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Formation of Unsaturated Vicinal Zr^+/P Frustrated Lewis Pairs by the Unique 1,1-Carbozirconation Reactions

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Supporting Information

ABSTRACT: Treatment of the metallocene cation complexes $[Cp^*_2MCH_3]^+[B(C_6F_5)_4]^-$ (M = Zr or Hf) with trimethylsilyl-(diarylphosphino)acetylenes $Ar_2P-C\equiv C-SiMe_3$ (Ar = Ph or *p*-tolyl) resulted in the formation of internal phosphane stabilized cations $[Cp^*_2M\text{-}C(CH_3)=C(SiMe_3)PAr_2]^+$ **4** through the unique 1,1-carbometalation reaction under mild conditions. In contrast, when the low Lewis basicity phosphane containing alkyne $(C_6F_5)_2P-C\equiv C-SiMe_3$ was used, normal 1,2-carbometalation occurred to produce complexes **5**, which show agostic coordination of a Me−Si group to the metal center. Complex **4a** reacts with *n*-butyl isocyanide to give the coordination product **6**, which has the Zr−P bond retained. Treatment of **4a** with N_2O gave the five-membered metallaheterocycle **7** by oxidation of the phosphane. The vicinal M^+/P complexes **4** also show some typical FLP reactivity. They add to cinnamaldehyde or paraformaldehyde, for example, to produce carbonyl addition products **8** and **9**, respectively. Complex **4a** adds to the N=O functionality of nitrosobenzene with formation of **10**. The vicinal M^+/P systems **4** behave as reactive frustrated Lewis pairs toward hetercumulenes, undergoing 1,2-addition to the C=O bond of CO_2 and the S=O bond of SO_2 to form the respective adducts **11** and **12**. The Zr^+/P FLP **4a** reacts with PhN=S=O to give the addition product **13**, in which the phosphane Lewis base has added to the nitrogen atom and the Zr^+ Lewis acid to both atoms of the S=O unit. The reaction of complex **4a** with the metal complex $[Ir(COD)Cl]_2$ affords a heterobimetallic Zr/Ir product **14**. The vicinal M^+/P complexes **4** can be also used as efficient catalysts for the regioselective dimerization of phenyl acetylene.

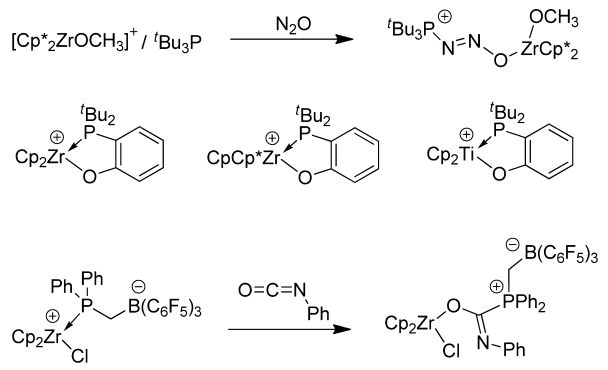
INTRODUCTION

Frustrated Lewis pairs (FLPs) were initially composed of combinations of main group element derived pairs of Lewis bases and Lewis acids.[1] Sufficient steric bulk prevented them from neutralizing strong adduct formation. Invariably such FLPs have shown transition metal reminiscent reaction behavior toward a variety of small molecules.[2] Dihydrogen activation is a most prominent feature,[3−5] often leading to metal-free hydrogenation catalysis. Main group element derived FLPs may also activate carbon monoxide for reductive hydroboration;[6] they also may bind to CO_2,[7,8] SO_2,[9] to alkenes and alkynes,[10] to azides,[11] to various carbonyl compounds, etc.[12,13] Some specific unsaturated P/B FLPs were shown to undergo cooperative C,C-addition to isonitriles[14] or to carbon monoxide[15] to form the respective five-membered heterocycles in a process that bears a remote resemblance to metal/isonitrile or metal/CO coordination chemistry as it is commonly described by the Dewar−Chatt−Duncanson model.[16] Many vicinal P/B FLPs react similarly by means of cooperative *N,N*-addition to nitric oxide (NO)[17] to form a new family of persistent FLP−NO aminoxyl radicals.[18]

There is a current tendency to explore the use of Lewis acid components other than boron in FLP chemistry. These recent developments include Al or Ga/P combinations[19] and also the use of strongly electrophilic phosphonium Lewis acids.[20] There is also some development toward the use of a few transition metal complex derived Lewis acids in FLP chemistry. Stephan et al. have described zirconocene cation/phosphane adducts of N_2O.[21] Wass et al. have described a series of cationic intramolecular zirconocene complexes with e.g. pendant aryloxyphosphanes that undergo quite a selection of typical FLP reactions (see Scheme 1).[22] We had used N. Shore's $Cp_2Zr(Cl)CH_2PPh_2$ complex[23] to generate the $[Cp_2Zr(Cl)\text{-}Ph_2PCH_2B(C_6F_5)_3]$ complex and explored its FLP chemistry.[24]

We had recently observed that phenyl(diphenylphosphino)-acetylene (**2a**) underwent a clean 1,2-insertion into the metal to

Scheme 1

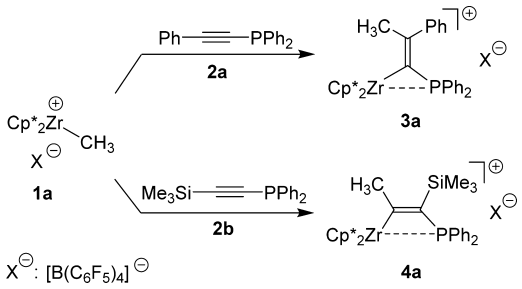


Received: July 7, 2014
Published: August 4, 2014

   dx.doi.org/10.1021/ja5068146 | J. Am. Chem. Soc. 2014, 136, 12431−12443

carbon σ-bond of $[Cp^*_2ZrCH_3]^+$ cation (**1a**)[25] (with $[B(C_6F_5)_4]^-$ anion) to give the geminal Zr^+/P Lewis pair **3a** featuring a substituted exomethylene unit (Scheme 2).[26] In

Scheme 2

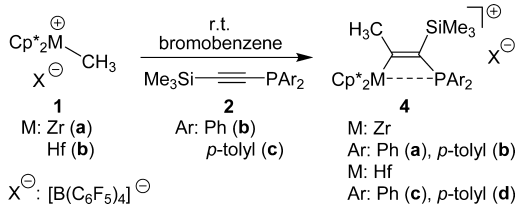


contrast, $[Cp^*_2ZrCH_3]^+$ (**1a**) reacted with trimethylsilyl(diphenylphosphino)acetylene (**2b**) by a unique 1,1-carbozirconation to yield the corresponding vicinal Zr^+/P Lewis pair **4a**.[27] Both the Zr^+/P systems **3a** and **4a** behaved as typical FLPs toward a variety of unsaturated substrates. The here observed 1,1-carbozirconation reaction appeared to be a rare example of a transition metal analogue of the 1,1-carboboration reaction,[28] which has seen quite some applications recently, especially with regard to its advanced variants using very electrophilic R-$B(C_6F_5)_2$ reagents.[29,30] It has become a very useful method for synthesizing substituted alkenyl boranes,[31] especially with sterically demanding substitution patterns.[32,33] It might be envisaged that our newly disclosed 1,1-carbozirconation reaction[27] of suitably functionalized alkynes could become a method of choice for generating respective functionalized alkenyl zirconocene cation systems. Therefore, we have explored this new reaction further and investigated the FLP behavior of the resulting (2-phosphinoalkenyl) group 4 metallocene cations in some detail. The current state of that development will be described in this article.

RESULTS AND DISCUSSION

Zr^+/P FLP Formation by 1,1-Carbometalation Reactions. We investigated the 1,1-carbometalation reaction using the trimethylsilyl(diarylphosphino)acetylenes **2b** (Ar = Ph) and **2c** (Ar = *p*-tolyl) (Scheme 3). Both of these were reacted with

Scheme 3



the group 4 metallocene cations $[Cp^*_2MCH_3]^+$ **1a** (M = Zr) and **1b** (M = Hf). The formation of the Zr^+/P 1,1-carbozirconation product **4a** (Ar = Ph, M = Zr) had been already described in our preliminary communication.[27]

The formation of the corresponding hafnium complex **4c** (Ar = Ph, M = Hf) shall here be described as a representative example. The salt $[Cp^*_2HfCH_3]^+[B(C_6F_5)_4]^-$ was in situ generated by treatment of $Cp^*_2Hf(CH_3)_2$ with 1 mol equiv of the trityl salt $[Ph_3C]^+[B(C_6F_5)_4]^-$ in bromobenzene solution (2 min, room temperature (RT)). Then, the alkyne Me_3Si—C≡C—PPh_2 (**2b**) was added, and the reaction mixture was kept at RT for 2 d. During this time, a crystalline precipitate of the 1,1-carbohafnation product **4c** was formed. The yellow crystalline product was isolated in 77% yield. It was characterized by X-ray diffraction, elemental analysis, and spectroscopy. It was found to be almost insoluble in bromobenzene and only slightly soluble in dichloromethane, the solvent used for the characterization by NMR. In CD_2Cl_2 solution, complex **4c** shows sharp ^1H NMR signals of the $SiMe_3$ substituent and the Cp^*_2Hf unit. The newly formed Hf-alkenyl ligand features a typical Hf—^{13}C═ NMR resonance at δ 265.9 and the signal of the neighboring ═C[P] carbon atom at δ 120.7 (with $^1J_{PC}$ = 15.2 Hz). The ^{31}P NMR resonance of complex **4c** occurs at δ 23.3 (see also Table 1 and the Supporting Information).

Table 1. Selected NMR Data of the 1,1-Carbometalation Products 4a–d

compound		4a[b,d]	4b[a]	4c[b]	4d[b]
M		Zr	Zr	Hf	Hf
Ar		Ph	*p*-tolyl	Ph	*p*-tolyl
yield		83%	70%	77%	81%[c]
NMR					
^{31}P		−6.8	−7.0	23.3	23.5
^{29}Si		−8.6	−8.8	−8.2	−8.3
	$^2J_{PSi}$[e]	4.4	4.3	5.1	5.0
^{13}C	M-C═	259.4	257.9	265.9	265.1
	═C[P]	122.8	121.1	120.7	120.5
	$^1J_{PC}$[e]	15.5	15.7	15.2	14.8
^1H	Cp*	1.78	1.50	1.85	1.84
	$SiMe_3$	0.36	0.31	0.37	0.35
	CH_3	2.24	1.96	2.38	2.37

[a]NMR spectra in C_6D_5Br. [b]In CD_2Cl_2. [c]In oil. [d]From ref 27. [e]In Hz.

The X-ray crystal structure analysis has confirmed that complex **4c** was formed by a 1,1-carbometalation reaction. It shows well separated cations and anions in the solid. The Cp^*_2Hf bent metallocene moiety has the tetra-substituted alkenyl unit σ-bonded to it (see Figure 1 and Table 2). This unit contains the CH_3 group at the former acetylenic carbon atom C1. This methyl group had migrated from hafnium to

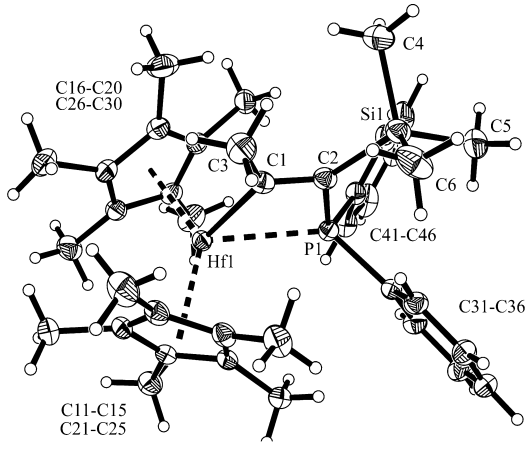


Figure 1. Molecular structure of the cation of the 1,1-carbometalation product **4c** (anion: $[B(C_6F_5)_4]^-$) (thermal ellipsoids are shown with 30% probability).

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Table 2. Selected Structural Data of the Complexes 4a–c[a]

compound	4a[b]	4b	4c
M	Zr	Zr	Hf
Ar	Ph	*p*-tolyl	Ph
M–C1	2.282(4)	2.290(4)	2.243(3)
C1–C2	1.363(5)	1.367(6)	1.376(5)
C2–P1	1.824(4)	1.803(6)	1.814(4)
M–P1	2.768(1)	2.768(1)	2.749(1)
C1–C3	1.505(5)	1.510(6)	1.499(5)
C2–Si	1.920(4)	1.904(8)	1.915(4)
M–C1–C2	110.7(3)	109.6(3)	110.3(2)
M–C1–C3	127.1(3)	127.8(3)	128.3(3)
M–C1–C2–P1	−6.7(3)	8.8(4)	−6.8(3)

[a]Bond lengths in Å, angles in deg. [b]From ref 27.

carbon in the 1,1-carbometalation reaction. This required a 1,2-silyl migration along the acetylenic backbone, and consequently, the $SiMe_3$ substituent is thus found attached to former acetylenic carbon atom C2, which also bears the bulky PPh_2 substituent originating from the reagent **2b**. The phosphane shows an internal coordination to the hafnium center inside the cation of complex **4c**.

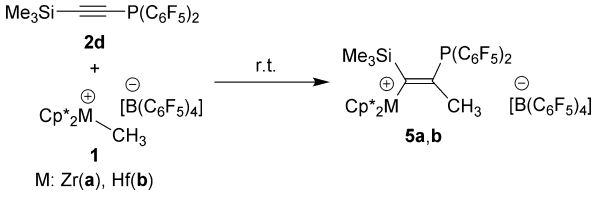
The alkenyl zirconocene cation complexes **4a,b** that were formed by the 1,1-carbozirconation reactions of the trimethylsilyl(diarylphosphino)acetylene starting materials **2b,c** show similar structural features (see Table 2). The structure of complex **4b** is depicted in the Supporting Information.

From our previous experiments (see Scheme 2) it was clear that the trimethylsilyl substituent played a key role for observing this rare type of a 1,1-carbozirconation reaction to prevail over the usual 1,2-[M]-CH_3 addition to the acetylenic substrate. From the related 1,1-carboboration, this favorable influence of the SiR_3 moieties as good migrating groups was well established.[28,33] The specific role of the diaryl-phosphino group remained to be specified for the 1,1-carbozirconation reaction. Was it a mere bystander or did it have a vital functional role in the reaction process?[34] For that reason, we went to some extreme measures and reacted the salt **1a** (M = Zr) with trimethylsilyl[bis(pentafluorophenyl)phosphino]-acetylene (**2d**), a system that contained a bulky diaryl-phosphane of very low Lewis basicity.

Treatment of the in situ generated salt **1a** (M = Zr) with the bis(pentafluorophenyl)phosphino substituted alkyne **2d** was carried out in the usual way (bromobenzene, RT, 2 d). Workup furnished the product **5a**, which we isolated from the reaction mixture as a red crystalline solid in 52% yield (Scheme 4).

The X-ray crystal structure analysis has revealed that compound **5a** was formed by a conventional alkyne insertion into the Zr–CH_3 linkage of the starting material **2d**. We found the regioisomer having the bulky $P(C_6F_5)_2$ group in the trans-vicinal position to the Cp^*_2Zr unit. The compound features an

Scheme 4



E-configurated *σ*-alkenyl ligand that was formed by regioselective 1,2-cis addition of the Zr-CH_3 moiety to the carbon–carbon triple bond. The overall core framework of complex **5a** is planar with dihedral angles Zr1–C1–C2–P1 −171.7(2)°, Zr1–C1–C2–C3 1.3(6)°, and P1–C2–C1–Si1 3.4(4)°. We note that one CH_3 substituent at silicon lies in the bent metallocene *σ*-ligand plane [Zr1–C1–Si1–C4 −6.6(2)°] and may have a weak contact with the strongly electrophilic metal center (Zr1···C4 = 2.639(4) Å), possibly indicating a stabilizing agostic metal–H–C interaction[35] between them (Figure 2).

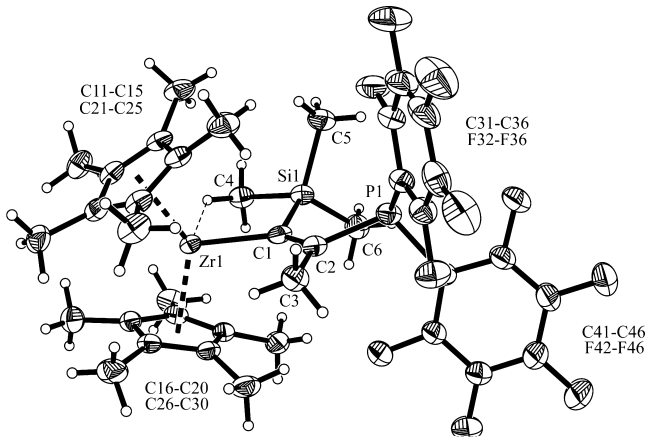


Figure 2. Molecular structure of the cation of complex **5a** (anion: $[B(C_6F_5)_4]^-$) (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): Zr1–C1 2.248(3), Zr1–C4(4) 2.639, Zr1–Si1 3.040(4), P1–Si1 3.225(5), C1–C2 1.342(5), C2–C3 1.511(5), C2–P1 1.854(4), C1–Si1 1.895(4), C4–Si1 1.947(4), C5–Si1 1.868(4), C6–Si1 1.858(4), Zr1–C1–C2 141.7(3), C1–C2–P1 116.1(3).

In solution, (CD_2Cl_2) complex **5a** features two sets of ^{19}F NMR signals in a 1:2 ratio of the $P(C_6F_5)_2$ group and the $[B(C_6F_5)_4]^-$ anion (for details see the Supporting Information). It shows a ^{31}P NMR resonance at δ −44.8 and a ^1H NMR signal of the transferred methyl group at δ 1.90. The peculiarity of the ^{29}Si NMR chemical shift at δ −51.6 ($^3J_{PSi}$ = 32.9 Hz) and the observation of $^1H/^{13}C$ NMR signals of a pair of methyl groups at silicon in a 1:2 ratio [^1H: δ −0.62 (3H), 0.63 (6H). ^{13}C: δ 8.6 ($^1J_{CH}$(average) ∼ 116 Hz), 2.3 ($^1J_{CH}$(average) ∼ 123 Hz)] are in agreement with an agostic *β*-Si-Me···Zr interaction.[35a–c] We also prepared the corresponding hafnium complex **5b**. It shows similar structural features and spectroscopic properties (for details see the Supporting Information).

We conclude that the Lewis basicity of the phosphanyl substituent has a profound influence on the observed reaction pathway. The low Lewis basic $P(C_6F_5)_2$ substituent has no special effect; in contrast, the markedly more strongly coordinating PPh_2 and $P(p\text{-tolyl})_2$ substituents direct the reaction away from the "normal" insertion pathway and (with the help of the good $SiMe_3$ migrating group) open the way toward realizing the unusual 1,1-carbozirconation (or 1,1-carbohafnation) pathway instead.

Reactions of the New Vicinal Zr^+/P Frustrated Lewis Pair. The Lewis acid and the Lewis base components in typical frustrated Lewis pairs can either react separately or, what is more exciting, they can react cooperatively with added substrates. We have observed both such reaction pathways for

dx.doi.org/10.1021/ja5068146 | J. Am. Chem. Soc. 2014, 136, 12431–12443

the typical example of the Zr^+/P FLP **4a** (R = Ph) and its Hf^+/P FLP congener **4c**.

The vicinal Zr^+/P system **4a** reacts rapidly with *n*-butylisocyanide. In a few instances, we had observed cooperative isonitrile coordination behavior with related B/P FLPs,[14] but here the isonitrile just adds to the strong Zr^+ Lewis acid. The reaction went to completion within 1 h at RT in dichloromethane and we isolated the adduct **6** (Figure 3) as

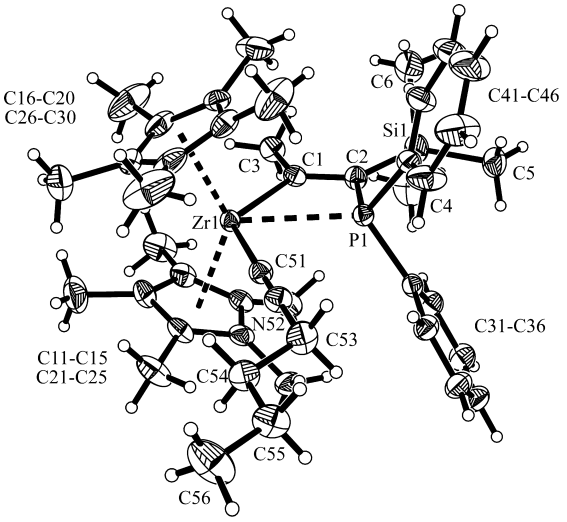


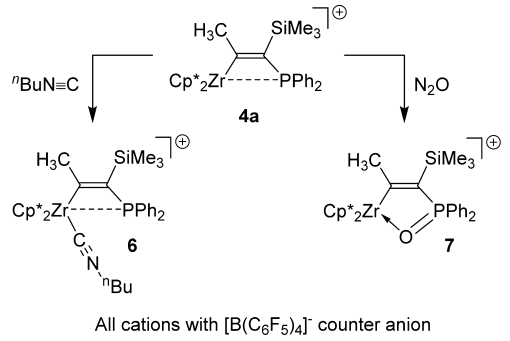
Figure 3. Molecular structure of the isonitrile adduct **6** (anion: $[B(C_6F_5)_4]^-$) (thermal ellipsoids are shown with 30% probability; one independent cation is depicted). Selected bond lengths (Å) and angles (deg): Zr1A−C1A 2.377(3), Zr1A−C51A 2.335(3), C1A−C2A 1.356(4), C1A−C3A 1.510(4), C2A−P1A 1.797(3), C2A−Si1A 1.909(3), C51A−N52A 1.147(4), Zr1A−C1A−C2A 116.2(2), Zr1A−C51A−N52A 178.7(3), C1A−C2A−P1A 102.7(2), Zr1A−C1A−C2A−P1A −1.5(3).

pale yellow crystals in 87% yield. The X-ray crystal structure analysis shows a structure that features the linear isonitrile ligand bonded to the bent metallocene cation at the lateral coordination site in the σ-ligand plane which bisects the Cp*−Zr−Cp* angle. The central position is occupied by the internal PPh_2 donor ligand [there are two independent molecules in the crystal: Zr1A−P1A 2.827(1) Å, Zr1B−P1B 2.833(1) Å].[36]

The Zr^+/P system is oxidized by treatment with N_2O. This led to the formation of the respective phosphinoxide, the oxygen atom of which was found bonded to zirconium.[37] The $[Zr(O)P]^+$ compound **7** was isolated in 84% yield. In solution it shows a ^{31}P NMR signal at δ 49.1. The tetra-substituted alkenyl bridge of complex **7** shows a typical C1 ^{13}C NMR signal at δ 267.1 ($^2J_{PC}$ = 13.2 Hz) and the C2 resonance at δ 140.6 ($^1J_{PC}$ = 67.7 Hz). There is a ^1H NMR $SiMe_3$ doublet at δ 0.34 ($^4J_{PH}$ = 0.4 Hz) [with a corresponding ^{29}Si NMR signal at δ −12.9 ($^2J_{PSi}$ = 33.2 Hz)] and the [=C]−CH_3 signal at δ 2.14 ($^4J_{PH}$ = 3.3 Hz).

Complex **7** (Scheme 5) was characterized by X-ray diffraction. It shows a five-membered heterocyclic core with relatively short bonds between oxygen and both phosphorus (P1−O1 1.535(2) Å) and zirconium (Zr1−O1 2.107 (4) Å). The endocyclic σ-alkenyl ligand has the methyl substituent attached at carbon atom C1 (C1−C3 1.525(4) Å, Zr1−C1 2.313(3) Å, C1−C2 1.375(4) Å, angle Zr1−C1−C2 120.8(2)°) and the pair of $SiMe_3$ and $P(O)Ph_2$ substituents bonded at carbon atom C2 (C2−Si1 1.916(3) Å, C2−P1 1.781(2) Å,

Scheme 5



angles Si1−C2−P1 124.6(2)°, P1−O1−Zr1 122.4(1)°) (see Figure 4).

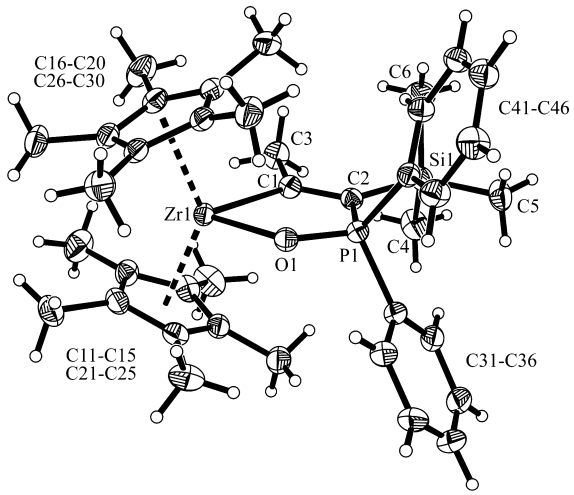


Figure 4. A view of the cation of the molecular structure of compound **7** (anion: $[B(C_6F_5)_4]^-$) (thermal ellipsoids are shown with 30% probability).

Many frustrated Lewis pairs add to carbonyl compounds and related reagents.[12] That was also observed for the metal containing Zr^+/P (**4a**) and Hf^+/P (**4c**) FLPs. The reaction of **4a** with *trans*-cinnamic aldehyde is a typical example. The Zr^+/P Lewis pair added rapidly to the carbonyl group (2h, RT) to give the six-membered heterocyclic product **8a**, which we isolated as a pale yellow crystalline solid in 84% yield. The X-ray crystal structure analysis (see Figure 5 and Table 3) shows a heterocyclic core that features a distorted cyclohexene-like half-chair conformation. This brings the *trans*-CH=CH−Ph substituent, that is attached at carbon atom C7, into a pseudoequatorial orientation. The endocyclic C1=C2 double bond of complex **8a** has the methyl group bonded at C1 and the −$SiMe_3$ substituent at C2.

In solution, complex **8a** (Scheme 6) features the ^1H NMR resonances of the *trans*-CH=CH−Ph substituent at δ 6.40 and 6.03 with a $^3J_{HH}$ coupling constant of 15.9 Hz. The former carbonyl carbon atom (C7) shows a $^1J_{PC}$ coupling constant of 55.3 Hz ($\delta^{13}C$ 82.9) and the bridging endocyclic C1=C2 unit features a C2 carbon resonance at 124.3 ppm with a $^1J_{PC}$ coupling constant of 45.8 Hz [$\delta^{13}C(1)$ 267.3]. Due to the newly formed carbon chirality center (C7), the pair of Cp* ligands at zirconium has become diastereotopic and, hence, give

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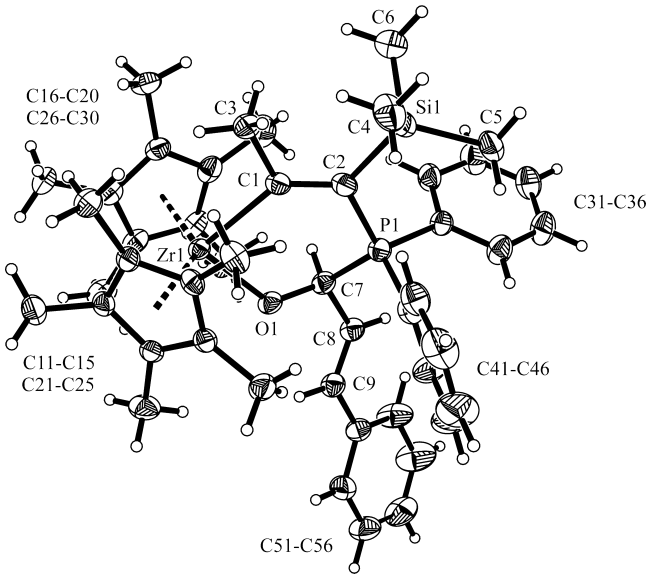


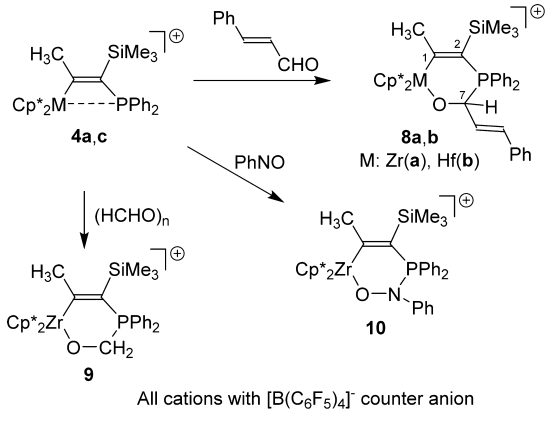
Figure 5. Molecular structure of complex **8a** (anion: $[B(C_6F_5)_4]^-$) (thermal ellipsoids are shown with 30% probability).

Table 3. Selected Structural Data of the Zr^+/P and Hf^+/P Addition Products 8 and 10[a]

compd	8a	8b	10
M	Zr	Hf	Zr
M1−O1	2.020(2)	1.998(3)	2.041(2)
M1−C1	2.327(4)	2.300(4)	2.321(3)
C1−C2	1.377(5)	1.367(6)	1.364(5)
C2−P1	1.791(4)	1.793(4)	1.789(3)
C1−C3	1.521(5)	1.517(5)	1.521(4)
C2−Si1	1.934(8)	1.941(8)	1.929(3)
P1−C7	1.863(4)	1.866(4)	1.704(3)[b]
C7−O1	1.380(4)	1.392(5)	1.432(3)[c]
M1−C1−C2	134.7(3)	133.8(3)	131.1(2)
C1−C2−P1	117.3(3)	118.2(3)	119.2(2)
C2−P1−C7	110.5(2)	110.0(2)	111.9(1)[d]
C7−O1−M1	127.2(2)	127.0(2)	124.3(2)[e]
O1−M1−C1	85.9(1)	86.8(1)	84.0(1)
M1−C1−C2−P1	−0.4(5)	−2.2(6)	−6.0(4)
P1−C7−O1−M1	74.0(3)	74.4(3)	82.9(2)[f]

[a]Bond lengths in Å, angles in deg. [b]P1−N1. [c]N1−O1. [d]C2−P1−N1. [e]N1−O1−Zr1. [f]P1−N1−O1−Zr1.

Scheme 6



rise to a pair of ^{13}C NMR methyl resonance at δ 12.5 and 11.5. For further details see Table 4 and the Supporting Information.

The hafnium complex **8b** was formed analogously. It was isolated in 78% yield. It shows similar NMR spectra (see Table 4) and similar structural data. The structure is depicted in the Supporting Information (see also Table 3).

We also prepared the parent compound of this series, namely, the formaldehyde addition product **9**. For that purpose, we reacted the cationic Zr^+/P FLP with a slight excess of paraformaldehyde in dichloromethane at room temperature (2 h). Workup involving washing with pentane eventually gave the six-membered heterocyclic product in 88% yield as a pale yellow oil. The compound was characterized by C, H elemental analysis and by NMR spectroscopy (see Table 4). It features the NMR signals of the newly introduced endocyclic [O]−CH_2 group at δ 5.11 (^1H, $^2J_{PH}$ = 0.8 Hz) and δ 68.8 (^{13}C, $^1J_{PC}$ = 60.1 Hz), respectively, and it features a single set of Cp* NMR resonances [^{13}C: δ 122.8, 11.9, for further details see Table 4 and the Supporting Information].

We had previously shown that the vicinal B/P FLP $(C_6F_5)_2BCH_2CH_2PMes_2$ undergoes 1,2-addition to the N═O functionality of nitrosobenzene.[12] The Zr^+/P system **4a** reacts similarly with this heterocarbonyl analogous functionality. The reaction between **4a** and Ph-NO went to completion within 2 h and we isolated the addition product **10** in 67% yield. Complex **10** showed the typical NMR features of the backbone (see Table 4). At room temperature, we have observed a single ^1H NMR Cp* resonance of the system that apparently undergoes a rapid conformational inversion of its half-chair shaped framework.

Complex **10** was also characterized by X-ray diffraction (see Table 3 and Figure 6). It shows a nonplanar framework built around the tetracoordinated zirconium and phosphorus atoms, both with pseudotetrahedral coordination geometries, and the nonplanar tricoordinate nitrogen atom ($\Sigma N1^{POC}$ 334.9°). The bond angle at oxygen is 124.3(2)°, at nitrogen (P1−N1−O1) 106.6(2)°, and the endocyclic bond angles at zirconium O1−Zr1−C1 and phosphorus N1−P1−C2 amount to 84.0(1)° and 110.9(1)°, respectively.

A variety of FLPs react readily with carbon dioxide.[7,8] So does the Zr^+/P Lewis pair as we had described in our preliminary communication.[27] We could now show that the Hf^+/P FLP **4c** also reacts rapidly with CO_2 (1 h, RT) to give the respective carbonyl addition product **11**. It was isolated in 81% yield. It was characterized by C,H elemental analysis and by spectroscopy (see Table 4). The Hf^+/P/CO_2 addition product shows a characteristic IR (C═O) band at 1690 cm^{-1}.

Both the Zr^+/P **4a** and the Hf^+/P **4c** system add to a sulfur−oxygen bond of sulfur dioxide. Both the addition products **12a** and **12b** were isolated as crystalline solids in ca. 80% yield and both were characterized by X-ray diffraction (see Scheme 7, Tables 3 and 4); as a typical example, the structure of the Hf complex **12b** is shown in Figure 7. The compound contains a near to planar O1−Hf1−C1−C2−P1 backbone. The coordination geometries at both hafnium and phosphorus are pseudotetrahedral. The sulfur atom lies outside the central plane and it features a trigonal-pyramidal coordination geometry ($\Sigma S1^{OOP}$ 313.8°). The zirconium complex **12a** shows similar structural features (for a view of the molecular structure see the Supporting Information, see also Table 3).

The sulfur chirality center makes the pairs of Cp* ligands at the group 4 metal centers in the complexes **12a** (Zr) and **12b** (Hf) diastereotopic, and consequently, we have monitored in

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Table 4. Selected NMR data of the Zr^+/P and Hf^+/P FLP addition products 8-12[a]

compd	8a	8b	9	10	11	12a	12b
M	Zr	Hf	Zr	Zr	Hf	Zr	Hf
reagent	PhCH=CHCHO		H_2CO	PhNO	CO_2	SO_2	SO_2
				^1H			
Cp*	2.01 1.70	2.06 1.75	1.81	1.80	1.88	1.93 1.81	2.00 1.88
$SiMe_3$	0.06	0.07	0.10	0.06	0.17	0.12	0.14
CH_3	2.13	2.14	2.08	2.19	1.87	1.40	1.68
				^{13}C			
C1	267.3	270.7	269.7	265.8	273.9	264.4	270.6
C2	124.3	125.3	122.2	127.0	125.9	131.6	130.8
$^1J_{PC}$ [b]	45.8	44.8	50.2	71.8	37.9	20.8	18.0
C7	82.9	82.7	68.8	-	164.3	-	-
$^1J_{PC}$ [b]	55.3	54.9	60.1	-	103.2	-	-
^{31}P	15.7	18.3	18.3	35.3	4.9	17.9	25.1
^{29}Si	−7.5	−6.9	−8.1	−8.6	−6.9	−5.3	−4.7

[a] In CD_2Cl_2. [b] In Hz.

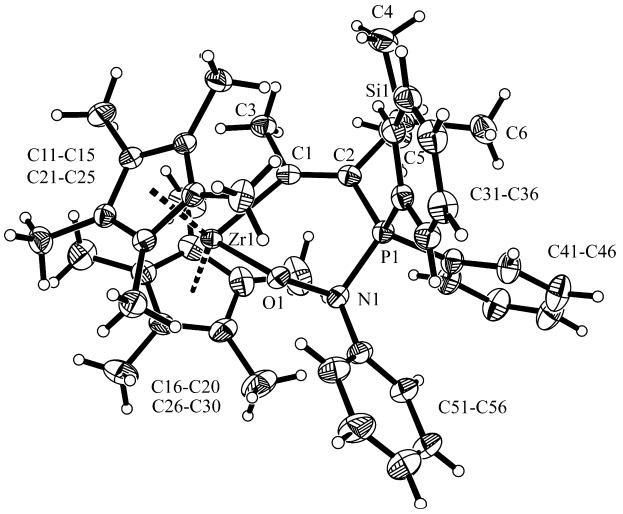


Figure 6. A projection of the molecular structure of compound **10** (only the cation is depicted; anion: $[B(C_6F_5)_4]^-$) (thermal ellipsoids are shown with 30% probability).

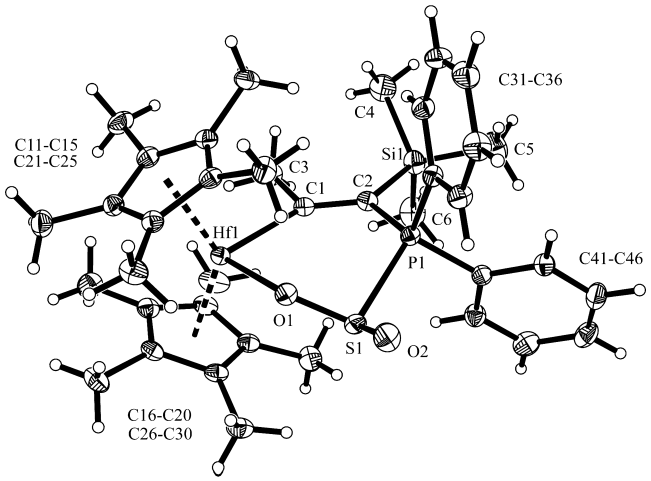
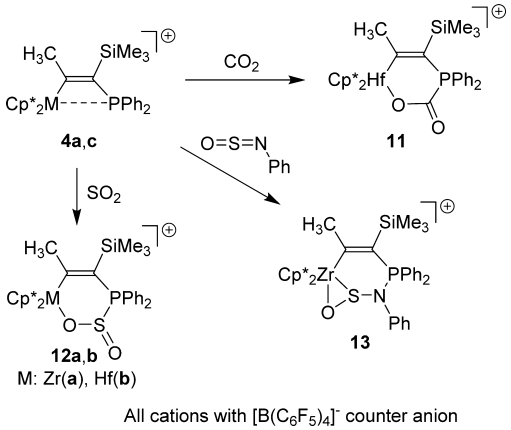


Figure 7. Molecular structure of the Hf^+/P/SO_2 addition product **12b** (only the cation is depicted; anion: $[B(C_6F_5)_4]^-$) (thermal ellipsoids are shown with 30% probability).

Scheme 7



such case equal intensity pairs of the respective $^1H/^{13}C$ NMR Cp* signals.

Many B/P FLPs have been shown to react rapidly with isocyanates. Both addition modes have been known, namely, 1,2-B/P addition to the carbonyl group of the heterocumulene[12] or to the C=NR moiety.[38] Knowing about the clean $Zr^+(Hf^+)$/P 1,2-addition to SO_2 we were tempted to investigate how these metal containing vicinal FLPs **4** would react with the heterocumulene moiety of N-sulfinyl benzene amine (Ph-N=S=O). One might have expected to see either addition to the S=O or the PhN=S moiety, similar as it was found in the related FLP isocyanate addition reactions. However, we found that a different bonding mode was favored which involved all three atoms of the heterocumulene chain.

The Zr^+/P FLP **4a** reacted rapidly with the PhN=S=O reagent to give the addition product **13** (see Scheme 7). The compound was isolated in 76% yield and characterized by X-ray diffraction. The X-ray crystal structure analysis revealed that the Zr^+/P FLP had principally added to the PhN=S moiety of the reagent. We find the phosphorus atom bonded to nitrogen (P1−N1 1.694(2) Å, angle P1−N1−S1 110.5(1)°) and the Zr atom bonded to sulfur. In addition, the Zr atom has also coordinated to the oxygen atom;[39,40] the system may be described as containing a η^2 (O=S)Zr unit with typical bonding parameters of Zr1−S1 2.734(2) Å, Zr1−O1 2.110(2) Å, S1−O1 1.587(2) Å, S1−N1 1.718(2) Å. The sulfur atom in

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complex **13** is trigonal-pyramidal ($\Sigma S1^{ZrON}$ 258.7°). The sulfur atom in complex **13** is a chirality center (see Figure 8).

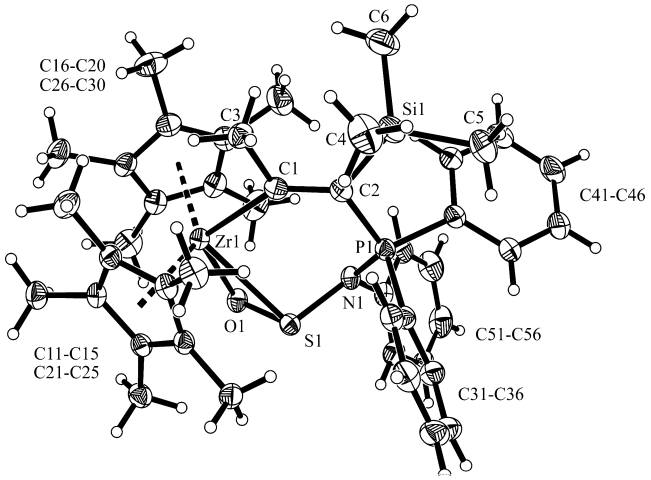
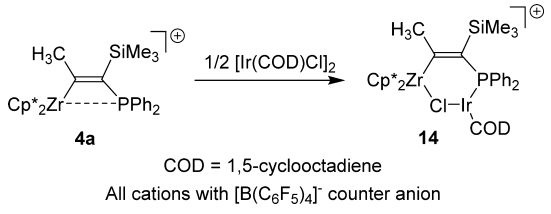


Figure 8. A view of the molecular structure of complex **13** (only the cation is depicted; anion: $[B(C_6F_5)_4]^-$) (thermal ellipsoids are shown with 30% probability).

Consequently, compound **13** shows the $^1H/^{13}C$ NMR resonance of a pair of diastereotopic Cp* ligands at zirconium; the Ph-substituents at P are also diastereotopic and show two sets of signals in a 1:1 intensity ratio as well. The product shows a ^{31}P NMR signal at δ 28.3 (for further details see the Supporting Information).

A few intramolecular B/P Lewis pairs had previously been shown to add to a number of transition metal complexes as bifunctional donor/acceptor ligands. Examples have been known where both the main group element FLP functions have formed direct bonds to the metal.[41] More examples are known where the Lewis base has added to the transition metal and the Lewis acid to a ligand atom (e.g., a halide ligand).[42] Such a coordination behavior was observed upon treatment of the Zr^+/P FLP **4a** with $[Ir(COD)Cl]_2$ (Scheme 8).

Scheme 8



The Zr^+/P system **4a** reacted with [Ir(COD)Cl] dimer in dichloromethane solution at RT to give the addition product **14** in 72% isolated yield. The compound shows the typical NMR features of the Zr^+/P FLP backbone [^{13}C: δ 239.2 ([Zr]C(1)═), δ 138.3 ($^1J_{PC}$ = 31.3 Hz, ═C[P]). ^1H: δ 1.84 (Cp*), 0.39 (CH_3), −0.13 ($SiMe_3$)]. In addition, we have monitored the typical NMR data of the 1,5-cyclooctadiene ligand coordinated to Ir [^1H: δ 2.30, 2.20, 1.80, 1.46 (each 2H, CH_2), δ 4.78, 2.84 (each 2H, HC═). ^{13}C: δ 89.6, 60.0 (HC═), δ 33.1, 29.4 (CH_2)].

Complex **14** was characterized by X-ray diffraction. It shows a structure that has the zirconium atom bonded to the chloride ligand of a monomeric Ir(COD)Cl unit and the phosphorus atom to iridium (Zr1−Cl1 2.556(1) Å, P1−Ir1 2.347(1) Å, Ir1−Cl1 2.366(1) Å, angle Zr1−Cl1−Ir1 124.4(1)°). The iridium atom has also both C═C double bonds of the 1,5-cyclooctadiene ligand bonded to it in a pseudo square-planar coordination environment (see Figure 9). The overall six-membered heterocyclic framework of the FLP addition product shows a slight deviation from planarity with dihedral angles P1−Ir1−Cl1−Zr1 −44.8(6)°, P1−C2−C1−Zr1 0.5(8)°, and Cl1−Zr1−C1−C2 −7.2(6)°. The C1═C2 bond of the backbone is short (C1−C2 1.349(6) Å) and the Zr1−C1 2.276(4) Å and C2−P1 1.842(4) Å bonds are in the typical range.

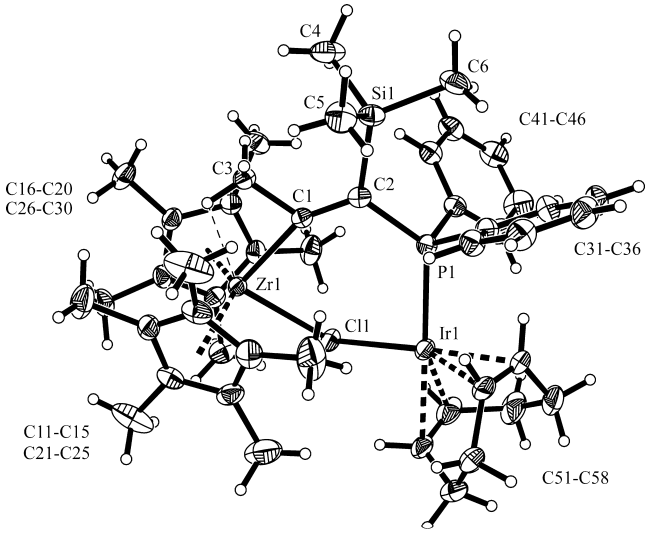
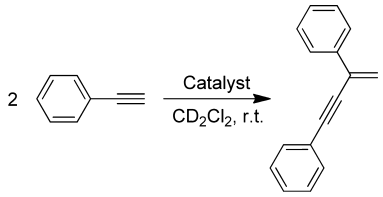


Figure 9. Molecular structure of the heterobimetallic complex **14** (only the cation is depicted; anion: $[B(C_6F_5)_4]^-$) (thermal ellipsoids are shown with 30% probability).

Catalytic Alkyne Dimerization. It is well-known that a variety of B/P and Zr^+/P FLPs react with terminal alkynes by deprotonation to form corresponding phosphonium salts.[22b,43] We also investigated the reactivity of our vicinal M^+/P systems with terminal alkynes, e.g., phenyl acetylene (PhC≡CH). We first monitored the reactions between hafnium complexes **4c** and **4d** with 1 equiv of phenyl acetylene in CD_2Cl_2 at room temperature. To our surprise, both of these compounds selectively dimerized the PhC≡CH to the head-to-tail dimer H_2C═C(Ph)C≡CPh. The usual FLP deprotonation product was not observed, indicating that our vicinal M^+/P Lewis pairs might be suitable for the regioselective dimerization of phenyl acetylene. We thus employed complexes **4** in this catalytic reaction and the results are showed in Table 5 (entries 1−4). Under our typical reaction conditions (0.8 mL of CD_2Cl_2 solution, 5 μmol of catalyst, RT), all these three vicinal M^+/P complexes behaved as highly efficient catalysts for the alkyne dimerization reaction. For zirconium complex **4a**, even with a very small amount of catalyst loading (0.5 mol %), the reaction still gave 86% conversion in 1 h (Table 5, entry 2). Its catalytic activity is comparable to that of the most active previously reported early transition metal catalysts.[44] In contrast, zirconium complex **5a** featuring the low Lewis basicity $P(C_6F_5)_2$ substituent formed by 1,2-carbozirconation showed markedly lower activities under similar conditions (32% conversion in 1.5 h, see Table 5, entry 5). To compare the reactivity of such vicinal M^+/P systems with their geminal

dx.doi.org/10.1021/ja5068146 | J. Am. Chem. Soc. 2014, 136, 12431−12443

Table 5. Dimerization of Phenyl Acetylene Catalyzed by M^+/P Frustrated Lewis Pairs[a]



entry	catalyst	[cat.]/[sub.] (mol %)	time (h)	conversion (%)[b]
1[c]	**4a**	1	0.5	98
2	**4a**	0.5	1	86
3	**4b**	1	1	80
4	**4c**	1	0.5	78
5	**5a**	1	1.5	32[d]
6	**3b**	5	3	2
7	**1b**	5	2	0[e]
8	**1b**/PPh_3[f]	5	2	5

[a]Room temperature, CD_2Cl_2 (0.8 mL) as the solvent. Catalysts **4** and **5** (5 μmol), catalysts **3** and **1** (10 μmol). [b]Conversion was determined by ^1H NMR analysis. [c]Isolated and determined by MS analysis. [d]With some polymer material. [e]Part of alkyne converted to a unidentified product and polymer material. [f]**1b** : PPh_3 = 1:1.

analogues, we prepared the geminal Hf^+/P complex **3b** by means of 1,2-carbohafnation in 72% isolated yield (for the details of the preparation and the X-ray structure of **3b** see the Supporting Information). However, it only produced trace amounts of the expected phenyl acetylene dimerization product even with as much as 5 mol % of catalyst loading in 3 h (Table 5, entry 6).

For early transition metal catalyzed alkyne dimerization reactions, it is generally believed that generation of $14e^-$ metal acetylide M−C≡CR compound by means of M−C σ-bond metathesis represents the initial step.[44] We assume that in our case the active $[Cp^*_2M{-}C{\equiv}C{-}Ph]^+$ species might be formed by a typical alkyne FLP deprotonation reaction generating $Cp^*_2M(-C{\equiv}CPh)[-C(Me){=}C(SiMe_3)PAr_2H^+]$. Subsequent protonolytic cleavage of the M−C(sp^2) σ-bond could then directly give the active (acetylide)metallocene cation species.[44] We also carried out a reference experiment by using $[Cp^*_2HfMe]^+[B(C_6F_5)_4]^-$ **1b**, in situ generated from $Cp^*_2HfMe_2$ with $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2, for the PhC≡CH dimerization (Table 5, entry 7). It only produced an unidentified species with 5 mol % catalyst loading in 2 h. Furthermore, we found that the system formed by combining **1b** with 1 equiv of PPh_3 gave the same head-to-tail dimer as that from complexes **4**, although with a very low activity (Table 5, entry 8). In summary, our transition metal containing FLPs derived from 1,1-carbometalation show high activities for the regioselective dimerization of phenyl acetylene, which cannot be achieved by using main group FLPs so far.

CONCLUSIONS

1,1-Carboboration has become a very useful method for the synthesis of alkenyl boranes, especially with regard to systems containing bulky substituents.[28,30] The 1,1-carbozirconation reaction had only recently been established.[27] It seems that for the observed examples this reaction has benefited from a combination of effects that let it prevail over the usual alkyne insertion reaction into the metal to carbon σ-bond, namely, steric bulk of the metallocene system, the good migratory ability of the trimethylsilyl group and a thermodynamic stabilization factor by the phosphane coordination in the product. Together these three factors let the 1,1-carbometalation reaction become favored over its competing alternatives, which include 1,2-M−CH_3 addition to the carbon−carbon triple bond or methyl cation abstraction by the adjacent phosphane.[45]

The bifunctional $Zr^+(Hf^+)$/P systems resulting from these rare cases of 1,1-carbometalation show a variety of typical features that one would expect from vicinal M^+/P frustrated Lewis pairs. This includes binding of small molecules such as carbon dioxide or sulfur dioxide or binding to carbonyl compounds or to metal−halide systems such as we have observed it for our Zr^+/P and Hf^+/P examples.

The main group element FLPs often react with terminal alkynes by deprotonation and alkynyl borate formation.[43] In the case of our new M^+/P FLPs, this reactivity is shifted toward the catalytic alkyne dimerization process, which we have observed instead. This may point to some new application potential that metal containing frustrated Lewis acid/Lewis base pairs may have over their purely main group element containing FLP congeners.

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 a Varian 600 MHz UNITY plus, a Varian 500 MHz UNITY plus, and a Bruker AC200 NMR spectrometer. Chemical shifts are given in ppm relative to solvents (^1H 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 was recorded on Foss-Heraeus CHNO-Rapid. IR spectra were recorded on a Varian 3100 FT-IR (Excalibur Series). X-ray crystal structure analyses: data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT;[46] data reduction Denzo-SMN;[47] absorption correction, Denzo;[48] structure solution SHELXS-97;[49] structure refinement SHELXL-97[50] and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Preparation of Compound 4b. Trimethylsilyl(di-*p*-tolylphosphanyl)acetylene (31 mg, 0.1 mmol) was added to a C_6H_5Br solution of $[Cp^*_2ZrMe][B(C_6F_5)_4]$ in situ generated by the reaction of $Cp^*_2ZrMe_2$ (39 mg, 0.1 mmol) with $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.1 mmol). After 2 days at room temperature, pentane (4 mL) was layered to the reaction mixture to give a orange oil which was separated and washed with pentane (3 × 2 mL) to eventually gave complex **4b** as a yellow-orange solid (95 mg, 70%). Crystals suitable for the X-ray single crystal structure analysis were obtained from a two-layer procedure using a CH_2Cl_2 solution of compound **4b** and cyclopentane in the fridge (ca. −35 °C). Anal. Calcd for $C_{64}H_{56}BF_{20}PSiZr{\cdot}C_6H_5Br$: C, 55.20; H, 4.04. Found: C, 54.61; H, 4.55. ^1H NMR (600 MHz, C_6D_5Br, 299 K): δ = 7.21 (m, 4H, *o*-tol), 7.07 (m, 4H, *m*-tol), 2.16 (s, 6H, CH_3^{tol}), 1.96 (d, $^4J_{PH}$ = 3.8 Hz, 3H, Me), 1.50 (s, 30H, C_5Me_5), 0.31 (s, $^2J_{SiH}$ = 6.3 Hz, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_5Br, 299 K): δ = 257.9 (ZrC), 148.5 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 141.5 (d, $^4J_{PC}$ = 2.5 Hz, *p*-tol), 138.3 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 136.4 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 133.2 (d, $^2J_{PC}$ = 10.3 Hz, *o*-tol), 129.2 (d, $^3J_{PC}$ = 10.1 Hz, *m*-tol), 127.1 (d, $^1J_{PC}$ = 32.6 Hz, *i*-tol), 125.1 (C_5Me_5), 121.8 (d, $^1J_{PC}$ = 15.7 Hz, =CP), 27.5 (d, $^3J_{PC}$ = 34.0 Hz, Me), 21.1 (CH_3^{tol}), 11.6 (C_5Me_5), 3.2 (d, $^3J_{PC}$ = 1.1 Hz, $SiMe_3$), n.o. (*i*-C_6F_5). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_5Br, 299 K): δ = −7.0 ($\nu_{1/2}$ ~ 3 Hz). ^{19}F NMR (564 MHz, C_6D_5Br, 299 K): δ = −133.1 (br, 2F, *o*-C_6F_5), −161.9 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*-C_6F_5), −165.6 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.7]. $^{11}B\{^1H\}$ NMR (192 MHz, C_6D_5Br, 299 K): δ =

dx.doi.org/10.1021/ja5068146 | J. Am. Chem. Soc. 2014, 136, 12431−12443

−15.8 ($\nu_{1/2}$ ∼ 30 Hz). ^{29}Si(dept) NMR (119 MHz, C_6D_5Br, 299 K): δ = −8.8 (d, $^2J_{PSi}$ = 4.3 Hz).

Preparation of Compound 4c. $(C_5Me_5)_2HfMe_2$ (96 mg, 0.2 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (184 mg, 0.2 mmol) were mixed in C_6H_5Br (2 mL). After ca. 2 min, trimethylsilyl(diphenylphosphanyl)-acetylene (57 mg, 0.2 mmol) was added to the reaction mixture. After standing at room temperature for 2 days, crystalline material had formed which was collected and washed with pentane (3 × 2 mL) to finally give complex **4c** as a yellow crystalline solid (220 mg, 77%). Crystals suitable for the X-ray crystal structure analysis were obtained from a C_6H_5Br solution of compound **4c**. Anal. Calcd for $C_{62}H_{52}BF_{20}PSiHf$: C, 52.24; H, 3.68. Found: C, 51.97; H, 3.73. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.53 (m, 2H, *p*-Ph_2P), 7.49 (m, 4H, *m*-Ph_2P), 7.43 (m, 4H, *o*-Ph_2P), 2.38 (d, $^4J_{PH}$ = 3.8 Hz, 3H, Me), 1.85 (s, 30H, C_5Me_5), 0.37 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 265.9 (d, $^2J_{PC}$ = 29.6 Hz, HfC), 148.5 (dm, $^1J_{FC}$ ∼ 240 Hz, C_6F_5), 138.6 (dm, $^1J_{FC}$ ∼ 245 Hz, C_6F_5), 136.7 (dm, $^1J_{FC}$ ∼ 245 Hz, C_6F_5), 134.0 (d, $^2J_{PC}$ = 9.9 Hz, *o*-Ph_2P), 131.6 (d, $^4J_{PC}$ = 2.6 Hz, *p*-Ph_2P), 130.9 (d, $^1J_{PC}$ = 34.3 Hz, *i*-Ph_2P)^t, 129.0 (d, $^3J_{PC}$ = 9.6 Hz, *m*-Ph_2P), 124.6 (C_5Me_5), 120.7 (d, $^1J_{PC}$ = 15.2 Hz, =CP)^t, 29.0 (d, $^3J_{PC}$ = 38.0 Hz, Me), 12.3 (C_5Me_5), 3.4 ($SiMe_3$), n.o. (*i*-C_6F_5), [^{t} tentative assignment]. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = 23.3 ($\nu_{1/2}$ ∼ 2 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ∼ 20 Hz). ^{29}S(dept) NMR (119 MHz, CD_2Cl_2, 299 K): δ = −8.2 (d, $^2J_{PSi}$ = 5.1 Hz).

Preparation of Compound 4d. Following the procedure described for the preparation of compound **4b**, reaction of complex $Cp^*_2HfMe_2$ (48 mg, 0.1 mmol) with $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.1 mmol) and subsequent reaction with trimethylsilyl(di-*p*-tolylphosphanyl)acetylene (31 mg, 0.1 mmol) finally gave compound **4d** as a brown oil (117 mg, 81%). Anal. Calcd for $C_{64}H_{56}BF_{20}PSiHf$: C, 52.89; H, 3.88. Found: C, 52.32; H, 3.73. ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.29 (m, 8H, tol), 2.41 (s, 6H, CH_3^{tol}), 2.37 (d, $^4J_{PC}$ = 3.7 Hz, 3H, Me), 1.84 (s, 30H, C_5Me_5), 0.35 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 265.1 (d, $^2J_{PC}$ = 30.4 Hz, HfC), 148.5 (dm, $^1J_{FC}$ ∼ 245 Hz, C_6F_5), 142.4 (d, $^4J_{PC}$ = 2.4 Hz, *p*-tol), 138.4 (dm, $^1J_{FC}$ ∼ 245 Hz, C_6F_5), 136.7 (dm, $^1J_{FC}$ ∼ 250 Hz, C_6F_5), 133.9 (d, $^2J_{PC}$ = 10.2 Hz, *o*-tol), 129.6 (d, $^3J_{PC}$ = 9.9 Hz, *m*-tol), 127.6 (d, $^1J_{PC}$ = 35.9 Hz, *i*-tol), 124.4 (C_5Me_5), 124.2 (br, *i*-C_6F_5), 120.5 (d, $^1J_{PC}$ = 13.8 Hz, =CP), 28.9 (d, $^3J_{PC}$ = 36.3 Hz, Me), 21.4 (CH_3^{tol}), 12.2 (C_5Me_5), 3.4 ($SiMe_3$). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = 23.5 ($\nu_{1/2}$ ∼ 3 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.2 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ∼ 20 Hz). ^{29}Si(dept) NMR (119 MHz, CD_2Cl_2, 299 K): δ = −8.3 (d, $^2J_{PSi}$ = 5.0 Hz).

Preparation of Compound 5a. $(C_5Me_5)_2ZrMe_2$ (78 mg, 0.2 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (184 mg, 0.2 mmol) were mixed in C_6H_5Br (1.5 mL). After ca. 2 min, the mixture was added to a solution of trimethylsilyl[bis(pentafluorophenyl)phosphanyl]acetylene (92 mg, 0.2 mmol) in 0.5 mL of C_6H_5Br. Then the reaction mixture was standing at room temperature for 2 days. After filtration, cyclopentane (4 mL) was layered to the obtained filtrate. A red solid was formed after several days at −35 °C. Crystallization of the collected red solid from a CH_2Cl_2 covered with cyclopentane (ca. 1:3) solution gave complex **5a** as a red crystalline solid (158 mg, 52%). Crystals suitable for the X-ray crystal structure analysis were grown from a two-layer procedure using a CH_2Cl_2 solution of compound **5a** and cyclopentane in the fridge (ca. −35 °C). Anal. Calcd for $C_{62}H_{42}BF_{30}PSiZr$: C, 49.05; H, 2.79. Found: C, 49.55; H, 2.95. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 1.99 (s, 30H, C_5Me_5), 1.90 (br d, $^3J_{PH}$ = 2.1 Hz, 3H, Me), 0.63 (d, J_{PH} = 3.3 Hz, 6H, SiMe), −0.62 (br, 3H, SiMe). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 250.3 (d, $^2J_{PC}$ = 24.4 Hz, ZrC), 154.0 (d, $^1J_{PC}$ = 31.4 Hz, =CP), 127.0 (C_5Me_5), 32.2 (br, $^1J_{CH}$ ∼ 129 Hz, Me), 12.4 ($^1J_{CH}$ ∼ 128 Hz, C_5Me_5), 8.6 (br, $^1J_{CH}$ ∼ 116 Hz, 1C, SiMe), 2.3 (d, J_{PC} = 12.5 Hz, $^1J_{CH}$ ∼ 123 Hz, 2C, SiMe), [C_6F_5 not listed]. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = −44.8 (quint, $^3J_{PF}$ = 21.4 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −128.9 (m, 2F, *o*), −149.7 (m, 1F, *p*), −160.0 (m, 2F, *m*) (PC_6F_5), [$\Delta\delta^{19}F_{mp}$ = 10.3], −133.1 (br, 4F, *o*), −163.8 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *p*), −167.6 (m, 4F, *m*) (BC_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ∼ 25 Hz). ^{29}Si(dept) NMR (99 MHz, CD_2Cl_2, 299 K): δ = −51.6 (d, $^3J_{PSi}$ = 32.9 Hz).

Preparation of Compound 5b. Following the procedure described for the preparation of compound **5a**, reaction of complex $Cp^*_2HfMe_2$ (48 mg, 0.1 mmol) with $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.1 mmol) and subsequent reaction with trimethylsilyl[bis-(pentafluorophenyl)phosphanyl]acetylene (46 mg, 0.1 mmol) gave compound **5b** as a yellow crystalline solid (107 mg, 66%). Crystals suitable for the X-ray crystal structure analysis were grown from a two-layer procedure using a CH_2Cl_2 solution of compound **5b** and cyclopentane at −35 °C. Anal. Calcd for $C_{62}H_{42}BF_{30}PSiHf$. C_5H_{10}: C, 48.03; H, 3.13. Found: C, 47.55; H, 3.07. ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 2.05 (s, 30H, C_5Me_5), 1.98 (br, 3H, Me), 0.67 (d, J_{PH} = 3.7 Hz, 6H, SiMe), −0.41 (br, 3H, SiMe). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 250.5 (d, $^2J_{PC}$ = 25.7 Hz, HfC), 155.4 (br d, $^1J_{PC}$ = 29.3 Hz, =CP), 125.0 (C_5Me_5), 33.1 (br, $^1J_{CH}$ ∼ 128 Hz, Me), 12.2 ($^1J_{CH}$ ∼ 128 Hz, C_5Me_5), 12.1 (br, $^1J_{CH}$ ∼ 116 Hz, SiMe), 2.4 (br d, J_{PC} = 13.1 Hz, $^1J_{CH}$ ∼ 124 Hz, 2C, SiMe), [C_6F_5 not listed]. ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = −41.2 (quint, $^3J_{PF}$ = 22.2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −128.9 (m, 2F, *o*), −149.6 (m, 1F, *p*), −160.0 (m, 2F, *m*) (PC_6F_5), [$\Delta\delta^{19}F_{mp}$ = 10.4], −133.1 (br m, 4F, *o*), −163.8 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *p*), −167.6 (m, 4F, *m*) (BC_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ∼ 20 Hz). ^{29}Si(dept) NMR (119 MHz, CD_2Cl_2, 299 K): δ = −48.2 (d, $^3J_{PSi}$ = 34.1 Hz).

Preparation of Compound 6. ***Caution!*** *Many isocyanides are toxic compounds that must be handled with due care.* ^{n}BuNC (ca. 5 mg, 0.06 mmol) was added to a suspension of complex **4a** (67 mg, 0.05 mmol) in CH_2Cl_2 (2 mL). Then the reaction mixture was stirred for 1 h at room temperature. Subsequently, the reaction solution was covered with cyclopentane (4 mL) and stored in the fridge (ca. −35 °C) for several days to give complex **6** as pale yellow crystals (62 mg, 87%). Some of the obtained crystals were suitable for the X-ray crystal structure analysis. Anal. Calcd for $C_{67}H_{61}BF_{20}NPSiZr$: C, 56.62; H, 4.33; N, 0.99. Found: C, 57.19; H, 4.49; N, 1.16. IR (KBr): 2196 (N≡C) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.58 (m, 4H, *o*-Ph_2P), 7.47 (m, 4H, *m*-Ph_2P), 7.46 (m, 2H, *p*-Ph_2P), 4.03 (m, 2H, NCH_2), 2.32 (d, $^4J_{PH}$ = 4.4 Hz, 3H, Me), 1.99 (m, 2H, CH_2), 1.67 (s, 30H, C_5Me_5), 1.60 (m, 2H, CH_2^{Me}), 1.07 (m, 3H, $^{CH2}CH_3$), 0.26 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 251.5 (d, $^2J_{PC}$ = 11.1 Hz, ZrC), 156.1 (m, N≡C), 148.6 (dm, $^1J_{FC}$ ∼ 240 Hz, C_6F_5), 145.4 (d, $^1J_{PC}$ = 24.2 Hz, =CP), 138.6 (dm, $^1J_{FC}$ ∼ 250 Hz, C_6F_5), 136.7 (dm, $^1J_{FC}$ ∼ 245 Hz, C_6F_5), 133.7 (d, $^1J_{PC}$ = 11.8 Hz, *i*-Ph_2P), 132.7 (d, $^2J_{PC}$ = 8.5 Hz, *o*-Ph_2P), 130.3 (d, $^4J_{PC}$ = 2.0 Hz, *p*-Ph_2P), 128.9 (d, $^3J_{PC}$ = 7.6 Hz, *m*-Ph_2P), 119.2 (C_5Me_5), 124.2 (br, i-C_6F_5), 45.5 (m, NCH_2), 31.5 (d, $^3J_{PC}$ = 46.9 Hz, Me), 31.1 (d, J = 1.5 Hz, CH_2), 20.5 (CH_2^{Me}), 13.3 ($^{CH2}CH_3$), 12.2 (C_5Me_5), 2.1 (d, $^3J_{PC}$ = 1.3 Hz, $SiMe_3$). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = −60.0 ($\nu_{1/2}$ ∼ 7 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ∼ 25 Hz). ^{29}Si(dept) NMR (99 MHz, CD_2Cl_2, 299 K): δ = −13.6 (d, $^2J_{PSi}$ = 5.5 Hz).

Preparation of Compound 7. A suspension of complex **4a** (67 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) was degassed and N_2O (1.5 bar) was introduced to the evacuated reaction flask for 10 min. The reaction mixture was layered with cyclopentane (4 mL) to gave complex **7** as yellow crystalline solids (57 mg, 84%). Crystals suitable for the X-ray crystal structure analysis were grown from a two-layer procedure using a CH_2Cl_2 solution of compound **7** and cyclopentane at −35 °C. Anal. Calcd for $C_{62}H_{52}BF_{20}OPSiZr$. CH_2Cl_2: C, 52.58; H, 3.78. Found: C, 51.76; H, 3.83. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.90 (m, 4H, *o*-Ph_2P), 7.71 (m, 2H, *p*-Ph_2P), 7.62 (m, 4H, *m*-

dx.doi.org/10.1021/ja5068146 | J. Am. Chem. Soc. 2014, 136, 12431−12443

Ph_2P), 2.14 (d, $^4J_{PH}$ = 3.3 Hz, 3H, Me), 1.78 (s, 30H, C_5Me_5), 0.34 (d, $^4J_{PH}$ = 0.4 Hz, $^2J_{SiH}$ = 6.4 Hz, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ = 267.1 (d, $^2J_{PC}$ = 13.2 Hz, ZrC), 148.5 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 140.6 (d, $^1J_{PC}$ = 67.7 Hz, =CP), 138.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 136.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 134.2 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Ph_2P), 133.2 (d, $^2J_{PC}$ = 10.3 Hz, *o*-Ph_2P), 131.6 (d, $^1J_{PC}$ = 98.3 Hz, *i*-Ph_2P), 129.4 (d, $^3J_{PC}$ = 11.8 Hz, *m*-Ph_2P), 125.7 (C_5Me_5), 124.2 (br, *i*-C_6F_5), 27.9 (d, $^3J_{PC}$ = 41.5 Hz, Me), 12.1 (C_5Me_5), 1.9 (d, $^3J_{PC}$ = 3.4 Hz, $SiMe_3$). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 299 K): δ = 49.1 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 25 Hz). ^{29}Si(dept) NMR (99 MHz, CD_2Cl_2, 299 K): δ = −12.9 (d, $^2J_{PSi}$ = 33.2 Hz).

Preparation of Compound 8a. Cinnamaldehyde (7 mg, 0.05 mmol) was added to a suspension of complex **4a** (67 mg, 0.05 mmol) in CH_2Cl_2 (2 mL), and then the reaction mixture was stirred for 2 h at room temperature. After filtration, the filtrate was covered with cyclopentane (4 mL) and the mixture was stored in the fridge (ca. −35 °C) for several days. Complex **8a** was obtained as a pale yellow crystalline solid (62 mg, 84%). Crystals suitable for the X-ray crystal structure analysis were grown from a two-layer procedure using a CH_2Cl_2 solution of compound **8a** and cyclopentane at −35 °C. Anal. Calcd for $C_{71}H_{60}BF_{20}OPSiZr.$ CH_2Cl_2: C, 55.60; H, 4.02. Found: C, 56.45; H, 4.00. ^1H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.92 (2H, *o*), 7.81 (1H, *p*), 7.68 (2H, *m*) (each m, PhP), 7.78 (1H, *p*), 7.70 (2H, *o*), 7.68 (2H, *m*) (each m, PhP), 7.34 (2H, *m*), 7.31 (1H, *p*), 7.24 (2H, *o*) (each m, Ph), 6.40 (ddd, $^3J_{HH}$ = 15.9 Hz, *J* = 5.2 Hz, *J* = 2.2 Hz, 1H, PhCH=), 6.03 (ddd, $^3J_{HH}$ = 15.9 Hz, *J* = 4.2 Hz, *J* = 2.6 Hz, 1H, =CH), 5.84 (m, 1H, OCH), 2.13 (d, $^4J_{PH}$ = 3.0 Hz, 3H, Me), 2.01, 1.70 (each s, each 15H, C_5Me_5), 0.06 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 267.3 (ZrC)[1], 148.5 (dm, $^1J_{FC}$ ~ 245 Hz), 137.8 (dm, $^1J_{FC}$ ~ 245 Hz), 136.7 (dm, $^1J_{FC}$ ~ 245 Hz), 124.5 (br) (C_6F_5), 136.0 (d, $^2J_{PC}$ = 7.2 Hz, *o*), 135.2 (d, $^4J_{PC}$ = 2.9 Hz, *p*), 130.1 (d, $^3J_{PC}$ = 10.9 Hz, *m*)[t], 124.4 (d, $^1J_{PC}$ = 75.5 Hz, *i*)[t](PhP), 135.8 (d, $^4J_{PC}$ = 3.5 Hz, *i*), 129.3 (*m*), 129.1 (*p*), 127.0 (d, $^5J_{PC}$ = 1.6 Hz, *o*)(Ph), 134.3 (d, $^4J_{PC}$ = 3.0 Hz, *p*), 132.4 (d, $^2J_{PC}$ = 8.7 Hz, *o*), 130.7 (d, $^3J_{PC}$ = 11.2 Hz, *m*)[t], 120.6 (d, $^1J_{PC}$ = 70.1 Hz, *i*)[t](PhP), 134.5 (d, $^3J_{PC}$ = 10.7 Hz, PhCH=), 124.7 (br, =CH), 124.3 (d, $^1J_{PC}$ = 45.8 Hz, =CP), 123.1, 122.9 (C_5Me_5), 82.9 (d, $^1J_{PC}$ = 55.3 Hz, OCH), 27.4 (d, $^3J_{PC}$ = 36.5 Hz, Me), 12.5, 11.5 (C_5Me_5), 2.7 (d, $^3J_{PC}$ = 2.2 Hz, $SiMe_3$), [[1] from the $^1H,^{13}C$ ghmbc experiment. [t] tentatively assigned]. $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = 15.7 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 25 Hz). ^{29}Si(dept) NMR (99 MHz, CD_2Cl_2, 299 K): δ = −7.5 (d, $^2J_{PSi}$ = 24.2 Hz).

Preparation of Compound 8b. Following the procedure described for the preparation of compound **8a**, reaction of complex **4c** (71 mg, 0.05 mmol) with cinnamaldehyde (7 mg, 0.05 mmol) gave compound **8b** as a pale yellow crystalline solid (61 mg, 78%). Crystals suitable for the X-ray crystal structure analysis were grown from a two-layer procedure using a CH_2Cl_2 solution of compound **8b** and cyclopentane at −35 °C. Anal. Calcd for $C_{71}H_{60}BF_{20}OPSiHf$: C, 54.75; H, 3.88. Found: C, 53.83; H, 3.99. ^1H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.92 (2H, *o*), 7.81 (1H, *p*), 7.68 (2H, *m*) (each m, PhP), 7.78 (1H, *p*), 7.70 (2H, *o*), 7.69 (2H, *m*) (each m, PhP), 7.34 (2H, *m*), 7.31 (1H, *p*), 7.24 (2H, *o*)(each m, Ph), 6.40 (ddd, $^3J_{HH}$ = 15.8 Hz, *J* = 5.1 Hz, *J* = 2.2 Hz, 1H, PhCH=), 6.02 (ddd, $^3J_{HH}$ = 15.8 Hz, *J* = 4.2 Hz, *J* = 2.7 Hz, 1H, =CH), 5.79 (m, 1H, OCH), 2.14 (d, $^4J_{PH}$ = 2.8 Hz, 3H, Me), 2.06, 1.75 (each s, each 15H, C_5Me_5), 0.07 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 270.7 (d, $^2J_{PC}$ = 23.6 Hz, ZrC), 148.5 (dm, $^1J_{FC}$ ~ 245 Hz), 138.7 (dm, $^1J_{FC}$ ~ 245 Hz), 136.7 (dm, $^1J_{FC}$ ~ 245 Hz), 124.5 (br) (C_6F_5), 136.0 (d, $^2J_{PC}$ = 7.1 Hz, *o*), 135.2 (d, $^4J_{PC}$ = 2.9 Hz, *p*), 130.7 (d, $^3J_{PC}$ = 11.3 Hz, *m*), 124.4 (d, $^1J_{PC}$ = 75.1 Hz, *i*) (PhP), 135.7 (d, $^4J_{PC}$ = 3.3 Hz, *i*), 129.3 (*m*), 129.1 (*p*), 127.0 (d, $^5J_{PC}$ = 1.8 Hz, *o*)(Ph), 134.3 (d, $^4J_{PC}$ = 2.8 Hz, *p*), 132.4 (d, $^2J_{PC}$ = 8.8 Hz, *o*), 130.0 (d, $^3J_{PC}$ = 10.8 Hz, *m*), 120.6 (d, $^1J_{PC}$ = 70.5 Hz, *i*)(PhP), 134.5 (d, $^3J_{PC}$ = 9.9 Hz, PhCH=), 125.3 (d, $^1J_{PC}$ = 44.8 Hz, =CP), 124.6 (br m, =CH), 121.9, 121.5 (C_5Me_5), 82.7 (d, $^1J_{PC}$ = 54.9 Hz, OCH), 28.4 (d, $^3J_{PC}$ = 36.0 Hz, Me), 12.6, 11.5 (C_5Me_5), 2.9 (d, $^3J_{PSi}$ = 2.2 Hz, $SiMe_3$). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = 18.3 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.8 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.9]. $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 25 Hz). ^{29}Si(dept) NMR (99 MHz, CD_2Cl_2, 299 K): δ = −6.9 (d, $^2J_{PSi}$ = 23.6 Hz).

Preparation of Compound 9. CH_2Cl_2 (2 mL) was added to a mixture of complex **4a** (67 mg, 0.05 mmol) and paraformaldehyde (ca. 2 mg, 0.07 mmol). Then the reaction mixture was stirred at room temperature for 2 h. After filtration, cyclopentane (4 mL) was layered to the filtrate to give a beige oil, which was separated and washed with pentane (3 × 2 mL) to eventually give compound **9** as a pale yellow oil (60 mg, 88%). Anal. Calcd for $C_{63}H_{54}BF_{20}OPSiZr.$ C_5H_{10}: C, 56.78; H, 4.49. Found: C, 56.94; H, 4.36. ^1H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.79 (m, 2H, *p*-Ph_2P), 7.70 (m, 8H, *o*, *m*-Ph_2P), 5.11 (d, $^2J_{PH}$ = 0.8 Hz, 2H, OCH_2), 2.08 (d, $^4J_{PH}$ = 3.2 Hz, 3H, Me), 1.81 (s, 30H, C_5Me_5), 0.10 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 269.7 (d, $^2J_{PC}$ = 25.3 Hz, ZrC), 148.5 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 138.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 136.7 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 134.7 (d, $^4J_{PC}$ = 2.9 Hz, *p*-Ph_2P), 133.7 (d, $^2J_{PC}$ = 8.7 Hz), 130.5 (d, $^3J_{PC}$ = 11.3 Hz)(*o*,*m*-Ph_2P), 124.2 (br, i-C_6F_5), 122.8 (C_5Me_5), 122.3 (d, $^1J_{PC}$ = 76.6 Hz, *i*-Ph_2P), 122.2 (d, $^1J_{PC}$ = 50.2 Hz, =CP), 68.8 (d, $^1J_{PC}$ = 60.1 Hz, OCH_2), 27.8 (d, $^3J_{PC}$ = 37.3 Hz, Me), 11.9 (C_5Me_5), 2.6 (d, $^3J_{PC}$ = 2.5 Hz, $SiMe_3$). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = 18.3 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 25 Hz). ^{29}Si(dept) NMR (119 MHz, CD_2Cl_2, 299 K): δ = −8.1 (d, $^2J_{PSi}$ = 25.9 Hz).

Preparation of Compound 10. Following the procedure described for the preparation of compound **8a**, reaction of complex **4a** (107 mg, 0.08 mmol) with PhNO (9 mg, 0.08 mmol) gave compound **10** as a pale yellow solid (78 mg, 67%). Crystals suitable for the X-ray crystal structure analysis were grown from a two-layer procedure using a CH_2Cl_2 solution of compound **10** and cyclopentane at −35 °C. Anal. Calcd for $C_{68}H_{57}BF_{20}NOPSiZr$: C, 56.51; H, 3.98; N, 0.97. Found: C, 56.20; H, 4.13; N, 0.85. ^1H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.83 (m, 2H, *p*-Ph_2P), 7.64 (br m, 8H, *o*,*m*-Ph_2P), 7.11 (br m, 2H, *m*-Ph^N), 7.08 (m, 1H, *p*-Ph^N), 6.47 (br, 2H, *o*-Ph^N), 2.19 (d, $^4J_{PC}$ = 3.4 Hz, 3H, Me), 1.80 (s, 30H, C_5Me_5), 0.06 (br, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 265.8 (d, $^2J_{PC}$ = 12.8 Hz, ZrC), 148.5 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 146.5 (d, $^2J_{PC}$ = 4.0 Hz, *i*-Ph^N)[t], 138.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 136.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 135.5 (d, $^4J_{PC}$ = 2.6 Hz, *p*-Ph_2P), 135.1 (br d, $^2J_{PC}$ = 9.2 Hz), 130.1 (d, $^3J_{PC}$ = 12.0 Hz)(*o*,*m*-Ph_2P), 129.0 (br, *m*-Ph^N), 127.0 (d, $^1J_{PC}$ = 71.8 Hz, =CP), 125.6 (*p*-Ph^N), 124.6 (d, $^1J_{PC}$ = 86.4 Hz, *i*-Ph_2P)[t], 123.6 (C_5Me_5), 120.8 (br, *o*-Ph^N)[t], 27.4 (d, $^3J_{PC}$ = 38.2 Hz, Me), 12.0 (C_5Me_5), 2.7 (d, $^3J_{PC}$ = 3.7 Hz, $SiMe_3$), n.o. (*i*-C_6F_5), [[t] tentative assignment]. $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = 35.3 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 20 Hz). ^{29}Si(dept) NMR (99 MHz, CD_2Cl_2, 299 K): −8.6 (d, $^2J_{PSi}$ = 39.4 Hz).

Preparation of Compound 11. A suspension of complex **4c** (143 mg, 0.1 mmol) in C_6H_5Br (2 mL) was degassed and CO_2 (1.5 bar) was introduced to the evacuated reaction flask for 1 h. Then the reaction mixture was covered with cyclopentane (4 mL) to eventually give complex **11** as a white solid (119 mg, 81%). Anal. Calcd for $C_{63}H_{52}BF_{20}O_2PSiHf$: C, 51.49; H, 3.57. Found: C, 51.31; H, 3.57. IR (KBr): 1690 (C=O) cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.95 (m, 4H, *o*-Ph_2P), 7.83 (m, 2H, *p*-Ph_2P), 7.72 (m, 4H, *m*-Ph_2P), 1.88 (s, 30H, C_5Me_5), 1.87 (d, $^4J_{PH}$ = 3.1 Hz, 3H, Me), 0.17 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ = 273.9 (d, $^2J_{PC}$ = 22.4 Hz, HfC), 164.3 (d, $^1J_{PC}$ = 103.2 Hz, C=O),

dx.doi.org/10.1021/ja5068146 | J. Am. Chem. Soc. 2014, 136, 12431−12443

148.5 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 138.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 136.7 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 135.1 (d, $^4J_{PC}$ = 3.1 Hz, *p*-Ph_2P), 133.8 (d, $^2J_{PC}$ = 9.2 Hz, *o*-Ph_2P), 130.4 (d, $^3J_{PC}$ = 11.9 Hz, *m*-Ph_2P), 125.9 (d, $^1J_{PC}$ = 37.9 Hz, =CP), 124.4 (br, i-C_6F_5), 123.3 (C_5Me_5), 122.4 (d, $^1J_{PC}$ = 77.7 Hz, *i*-Ph_2P), 26.2 (d, $^3J_{PC}$ = 37.0 Hz, Me), 11.9 (C_5Me_5), 2.7 (d, $^3J_{PC}$ = 2.6 Hz, $SiMe_3$). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 299 K): δ = 4.9 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 20 Hz). ^{29}Si(dept) NMR (99 MHz, CD_2Cl_2, 299 K): δ = −6.9 (d, $^2J_{PSi}$ = 22.5 Hz).

Preparation of Compound 12a. Following the procedure described for the preparation of compound **7**, reaction of complex **4a** (134 mg, 0.1 mmol) with SO_2 (1.5 bar) gave compound **12a** as a yellow crystalline solid (112 mg, 80%). Crystals suitable for the X-ray crystal structure analysis were grown from a two-layer procedure using a CH_2Cl_2 solution of compound **12a** and cyclopentane at −35 °C. Anal. Calcd for $C_{62}H_{52}BF_{20}O_2PSSiZr$: C, 53.11; H, 3.74. Found: C, 53.14; H, 3.77. ^1H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.86 (*o*), 7.81 (*p*), 7.80 (*p*), 7.75 (*o*), 7.75 (*m*), 7.72 (*m*)(each m, Σ10H, Ph_2P)[1], 1.93, 1.81 (each s, each 15H, C_5Me_5), 1.40 (d, $^4J_{PC}$ = 3.9 Hz, 3H, Me), 0.12 (s, $^2J_{SiH}$ = 6.5 Hz, 9H, $SiMe_3$), [1 from the ghsqc experiment]. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ = 264.4 (d, $^2J_{PC}$ = 27.9 Hz, ZrC), 148.5 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 138.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 136.7 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 135.0 (d, $^4J_{PC}$ = 4.0 Hz), 134.6 (d, $^4J_{PC}$ = 3.6 Hz)(*p*-Ph_2P), 134.7 (d, $^2J_{PC}$ = 6.5 Hz), 133.3 (d, $^2J_{PC}$ = 7.7 Hz)(*o*-Ph_2P), 130.7 (d, $^3J_{PC}$ = 11.7 Hz), 130.2 (d, $^3J_{PC}$ = 11.6 Hz)(*m*-Ph_2P), 131.6 (d, $^1J_{PC}$ = 20.8 Hz, =CP), 124.9, 124.6 (C_5Me_5), 124.3 (br, i-C_6F_5), 123.2 (d, $^1J_{PC}$ = 61.2 Hz), 121.2 (d, $^1J_{PC}$ = 50.2 Hz)(*i*-Ph_2P), 19.6 (d, $^3J_{PC}$ = 40.5 Hz, Me), 12.4, 12.0 (C_5Me_5), 2.2 (d, $^3J_{PC}$ = 1.7 Hz, $SiMe_3$). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 299 K): δ = 17.9 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −133.1 (brm, 2F, *o*-C_6F_5), −163.8 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.6 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 20 Hz). ^{29}Si(dept) NMR (99 MHz, CD_2Cl_2, 299 K): δ = −5.3 (d, $^2J_{PSi}$ = 10.6 Hz).

Preparation of Compound 12b. Following the procedure described for the preparation of compound **7**, reaction of complex **4c** (143 mg, 0.1 mmol) with SO_2 (1.5 bar) gave compound **12b** as a pale yellow crystalline solid (116 mg, 78%). Crystals suitable for the X-ray crystal structure analysis were grown from a two-layer procedure using a CH_2Cl_2 solution of compound **12b** and cyclopentane at −35 °C. Anal. Calcd for $C_{62}H_{52}BF_{20}O_2PSSiHf$: C, 50.00; H, 3.52. Found: C, 49.69; H, 3.41. ^1H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.88 (*o*), 7.86 (*p*), 7.81 (*p*), 7.78 (*o*), 7.76 (*m*), 7.73 (*m*)(each m, Σ10H, Ph_2P)[1], 2.00, 1.88 (each s, each 15H, C_5Me_5), 1.68 (d, $^4J_{PC}$ = 3.3 Hz, 3H, Me), 0.14 (s, $^2J_{SiH}$ = 6.5 Hz, 9H, $SiMe_3$), [1 from the ghsqc and ghmbc experiment]. $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 270.6 (d, $^2J_{PC}$ = 27.2 Hz, HfC), 148.5 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 138.6 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 136.6 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 135.2 (d, $^4J_{PC}$ = 3.8 Hz), 134.71 (d, $^4J_{PC}$ = 3.6 Hz)(*p*-Ph_2P), 134.73 (d, $^2J_{PC}$ = 6.9 Hz), 133.3 (d, $^2J_{PC}$ = 7.8 Hz)(*o*-Ph_2P), 130.7 (d, $^3J_{PC}$ = 11.5 Hz), 130.2 (d, $^3J_{PC}$ = 11.7 Hz)(*m*-Ph_2P), 130.8 (d, $^1J_{PC}$ = 18.0 Hz, =CP), n.o. (br, i-C_6F_5), 123.7, 123.5 (C_5Me_5), 120.8 (d, $^1J_{PC}$ = 52.2 Hz), 123.1 (d, $^1J_{PC}$ = 63.5 Hz)(*i*-Ph_2P), 24.3 (d, $^3J_{PC}$ = 40.9 Hz, Me), 12.4, 11.9 (C_5Me_5), 2.7 (d, $^3J_{PC}$ = 1.7 Hz, $SiMe_3$). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = 25.1 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 20 Hz). ^{29}Si(dept) NMR (119 MHz, CD_2Cl_2, 299 K): δ = −4.7 (d, $^2J_{PSi}$ = 11.0 Hz).

Preparation of Compound 13. Following the procedure described for the preparation of compound **8a**, reaction of complex **4a** (67 mg, 0.05 mmol) with PhNSO (7 mg, 0.05 mmol) gave compound **13** as a pale yellow solid (56 mg, 76%). Crystals suitable for the X-ray crystal structure analysis were grown from a two-layer procedure using a CH_2Cl_2 solution of compound **13** and cyclopentane at −35 °C. Anal. Calcd for $C_{68}H_{57}BF_{20}NOPSSiZr$: C, 55.28; H, 3.89; N, 0.95. Found: C, 55.35; H, 4.24; N, 0.98. ^1H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.90 (2H, *o*), 7.82 (1H, *p*), 7.73 (2H, *m*)(each m, Ph_2P), 7.68 (1H, *p*), 7.52 (2H, *m*) 7.72 (2H, *o*)(each m, Ph_2P'), 7.12 (3H, *m*, *p*), 6.96 (2H, *o*)(each m, Ph^N), 1.95 (d, $^4J_{PC}$ = 3.5 Hz, 3H, Me), 1.91, 1.84 (each s, each 15H, C_5Me_5), 0.05 (br, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 260.8 (d, $^2J_{PC}$ = 14.7 Hz, ZrC), 148.5 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 136.6 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 135.7 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 145.0 (d, $^2J_{PC}$ = 2.3 Hz, *i*), 129.1 (d, $^4J_{PC}$ = 1.3 Hz, *m*), 127.2 (d, $^5J_{PC}$ = 1.5 Hz, *p*), 127.0 (d, $^3J_{PC}$ = 1.8 Hz, *o*)(Ph^N), 135.2 (d, $^4J_{PC}$ = 2.9 Hz, *p*), 133.9 (d, $^2J_{PC}$ = 9.9 Hz, *o*), 130.0 (d, $^3J_{PC}$ = 11.7 Hz, *m*), 126.2 (d, $^1J_{PC}$ = 93.2 Hz, *i*)(Ph_2P'), 134.9 (d, $^4J_{PC}$ = 3.2 Hz, *p*), 133.3 (d, $^2J_{PC}$ = 9.8 Hz, *o*), 129.9 (d, $^3J_{PC}$ = 12.1 Hz, *m*), 128.5 (d, $^1J_{PC}$ = 95.5 Hz[t], *i*)(Ph_2P), 128.4 (d, $^1J_{PC}$ = 60.3 Hz[t], =CP), 124.4 (br, i-C_6F_5), 122.9, 122.6 (C_5Me_5), 25.9 (d, $^3J_{PC}$ = 43.8 Hz, Me), 12.5, 12.4 (C_5Me_5), 3.3 (d, $^3J_{PC}$ = 3.9 Hz, $SiMe_3$), [t tentative assignment]. $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = 28.3 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 20 Hz). ^1H, ^{29}Si ghmqc (600 MHz/119 MHz, CD_2Cl_2, 299 K): δ $^1H/\delta$ ^{29}Si = 0.05/-7.1

Preparation of Compound 14. Following the procedure described for the preparation of complex **8a**, the reaction of complex **4a** (107 mg, 0.08 mmol) with $[Ir(cod)Cl]_2$ (27 mg, 0.04 mmol) in CH_2Cl_2 (2 mL) gave compound **14** as a red-orange solid (96 mg, 72%). Crystals suitable for the X-ray crystal structure analysis were grown from a two-layer procedure using a CH_2Cl_2 solution of compound **14** and cyclopentane at −35 °C. Anal. Calcd for $C_{70}H_{64}BClF_{20}IrPSiZr \cdot CH_2Cl_2$: C, 48.48; H, 3.78. Found: C, 48.95; H, 3.70. ^1H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.74 (m, 4H, *o*-Ph_2P), 7.49 (m, 6H, *m*, *p*-Ph_2P), 4.78, 2.84 (each m, each 2H, CH^{cod}), 2.30, 2.20, 1.80, 1.46 (each m, each 2H, CH_2^{cod}), 1.84 (s, 30H, C_5Me_5), 0.39 (d, $^4J_{PH}$ = 3.2 Hz, 3H, Me), −0.13 (s, $^2J_{SiH}$ = 6.1 Hz, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 239.2 (d, $^2J_{PC}$ = 44.6 Hz, ZrC), 148.5 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 138.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 138.3 (d, $^1J_{PC}$ = 31.3 Hz, =CP), 136.7 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 134.3 (d, $^2J_{PC}$ = 10.3 Hz, *o*-Ph_2P), 133.2 (d, $^1J_{PC}$ = 46.6 Hz, *i*-Ph_2P), 131.2 (d, $^4J_{PC}$ = 2.1 Hz, *p*-Ph_2P), 128.8 (d, $^3J_{PC}$ = 9.6 Hz, *m*-Ph_2P), 124.2 (br, *i*-C_6F_5), 122.3 (C_5Me_5), 89.6 (d, $^2J_{PC}$ = 12.3 Hz, CH^{cod}), 60.0 (CH^{cod}), 33.1 (d, *J* = 3.3 Hz, CH_2^{cod}), 29.4 (d, *J* = 2.1 Hz, CH_2^{cod}), 12.4 (C_5Me_5), 3.4 ($SiMe_3$), 3.0 (d, $^3J_{PC}$ = 35.8 Hz, $^1J_{CH}$ ~ 124 Hz[1], Me), [1 from the ghmbc experiment]. $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = 31.0 ($\nu_{1/2}$ ~ 2 Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = −133.1 (br m, 2F, *o*-C_6F_5), −163.9 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), −167.7 (br m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 3.8]. $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = −16.7 ($\nu_{1/2}$ ~ 25 Hz). ^{29}Si(dept) NMR (119 MHz, CD_2Cl_2, 299 K): δ = −4.4 (d, $^2J_{PSi}$ = 13.8 Hz).

■ ASSOCIATED CONTENT

Supporting Information

Experimental and analytical details. Crystallographic data and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the Alexander von Humboldt-Stiftung and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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