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Electrophilic d^0 Cations of Group 4 Metals (M = Ti, Zr, Hf) Derived from Monopentafulvene Complexes: Direct Formation of Tridentate *Cp,O,P*-Ligands

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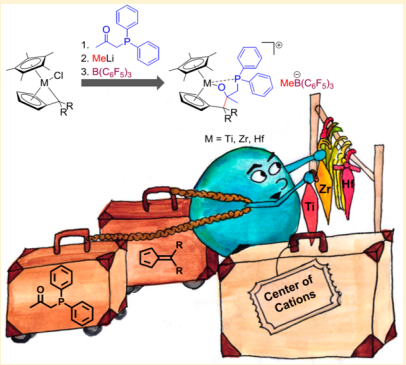
Supporting Information

ABSTRACT: The reactions of the monopentafulvene complexes **Ti1a** and **Ti1b** with the general formula $[Cp^*Ti(Cl)(\pi\text{-}\eta^5\text{:}\sigma\text{-}\eta^1\text{-}C_5H_4{=}CR_2)]$ (R = *p*-tolyl (**Ti1a**); CR_2 = adamantylidene (**Ti1b**)) with the bidentate *P,O*-ligand precursor **L1**, featuring a diphenylphosphine and a hydroxyl functional group, are reported, yielding the corresponding complexes **Ti2a** and **Ti2b** in good yields as the result of deprotonation. A chloride/methyl exchange reaction and subsequent reaction with $B(C_6F_5)_3$ was envisaged to yield the corresponding cationic complexes. Instead, the methylation reactions of **Ti2a** and **Ti2b** with methyllithium or methylmagnesium bromide selectively yielded the doubly methylated titanium complexes **Ti3a** and **Ti3b** with abstraction of LiCl and the lithium salt of the bidentate *P,O*-ligand. To avoid this reaction, the *P,O*-ligand precursor **L2** was prepared, featuring a carbonyl group instead of the hydroxyl functional group. This change in the general reaction sequence allowed the preparation of a new family of cationic titanium complexes **Ti6a** and **Ti6b** and was transferred to the heavier congeners zirconium (**Zr4**) and hafnium (**Hf4**). Every step of the reaction pathway was performed under mild reaction conditions and in good to very good yields. The insertion of the carbonyl group into the $M{-}C_{exo}$ bond of the monopentafulvene complexes **Ti1a**, **Ti1b**, **Zr1**, and **Hf1**, and consequently the formation of a C−C bond, proved to be mandatory for the methylation and subsequent abstraction of the methyl group by $B(C_6F_5)_3$. In effect, a tridentate *Cp,O,P*-ligand was directly introduced into the coordination spheres of the respective group 4 metals within the cationic complexes. In all cases the phosphorus shows a persistent interaction between the Lewis acidic metal center and the Lewis basic phosphine moiety, as shown by NMR analyses and in the solid state. Every complex was thoroughly characterized, including several X-ray diffraction analyses of each class of compounds reported here.



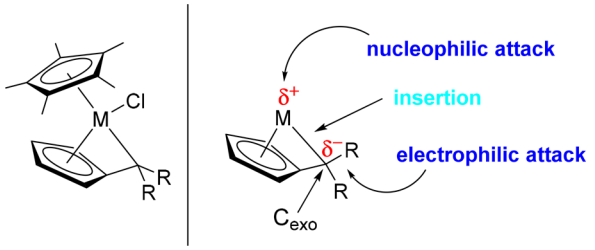
INTRODUCTION

Well-defined, highly electrophilic d^0 cationic complexes of group 4 metals are of great academic and industrial interest, especially due to their use as olefin polymerization catalysts.[1] In particular, methylzirconocene cations, e.g. the so-called Jordan cation $[Cp_2ZrMe]^+$, are the active catalytic species in homogeneous single-site Ziegler−Natta catalysis.[2,3] Numerous substitution patterns for the ancillary ligands of d^0 cationic group 4 systems have been developed to direct their catalytic activity. Moreover, such cationic species are able to catalyze organic transformations. In this context the Jordan cation is able to couple olefins and α-picoline through sequential aryl C−H activation, olefin insertion, Zr−R bond hydrogenolysis, and steps involving ligand exchange.[4]

We recently reported on the convenient syntheses of mixed pentamethylcyclopentadienyl/pentafulvene complexes of titanium,[5,6] as well as of the heavier congeners zirconium[7] and hafnium,[7] via a reductive complexation route. The $\pi\text{-}\eta^5\text{:}\sigma\text{-}\eta^1$ bonding mode, or more specifically the reactive $M{-}C_{exo}$ bond (C_{exo} = exocyclic carbon atom of the pentafulvene ligand) of the fulvene moiety, allows many subsequent transformations under mild reaction conditions in terms of E−H bond activation reactions and insertion reactions of polar multiple bond substrates (Scheme 1).[8−14]

Hemilabile bidentate *P,O*-ligands constitute an important ligand class for transition-metal-catalyzed transformations within the Shell Higher Olefin Process (SHOP) and the palladium-catalyzed alternating copolymerization of alkenes and

Scheme 1. Synthesized Mixed Pentamethylcyclopentadienyl/Pentafulvene Complexes (M = Ti, Zr, Hf) and General Reactivity of the $\pi\text{-}\eta^5\text{:}\sigma\text{-}\eta^1$ Pentafulvene Moiety



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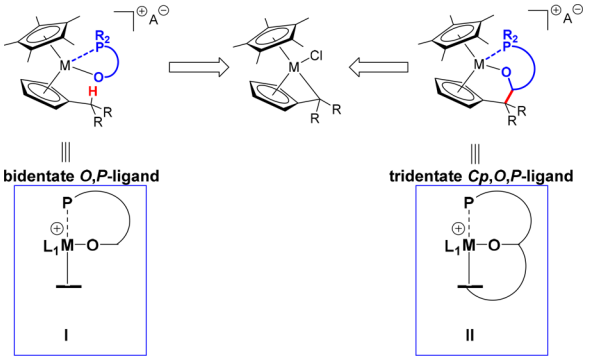
carbon monoxide, which use simple phosphinocarboxylic and phosphinosulfonic acid ligands; these are probably the most famous examples.[15−17]

We initially targeted cationic group 4 metal complexes derived from the established monopentafulvene complexes reported previously and bidentate *P,O*-ligands, utilizing the general reactivity of pentafulvene complexes in the form of E−H activation reactions (Scheme 2, left) or insertion reactions (Scheme 2, right).

Scheme 2. Targeted Cationic Group 4 Metal Complexes I and II Derived from Monopentafulvene Complexes and a Bidentate *P,O*-Ligand (M = Ti, Zr, Hf), and Illustration of the General Ligand Frameworks



P,O-Ligands featuring a carbonyl function to insert into the M−C_{exo} bond would lead to a new type of tridentate ligand, built directly at the metal center, with inclusion of the cyclopentadienyl moiety together with the strong M−O bond and the donor side of the phosphine functional group (Scheme 2, right (**II**)), whereas the E−H activation reaction pathway would lead to similar systems (**I**) without the link between the oxygen and cyclopentadienyl donor sites.

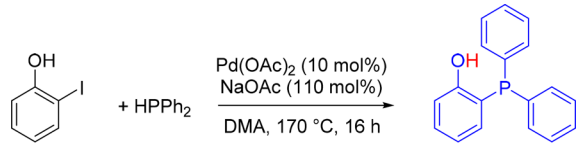
Such cationic species received an immense increase in interest during the last few years due to the development of transition-metal frustrated Lewis pairs (tm-FLPs).[18−20] FLPs have been shown to be a powerful tool for numerous bond activation reactions and small-molecule activations. Replacing the Lewis acid compound, which is usually a polyfluorinated arylborane, with an electrophilic transition-metal center offers the promising ability to combine the powerful small-molecule activation chemistry of FLPs with the extensively studied suite of catalytically relevant reactions and has already shown new reaction pathways.[18−20] It has to be mentioned that examples of tm-FLPs in which the Lewis acid is replaced by a transition metal have been mostly focused on zirconium,[21−34] whereas only a few examples with titanium,[35−37] hafnium,[26,31,38] and ruthenium[39,40] have been reported. Whether the frustrated character between the Lewis acid and the Lewis base is present is strongly dependent on the steric and electronic properties of each part. This makes intensive studies and screening of appropriate ligand systems mandatory.

We thought that the monopentafulvene complexes [Cp*Ti(Cl)(π-η^5:σ-η^1-C_5H_4=CR_2)] (R = alkyl, aryl) of the group 4 metal centers would be ideal precursor compounds for synthesizing cationic group 4 metal complexes with a specific ligand backbone generally suitable for the applications mentioned above. In this contribution, we report on a convenient, atom-economical, and high-yielding reaction pathway under mild reaction conditions to obtain such complexes, where the modular synthesis of the ligand framework takes place directly at the precursor complex, resulting in a tridentate *Cp,O,P*-ligand framework.

RESULTS AND DISCUSSION

We started the investigation with the synthesis of the bidentate *P,O*-ligand precursor **L1** with a hydroxyl and a diphenylphosphino functional group by employing a procedure slightly modified from that described by Spring et al. (Scheme 3).[41]

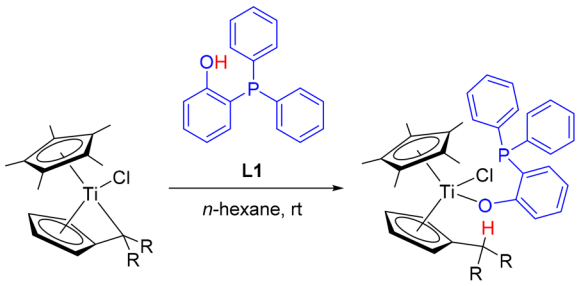
Scheme 3. Synthesis of Compound L1



The hydroxyl functional group should be suitable for O−H activation by pentafulvene complexes in analogy to the reactivity of amines.[10,11] **L1** was synthesized by a palladium-catalyzed coupling of 2-iodophenol and diphenylphosphine under basic reaction conditions in dimethylacetamide (DMA) and isolated as a colorless solid in 69% yield after purification by column chromatography. For reasons of comparison we recollected NMR data of **L1** in deuterobenzene.[42]

This compound exhibits the envisaged design features of a resulting strong M−O bond and an intramolecular phosphine donor side for reactions with the mixed pentamethylcyclopentadienyl/pentafulvene complexes of group 4 metal centers. Therefore, the titanium complexes **Ti1a**[5] and **Ti1b**[6] with sterically encumbered pentafulvene ligands were used. Indeed, by reaction with **L1** in *n*-hexane under mild reaction conditions, the novel compounds **Ti2a** and **Ti2b** were isolated as analytically pure orange (**Ti2a**) and red-brown (**Ti2b**) solids in good yields of 70% and 76%, respectively (Scheme 4). The air- and moisture-sensitive complexes show good solubilities in aromatic and polar solvents and slight solubilities in aliphatic solvents.

Scheme 4. Synthesis of Complexes Ti2a and Ti2b



Complexes **Ti2a** and **Ti2b** both crystallize in the monoclinic space group $P2_1/n$. The molecular structures (Figure 1) of **Ti2a** and **Ti2b** display the expected pseudotetrahedral coordination environment at the titanium centers (Cl1−Ti1−O1 95.00(4)°, Ct1−Ti1−Ct2 131.5° (**Ti2a**), Cl1−Ti1−O1 94.50(3)°, Ct1−Ti1−Ct2 132.9° (**Ti2b**)).

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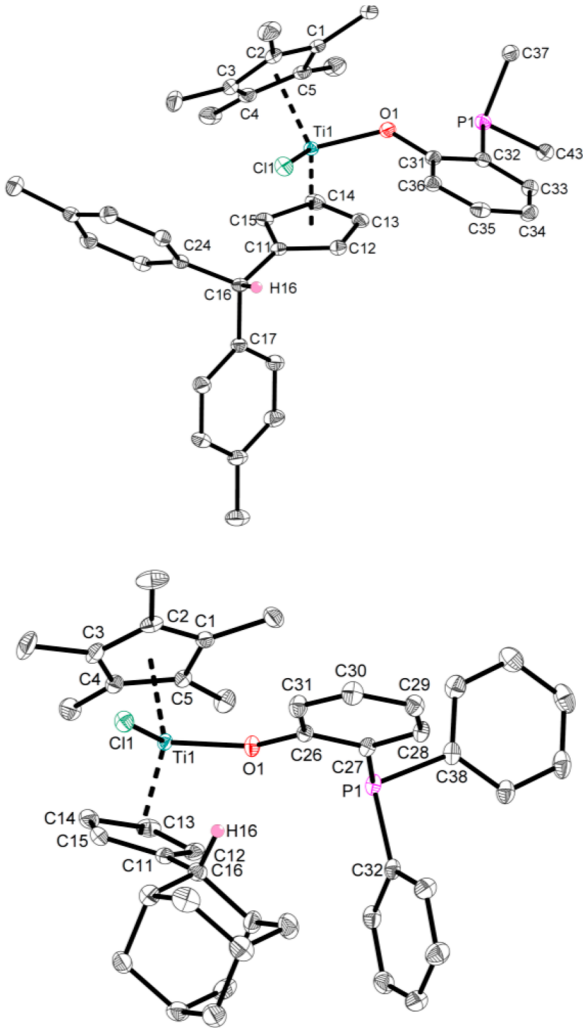


Figure 1. Molecular structures of complexes **Ti2a** (top) and **Ti2b** (bottom). Hydrogen atoms (except H16) and the phenyl groups of the phosphine moiety (only for **Ti2a**) are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): **Ti2a**, Ti1−O1 1.9199(13), Ti1−Cl1 2.3266(19), Ti1···P1 4.39, O1−C31 1.345(2), P1−C32 1.8348(19), C11−C16 1.510(2), Ti1−O1−C31 136.22(11), Cl1−Ti1−O1 95.00(4), Ct1−Ti1−Ct2 131.5, ∑∠P1 304.1 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15); **Ti2b**, Ti1−O1 1.8775(9), Ti1−Cl1 2.3950(4), Ti1···P1 4.48, O1−C26 1.3369(14), P1−C27 1.8288(12), C11−C16 1.5076(17), Ti1−O1−C26 158.09(8), Cl1−Ti1−O1 94.50(3), Ct1−Ti1−Ct2 132.9, ∑∠P1 305.8 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15).

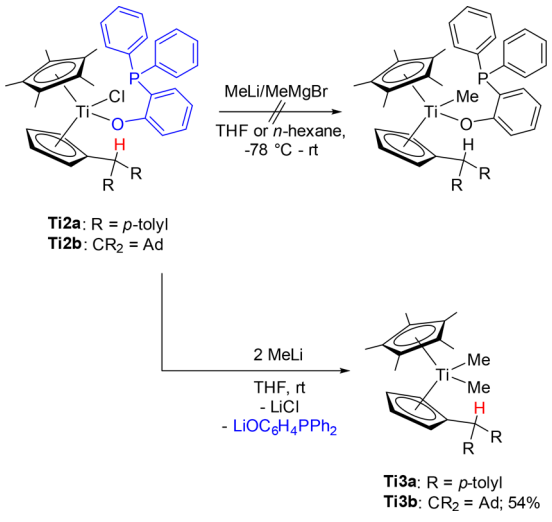
The newly formed Ti1−O1 bonds with bond lengths of 1.9199(13) Å (**Ti2a**) and 1.8775(9) Å (**Ti2b**) are shortened single bonds due to Ti(d_π)−O(p_π) interactions, and the Ti1−Cl1 bond lengths (2.3266(19) Å (**Ti2a**), 2.3950(4) Å (**Ti2b**)) are typical of single bonds.[43,44] In contrast to the starting compounds **Ti1a** (C_{ipso}−C_{exo} 1.428(7) Å)[5] and **Ti1b** (C_{ipso}−C_{exo} 1.422(4) Å)[6] the C11−C16 bonds (1.510(2) Å (**Ti2a**), 1.5076(17) Å (**Ti2b**)) are elongated and now constitute C(sp^2)−C(sp^3) single bonds.[45]

The NMR parameters are discussed for **Ti2a** as an example. In the high-field region the ^{1}H NMR spectrum of **Ti2a** shows two separate signals for the methyl groups of the *p*-tolyl groups at $\delta(^1H)$ 2.05 and 2.09 ppm, respectively, due to the chirality at the central metal atom. Of high diagnostic value are the four signals of the chemically inequivalent hydrogen atoms of the coordinated five-membered ring of the former pentafulvene ligand at $\delta(^1H)$ 5.44, 5.96, 6.05, and 6.34 ppm and the chemical shift of the CH_{exo} atom at $\delta(^1H)$ 6.12 ppm ($\delta(^{13}C)$ 52.2 ppm); all arein good agreement with those of other di-*p*-tolyl-substituted pentafulvene complexes, protonated at the exocyclic carbon position.[10−12] In the low-field region of the ^{1}H NMR spectrum, the expected distinct signals for the aromatic hydrogen atoms are observed and, in contrast to **L1**, separate signals are obtained for the *o*-, *m*-, and *p*-hydrogen atoms of each phenyl group, again caused by the chirality of the central titanium atom. The corresponding $^{31}P\{^1H\}$ NMR chemical shift of **Ti2a** at $\delta(^{31}P\{^1H\})$ 21.3 ppm is shifted only 6.4 ppm to lower field in comparison to free **L1**, indicating a very similar chemical environment at the phosphorus atom, and also lies in the same range as that observed for other aryl-substituted phosphorus(III) compounds and complexes. In the ^{13}C NMR spectra, the ubiquitous doubled coupling patterns of the carbon atoms close to the phosphorus are observed.

After the successful preparation of the complexes **Ti2a** and **Ti2b**, the next step was the installation of the electrophilic position at the metal atom. The abstraction of methyl groups by strong Lewis acids, e.g. by boranes or aluminum derivatives, is an established method to generate electrophilic metal centers.[32,33] We therefore started to investigate the possibility of reacting **Ti2a** and **Ti2b** with 1.0 equiv of methyllithium under mild reaction conditions in THF or *n*-hexane.

The reaction of **Ti2a** with 1.0 equiv of a methyllithium solution (1.6 M in Et_2O) at room temperature in THF yielded a mixture of products after removal of all volatiles without further purification steps. The main product was the starting material **Ti2a**, as indicated by ^{31}P NMR spectroscopy ($\delta(^{31}P\{^1H\})$ −21.3 ppm), and only one other phosphorus species was observed ($\delta(^{31}P\{^1H\})$ −24.3 ppm). The most significant signal in the ^{1}H NMR spectrum of the product mixture has a chemical shift of $\delta(^1H)$ −0.18 ppm with the corresponding ^{13}C NMR resonance at $\delta(^{13}C\{^1H\})$ 47.0 ppm, which is in the typical range of comparable complexes bearing two terminal Ti−CH_3 groups (e.g., $Cp_2Ti(CH_3)_2$: $\delta(^1H)$ −0.07 ppm, $\delta(^{13}C\{^1H\})$ 46.1 ppm).[46a] The same results were obtained when MeMgBr was used as the methylation reagent and/or the reaction was started at −78 °C (Scheme 5).

Scheme 5. Attempted Methylation of Ti2a and Ti2b



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Due to the remaining starting material **Ti2a** in the reaction mixture, we increased the stoichiometry of the methylation reagent to 2.0 equiv of methyllithium. After purification and removal of all volatiles no more starting material was observable in the NMR spectra. Instead, in the low-field area of the ^{1}H NMR spectrum resonances at $\delta(^1H)$ −0.18 (s, 6H) ($\delta(^{13}C\{^1H\})$ 47.3 ppm), 1.56 (s, 15H) ($\delta(^{13}C\{^1H\})$ 12.1 ppm), and 2.09 (s, 6H) ($\delta(^{13}C\{^1H\})$ 21.0 ppm) ppm were detected together with three signals for the four hydrogen atoms of the C_5H_4 moiety and one signal with a chemical shift of $\delta(^1H)$ 5.43 ppm ($\delta(^{13}C)$ 52.7 ppm), clearly indicating the formation of the doubly methylated complex **Ti3a** and $LiOC_6H_4PPh_2$ (**III**) as the byproduct (NMR data and spectra of this procedure as well as the crystal structure of $LiOC_6H_4PPh_2$ (**III**) are shown in the Supporting Information[42]). We repeated this procedure for the synthesis of the adamantyl-substituted complex **Ti3b**, which was also characterized by NMR spectroscopy and single-crystal X-ray diffraction. Single crystals were obtained from a saturated *n*-hexane solution at −4 °C (Figure 2).

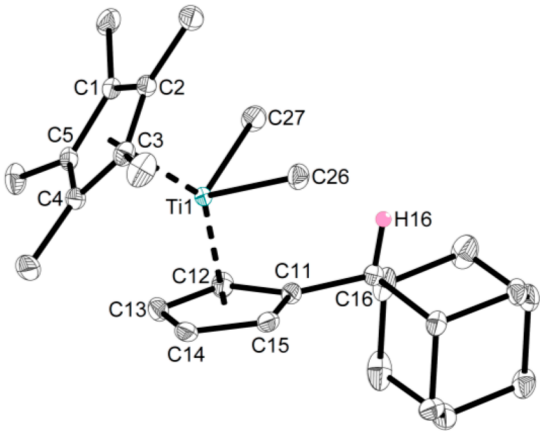
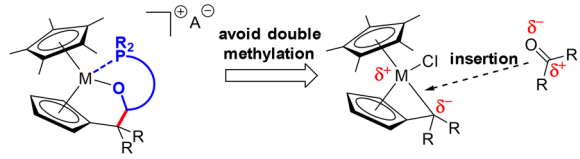


Figure 2. Molecular structure of complex **Ti3b**. Hydrogen atoms (except H16) are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1−C26 2.1774(10), Ti1−C27 2.1685(11), C11−C16 1.5095(13), C26−Ti1−C27 92.02(5), Ct1−Ti1−Ct2 135.7 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15).

Complex **Ti3b** crystallizes in the monoclinic space group $P2_1/c$, and the central titanium atom shows a distorted-tetrahedral coordination environment (C26−Ti1−C27 92.02(5)°, Ct1−Ti1−Ct2 135.7°). The titanium−carbon bond lengths of the terminal methyl groups (Ti1−C26 2.1774(10) Å, Ti1−C27 2.1685 Å) lie in the expected range and are comparable to those of Cp_2TiMe_2 (2.181(2) and 2.170(2) Å).[46b] As for **Ti2a** and other complexes with a protonated exocyclic carbon atom of the former pentafulvene moiety, the C11−C16 bond length of 1.5095(13) Å is characteristic of a C(sp^2)−C(sp^3) single bond.[45]

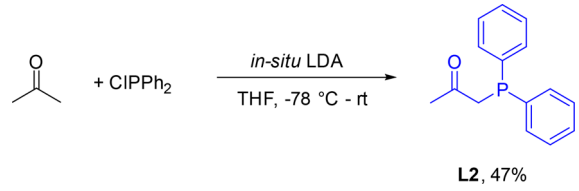
Because of this reactivity, namely the double-methylation reaction of **Ti2a** and **Ti2b**, we thought about a method to avoid the elimination of the previously installed hemilabile bidentate *P,O*-ligand framework. Meanwhile we wanted to maintain the general properties of the pursued ligand framework (strong M−O bond and a five-membered chelating *P,O*-ligand system) and the reaction pathway. Therefore, we thought about using a proper ketone or aldehyde satisfying these characteristics because carbonyl compounds can react with pentafulvene complexes via an insertion reaction.[47] Consequently, a new C−C bond should be formed, which might be able to stabilize the ligand framework and, in addition, should avoid the second methylation seen above, resulting in metallacycles with $\sigma-\pi$ chelating ligands (Scheme 6).

Scheme 6. Attempted Stabilization through C−C Linkage via Insertion of a Carbonyl Compound To Avoid the Second Methylation Reaction



We found that the ligand precursor **L2** features all criteria and synthesized it according to a procedure slightly modified from that by Ugozzolli et al. (Scheme 7).[48] As for **L1**, we recollected NMR data of **L2** in deuterobenzene (Supporting Information[42]). **L2** is a yellow oil which was purified by distillation in 47% isolated yield.

Scheme 7. Synthesis of Compound L2



The reactions of **L2** with the mixed pentamethylcyclopentadienyl/monopentafulvene complexes **Ti1a** and **Ti1b** were accompanied by a slight color change and precipitation of the insertion products **Ti4a** and **Ti4b** as yellow solids in good yields of 81% each (Scheme 8). Both complexes are air and

Scheme 8. Syntheses of Complexes Ti4a, Ti4b, Zr2, and Hf2 by Reacting Ti1a, Ti1b, Zr1, and Hf1 with L2 and Further Installation of the Methyl Group To Yield Complexes Ti5a, Ti5b, Zr3, and Hf3

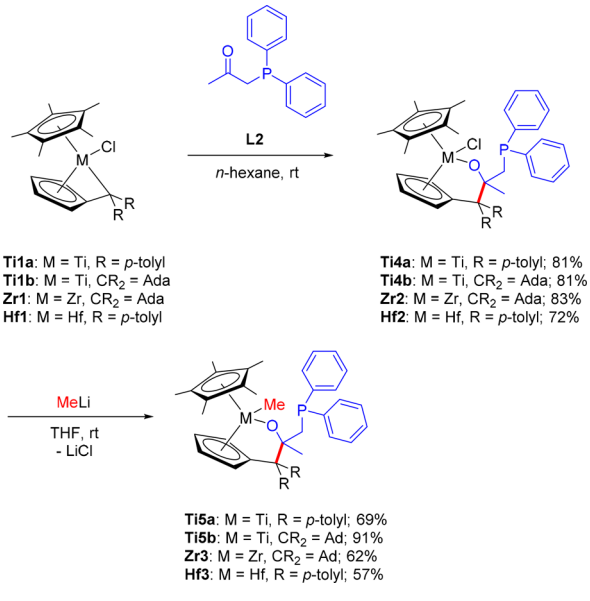


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Table 1. Selected NMR Parameters of Complexes Ti4a, Ti4b, Zr2, Hf2, Ti5a, Ti5b, Zr3, and Hf3[a]

compd	$\delta(^1H)/\delta(^{13}C\{^1H\})$ PCH_2, $^2J_{P,H}/^1J_{C,P}(PCH_2)$	$\delta^1H/\delta^{13}C\{^1H\}$ MCH_3	$\delta(^{13}C\{^1H\})$ OC_q, $^2J_{C,P}(OC_q)$	$\delta^1H/\delta^{13}C\{^1H\}$ OC_qCH_3, $^3J_{C,P}(OC_qCH_3)$	$\delta(^{13}C\{^1H\})$ $C_{q,exo}$, $^3J_{C,P}(C_{q,exo})$	$\delta(^{31}P\{^1H\})$
Ti4a	2.87 and 3.80/46.9		112.0	1.79/32.5	66.2	−20.3
	$^2J_{P,H}$ = 6.0/$^1J_{C,P}$ = 17.9		$^2J_{C,P}$ = 11.0	$^3J_{C,P}$ = 13.5	$^3J_{C,P}$ = 2.6 Hz	
Ti4b[b]	2.45 and 3.24/41.2		112.1	1.39/35.8	55.3	−22.0
	$^2J_{P,H}$[c]/$^1J_{C,P}$ = 18.6		$^2J_{C,P}$ = 9.2	$^3J_{C,P}$ = 13.4	$^3J_{C,P}$ = 2.2 Hz	
Ti5a	2.77 and 3.69/46.5	0.43/38.7	107.8	1.51/33.0	66.6	−20.2
	$^2J_{P,H}$ = 6.2/$^1J_{C,P}$ = 17.2		$^2J_{C,P}$ = 13.8	$^3J_{C,P}$ = 13.8	$^3J_{C,P}$ = 2.5 Hz	
Ti5b	2.79 and 3.15/42.6	0.33/36.3	107.9	1.41/35.1	55.6	−23.9
	$^2J_{P,H}$[c]/$^1J_{C,P}$ = 15.9		$^2J_{C,P}$ = 9.4	$^3J_{C,P}$ = 13.1	$^3J_{C,P}$[c]	
Zr2[b]	2.88 and 3.12/44.2		107.8	[b]	55.9	−21.5
	$^2J_{P,H}$[c]/$^1J_{C,P}$ = 16.7		$^2J_{C,P}$ = 9.1		$^3J_{C,P}$[c]	
Hf2	2.88 and 3.93/42.3		104.9	1.71/32.6	66.4	−20.5
	$^2J_{P,H}$[c]/$^1J_{C,P}$ = 17.1		$^2J_{C,P}$ = 10.8	$^3J_{C,P}$ = 12.0	$^3J_{C,P}$ = 12.0 Hz	
Zr3[b]	[b]	−0.05/23.1	[b]	[b]	56.0	−22.2
					$^3J_{C,P}$[c]	
Hf3	2.79 and 3.90/46.0	−0.04/28.3	103.0	1.52/33.1	66.6	−20.7
	$^2J_{P,H}$ = 14.5/$^1J_{C,P}$ = 16.8		$^2J_{C,P}$ = 10.9	$^3J_{C,P}$ = 11.9	$^3J_{C,P}$[c]	

[a] δ values are given in ppm and J values in Hz. Measurements were carried out in C_6D_6 at room temperature. [b] Product is a mixture of diastereoisomers; therefore, only clearly assignable signals of the main diastereoisomer are given. [c] Coupling constant not observed.

moisture sensitive but can be stored under inert conditions without indication of decomposition. Ideal for purification purposes are the slight solubilities in aliphatic solvents and good solubilities in aromatic and polar solvents. Our strategy to produce singly methylated complexes with maintenance of the ligand framework worked via subsequent methylation of **Ti4a** and **Ti4b** with methyllithium under mild reaction conditions and readily yielded the corresponding complexes **Ti5a** and **Ti5b** in yields up to 91% as pale yellow solids. Encouraged by these results, we could successfully transfer these reactions to the heavier congeners zirconium and hafnium to yield the complexes **Zr2**, **Hf2**, **Zr3**, and **Hf3**.

The compounds **Ti4a**, **Ti4b**, **Zr2**, **Hf2**, **Ti5a**, **Ti5b**, **Zr3**, and **Hf3** were fully characterized by NMR analyses. Due to the high similarity of the most important and characteristic NMR parameters of these complexes, the NMR data are discussed for compounds **Ti4a** and **Ti5a** as examples and summarized for all in Table 1.

The ^1H NMR spectrum of complex **Ti4a** shows at lower field one signal for the methyl group located at the quaternary carbon atom of the former carbonyl group at a chemical shift of $\delta(^1H)$ 1.79 ppm with the respective ^{13}C resonance at $\delta(^{13}C\{^1H\})$ 32.5 ppm (doublet) and a characteristic $^3J_{C,P}$ coupling constant of 13.5 Hz. The methyl groups of the *p*-tolyl groups show one signal each at $\delta(^1H)$ 2.10 and 2.17 ppm, characteristic of the C_1 symmetry of this complex. The methylene group in a position α to the phosphorus has ^1H NMR chemical shifts at $\delta(^1H)$ 2.87 and 3.80 ppm (due to diastereotopicity) and a ^{13}C NMR chemical shift of $\delta(^{13}C\{^1H\})$ 46.9 ppm (doublet) with coupling constants of $^2J_{P,H}$ = 6.0 Hz and $^1J_{C,P}$ = 17.9 Hz. Of high diagnostic value for this class of compounds is the ^{13}C chemical shift of the exocyclic carbon atom at $\delta(^{13}C\{^1H\})$ 66.2 ppm (doublet), which, together with the coupling constant of $^3J_{C,P}$ = 2.6 Hz, confirms the insertion of the carbonyl group into the former Ti−C_{exo} bond. As expected, the $^{31}P\{^1H\}$ chemical shift of $\delta(^{31}P\{^1H\})$ −20.3 ppm is in the same range as for free **L2**, indicating the same chemical environment at the phosphorus atom. The other chemical shifts of the Cp* and C_5H_4 moieties are in the same characteristic range as for other complexes derived from pentafulvene complexes of titanium.[5,7] The ^1H and ^{13}C NMR signals of the titanium methyl group of **Ti5a** are localized at $\delta(^1H)$ 0.43 ppm and $\delta(^{13}C\{^1H\})$ 38.7 ppm, which are in the range for other terminal monomethylated complexes of titanium (e.g., $(Cy_2N)_3TiCH_3$).[49] The corresponding chemical shifts of **Ti5a** in comparison to **Ti4a** are overall slightly shifted to higher field. Particularly noteworthy is the isolation of the *p*-tolyl-substituted products **Ti4a** and **Hf2** as diastereomerically pure products, whereas the adamantyl-substituted products **Ti4b** and **Zr2** are obtained as mixtures of diastereoisomers (ratio of diastereoisomers for **Ti4b** and **Zr2**: approximately 3:1). Figure 3 shows an extract of the ^1H NMR and $^{31}P\{^1H\}$ NMR of complex **Ti4b** to illustrate the occurrence of diastereoisomers.

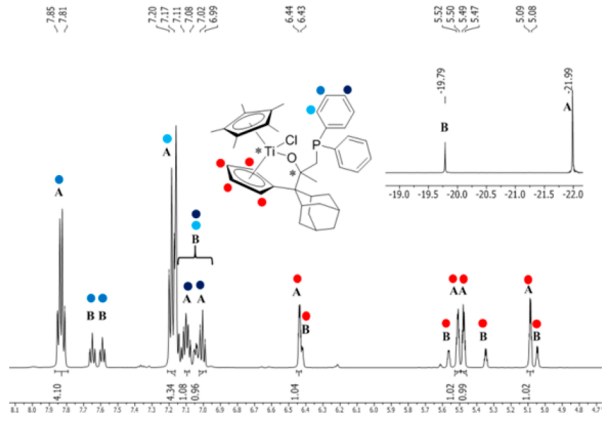

Figure 3. Excerpt of the ^1H NMR spectrum (500 MHz, C_6D_6, room temperature) and of the $^{31}P\{^1H\}$ NMR spectrum (202 MHz, C_6D_6, room temperature) of complex **Ti4b**: (**A**) first diastereoisomer; (**B**) second diastereoisomer.

The molecular structures of complexes **Zr2**, **Hf2**, **Ti5b**, and **Hf3** were determined by single-crystal X-ray diffraction and are shown in Figures 4 and 5. Crystals were obtained from either the mother liquor of the reacted mixtures or from saturated *n*-hexane solutions at −4 or −26 °C.

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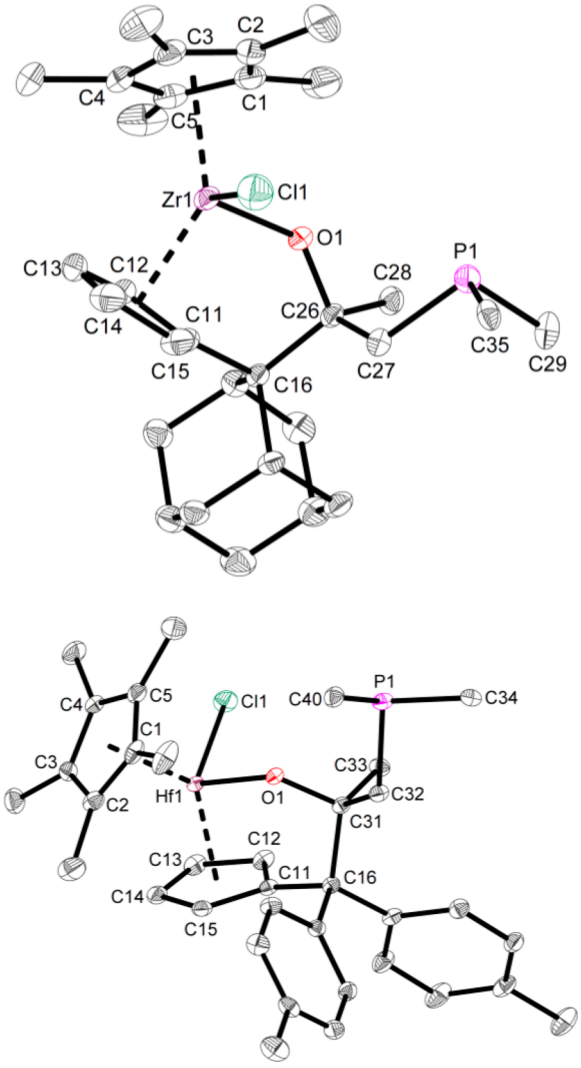

Figure 4. Molecular structures of complexes **Zr2** (top) and **Hf2** (bottom). Hydrogen atoms and the phenyl groups of the phosphine moiety are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): **Zr2**, Zr1−O1 1.9596(7), Zr1−Cl1 2.4604(3), Zr1···P1 4.57, O1−C26 1.4236(11), P1−C27 1.8601(10), C16−C26 1.6036(12), C26−C27 1.5544(13), C26−C28 1.5325(12), Cl1−Zr1−O1 102.71(2), Ct1−Zr1−Ct2 135.1, ∑∠P1 301.3, ∑∠C26 (C27−C26−C28 + C27−C26−O1 + C28−C26−O1) 320.3 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15); **Hf2**, Hf1−O1 1.9801(10), Hf1−Cl1 2.4394(3), Hf1···P1 4.96, O1−C31 1.4322(16), P1−C32 1.8691(14), C16−C31 1.6267(18), C31−C32 1.5463(19), C31−C33 1.5298(18), Cl1−Hf1−O1 100.70(3), Ct1−Hf1−Ct2 132.0, ∑∠P1 304.9, ∑∠C31 (C32−C31−C33 + C32−C31−O1 + C33−C31−O1) 323.5 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15).

Complexes **Ti5b**, **Hf2**, and **Hf3** crystallize in the monoclinic space group $P2_1/n$, and **Zr2** crystallizes in the triclinic space group $P\bar{1}$. The crystallographic features of these complexes are, as expected, quite similar and follow the general tendency of increasing atomic radii within group 4.[43] The central metal atoms are consistently in distorted-tetrahedral coordination environments. The M−Cl and M−CH_3 bond lengths are typical of single bonds.[44] The M−O bond lengths are shorter than typical single bonds due to M(d_π)−O(p_π) interactions between the free electron pair of the oxygen and the metal atoms.[44] Moreover, the C(sp^3)−O distances of 1.425 Å on

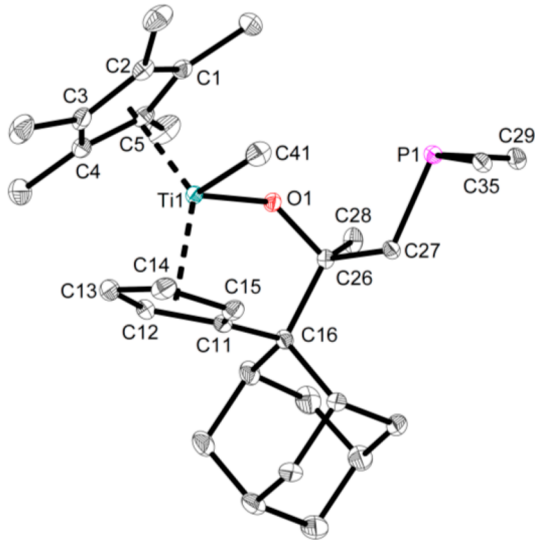

Figure 5. Molecular structures of complexes **Ti5b** (top) and **Hf3** (bottom). Hydrogen atoms and the phenyl groups of the phosphane moiety are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): **Ti5b**, Ti1−O1 1.8621(8), Ti1−C41 2.1805(12), Ti1···P1 4.35, O1−C26 1.4256(13), P1−C27 1.8630(11), C16−C26 1.6290(15), C26−C27 1.5509(15), C26−C28 1.5274(15), C41−Ti1−O1 98.13(4), Ct1−Ti1−Ct2 134.9, ∑∠P1 301.6, ∑∠C26 (C27−C26−C28 + C27−C26−O1 + C28−C26−O1) 320.7 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15); **Hf3**, Hf1−O1 1.9833(10), Hf1−C46 2.2751(15), Hf1···P1 4.95, O1−C31 1.4289(17), P1−C32 1.8692(14), C16−C31 1.6321(19), C31−C32 1.543(2), C31−C33 1.5297(19), C46−Hf1−O1 99.97(5), Ct1−Hf1−Ct2 132.8, ∑∠P1 305.2, ∑∠C31 (C32−C31−C33 + C32−C31−O1 + C33−C31−O1) 323.7 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15).

average are in accordance with single bonds (1.43 Å).[45] The newly formed C−C bonds C16−C26 (adamantyl substitution at C_{exo}) and C16−C31 (*p*-tolyl substitution at C_{exo}) with bond lengths above 1.60 Å are comparable to those of extremely long C−C single bonds.[50] This elongation is caused by the strong ring strain of the newly formed σ−π chelate ligand.[51] The C16−C26 bond length in **Hf3** (1.6321(19) Å) is the longest C−C bond reported so far for these types of carbonyl insertion products. The former carbonyl carbon atoms are sp^3-hybridized, as indicated by the sum of angles around C26 or C31, respectively (320.3° (**Zr2**), 323.5° (**Hf2**), 320.7° (**Ti5b**), and 323.7 (**Hf3**)).

The reactions of complexes **Ti5a**, **Ti5b**, **Zr3**, and **Hf3** with the highly Lewis acidic borane $B(C_6F_5)_3$ in toluene at room temperature resulted in the facile formation of the cationic complexes **Ti6a**, **Ti6b**, **Zr4**, and **Hf4** in very good yields of up to 91% after purification as orange (**Ti6a** and **Ti6b**) and yellow (**Zr4** and **Hf4**) solids, which proved to be the products of methyl abstraction by the polyfluorinated borane $B(C_6F_5)_3$ (Scheme 9). In addition, the aforementioned tridentate *Cp*,*O*,*P*-ligands were formed.

The cationic group 4 complexes are perfectly stable in the solid state and can be stored for months under inert conditions but, like their precursor complexes, are sensitive toward air and moisture. Under ambient conditions, the cationic complexes are insoluble in aromatic and aliphatic hydrocarbons, already indicating the formation of ionic species, and solutions of these complexes in THF immediately start to polymerize the THF. Compounds **Ti6a**, **Ti6b**, **Zr4**, and **Hf4** proved to be

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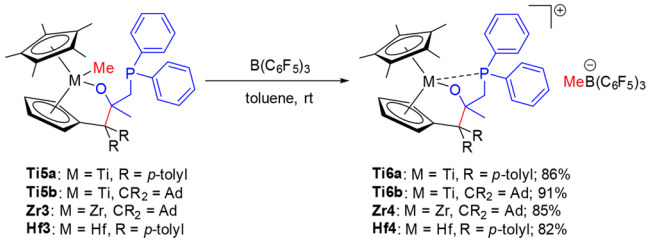
Scheme 9. Syntheses of Cationic Complexes Ti6a, Ti6b, Zr4, and Hf4



Ti5a: M = Ti, R = *p*-tolyl
Ti5b: M = Ti, CR_2 = Ad
Zr3: M = Zr, CR_2 = Ad
Hf3: M = Hf, R = *p*-tolyl

Ti6a: M = Ti, R = *p*-tolyl; 86%
Ti6b: M = Ti, CR_2 = Ad; 91%
Zr4: M = Zr, CR_2 = Ad; 85%
Hf4: M = Hf, R = *p*-tolyl; 82%

stable in dichloromethane, enabling multinuclear NMR spectroscopy.

^{1}H, $^{11}B\{^{1}H\}$, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectroscopy clearly indicates the abstraction of the methyl group and the formation of the corresponding $MeB(C_6F_5)^-$ anion. The $^{11}B\{^{1}H\}$ NMR chemical shifts of compounds **Ti6a**, **Ti6b**, **Zr4**, and **Hf4** at $\delta(^{11}B\{^{1}H\})$ −14.9 ppm and the $^{19}F\{^{1}H\}$ chemical shifts between $\delta(^{19}F\{^{1}H\})$ −167.9 and 167.7 (*m*-$F_{Ar}B$), −165.4 and −165.0 (*p*-$F_{Ar}B$), and −133.4 and −133.0 (*o*-$F_{Ar}B$) ppm are in accordance with other cationic complexes with this borate anion.[23,31] The difference in the chemical shifts of the meta and para fluorine atoms of the borate anion is a characteristic parameter to probe whether the anion coordinates to the cationic d^0 metal center in solution and was first introduced by Horton et al.[52,53] According to their work, coordinative interactions are assumed for $\Delta\delta(m,p\text{-F})$ values greater than 3.5 ppm. The $\Delta\delta(m,p\text{-F})$ values for the complexes reported here range from 2.5 to 2.7 ppm, indicating no coordination of the anion to the d^0 metal centers. The bright singlet resonances in the ^{1}H NMR spectra of $\delta(^{1}H)$ 0.50−0.51 ppm with the corresponding $^{13}C\{^{1}H\}$ signals at $\delta(^{13}C\{^{1}H\})$ 9.8−10.0 ppm are also in accordance with other cationic group 4 complexes with the noncoordinating anion $MeB(C_6F_5)^-$.[23,31] Of high diagnostic value are the $^{31}P\{^{1}H\}$ resonances of complexes **Ti6a** ($\delta(^{31}P\{^{1}H\})$ 22.0 ppm), **Ti6b** ($\delta(^{31}P\{^{1}H\})$ 28.4 ppm), **Zr4** ($\delta(^{31}P\{^{1}H\})$ 19.1 ppm), and **Hf4** ($\delta(^{31}P\{^{1}H\})$ 22.0 ppm), which show a significant shift toward lower field of at least 41.3 ppm in comparison to the methylated starting compounds **Ti5a**, **Ti5b**, **Zr3**, and **Hf3**. This strongly indicates an interaction between the Lewis acidic metal centers and the Lewis basic phosphine moiety in all cases. For comparison, Wass et al. prepared the complex $[Cp_2Zr(Me)OC_6H_4P(^tBu_2)]$ and the corresponding cationic species. For this reaction step a downfield shift of 44.4 ppm in the $^{31}P\{^{1}H\}$ NMR was observed.[32,33] All chemical shifts in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the cationic complexes are in the expected ranges, and the characteristic coupling patterns for the nuclei close to the phosphorus are observed. In addition, all compounds are obtained in a diastereoselective manner. For example, Figure 6 shows the ^{1}H NMR spectrum of complex **Ti6b**.

The formation of the cationic complexes is furthermore confirmed by the molecular structure of complex **Ti6b** in the solid state (Figure 7). Single crystals of **Ti6b** were obtained from a saturated dichloromethane solution of **Ti6b**, layered with cyclohexane at −4 °C. The solution NMR data of complex **Ti6b** are in accordance with its solid-state structure.

Complex **Ti6b** crystallizes in the triclinic space group $P\bar{1}$ and displays distorted-tetrahedral geometry (P1−Ti1−O1 72.94(3)°, Ct1−Ti1−Ct2 136.1°) at the central titanium atom and a five-membered-ring system due to the coordination

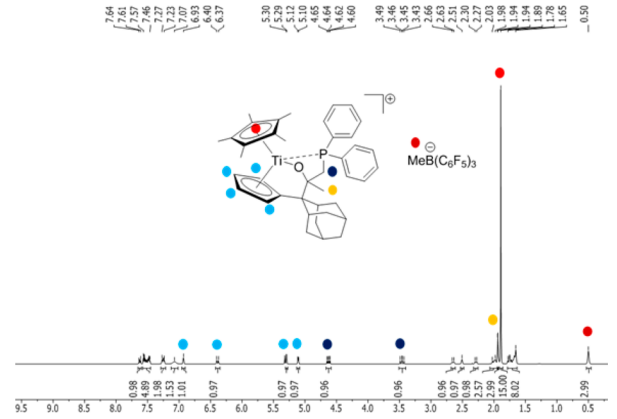


Figure 6. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, rt) of complex **Ti6b**, with corresponding signals highlighted by colored symbols.

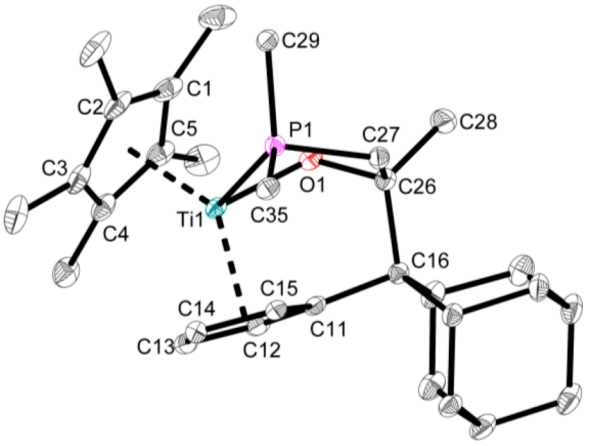


Figure 7. Molecular structure of complex **Ti6b**. Hydrogen atoms, the borate anion, and the phenyl groups of the phosphane moiety are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1−O1 1.8677(9), Ti1−P1 2.6039(4), O1−C26 1.4402(15), P1−C27 1.8502(12), C16−C26 1.6166(17), C26−C27 1.5675(17), C26−C28 1.5370(17), P1−Ti1−O1 72.94(3), Ct1−Ti1−Ct2 136.1, ∑∠P1 310.6, ∑∠C31 (C27−C26−C28 + C27−C26−O1 + C28−C26−O1) 317.9 (Ct1 = centroid of C1−C5; Ct2 = centroid of C11−C15).

of the phosphorus. In this regard, an elongated Ti−P bond is present and at 2.6039(4) Å lies in the same range as comparable Ti(IV)−arylphosphine bonds (e.g., 2.636(3) Å for $[Cp_2Ti(PPh_2)PMe_3]$).[54] The Ti1−O1 bond length of 1.8677(9) Å remains unchanged (**Ti5b** (1.8621(8) Å)) and hence is still shorter than a Ti−O single bond, indicating $Ti(d_\pi)-O(p_\pi)$ interaction. Noteworthy, the C16−C26 bond length (1.6166(17) Å) is still significantly elongated in comparison to a typical $C(sp^3)-C(sp^3)$ single bond (1.53 Å) and the former carbonyl carbon atom is sp^3 hybridized.[45] The molecular structure of **Ti6b** shows an *S* configuration at the metal center and *R* configuration at the C26 atom or, due to crystallographic symmetry, *R* and *S* configurations, respectively. Consequently, **Ti6b** is obtained as an *S*,*R* and *R*,*S* pair of diastereoisomers.

CONCLUSION

We have successfully developed a strategy to synthesize the highly electrophilic cationic d^0 complexes **Ti6a**, **Ti6b**, **Zr4**, and **Hf4** by a two-step synthetic pathway, starting from the

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corresponding monopentafulvene complexes **Ti1a**, **Ti1b**, **Zr1**, and **Hf1** and the readily accessible bidentate *P*,*O*-ligand precursor **L2** with a phosphine moiety and a carbonyl functional group. The driving force of the reaction is the strong nucleophilic character of the C_{exo} atom of the pentafulvene ligand in the coordination sphere of the metal. All reaction steps were performed under mild reaction conditions, providing good to very good yields. The insertion reaction of the carbonyl compound proved to be mandatory to stabilize the ligand framework for the subsequent methylation reaction. In contrast, the use of the bidentate *P*,*O*-ligand precursor **L1** with a phosphine moiety and a hydroxyl functional group provided the corresponding complexes **Ti2a** and **Ti2b** as the result of O−H deprotonation, but the subsequent methylation reactions selectively yield the doubly methylated complexes **Ti3a** and **Ti3b** with abstraction of the previously installed *P*,*O*-ligand. **Ti6a**, **Ti6b**, **Zr4**, and **Hf4** feature a novel tridentate *Cp*,*O*,*P*-ligand system, which is built directly at the metal through insertion of the carbonyl group into the M−C_{exo} bond and simultaneous generation of the cationic species by methyl abstraction with $B(C_6F_5)_3$. In all cases the phosphorus shows a persistent interaction between the Lewis acidic metal center and the Lewis basic phosphine moiety. Every new compound was fully characterized by NMR analyses, high-resolution mass spectroscopy, and additionally single-crystal X-ray diffraction of at least one member of each type of compound. The expansion of this strategy and investigations of the general reactivity with regard to tm-FLP chemistry is currently the subject of intense experimental investigations in our laboratories.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an inert atmosphere of argon or nitrogen with rigorous exclusion of oxygen and moisture using standard glovebox and Schlenk techniques. The glass equipment was stored in an oven at 120 °C and evacuated prior to use. Solvents and liquid educts were dried according to standard procedures. Solvents were distilled over Na/K alloy and benzophenone or CaH_2 under a nitrogen atmosphere. Solid materials were stored and weighed in a glovebox or dried under high vacuum before use. Methyllithium was used as a 1.6 M solution in diethyl ether, and *n*-butyllithium was used as a 1.6 M solution in *n*-hexane. The pentafulvene complexes **Ti1a**, **Ti1b**, **Zr1**, and **Hf1** were synthesized according to literature procedures.[5−7] 2-Iodophenol, $Pd^{II}(CH_3COO)_2$, Ph_2PH, and Ph_2PCl were purchased from commercial sources. 2-Iodophenol and $Pd^{II}(CH_3COO)_2$ were used as received. Ph_2PH and Ph_2PCl were distilled over $CaCl_2$ and stored under nitrogen.

Thin-layer chromatography was performed using commercially available Alugram SIL/G UV254 sheets with fluorescent indicator (254 nm) from Macherey Nagel. Silica gel from Grace (particle size 40−63 μm) was used for column chromatography.

High-resolution mass spectra were measured on a Finnigan-MAT95 spectrometer using ESI.

Infrared spectra were performed on a Bruker Tensor 27 spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system.

NMR spectra were recorded on Bruker Avance 300, Bruker Avance 500, and Bruker Avance III 500 spectrometers. ^{1}H NMR spectra were referend to the residual solvent resonance as internal standard (benzene-d_6 (C_6D_6):, $\delta(^1H)$ C_6D_5H 7.16 ppm; dichloromethane-d_2 (CD_2Cl_2), $\delta(^1H)$ $CDHCl_2$ 5.32 ppm) and ^{13}C spectra by using the central line of the solvent signal (benzene-d_6 (C_6D_6), $\delta(^{13}C\{^1H\})$ C_6D_6 128.06 ppm; dichloromethane-d_2 (CD_2Cl_2), $\delta(^{13}C\{^1H\})$ CD_2Cl_2 53.84 ppm). $^{11}B\{^1H\}$ NMR, $^{19}F\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR spectra were referenced against external standards ($BF_3{\cdot}OEt_2$, $\delta(^{11}B\{^1H\})$ $BF_3{\cdot}OEt_2$ 0.0 ppm; $CFCl_3$, $\delta(^{19}F\{^1H\})$ $CFCl_3$ 0.0 ppm); H_3PO_4, $\delta(^{31}P\{^1H\})$ H_3PO_4 0.0 ppm).

Elemental analyses were carried out on a EuroEA 3000 Elemental Analyzer. The carbon value in the elemental analysis is often lowered by carbide formation. The hydrogen value is found in some cases to be higher, due to residual traces of solvents.

Melting points were determined using a "Mel-Temp" apparatus by Laboratory Devices, Cambridge, U.K. Further exact details of the individually synthesized products, crystallographic data, and NMR spectra are given in the Supporting Information.

Synthesis and Characterization of Compounds. *Synthesis of **L1**.* **L1** was prepared according to a slightly modified literature procedure.[41] 2-Iodophenol (2.000 g, 9.090 mmol), $Pd(OAc)_2$ (0.020 g, 0.909 mmol), and NaOAc (0.820 g, 10.000 mmol) were dissolved in 20 mL of dimethylacetamide. Diphenylphosphine (1.6 mL, 9.090 mmol) was added, and the reaction mixture was refluxed for 16 h. The reaction mixture was filtered, and the filtrate was washed with dimethylacetamide (3 × 3 mL). All volatiles were evaporated under vacuum. The crude product was purified by column chromatography (SiO_2; dichloromethane). The product **L1** was obtained as a colorless solid.

Data for **L1** are as follows. Yield: 1.737 g (69%). R_f = 0.76 (SiO_2; dichloromethane). ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ 6.01 (s(br), 1H, OH), 6.65−6.68 (m, 1H, C_6H_4), 6.77−6.80 (m, 1H, C_6H_4), 7.00−7.03 (m, 7H, 6 × CH_{Ph}, C_6H_4), 7.06−7.09 (m, 1H, C_6H_4), 7.31−7.35 (m, 4H, 4 × CH_{Ph}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 300 K): δ 116.0 (C_6H_4), 121.3 (C_6H_4), 121.8 (d, $^1J_{C,P}$ = 6.8 Hz, $C_{q,C6H4}P$), 128.95 (d, $J_{C,P}$ = 7.0 Hz, 4 × CH_{Ph}), 129.0 (2 × CH_{Ph}), 131.8 (C_6H_4), 133.8 (d, $J_{C,P}$ = 19.0 Hz, 4 × CH_{Ph}), 135.1 (d, $J_{C,P}$ = 4.1 Hz, C_6H_4), 135.9 (d, $^1J_{C,P}$ = 6.6 Hz, 2 × $C_{q,Ph}$), 159.9 (d, $^2J_{C,P}$ = 18.7 Hz, $C_{q,C6H4}OH$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 300 K): δ −27.7 ppm. Analytical data of compound **L1** are in accordance with the literature.[41]

*Synthesis of **Ti2a**.* Complex **Ti1a** (0.500 g, 1.049 mmol) and ligand **L1** (0.292 g, 1.049 mmol) were suspended in 10 mL of *n*-hexane, resulting in an orange suspension. The reaction mixture was stirred for 16 h at room temperature. The solid was separated, washed with *n*-hexane (3 × 5 mL) and dried under vacuum to give **Ti2a** as an orange solid.

Crystals suitable for single crystal X-ray diffraction were obtained from a saturated *n*-hexane/toluene solution at −26 °C.

Data for **Ti2a** are as follows. Yield: 0.553 g (70%). Mp: 142−144 °C. IR (ATR): $\tilde{\nu}$ 3053, 3027, 2915, 1557, 1556, 1509, 1486, 1456, 1431, 1376, 1275, 1264, 1190, 1155, 1122, 1107, 1089, 1064, 1023, 872, 862, 829, 816, 763, 741, 694, 677, 611, 597, 577 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 1.74 (s, 15H, C_5Me_5), 2.05 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 5.44−5.45 (m, 1H, C_5H_4), 5.96−5.97 (m, 1H, C_5H_4), 6.05−6.06 (m, 1H, C_5H_4), 6.12 (s, 1H, CH_{exo}), 6.34−6.35 (m, 1H, C_5H_4), 6.59−6.62 (m, 1H, C_6H_4), 6.85−6.87 (m, 2H, 2 × *m*-$CH_{p\text{-}tolyl}CH_3$), 6.96−6.97 (m, 2H, 2 × *m*-$CH_{p\text{-}tolyl}CH_3$), 7.01−7.09 (m, 9H, 3 × C_6H_4, 4 × *o*-$CH_{Ph}P$, 2 × *p*-$CH_{Ph}P$), 7.11−7.13 (m, 2H, 2 × *o*-$CH_{p\text{-}tolyl}CH_3$), 7.33−7.38 (m, 6H, 2 × *o*-$CH_{p\text{-}tolyl}CH_3$, 4 × *m*-$CH_{Ph}P$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ 12.9 (C_5Me_5), 21.0 (CH_3), 21.1 (CH_3), 52.2 (CH_{exo}), 110.5 (C_5H_4), 113.1 (C_5H_4), 117.4 (C_5H_4), 120.0 (C_5H_4), 127.5 (C_5Me_5), 128.1 (2 × *m*-$CH_{p\text{-}tolyl}CH_3$)*, 128.2 (2 × *m*-$CH_{p\text{-}tolyl}CH_3$)*, 128.5 (2 × *o*-$CH_{p\text{-}tolyl}CH_3$), 128.9 (C_6H_4), 128.92 (C_6H_4), 129.0 (C_6H_4), 129.3 (d, $^2J_{C,P}$ = 9.8 Hz, 4 × *o*-$CH_{Ph}P$), 129.4 (2 × *p*-$CH_{Ph}P$), 130.3 (2 × *o*-$CH_{p\text{-}tolyl}CH_3$), 133.8 (d, $^2J_{C,P}$ = 18.7 Hz, C_6H_4), 134.2 (d, $^3J_{C,P}$ = 20.2 Hz, 4 × *m*-$CH_{Ph}P$), 135.4 ($C_{q,p\text{-}tolyl}CH_3$), 135.8 ($C_{q,p\text{-}tolyl}CH_3$), 138.8 (d, $^1J_{C,P}$ = 12.8 Hz, 2 × $C_{q,Ph}P$), 139.4 (d, $^1J_{C,P}$ = 12.2 Hz, $C_{q,C6H4}P$), 141.5 (*p*-$C_{q,p\text{-}tolyl}CH_3$), 142.9 (*p*-$C_{q,p\text{-}tolyl}CH_3$), 145.3 ($C_{q,ipso}$), 174.0 ($C_{q,C6H4}O$) ppm (the asterisk indicates overlap with C_6D_6 signal). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K): δ −21.3 ppm. Anal. Calcd for $C_{48}H_{48}ClOPTi$: C, 76.34; H, 6.41. Found: C, 76.12; H, 6.49.

*Synthesis of **Ti2b**.* Complex **Ti1b** (0.500 g, 1.199 mmol) and ligand **L1** (0.334 g, 1.199 mmol) were suspended in 10 mL of *n*-hexane, resulting in a red suspension. The reaction mixture was stirred for 16 h at room temperature. The solid was separated, washed with *n*-hexane

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(3 × 5 mL), and dried under vacuum to give **Ti2b** as a red-brown solid.

Data for **Ti2b** are as follows. Yield: 0.631 g (76%). Mp: 217−219 °C. IR (ATR): $\tilde{\nu}$ 2907, 2844, 1575, 1548, 1483, 1455, 1428, 1380, 1291, 1244, 1183, 1156, 1122, 1101, 1068, 1025, 883, 860, 851, 828, 816, 782, 762, 748, 738, 694, 680, 644, 620 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 298 K): δ 1.39−1.42 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 1.49−1.52 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 1.67−1.76 (m, 7H, $CH_{Ad}/CH_{2,Ad}$), 1.83 (s, 15H, C_5Me_5), 1.87−2.05 (m, 4H, $CH_{Ad}/CH_{2,Ad}$), 2.26−2.27 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 3.38 (s, 1H, CH_{exo}), 5.77−5.78 (m, 2H, 2 × C_5H_4), 6.18−6.20 (m, 1H, C_5H_4), 6.40−6.41 (m, 1H, C_5H_4), 6.64−6.67 (m, 1H, CH_{Aryl}), 7.04−7.14 (m, 8H, 8 × CH_{Aryl}), 7.34−7.41 (m, 2H, 2 × CH_{Aryl}), 7.50−7.53 (m, 2H, 2 × CH_{Aryl}), 7.61−7.62 (m, 1H, CH_{Aryl}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): due to slight solubility in C_6D_6 no satisfying spectrum was obtained. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 300 K): δ −21.4 ppm. Anal. Calcd for $C_{43}H_{48}ClOPTi$: C, 74.30; H, 6.96. Found: C, 74.55; H, 7.22. HR/MS: calculated m/z 695.2689 $[M + H^+]$; measured (ESI) m/z 695.2686.

*Synthesis of **Ti3a**. Method A.* Complex **Ti1a** (0.250 g, 0.331 mmol) was dissolved in 10 mL of tetrahydrofuran, and methyllithium (0.2 mL, 0.331 mmol; 1.6 M in diethyl ether) was added at room temperature. The reaction mixture was stirred for 16 h at room temperature. All volatiles were evaporated under vacuum. The residue was dissolved in 12 mL of toluene, the solution was filtered, and the precipitate of LiCl was washed with toluene (2 × 10 mL). The combined filtrates were evaporated under vacuum. The analyses of the NMR data showed that a mixture of the starting material **Ti1a**, complex **Ti3a**, and byproducts was obtained. The same results were obtained by using methylmagnesium bromide (1.0 equiv) and/or starting the reaction at −78 °C.

Method B. Complex **Ti1a** (0.150 g, 0.199 mmol) was dissolved in 10 mL of tetrahydrofuran, and methyllithium (0.25 mL, 0.397 mmol) was added at room temperature. The reaction mixture was stirred for 16 h at room temperature. All volatiles were evaporated under vacuum. The residue was was dissolved in 10 mL of toluene, the solution was filtered, and the precipitate of LiCl was washed with toluene (2 × 8 mL). The combined filtrates were evaporated under vacuum. The product was obtained as a mixture of complex **Ti3a** and $LiOC_6H_4PPh_2$ as a yellow solid (0.062 g).

Single crystals of $LiOC_6H_4PPh_2$ were obtained from a saturated *n*-hexane/toluene solution of the crude product at −26 °C.

Data for **Ti3a** are as follows. ^1H NMR (500 MHz, C_6D_6, 305 K): δ −0.18 (s, 6H, 2 × $TiCH_3$), 1.56 (s, 15H, C_5Me_5), 2.09 (s, 6H, 2 × $CH_{3,p\text{-tolyl}}$), 5.31−5.32 (m, 2H, 2 × C_5H_4), 5.43 (s, 1H, CH_{exo}), 5.85−5.86 (m, 2H, 2 × C_5H_4), 6.94−6.98 (m, 4H, 4 × *m*-$CH_{p\text{-tolyl}}CH_3$), 7.33−7.36 (m, 4H, 4 × *o*-$CH_{p\text{-tolyl}}CH_3$) ppm. ^{13}C NMR (126 MHz, C_6D_6, 305 K): δ 12.1 (C_5Me_5), 21.0 (2 × $CH_{3,p\text{-Tol}}$), 47.3 (2 × $TiCH_3$), 52.7 (CH_{exo}), 111.9 (2 × C_5H_4), 115.3 (2 × C_5H_4), 120.0 (C_5Me_5), 128.5 (4 × *m*-$CH_{p\text{-tolyl}}CH_3$), 129.4 (4 × *o*-$CH_{p\text{-tolyl}}CH_3$), 135.7 (2 × $C_{q,p\text{-tolyl}}CH_3$), 137.7 (2 × *p*-$C_{q,p\text{-tolyl}}CH_3$), 143.4 ($C_{q,ipso}$) ppm.

*Synthesis of **Ti3b**.* Complex **Ti1b** (0.250 g, 0.371 mmol) was dissolved in 15 mL of tetrahydrofuran, and methyllithium (0.2 mL, 0.371 mmol; 1.6 M in diethyl ether) was added at room temperature. The reaction mixture was stirred for 16 h at room temperature. All volatiles were evaporated under vacuum. The residue was dissolved in 12 mL of toluene, the solution was filtered, and the precipitate of LiCl was washed with toluene (2 × 10 mL). The combined filtrates were evaporated under vacuum. The same results were obtained by using methyl magnesium bromide (1.0 equiv) and/or starting the reaction at −78 °C. The product **Ti3b** was obtained as a yellow solid.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane solution at −4 °C.

Data for **Ti3b** are as follows. Yield: 0.083 g (54%). ^1H NMR (500 MHz, C_6D_6, 305 K): δ −0.27 (s, 6H, 2 × $TiCH_3$), 1.62−2.03 (m, 10H, 10 × $CH_{Ad}/CH_{2,Ad}$), 1.66 (s, 15H, C_5Me_5), 2.26−2.28 (m, 2H, 2 × $CH_{Ad}/CH_{2,Ad}$), 2.40−2.41 (m, 2H, 2 × $CH_{Ad}/CH_{2,Ad}$), 2.75 (s, 1H, CH_{exo}), 5.24−5.25 (m, 2H, 2 × C_5H_4), 5.92−5.93 (m, 2H, 2 × C_5H_4) ppm. ^{13}C NMR (126 MHz, C_6D_6, 305 K): δ 12.2 (C_5Me_5), 28.3 (CH_{Ad}), 28.4 (CH_{Ad}), 32.6 (2 × $CH_{2,Ad}$), 32.9 (2 × CH_{Ad}), 38.5 ($CH_{2,Ad}$), 38.9 (2 × $CH_{2,Ad}$), 44.8 (CH_{exo}), 44.9 (2 × $TiCH_3$), 110.8 (2 × C_5H_4), 114.6 (2 × C_5H_4), 119.6 (C_5Me_5), 132.3 ($C_{q,ipso}$) ppm.

*Synthesis of **L2**.* **L2** was prepared according to a slightly modified literature procedure.[48] To a solution of diisopropylamine (12.7 mL, 90.00 mmol) in 50 mL of tetrahydrofuran was added *n*-butyllithium (36.0 mL, 90.00 mmol; 2.5 M in *n*-hexane) at −78 °C. The solution was stirred for 30 min at −78 °C. Acetone (6.6 mL, 90.00 mmol) in 20 mL of tetrahydrofuran was added slowly at −78 °C to the in situ prepared LDA solution, and the reaction mixture was stirred for another 2 h at −78 °C. The reaction mixture was added via cannula to a solution of chlorodiphenylphosphine (16.1 mL, 90.00 mmol) in 50 mL of tetrahydrofuran, resulting in an orange suspension. The suspension was stirred for 16 h at room temperature. All volatiles were removed under vacuum, and 20 mL of toluene was added to the residue. The residue was filtered and washed with toluene (2 × 20 mL). The volatiles were removed under vacuum, and the residue was purified by distillation to give compound **L2** as a yellow oil.

Data for **L2** are as follows. Yield: 10.328 g (47%; bp: 130 °C at 2 × 10^{-2} mbar). ^1H NMR (500 MHz, C_6D_6, 305 K): δ 1.78 (s, 3H, CH_3), 2.89 (s, 2H, CH_2), 7.01−7.07 (m, 6H, 4 × *o*-$CH_{Ph}P$, 2 × *p*-$CH_{Ph}P$), 7.35−7.39 (m, 4H, 4 × *m*-$CH_{Ph}P$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ 30.3 (CH_3), 45.5 (d, $^1J_{C,P}$ = 22.4 Hz, CH_2), 128.8 (d, $^2J_{C,P}$ = 6.8 Hz, 4 × *o*-$CH_{Ph}P$), 129.1 (2 × *p*-$CH_{Ph}P$), 133.0 (d, $^3J_{C,P}$ = 19.8 Hz, 4 × *m*-$CH_{Ph}P$), 138.3 (d, $^1J_{C,P}$ = 14.9 Hz, 2 × $C_{q,Ph}P$), 203.3 (d, $^2J_{C,P}$ = 9.5 Hz, C═O) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 305 K): δ −18.4 ppm. Analytical data of compound **L2** are in accordance with the literature.[48]

*Synthesis of **Ti4a**.* In a glovebox compound **L2** (0.354 g, 1.461 mmol) in *n*-hexane (3 × 3 mL) was added to a solution of complex **Ti1a** (0.697 g, 1.461 mmol) in 10 mL of *n*-hexane. The suspension was stirred for 16 h at room temperature. The solid was separated, washed with *n*-hexane (2 × 5 mL), and dried under vacuum to give **Ti4a** as a yellow solid.

Data for **Ti4a** are as follows. Yield: 0.852 g (0.852 mmol, 81%). Mp: 145−147 °C dec. IR (ATR): $\tilde{\nu}$ 2906, 2854, 1586, 1510, 1480, 1433, 1373, 1250, 1193, 1166, 1150, 1121, 1070, 1047, 1024, 969, 943, 909, 866, 818, 799, 786, 742, 695, 653, 638, 585, 564 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 305 K): δ 1.79 (s, 3H, OC_qCH_3), 2.00 (s, 15H, C_5Me_5), 2.10 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.17 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.87 (dd, $^2J_{H,H}$ = 14.6 Hz, $^2J_{P,H}$ = 6.0 Hz, 1H, CH_2), 3.80 (d, $^2J_{H,H}$ = 14.6 Hz, 1H, CH_2), 5.01−5.02 (m, 1H, C_5H_4), 5.46−5.47 (m, 2H, 2 × C_5H_4), 6.89−6.90 (m, 1H, *o*-$CH_{p\text{-tolyl}}CH_3$), 6.94−7.04 (m, 9H, C_5H_4, 8 × CH_{Aryl}), 7.10−7.13 (m, 2H, 2 × *o*-$CH_{Ph}P$), 7.30−7.31 (m, 1H, *m*-$CH_{p\text{-tolyl}}CH_3$), 7.43−7.46 (m, 2H, 2 × *m*-$CH_{Ph}P$), 7.49−7.52 (m, 2H, 2 × *m*-$CH_{Ph}P$), 7.63−7.70 (m, 2H, 2 × *m*-$CH_{p\text{-tolyl}}CH_3$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ 13.1 (C_5Me_5), 20.9 ($CH_{3,p\text{-tolyl}}$), 21.0 ($CH_{3,p\text{-tolyl}}$), 32.5 (d, $^3J_{C,P}$ = 13.5 Hz, OC_qCH_3), 46.9 (d, $^1J_{C,P}$ = 17.9 Hz, CH_2), 66.2 (d, $^3J_{C,P}$ = 2.6 Hz, $C_{q,exo}$), 110.5 (C_5H_4), 112.0 (d, $^2J_{C,P}$ = 11.0 Hz, OC_q), 112.5 (C_5H_4), 113.2 (C_5H_4), 124.4 (C_5H_4), 125.3 (C_5Me_5), 127.8 (*p*-$CH_{Ph}P$)*, 128.6 (d, $^2J_{C,P}$ = 5.5 Hz, 2 × *o*-$CH_{Ph}P$), 128.65 (*p*-$CH_{Ph}P$), 128.69 (2 × *o*-$CH_{p\text{-tolyl}}CH_3$), 128.71 (d, $^2J_{C,P}$ = 6.9 Hz, 2 × *o*-$CH_{Ph}P$), 129.0 (2 × *o*-$CH_{p\text{-tolyl}}CH_3$), 130.1 (2 × *m*-$CH_{p\text{-tolyl}}CH_3$), 131.4 (2 × *m*-$CH_{p\text{-tolyl}}CH_3$), 132.9 (d, $^3J_{C,P}$ = 18.3 Hz, 2 × *m*-$CH_{Ph}P$), 134.2 (d, $^3J_{C,P}$ = 21.2 Hz, 2 × *m*-$CH_{Ph}P$), 136.2 ($C_{q,p\text{-tolyl}}CH_3$), 136.5 ($C_{q,p\text{-tolyl}}CH_3$), 141.3 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 141.9 (d, $^1J_{C,P}$ = 18.3 Hz, $C_{q,Ph}P$), 142.4 (d, $^1J_{C,P}$ = 16.5 Hz, $C_{q,Ph}P$), 143.7 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 150.1 ($C_{q,ipso}$) ppm (asterisk indicates overlay with C_6D_6 signal). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 305 K): δ −20.3 ppm.

*Synthesis of **Ti4b**.* In a glovebox compound **L2** (1.395 g, 5.757 mmol) in *n*-hexane (3 × 5 mL) was added to a solution of complex **Ti1b** (2.400 g, 5.757 mmol) in 20 mL of *n*-hexane. The suspension was stirred for 16 h at room temperature. The solid was separated, washed with *n*-hexane (3 × 10 mL), and dried under vacuum to give **Ti4b** as a yellow solid as a mixture of both diastereoisomers. NMR data are only given for the main diastereoisomer.

Data for **Ti4b** are as follows. Yield: 3.075 g (81%). Mp: 162−164 °C dec. IR (ATR): $\tilde{\nu}$ 3013, 2997, 2975, 2900, 2878, 2847, 1480, 1451, 1432, 1375, 1364, 1209, 1195, 1168, 1155, 1141, 1116, 1095, 1059, 1046, 1026, 995, 983, 943, 917, 880, 828, 816, 754, 742, 732, 697, 672, 659, 631, 563 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 305 K): δ 1.39 (s, 3H,

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OC_qCH_3), 1.42−2.51 (m, 15H, PCH_2, $CH/CH_{2,Ad}$), 1.91 (s, 15H, C_5Me_5), 3.23−3.25 (m, 1H, PCH_2), 5.08−5.09 (m, 1H, C_5H_4), 5.47−5.49 (m, 1H, C_5H_4), 5.50−5.52 (m, 1H, C_5H_4), 6.43−6.44 (m, 1H, C_5H_4), 6.99−7.02 (m, 1H, *p*-CH_{Ph}P), 7.08−7.11 (m, 1H, *p*-CH_{Ph}P), 7.17−7.20 (m, 4H, 4 × *o*-CH_{Ph}P), 7.81−7.85 (m, 4H, 4 × *m*-CH_{Ph}P) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ 12.9 (C_5Me_5), 25.9 (CH_{Ad}), 27.6 (CH_{Ad}), 27.9 (CH_{Ad}), 33.6 ($CH_{2,Ad}$), 33.63 (CH_{Ad}), 34.7 ($CH_{2,Ad}$), 35.8 (d, $^3J_{C,P}$ = 13.4 Hz, OC_qCH3), 37.3 ($CH_{2,Ad}$), 37.5 ($CH_{2,Ad}$), 39.3 ($CH_{2,Ad}$), 41.2 (d, $^1J_{C,P}$ = 18.6 Hz, PCH_2), 55.3 (d, $^3J_{C,P}$ = 2.2 Hz, $C_{q,exo}$), 104.3 (C_5H_4), 111.9 (C_5H_4), 112.1 (d, $^2J_{C,P}$ = 9.2 Hz, OC_q), 112.8 (C_5H_4), 120.1 (C_5H_4), 124.3 (C_5Me_5), 127.4 (*p*-CH_{Ph}P), 128.2 (d, $^2J_{C,P}$ = 5.0 Hz, 2 × *o*-CH_{Ph}P)*, 128.8 (d, $^2J_{C,P}$ = 7.4 Hz, 2 × *o*-CH_{Ph}P), 129.0 (*p*-CH_{Ph}P), 133.1 (d, $^2J_{C,P}$ = 16.8 Hz, 2 × *m*-CH_{Ph}P), 135.1 (d, $^2J_{C,P}$ = 22.8 Hz, 2 × *m*-CH_{Ph}P), 142.6 (d, $^1J_{C,P}$ = 19.7 Hz, $C_{q,Ph}$P), 142.9 (d, $^1J_{C,P}$ = 16.9 Hz, $C_{q,Ph}$P), 156.4 ($C_{q,ipso}$) ppm (asterisk indicates overlay with C_6D_6 signal). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 305 K): δ −22.0 ppm. HR/MS: calculated: *m*/*z* 659.2689 [M + H^+]; measured (ESI): *m*/*z* 659.2682.

Synthesis of ***Zr2***. In a glovebox compound **L2** (0.263 g, 1.086 mmol) in *n*-hexane (3 × 2 mL) was added to a solution of complex **Zr1** (0.500 g, 1.086 mmol) in 12 mL of *n*-hexane. The suspension was stirred for 16 h at room temperature. The solid was separated, washed with *n*-hexane (3 × 5 mL), and dried under vacuum to give **Zr2** as a pale yellow solid.

Only the clearly assignable signals of the main diastereoisomer are stated.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane solution at −4 °C.

Data for **Zr2** are as follows. Yield: 0.630 g (83%). Mp: 102−104 °C. IR (ATR): $\tilde{\nu}$ 2902, 2851, 1705, 1584, 1480, 1450, 1433, 1376, 1277, 1217, 1197, 1154, 1092, 1049, 1025, 995, 980, 954, 878, 801, 735, 695, 657, 627, 595, 561 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 305 K): δ 1.94 (s, 15H, C_5Me_5), 2.88 (d, $^2J_{H,H}$ = 16.7 Hz, 1H, PCH_2), 3.10−314 (m, 1H, PCH_2), 5.35−5.37 (m, 1H, C_5H_4), 5.55−5.57 (m, 1H, C_5H_4), 5.75−5.77 (m, 1H, C_5H_4), 6.27−6.29 (m, 1H, C_5H_4), 7.76−7.81 (m, 4H, 4 × *m*-CH_{Ph}P) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ 12.0 (C_5Me_5), 44.2 (d, $^1J_{C,P}$ = 16.7 Hz, CH_2), 55.9 ($C_{q,exo}$), 104.8 (C_5H_4), 107.8 (d, $^2J_{C,P}$ = 9.1 Hz, OC_q), 110.31 (C_5H_4), 110.32 (C_5H_4), 115.1 (C_5H_4), 120.9 (C_5Me_5), 154.9 ($C_{q,ipso}$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 305 K): δ −21.5 ppm. Anal. Calcd for $C_{40}H_{48}ClOPZr$: C, 68.39; H, 6.89. Found: C, 69.68; H, 6.89. HR/MS: calculated *m*/*z* 701.2257 [M + H^+]; measured (ESI) *m*/*z* 701.2249.

Synthesis of ***Hf2***. In a glovebox compound **L2** (0.199 g, 0.823 mmol) in *n*-hexane (3 × 3 mL) was added to a solution of complex **Hf1** (0.500 g, 0.823 mmol) in 20 mL of *n*-hexane. The suspension was stirred for 16 h at room temperature. The solid was separated, washed with *n*-hexane (3 × 8 mL), and dried under vacuum to give **Hf2** as a pale yellow solid.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane solution at −4 °C.

Data for **Hf2** are as follows. Yield: 0.505 g (72%). Mp: 91−93 °C dec. IR (ATR): $\tilde{\nu}$ 2955, 2914, 2861, 1510, 1450, 1433, 1377, 1285, 1243, 1189, 1174, 1104, 1069, 1038, 1025, 986, 984, 945, 912, 876, 844, 813, 798, 736, 695, 667 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 300 K): δ 1.71 (s, 3H, OC_qCH_3), 2.02 (s, 15H, C_5Me_5), 2.09 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.18 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.86−2.90 (m, 1H, PCH_2), 3.91−3.94 (m, 1H, PCH_2), 4.97−5.00 (m, 1H, C_5H_4), 5.46−5.47 (m, 1H, C_5H_4), 5.69−5.70 (m, 1H, C_5H_4), 6.79−6.80 (m, 1H, C_5H_4), 6.85−6.87 (m, 1H, CH_{Aryl}), 6.96−7.07 (m, 8H, 8 × CH_{Aryl}), 7.31−7.38 (m, 3H, 3 × CH_{Aryl}), 7.43−7.46 (m, 2H, 2 × *m*-CH_{Ph}P), 7.56−7.59 (m, 2H, 2 × *m*-CH_{Ph}P), 7.72−7.74 (m, 1H, CH_{Aryl}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 300 K): δ 12.0 (d, $^{TS}J_{C,P}$ = 1.9 Hz, C_5Me_5), 20.9 ($CH_{3,p\text{-tolyl}}$), 21.0 ($CH_{3,p\text{-tolyl}}$), 32.6 (d, $^3J_{C,P}$ = 12.0 Hz, OC_qCH_3), 42.3 (d, $^1J_{C,P}$ = 17.1 Hz, PCH_2), 66.4 (d, $^3J_{C,P}$ = 2.3 Hz, $C_{q,exo}$), 104.9 (d, $^2J_{C,P}$ = 10.8 Hz, OC_q), 109.2 (C_5H_4), 109.6 (C_5H_4), 110.4 (C_5H_4), 118.5 (C_5H_4), 120.1 (C_5Me_5), 128.0 (2 × *o*-$CH_{p\text{-tolyl}}CH_3$), 128.5 (*p*-CH_{Ph}P), 128.54 (*p*-CH_{Ph}P), 128.6 (d, $^2J_{C,P}$ = 5.7 Hz, 2 × *o*-CH_{Ph}P), 128.7 (d, $^2J_{C,P}$ = 6.9 Hz, 2 × *o*-CH_{Ph}P), 129.1 (2 × *o*-$CH_{p\text{-tolyl}}CH_3$), 130.1 (2 × *m*-$CH_{p\text{-tolyl}}CH_3$), 131.0 (2 × *m*-$CH_{p\text{-tolyl}}CH_3$), 133.3 (d, $^3J_{C,P}$ = 18.9 Hz, 2 × *m*-CH_{Ph}P), 133.9 (d, $^3J_{C,P}$ = 20.8 Hz, 2 × *m*-CH_{Ph}P), 136.2 ($C_{q,p\text{-tolyl}}CH_3$), 136.3 ($C_{q,p\text{-tolyl}}CH_3$), 141.5 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 141.8 (d, $^1J_{C,P}$ = 16.7 Hz, $C_{q,Ph}$P), 142.1 (d, $^1J_{C,P}$ = 18.4 Hz, $C_{q,Ph}$P), 144.3 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 146.5 ($C_{q,ipso}$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 300 K): δ −20.5 ppm. Anal. Calcd for $C_{45}H_{48}ClHfOP$: C, 63.60; H, 5.69. Found: C, 63.55; H, 5.61. HR/MS: calculated *m*/*z* 815.2908 [M − Cl^-]; measured (ESI) *m*/*z* 815.2909.

Synthesis of ***Ti5a***. To a solution of complex **Ti4a** (0.400 g, 0.556 mmol) in 10 mL of tetrahydrofuran was added a methyllithium solution (0.4 mL, 0.556 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 10 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 8 mL). All volatiles were removed under vacuum to give complex **Ti5a** as a pale yellow solid.

Data for **Ti5a** are as follows. Yield: 0.268 g (69%). Mp: 85−87 °C dec. IR (ATR): $\tilde{\nu}$ 3052, 3019, 2966, 2904, 1510, 1479, 1433, 1375, 1261, 1147, 1120, 1070, 1039, 1024, 943, 911, 866, 841, 813, 797, 733, 695, 652, 636, 586, 565 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 305 K): δ 0.43 (s, 3H, $TiCH_3$), 1.51 (s, 3H, OC_qCH_3), 1.87 (s, 15H, C_5Me_5), 2.14 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.17 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.77 (dd, $^2J_{H,H}$ = 14.6 Hz, $^2J_{P,H}$ = 6.2 Hz, 1H, CH_2), 3.69 (d, $^2J_{H,H}$ = 14.6 Hz, 1H, CH_2), 4.84−4.85 (m, 1H, C_5H_4), 5.13−5.17 (m, 2H, 2 × C_5H_4), 6.81−6.83 (m, 1H, C_5H_4), 6.92−6.94 (m, 1H, $CH_{p\text{-tolyl}}$), 6.97−7.05 (m, 7H, 2 × *o*-CH_{Ph}P, 5 × $CH_{p\text{-tolyl}}$), 7.10−7.13 (m, 2H, 2 × *o*-CH_{Ph}P) 7.32−7.34 (m, 1H, $CH_{p\text{-tolyl}}$), 7.42−7.46 (m, 2H, 2 × *m*-CH_{Ph}P), 7.49−7.52 (m, 2H, 2 × *m*-CH_{Ph}P), 7.55−7.57 (m(br), 2H, 2× $CH_{p\text{-tolyl}}$), 7.88−7.90 (m, 1H, $CH_{p\text{-tolyl}}$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ 12.3 (C_5Me_5), 21.0 ($CH_{3,p\text{-tolyl}}$), 21.02 ($CH_{3,p\text{-tolyl}}$), 33.0 (d, $^3J_{C,P}$ = 13.8 Hz, $OCqCH_3$), 38.7 ($TiCH_3$), 46.5 (d, $^1J_{C,P}$ = 17.2 Hz, PCH_2), 66.6 (d, $^3J_{C,P}$ = 2.5 Hz, $C_{q,exo}$), 107.8 (d, $^2J_{C,P}$ = 10.9 Hz, OC_q), 109.1 (C_5H_4), 109.2 (C_5H_4), 109.3 (C_5H_4), 119.8 (C_5Me_5), 120.3 (C_5H_4), 127.8 (*p*-CH_{Ph}P)*, 128.4 (*p*-CH_{Ph}P), 128.5 (d, $^2J_{C,P}$ = 5.5 Hz, 2 × *o*-CH_{Ph}P), 128.54 (2 × *o*-$CH_{p\text{-tolyl}}CH_3$), 128.6 (d, $^2J_{C,P}$ = 6.9 Hz, 2 × *o*-CH_{Ph}P), 128.9 (2 × *o*-$CH_{p\text{-tolyl}}CH_3$), 130.3 (2 × *m*-$CH_{p\text{-tolyl}}CH_3$), 131.6 (2 × *m*-$CH_{p\text{-tolyl}}CH_3$), 133.0 (d, $^3J_{C,P}$ = 18.5 Hz, 2 × *m*-CH_{Ph}P), 133.2 ($C_{q,p\text{-tolyl}}CH_3$), 133.3 ($C_{q,p\text{-tolyl}}CH_3$), 134.1 (d, $^3J_{C,P}$ = 21.0 Hz, 2 × *m*-CH_{Ph}P), 136.0 (d, $^1J_{C,P}$ = 35.1 Hz, $C_{q,Ph}$P), 136.1 (d, $^1J_{C,P}$ = 26.5 Hz, $C_{q,Ph}$P), 142.3 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 144.1 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 145.2 ($C_{q,ipso}$) ppm (asterisk indicates overlay with C_6D_6 signal). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 305 K): δ −20.2 ppm.

Synthesis of ***Ti5b***. To a solution of complex **Ti4b** (1.000 g, 1.517 mmol) in 20 mL of tetrahydrofuran was added a methyllithium solution (1.0 mL, 1.517 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 15 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 10 mL). All volatiles were removed under vacuum to give complex **Ti5b** as a pale yellow solid.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane solution at −26 °C.

Data for **Ti5b** are as follows. Yield: 0.880 g (91%). Mp: 170−172 °C dec. IR (ATR): $\tilde{\nu}$ 3014, 2990, 2965, 2890, 2848, 1479, 1464, 1450, 1432, 1374, 1364, 1233, 1209, 1196, 1165, 1141, 1116, 1091, 1059, 1045, 1026, 982, 952, 912, 878, 847, 814, 754, 745, 732, 696, 657, 631, 583, 560 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 305 K): δ 0.33 (s, 3H, $TiCH_3$), 1.41 (s, 3H, OC_qCH_3), 1.51−1.72 (m, 8H, $CH_{Ad}/CH_{2,Ad}$), 1.85 (s, 15H, C_5Me_5), 2.09−2.12 (m, 2H, $CH_{Ad}/CH_{2,Ad}$), 2.25−2.26 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.36−2.39 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.58−2.59 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.72−2.75 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.78−2.81 (m, 1H, CH_2), 3.13−3.17 (m, 1H, CH_2), 4.91−4.92 (m, 1H, C_5H_4), 5.16−5.17 (m, 1H, C_5H_4), 5.36−5.36 (m, 1H, C_5H_4), 6.20−6.21 (m, 1H, C_5H_4), 7.03−7.09 (m, 2H, 2 × *p*-CH_{Ph}P), 7.14−7.19 (m, 4H, 4 × *o*-CH_{Ph}P)*, 7.64−7.67 (m, 2H, 2 × *m*-CH_{Ph}P), 7.77−7.80 (m, 2H, 2 × *m*-CH_{Ph}P) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ 12.2 (C_5Me_5), 27.8 (CH_{Ad}), 28.1 (CH_{Ad}), 33.0 (CH_{Ad}), 33.9 (CH_{Ad}), 34.0 ($CH_{2,Ad}$), 34.8 ($CH_{2,Ad}$), 35.1 (d, $^3J_{C,P}$ = 13.1 Hz, OC_qCH_3), 36.3 (d, $^{TS}J_{C,P}$ = 5.1 Hz, $TiCH_3$), 37.5 ($CH_{2,Ad}$), 37.6 ($CH_{2,Ad}$), 39.6 ($CH_{2,Ad}$), 42.6 (d, $^1J_{C,P}$ = 15.9 Hz, PCH_2), 55.6 ($C_{q,exo}$), 103.1 (C_5H_4), 107.9 (d, $^2J_{C,P}$ = 9.4 Hz, OC_q), 108.0 (C_5H_4), 108.7 (C_5H_4), 116.6 (C_5H_4), 119.0 (C_5Me_5), 127.8 (*p*-CH_{Ph}P)*, 128.4 (d, $^2J_{C,P}$ = 5.8 Hz, 2 × *o*-

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$CH_{Ph}P$) 128.8 (d, $^2J_{C,P}$ = 7.4 Hz, 2 × *o*-$CH_{Ph}P$), 128.82 (*p*-$CH_{Ph}P$), 132.9 (d, $^3J_{C,P}$ = 18.8 Hz, 2 × *m*-$CH_{Ph}P$), 134.4 (d, $^3J_{C,P}$ = 22.2 Hz, 2 × *m*-$CH_{Ph}P$), 142.6 (d, $^1J_{C,P}$ = 20.1 Hz, $C_{q,Ph}P$), 143.0 (d, $^1J_{C,P}$ = 16.8 Hz, $C_{q,Ph}P$), 151.0 ($C_{q,ipso}$) ppm (asterisk indicates overlay with C_6D_6 signal). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 305 K): δ −23.9 ppm. HR/MS: calculated *m*/*z* 639.3235 [M + H^+]; measured (ESI) *m*/*z* 639.3242.

Synthesis of ***Zr3***. To a solution of complex **Zr2** (0.500 g, 0.712 mmol) in 15 mL of tetrahydrofuran was added a methyllithium solution (0.4 mL, 0.712 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 12 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 8 mL). All volatiles were removed under vacuum to give complex **Zr3** as a pale yellow solid.

Only the clearly assignable signals of the main diastereoisomer are stated.

Data for **Zr3** are as follows. Yield: 0.303 g (62%). Mp: 94−96 °C dec. IR (ATR): $\tilde{\nu}$ 3014, 2990, 2965, 2890, 2848, 1479, 1464, 1450, 1432, 1374, 1364, 1233, 1209, 1196, 1165, 1141, 1116, 1091, 1059, 1045, 1026, 982, 952, 912, 878, 847, 814, 754, 745, 732, 696, 657, 631, 583, 560 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 298 K): δ −0.05 (s, 3H, $ZrCH_3$), 1,86 (s, 15H, C_5Me_5), 5.11−5.13 (m, 1H, C_5H_4), 5.42−5.44 (m, 1H, C_5H_4), 5.57−5.58 (m, 1H, C_5H_4), 6.19−6.21 (m, 1H, C_5H_4), 7.57−7.60 (m, 2H, 2 × *m*-$CH_{Ph}P$), 7.69−7.72 (m, 2H, 2 × *m*-$CH_{Ph}P$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ 11.6 (C_5Me_5), 23.1 ($ZrCH_3$), 56.0 ($C_{q,exo}$), 104.0 (C_5H_4), 105.4 (C_5H_4), 105.5 (C_5H_4), 114.1 (C_5H_4), 117.5 (C_5Me_5), 150.1 ($C_{q,ipso}$) ppm $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K): δ −22.2 ppm. HR/MS: calculated *m*/*z* 681.2797 [M + H^+]; measured (ESI) *m*/*z* 681.2793.

Synthesis of ***Hf3***. To a solution of complex **Hf2** (0.400 g, 0.471 mmol) in 15 mL of tetrahydrofuran was added a methyllithium solution (0.3 mL, 0.471 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed, and the residue was dissolved in 12 mL of toluene. The solution was filtered, and the residue was washed with toluene (2 × 8 mL). All volatiles were removed under vacuum to give complex **Hf3** as a colorless solid.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated *n*-hexane solution at −4 °C.

Data for **Hf3** are as follows. Yield: 0.222 g (57%). Mp: 109−111 °C dec. IR (ATR): $\tilde{\nu}$ 3023, 2916, 2863, 1585, 1510, 1480, 1433, 1377, 1261, 1194, 1166, 1149, 1120, 1069, 1039, 1024, 967, 945, 911, 870, 809, 797, 736, 695 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 300 K): δ −0.04 (s, 3H, $HfCH_3$), 1.52 (s, 3H, OC_qCH_3), 1.91 (s, 15H, C_5Me_5), 2.12 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.20 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.79 (dd, 1H, $^2J_{P,H}$ = 5.7 Hz, $^2J_{H,H}$ = 14.5 Hz, PCH_2), 3.89−3.91 (m, 1H, PCH_2), 5.00−5.02 (m, 1H, C_5H_4), 5.15−5.16 (m, 1H, C_5H_4), 5.44−5.45 (m, 1H, C_5H_4), 6.67−6.68 (m, 1H, C_5H_4), 6.87−6.88 (m, 1H, CH_{Aryl}), 6.94−7.15 (m, 11H, 11 × CH_{Aryl}), 7.32−7.34 (m, 1H, CH_{Aryl}), 7.43−7.46 (m, 2H, 2 × *m*-$CH_{Ph}P$), 7.57−7.60 (m, 2H, 2 × *m*-$CH_{Ph}P$), 7.89−7.91 (m, 1H, CH_{Aryl}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 300 K): δ 11.6 (C_5Me_5), 20.9 ($CH_{3,p\text{-tolyl}}$), 21.1 ($CH_{3,p\text{-tolyl}}$), 28.3 ($HfCH_3$), 33.1 (d, $^3J_{C,P}$ = 11.9 Hz, OC_qCH_3), 46.0 (d, $^1J_{C,P}$ = 16.8 Hz, PCH_2), 66.6 ($C_{q,exo}$), 103.0 (d, $^2J_{C,P}$ = 10.9 Hz, OC_q), 106.3 (C_5H_4), 108.7 (C_5H_4), 109.0 (C_5H_4), 116.7 (C_5H_4), 117.0 (C_5Me_5), 128.1 (*p*-$CH_{Ph}P$)*, 128.5 (*p*-$CH_{Ph}P$), 128.58 (d, $^2J_{C,P}$ = 3.3 Hz, 2 × *o*-$CH_{Ph}P$), 128.6 (d, $^2J_{C,P}$ = 6.7 Hz, 2 × *o*-$CH_{Ph}P$), 129.0 (2 × *o*-$CH_{p\text{-tolyl}}CH_3$), 129.3 (2 × *o*-$CH_{p\text{-tolyl}}CH_3$), 130.2 (2 × *m*-$CH_{p\text{-tolyl}}CH_3$), 131.1 (2 × *m*-$CH_{p\text{-tolyl}}CH_3$), 133.4 (d, $^3J_{C,P}$ = 19.2 Hz, 2 × *m*-$CH_{Ph}P$), 133.8 (d, $^3J_{C,P}$ = 20.4 Hz, 2 × *m*-$CH_{Ph}P$), 136.0 ($C_{q,p\text{-tolyl}}CH_3$), 136.1 ($C_{q,p\text{-tolyl}}CH_3$), 137.9 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 141.7 (d, $^1J_{C,P}$ = 16.5 Hz, $C_{q,Ph}P$), 142.2 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 142.4 (d, $^1J_{C,P}$ = 15.8 Hz, $C_{q,Ph}P$), 144.7 ($C_{q,ipso}$) ppm (asterisk indicates overlay with C_6D_6 signal). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 300 K): δ −20.7 ppm. Anal. Calcd for $C_{46}H_{51}HfOP$: C, 66.62; H, 6.20. Found: C, 66.45; H, 6.50. HR/MS: calculated *m*/*z* 853.3041 [M + Na^+]; measured (ESI) *m*/*z* 853.3040.

Synthesis of ***Ti6a***. A mixture of complex **Ti5a** (0.200 g, 0.290 mmol) and $B(C_6F_5)_3$ (0.147 g, 0.290 mmol) was stirred in 10 mL of toluene. By stopping the stirring process after a few minutes, the development of two phases can be observed due to the formation of complex **Ti6a**. The solvent was decanted, and the residue was washed with *n*-hexane (3 × 8 mL) and dried under vacuum to give complex **Ti6a** as an orange solid.

Data for **Ti6a** are as follows. Yield: 0.303 g (86%). Mp: 90−92 °C. IR (ATR): $\tilde{\nu}$ 3021, 2924, 2863, 1640, 1509, 1454, 1380, 1267, 1195, 1082, 1022, 952, 935, 895, 864, 835, 800, 740, 696, 659, 636, 604, 568 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 305 K): δ 0.50 (s(br), 3H, BCH_3), 1.95 (s, 15H, C_5Me_5), 2.19 (d, $^4J_{P,H}$ = 2.1 Hz, 3H, OC_qCH_3), 2.30 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.35 (s, 3H, $CH_{3,p\text{-tolyl}}$), 3.50 (dd, $^2J_{P,H}$ = 13.6 Hz, $^2J_{H,H}$ = 16.7 Hz, 1H, CH_2), 4.48 (dd, $^2J_{P,H}$ = 5.7 Hz, $^2J_{H,H}$ = 16.7 Hz, 1H, CH_2), 4.64−4.65 (m, 1H, C_5H_4), 5.17−5.19 (m, 1H, C_5H_4), 6.67−6.71 (m, 1H, CH_{Aryl}), 6.77−6.81 (m, 1H, C_5H_4), 6.83−6.84 (m, 1H, C_5H_4), 6.95−6.96 (m, 2H, 2 × CH_{Aryl}), 6.99−7.01 (m, 2H, 2 × CH_{Aryl}), 7.09−7.19 (m, 4H, 4 × CH_{Aryl}), 7.26−7.31 (m, 2H, 2 × CH_{Aryl}), 7.43−7.45 (m, 1H, CH_{Aryl}), 7.48−7.55 (m 5H, 5 × CH_{Aryl}), 7.59−7.63 (m, 1H, CH_{Aryl}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 305 K): δ 9.8 (BCH_3)*, 13.1 (C_5Me_5), 21.0 ($CH_{3,p\text{-tolyl}}$), 21.1 ($CH_{3,p\text{-tolyl}}$), 32.9 (d, $^3J_{C,P}$ = 2.7 Hz, OCqCH3), 59.6 (d, $^1J_{C,P}$ = 35.8 Hz, CH_2), 66.6 ($C_{q,exo}$), 108.4 (C_qO), 110.6 (C_5H_4), 118.2 (C_5H_4), 118.6 (d, $^{TS}J_{C,P}$ = 3.1 Hz, C_5H_4), 120.6 (C_5H_4), 128.6 (C_5Me_5), 129.0 ($C_{q,Ar}B$)*, 129.3 (d, $^2J_{C,P}$ = 9.0 Hz, 2 × *o*-$CH_{Ph}P$), 129.33 (d, $^2J_{C,P}$ = 5.3 Hz, 2 × *o*-$CH_{Ph}P$), 129.4 (*p*-$CH_{Ph}P$), 130.4 (*p*-$CH_{Ph}P$), 130.7 (2 × $CH_{p\text{-tolyl}}$), 130.8 (2 × $CH_{p\text{-tolyl}}$), 131.68 (2 × $CH_{p\text{-tolyl}}$, 131.7 (2 × $CH_{p\text{-tolyl}}$), 132.7 (2 × *m*-$CH_{Ph}P$), 132.73 (d, $^1J_{C,P}$ = 34.4 Hz, $C_{q,Ph}P$), 133.3 (d, $^1J_{C,P}$ = 28.6 Hz, $C_{q,Ph}P$), 133.9 (d, $^3J_{C,P}$ = 9.3 Hz, 2 × *m*-$CH_{Ph}P$), 136.9 (dm, $^1J_{C,F}$ = 241.9 Hz, $C_{q,Ar}F$), 137.8 ($C_{q,p\text{-tolyl}}CH_3$), 137.9 (dm, $^1J_{C,F}$ = 241.9 Hz, $C_{q,Ar}F$), 138.3 ($C_{q,p\text{-tolyl}}CH_3$), 140.1 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 140.9 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 148.7 (dm, $^1J_{C,F}$ = 237.6 Hz, $C_{q,Ar}F$), 149.2 ($C_{q,ipso}$) ppm (asterisk indicates assignment by $^1H/^{13}C$-HMQC/HMBC spectra). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 305 K): δ −14.9 ppm. $^{19}F\{^1H\}$ NMR (470 MHz, CD_2Cl_2, 305 K): δ −167.9 (m, 6F, *m*-$F_{Ar}B$), −165.4 (t, $^3J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), −133.0 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 305 K): δ 22.0 ppm.

Synthesis of ***Ti6b***. A mixture of complex **Ti5b** (0.400 g, 0.626 mmol) and $B(C_6F_5)_3$ (0.321 g, 0.626 mmol) was stirred in 10 mL of toluene. When the stirring process was stopped after a few minutes, the development of two phases could be observed due to the formation of complex **Ti6b**. The solvent was decanted, and the residue was washed with *n*-hexane (3 × 10 mL) and dried under vacuum to give complex **Ti6b** as an orange solid.

Crystals suitable for single-crystal X-ray diffraction were obtained from a saturated dichloromethane solution, layered with cyclohexane at −4 °C.

Data for **Ti6b** are as follows. Yield: 0.657 g (91%). Mp: 180−182 °C. IR (ATR): $\tilde{\nu}$ 2895, 2859, 1638, 1509, 1482, 1453, 1436, 1379, 1368, 1265, 1191, 1077, 1027, 995, 982, 963, 949, 934, 922, 876, 838, 801, 753, 737, 695, 660, 635, 617, 604, 591, 566 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 305 K): δ 0.50 (s(br), 3H, BCH_3), 1.65−1.78 (m, 8H, $CH_{Ad}/CH_{2,Ad}$), 1.89 (s, 15H, C_5Me_5), 1.94 (d, $^4J_{H,P}$ = 2.2 Hz, 3H, CH_3), 1.98−2.03 (m, 3H, $CH_{Ad}/CH_{2,Ad}$), 2.27−2.30 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.51−2.52 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.63−2.66 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 3.48 (dd, $^2J_{P,H}$ = 13.6 Hz, $^2J_{H,H}$ = 16.8 Hz, 1H, CH_2), 4.63 (dd, $^2J_{P,H}$ = 7.5 Hz, $^2J_{H,H}$ = 16.8 Hz, 1H, CH_2), 5.10−5.12 (m, 1H, C_5H_4), 5.29−5.30 (m, 1H, C_5H_4), 6.37−6.40 (m, 1H, C_5H_4), 6.93−6.94 (m, 1H, C_5H_4), 7.05−7.08 (m(br), 2H, 2 × CH_{Ph}), 7.23−7.27 (m, 2H, 2 × CH_{Ph}), 7.46−7.57 (m, 5H, 5 × CH_{Ph}), 7.61−7.64 (m, 1H, CH_{Ph}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 305 K): δ 9.9 (BCH_3)**, 13.0 (C_5Me_5), 27.3 (CH_{Ad}), 27.8 (CH_{Ad}), 31.5 (CH_{Ad}), 32.2 ($CH_{2,Ad}$), 34.3 ($CH_{2,Ad}$), 36.1 ($CH_{2,Ad}$), 36.6 (CH_{Ad}), 37.2 (d, $^3J_{C,P}$ = 2.2 Hz, CH_3), 38.1 ($CH_{2,Ad}$), 39.2 ($CH_{2,Ad}$), 53.5 (d, $^1J_{C,P}$ = 31.6 Hz, CH_2)*, 54.6 ($C_{q,exo}$), 108.3 (C_5H_4), 108.8 (C_qO), 113.4 (C_5H_4), 115.6 (d, $^{TS}J_{C,P}$ = 3.0 Hz, C_5H_4), 121.6 (C_5H_4), 127.9 (C_5Me_5), 129.2 (d, $^2J_{C,P}$ = 9.2 Hz, 4 × *o*-$CH_{Ph}P$), 130.5 ($C_{q,Ar}B$)**, 131.5 (*p*-$CH_{Ph}P$), 132.5 (*p*-$CH_{Ph}P$), 133.2 (d, $^1J_{C,P}$ = 28.1 Hz, $C_{q,Ph}P$), 133.8 (d, $^3J_{C,P}$ = 9.5 Hz, 4 × *m*-$CH_{Ph}P$), 134.1 (d, $^1J_{C,P}$ = 34.0 Hz,

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$C_{q,Ph}P$), 136.9 (dm, $^{1}J_{C,F}$ = 244.0 Hz, $C_{q,Ar}F$), 138.0 (dm, $^{1}J_{C,F}$ = 242.6 Hz, $C_{q,Ar}F$), 148.8 (dm, $^{1}J_{C,F}$ = 238.5 Hz, $C_{q,Ar}F$), 153.4 (d, $^{TS}J_{C,P}$ = 2.8 Hz, $C_{q,ipso}$) ppm (asterisk indicates overlay with C_6D_6 signal). ** = assignment by $^{1}H/^{13}C$-HMQC/HMBC spectra $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 305 K): δ −14.9 ppm. $^{19}F\{^{1}H\}$ NMR (470 MHz, CD_2Cl_2, 305 K): δ −167.9 (m, 6F, *m*-$F_{Ar}B$), −165.4 (t, $^{3}J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), −133.0 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 305 K): δ 28.4 ppm. Anal. Calcd for $C_{59}H_{51}BF_{15}OPTi$: C, 61.59; H, 4.47. Found: C, 61.67; H, 4.76. HR/MS: calculated *m*/*z* 623.2922 [M^+]; measured (ESI) *m*/*z* 623.2930.

Synthesis of ***Zr4***. A mixture of complex **Zr3** (0.250 g, 0.367 mmol) and $B(C_6F_5)_3$ (0.188 g, 0.367 mmol) was stirred in 10 mL of toluene. When the stirring process was stopped after a few minutes, the development of two phases could be observed due to the formation of complex **Zr4**. The solvent was decanted, and the residue was washed with *n*-hexane (3 × 5 mL) and dried under vacuum to give complex **Zr4** as a yellow solid.

Data for **Zr4** are as follows. Yield: 0.371 g (85%). Mp: 84−86 °C. IR (ATR): $\tilde{\nu}$ 2895, 2859, 1638, 1509, 1482, 1453, 1436, 1379, 1368, 1265, 1191, 1077, 1027, 995, 982, 963, 949, 934, 922, 876, 838, 801, 753, 737, 695, 660, 635, 617, 604, 591, 566 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 305 K): δ 0.51 (s(br), 3H, BCH_3), 1.65−1.76 (m, 8H, $CH_{Ad}/CH_{2,Ad}$), 1.89 (s, 15H, C_5Me_5), 1.93 (d, 3H, CH_3), 1.97−2.01 (m, 3H, $CH_{Ad}/CH_{2,Ad}$), 2.28−2.30 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.39−2.40 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.70−2.73 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 3.38 (dd, $^{2}J_{P,H}$ = 14.7 Hz, $^{2}J_{H,H}$ = 16.8 Hz, 1H, CH_2), 4.42 (dd, $^{2}J_{P,H}$ = 7.5 Hz, $^{2}J_{H,H}$ = 16.8 Hz, 1H, CH_2), 5.45−5.47 (m, 1H, C_5H_4), 5.63−5.64 (m, 1H, C_5H_4), 6.38−6.41 (m, 1H, C_5H_4), 6.83−6.85 (m, 1H, C_5H_4), 7.21−7.26 (m, 4H, 4 × CH_{Ph}), 7.49−7.51 (m, 3H, 3 × CH_{Ph}), 7.59−7.62 (m, 2H, 2 × CH_{Ph}), 7.66−7.70 (m, 1H, CH_{Ph}) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 305 K): δ 10.0 (BCH_3)*, 11.8 (C_5Me_5), 27.3 (CH_{Ad}), 27.8 (CH_{Ad}), 31.8 (CH_{Ad}), 32.1 ($CH_{2,Ad}$), 34.4 ($CH_{2,Ad}$), 36.5 ($CH_{2,Ad}$), 36.8 (CH_{Ad}), 38.0 ($CH_{2,Ad}$), 38.5 (d, $^{3}J_{C,P}$ = 3.7 Hz, CH_3), 39.4 ($CH_{2,Ad}$), 51.7 (d, $^{1}J_{C,P}$ = 26.9 Hz, CH_2), 55.2 ($C_{q,exo}$), 105.7 (C_qO), 108.1 (C_5H_4), 113.4 (C_5H_4), 113.8 (d, $^{TS}J_{C,P}$ = 2.6 Hz, C_5H_4), 118.7 (C_5H_4), 125.0 (C_5Me_5), 129.2 ($C_{q,Ar}B$)*, 129.7 (d, $^{2}J_{C,P}$ = 9.5 Hz, 2 × *o*-$CH_{Ph}P$), 130.7 (d, $^{2}J_{C,P}$ = 10.7 Hz, 2 × *o*-$CH_{Ph}P$), 131.5 (d, $^{1}J_{C,P}$ = 37.9 Hz, $C_{q,Ph}P$), 131.6 (*p*-$CH_{Ph}P$), 131.9 (d, $^{1}J_{C,P}$ = 33.4 Hz, $C_{q,Ph}P$), 132.7 (d, $^{3}J_{C,P}$ = 10.5 Hz, 2 × *m*-$CH_{Ph}P$), 133.0 (*p*-$CH_{Ph}P$), 134.0 (d, $^{3}J_{C,P}$ = 12.8 Hz, 2 × *m*-$CH_{Ph}P$), 136.9 (dm, $^{1}J_{C,F}$ = 245.9 Hz, $C_{q,Ar}F$), 138.0 (dm, $^{1}J_{C,F}$ = 244.3 Hz, $C_{q,Ar}F$), 148.8 (dm, $^{1}J_{C,F}$ = 242.6 Hz, $C_{q,Ar}F$), 151.7 ($C_{q,ipso}$) ppm (asterisk indicates assignment by $^{1}H/^{13}C$-HMQC/HMBC spectra). $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 305 K): δ −14.9 ppm. $^{19}F\{^{1}H\}$ NMR (470 MHz, CD_2Cl_2, 305 K): δ −167.7 (m, 6F, *m*-$F_{Ar}B$), −165.0 (t, $^{3}J_{F,F}$ = 20.2 Hz, 3F, *p*-$F_{Ar}B$), −133.4 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 305 K): δ 19.1 ppm. Anal. Calcd for $C_{59}H_{51}BF_{15}OPZr$: C, 59.35; H, 4.31. Found: C, 59.32; H, 4.31. HR/MS: calculated *m*/*z* 665.2490 [M^+]; measured (ESI) *m*/*z* 665.2487.

Synthesis of ***Hf4***. A mixture of complex **Hf3** (0.100 g, 0.121 mmol) and $B(C_6F_5)_3$ (0.062 g, 0.121 mmol) was stirred in 10 mL of toluene. By stopping the stirring process after a few minutes, the development of two phases can be observed due to the formation of complex **Hf4**. The solvent was decanted, the residue was washed with *n*-hexane (3 × 5 mL), and dried under vacuum to give complex **Hf4** as a yellow solid.

Data for **Hf4** are as follows. Yield: 0.132 g (82%). Mp: 94−96 °C. IR (ATR): $\tilde{\nu}$ 2919, 2860, 1640, 1509, 1452, 1379, 1265, 1195, 1081, 1023, 964, 951, 935, 868, 815, 799, 764, 738, 690, 659, 639 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ 0.50 (s(br), 3H, BCH_3), 2.00 (s, 15H, C_5Me_5), 2.16 (d, 3H, $^{4}J_{P,H}$ = 2.1 Hz, CH_3), 2.33 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.34 (s, 3H, $CH_{3,p\text{-tolyl}}$), 3.49 (dd, $^{2}J_{P,H}$ = 14.7 Hz, $^{2}J_{H,H}$ = 16.8 Hz, 1H, CH_2), 4.25 (dd, $^{2}J_{P,H}$ = 5.8 Hz, $^{2}J_{H,H}$ = 16.8 Hz, 1H, CH_2), 4.79−4.81 (m, 1H, C_5H_4), 5.43−5.45 (m, 1H, C_5H_4), 6.69−6.74 (m, 2H, 2 × C_5H_4), 7.04−7.17 (m, 9H, 9 × CH_{Aryl}), 7.28−7.31 (m, 2H, 2 × CH_{Aryl}) 7.46−7.48 (m, 1H, CH_{Aryl}), 7.50−7.60 (m, 5H, 5 × CH_{Aryl}), 7.67−7.69 (m, 1H, CH_{Aryl}) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ 9.9 (BCH_3)*, 11.8 (C_5Me_5), 20.97 ($CH_{3,p\text{-tolyl}}$), 21.0 ($CH_{3,p\text{-tolyl}}$), 33.9 (d, $^{3}J_{C,P}$ = 2.9 Hz, CH_3), 56.7 (d, $^{1}J_{C,P}$ = 33.4 Hz, CH_2), 66.7 ($C_{q,exo}$), 102.4 (OC_q), 108.8 (C_5H_4), 115.8 (C_5H_4), 116.0 (d, $^{TS}J_{C,P}$ = 4.1 Hz, C_5H_4), 117.0 (C_5H_4), 123.8 (C_5Me_5), 129.0 ($C_{q,Ar}B$)*, 129.3 (*p*-$CH_{Ph}P$), 129.6 (*p*-$CH_{Ph}P$), 129.7 (d, $^{2}J_{C,P}$ = 8.2 Hz, 2 × *o*-$CH_{Ph}P$), 130.1 (d, $^{1}J_{C,P}$ = 42.4 Hz, $C_{q,Ph}P$), 130.2 (2 × *o*-$CH_{p\text{-tolyl}}CH_3$), 130.5 (2 × *o*-$CH_{p\text{-tolyl}}CH_3$), 130.8 (d, $^{2}J_{C,P}$ = 10.2 Hz, 2 × *o*-$CH_{Ph}P$), 131.5 (d, $^{1}J_{C,P}$ = 37.5 Hz, $C_{q,Ph}P$), 131.9 (2 × *m*-$CH_{p\text{-tolyl}}CH_3$), 133.1 (d, $^{3}J_{C,P}$ = 10.0 Hz, 2 × *m*-$CH_{Ph}P$), 133.2 (2 × *m*-$CH_{p\text{-tolyl}}CH_3$), 133.9 (d, $^{3}J_{C,P}$ = 12.2 Hz, 2 × *m*-$CH_{Ph}P$), 136.9 (dm, $^{1}J_{C,F}$ = 245.7 Hz, $C_{q,Ar}F$), 137.7 ($C_{q,p\text{-tolyl}}CH_3$), 137.9 (dm, $^{1}J_{C,F}$ = 250.2 Hz, $C_{q,Ar}F$), 138.3 ($C_{q,p\text{-tolyl}}CH_3$), 140.0 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 141.5 (*p*-$C_{q,p\text{-tolyl}}CH_3$), 145.3 ($C_{q,ipso}$), 148.8 (dm, $^{1}J_{C,F}$ = 227.1 Hz, $C_{q,Ar}F$) ppm. * = assignment by $^{1}H/^{13}C$-HMQC/HMBC spectra $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 299 K): δ −14.9 ppm. $^{19}F\{^{1}H\}$ NMR (470 MHz, CD_2Cl_2, 299 K): δ −167.9 (m, 6F, *m*-$F_{Ar}B$), −165.4 (t, $^{3}J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), −133.0 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 299 K): δ 22.0 ppm. Anal. Calcd for $C_{64}H_{51}BF_{15}HfOP$: C, 57.31; H, 3.83. Found: C, 57.37; H, 4.49. HR/MS: calculated *m*/*z* 815.2908 [M^+]; measured (ESI) *m*/*z* 815.2905.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00088.

Crystallographic parameterd for compounds **Ti2a**, **Ti2b**, **Ti3b**, **Ti5b**, **Ti6b**, **Zr2**, **Hf2**, **Hf3**, and **LiOC$_6$H$_4$PPh$_2$** and ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$, $^{19}F\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra of all compounds (PDF)

Accession Codes

CCDC 1822963−1822971 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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