), 6.39 (1H) (each br, Ph), 5.98 (d, $^2J_{PH}$ = 21.2 Hz, 1H, CHPh), 2.34 (s, 15H, C_5Me_5), 1.83 (br, 3H, Me), 1.75 (s, 15H, C_5Me_5'). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K)[selected resonances]: δ = 172.2 (d, $^2J_{PC}$ = 7.6 Hz, C=), 159.0 (d, $^3J_{PC}$ = 7.1 Hz, OC=), 157.1 (d, $^1J_{PC}$ = 38.2 Hz, =CZr), 145.2 (*i*-Ph), 125.3 (C_5Me_5'), 125.1 (C_5Me_5), 110.2 (d, $^2J_{PC}$ = 8.3 Hz, PhC=), 51.3 (d, $^1J_{PC}$ = 50.7 Hz, CHPh), 38.8 (d, $^3J_{PC}$ = 37.0 Hz, Me), 13.6 (C_5Me_5), 12.8 (C_5Me_5'). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 299 K): δ = 26.6 ($\nu_{1/2} \sim 1$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), −167.7 (m, 2F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2} \sim 25$ Hz).

X-ray Crystal Structure Analysis of Complex 25b. Formula $C_{86}H_{64}BF_{20}OPZr \cdot C_5H_{10}$, M = 1696.50, pale yellow crystal, 0.20 × 0.10 × 0.02 mm^3, a = 13.8374(4), b = 14.5871(5), c = 21.9553(8) Å, α = 86.185(1), β = 88.823(1), γ = 77.638(2)°, V = 4319.2(2) Å^3, ρ_{calc} = 1.304 gcm^{-3}, μ = 0.233 mm^{-1}, empirical absorption correction (0.954 ≤ T ≤ 0.995), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 36922 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.59 Å^{-1}, 14614 independent (R_{int} = 0.057) and 11404 observed reflections [$I > 2\sigma(I)$], 1093 refined parameters, R = 0.081, wR^2 = 0.192, max. (min.) residual electron density 0.94 (−0.49) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 27. Following the procedure described for the preparation of **25a**: reaction of complex **10** (22.1 mg, 15.6 μmol) with 1-phenylbut-2-yn-1-one (2.3 mg, 15.6 μmol) gave **27** as a red crystalline solid (12.8 mg, 55% yield). Crystals suitable for X-ray single crystal analysis were grown from a two layer procedure using CH_2Cl_2/cyclopentane at room temperature. Elemental Analysis: calcd. for $C_{75}H_{56}BF_{20}OPZr \cdot CH_2Cl_2$: C, 58.10; H, 3.72. Found: C, 57.22; H, 4.09. IR (KBr): 1643 (m), 1513 (s), 1464 (s), 980 (s) cm^{-1}. ^1H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.70 (m, 2H, *o*-Ph^O), 7.68 (m, 1H, *p*-Ph^O), 7.61 (m, 2H, *p*-Ph_2P), 7.53 (m, 2H, *m*-Ph^O), 7.46 (m, 4H, *m*-Ph_2P), 7.34 (m, 4H, *o*-Ph_2P), 7.02 (m, 1H, *p*-Ph), 6.87 (m, 2H, *m*-Ph),

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6.71 (m, 2H, *o*-Ph), 2.07 (s, 3H, Me), 1.97 (d, $^3J_{PH}$ = 11.3 Hz, 3H, MeC═), 1.89 (s, 30H, C_5Me_5). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 199.8 (d, $^2J_{PC}$ = 49.3 Hz, ═C═), 197.4 (d, $^3J_{PC}$ = 28.9 Hz, OC═), 173.2 (d, $^2J_{PC}$ = 1.7 Hz, C═), 158.9 (d, $^1J_{PC}$ = 21.8 Hz, ZrC═), 148.5 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 145.0 (d, $^3J_{PC}$ = 18.4 Hz, *i*-Ph), 144.0 (d, $^1J_{PC}$ = 100.4 Hz, MeC═), 138.7 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 136.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 135.3 (*p*-Ph^O), 134.1 (d, $^2J_{PC}$ = 8.9 Hz, *o*-Ph_2P), 133.6 (d, $^4J_{PC}$ = 1.4 Hz, *i*-Ph^O), 133.3 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Ph_2P), 129.8 (*m*-Ph^O), 129.7 (*o*-Ph^O), 129.2 (d, $^3J_{PC}$ = 10.9 Hz, *m*-Ph_2P), 128.5 (*m*-Ph), 127.5 (d, $^4J_{PC}$ = 1.8 Hz, *o*-Ph), 127.4 (*p*-Ph), 126.8 (d, $^1J_{PC}$ = 64.1 Hz, *i*-Ph_2P), 124.3 (br, *i*-C_6F_5), 121.9 (C_5Me_5), 38.8 (d, $^3J_{PC}$ = 36.1 Hz, CH_3), 22.3 (d, $^2J_{PC}$ = 19.9 Hz, MeC═), 12.9 (C_5Me_5). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = 33.2 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.2 (br, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (m, 2F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 20 Hz).

X-ray Crystal Structure Analysis of Complex 27. Formula $C_{75}H_{56}BF_{20}OPZr \cdot CH_2Cl_2$, M = 1571.12, yellow-orange crystal, 0.30 × 0.17 × 0.07 mm^3, a = 13.0151(2), b = 14.7358(2), c = 19.3515(3) Å, α = 72.626(1), β = 73.566(1), γ = 82.426(1)°, V = 3392.81(9) Å^3, ρ_{calc} = 1.538 gcm^{-3}, μ = 0.366 mm^{-1}, empirical absorption correction (0.898 ≤ T ≤ 0.974), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 37649 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.67 Å^{-1}, 16542 independent (R_{int} = 0.041) and 13818 observed reflections [$I > 2\sigma(I)$], 931 refined parameters, R = 0.052, wR^2 = 0.115, max. (min.) residual electron density 0.54 (−0.53) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and physical characterization of the new compounds, crystallographic data, and CIF files. 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 analysis.

Notes

The authors declare no competing financial interest.

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In the version published ASAP April 17, 2013, Figures 1 and 3 were transposed, this was corrected and reposted April 19, 2013.