EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201801016

Link to VoR: http://dx.doi.org/10.1002/ejic.201801016

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10.1002/ejic.201801016

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Cationic Group 4 Complexes (M = Ti, Zr, Hf): Modifications and Limitations in the Design of Tridentate *Cp*,*O*,*P*-Ligand Frameworks Built Directly in the Coordination Sphere of the Metal

Malte Fischer,[a] Maximilian Jaugstetter,[a] Raoul Schaper,[a] Marc Schmidtmann,[a] and Rüdiger Beckhaus*[a]

Abstract: The reactions of the monopentafulvene complexes **Ti1**, **Zr1**, and **Hf1** with bidentate *O*,*P*-ligand precursors **L1-3** to form the corresponding cationic complexes employing an established three-step synthetic protocol (insertion, methylation, activation with $B(C_6F_5)_3$) are investigated. The ligands **L1-3** are designed to have different sized spacers between the carbonyl and diphenylphosphine functional groups. The attempts to react **Ti1**, **Zr1**, and **Hf1** with acetyldiphenylphosphine (**L1**) proved to yield undesired products at various steps in the synthetic sequence. Employing **Ti1** the formation of **Ti2** is observed accompanied by release of diphenylphosphine. **Ti2**, with the exocyclic double bond, is the formal product of insertion of the smallest ketene ($H_2C=C=O$) into the Ti–C_{exo} bond. Starting with **Zr1** results in isolation of the insertion product **Zr2** without loss of diphenylphosphine, but a byproduct is formed during the reaction with **L1**. Subsequent methylation with methyllithium yielded a complex reaction mixture. **Hf1** reacts cleanly with **L1** to the insertion product **Hf2**. Also, the methylation reaction selectively yielded **Hf3** as the result of chloride/methyl exchange, but final activation with $B(C_6F_5)_3$ causes decomposition and release of diphenylphosphine. The use of the ligand precursors **L2** and **L3** with two methylene groups or an aryl group as linkers between the functional groups selectively yielded the desired cationic complexes **Ti6**, **Zr6**, **Hf6**, and **Ti9** in good to excellent overall yields.

Introduction

Ligand design is one of the key features of modern organometallic and transition metal based chemistry with homogeneous catalysis as the main area of application.[1] Bonding interactions between the central metal atom and the ancillary ligand system prove to be crucial for influencing the electronic properties of the complexes as well as the steric environment around the reactive part of the molecules. Therefore even small changes in the ligand system can be essential to allow for further reactivity or to make new reactions pathways accessible.

In regard to the achievements of the use of well-defined cationic group 4 metal complexes and their role as important olefin polymerization catalysts, numerous substitution patterns for the ancillary ligand systems have been developed do direct their catalytic activity.[2] For example, Brintzinger et al. synthesized a silaspiro zirconocene complex, which posseses C_2-symmetry, and showed that this complex is able to polymerize propylene to isotactic polypropylene after activation with methylaluminoxan (MAO) to the corresponding cationic complex.[3] In contrast a quite similar C_s-symmetric complex affords almost only atactic polypropylene.[4]

Cationic group 4 species receive growing interest as Lewis acid components in frustrated Lewis pair chemistry.[5] Such transition metal based frustrated Lewis pairs (tm-FLPs) benefit from the overall greater structural diversity compared to their main group counterparts and, beyond that, show a long history as Lewis acid catalysts in numerous reactions.[6] The fact that the appropriate ligand system, and assumingly even slight changes within the ligand-framework can have a tremendous influence on the reactivity, can be exemplified by the cationic zirconocene phosphinoaryloxide complexes **I** and **II** by Wass and co-workers.[7] Whereas the dicyclopentadienyl derivative **I** with a long but persistent zirconium–phosphorus bond is not able to cleave dihydrogen heterolytically, the dipentamethylcyclopentadienyl derivative **II**, which shows no interaction between the Lewis acidic zirconium center and the Lewis basic phosphine moiety at all, readily cleaves dihydrogen under the same reaction conditions to give complex **III** (Scheme 1, **A**).

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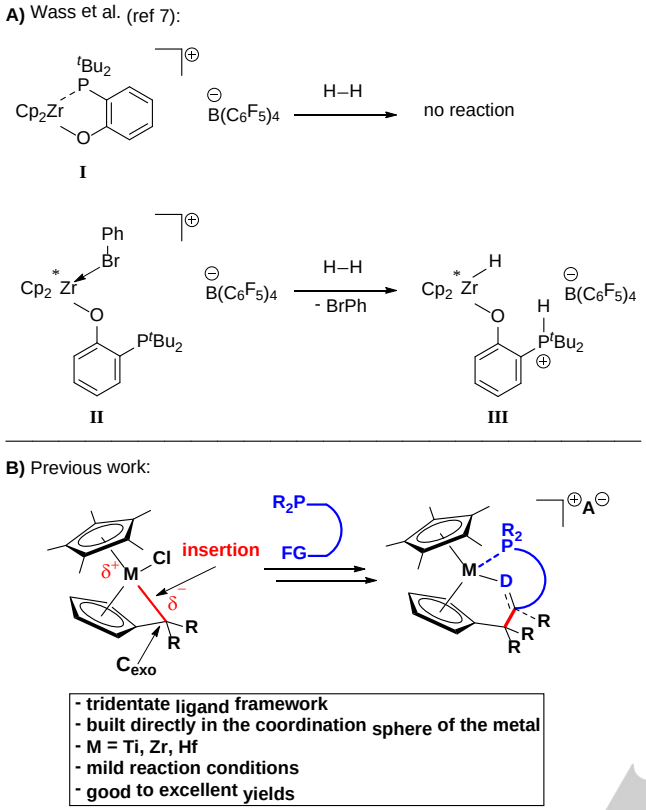
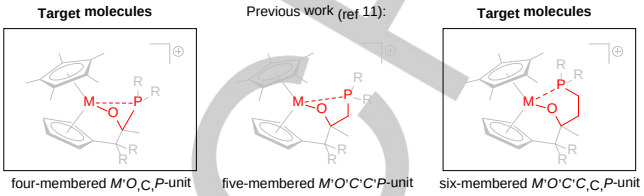


Scheme 1. Effects of ligand design on cationic group 4 metal complexes within tm-FLP chemistry (**A**) and synthetic concept of cationic group 4 metal complexes with tridentate *Cp*,*D*,*P*-ligand framework (**B**) (M = Ti, Zr, Hf; FG = RC=O or CN; D = O, N; R = alkyl, aryl).

Previously, we have established an efficient synthetic protocol for the synthesis of cationic complexes of all group 4 metals with tridentate *Cp*,*D*,*P*-ligand frameworks (D = O, N) by reacting mixed cyclopentadienyl/monopentafulvene precursor complexes[8-10] with bifunctional ligand precursors (Scheme 1, **B**).[11,12] Those bidentate ligand precursors feature one functional group (FG), which is able to undergo an insertion reaction into the polarized bond between the metal and the exocyclic carbon atom (C_{exo}) of the π-η^5:σ-η^1 bonded monopentafulvene ligand (carbonyl or nitrile functional group) and one phosphine functional group to enable interactions between the Lewis acidic metal center and the Lewis basic phosphine moiety in the cationic complexes. This concept includes the characteristics of hemilabile *O*,*P*-ligands, in which the unoccupied coordination side can become available for further reactions by cleavage of the labile metal–ligand bond.[13] Recent investigations have already shown that our reported complexes act as tm-FLPs.[12]
In most cases, multidentate ligand precursors are synthesized by multistep organic syntheses, which require multiple isolation and purification steps before synthesizing the corresponding complexes. In contrast, our approach allows the preparation of densely functionalized *Cp*,*D*,*P*-tridentate ligands directly in the coordination sphere of the respective group 4 metals in good to excellent yields and under mild reaction conditions.[11,12] As a continuation of our efforts, we herein report on limitations and possibilities to expand and modify the tridentate *Cp*,*O*,*P*-ligand framework of this family of cationic complexes with focus on the ring size of the resulting *M*,*O*,*P*-heterocycles (Scheme 2).

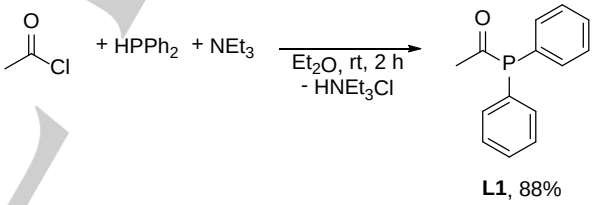


Scheme 2. Targeted cationic group 4 metal complexes of this work.

Results and Discussion

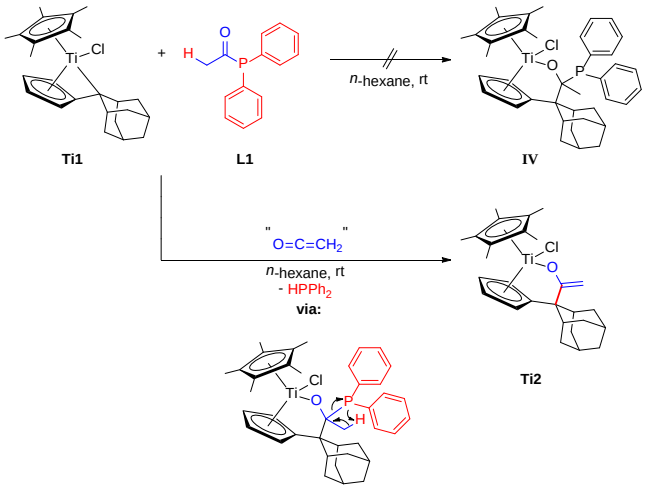
Attempts to synthesize Cationic Group 4 Metal Complexes With Four-Membered *M*,*O*,*C*,*P*-units

The bidentate *P*,*O*-ligand precursor **L1** was prepared according to a slightly modified method described by Wang and co-workers and isolated as a colorless oil in 88% yield (Scheme 3).[14]



Scheme 3. Synthesis of the ligand precursor **L1**.

For reasons of comparison we recollected NMR data of **L1** in deuterobenzene ($\delta(^{31}P\{^1H\})$ = 17.0 ppm[15]). With **L1** in hand we envisaged to synthesize cationic group 4 metal complexes (M = Ti, Zr, Hf) with tridentate *Cp*,*O*,*P*-ligand framework and a four-membered *M*,*O*,*C*,*P*-chelating subunit by employing the established synthetic pathway reported previously.[11,12] Therefore, we started with the reaction of the mixed pentamethylcyclopentadienyl/pentafulvene titanium complex **Ti1** with **L1** in *n*-hexane at room temperature. After purification an oily orange compound was isolated. Analysis of the NMR data revealed that clean conversion to **Ti2** has taken place and diphenylphosphine was formed as the byproduct (which explains the oily consistency), verified by its characteristic NMR chemical shifts ($\delta(^{31}P\{^1H\})$ = -40.8 ppm; $\delta(^1H)$ = 5.20 (d, $^1J_{P,H}$ = 215.8 Hz, 1H, *H*PPh_2) ppm) (Scheme 4).



Scheme 4. Synthesis of Complex **Ti2** via release of diphenylphospine.

In other words, the release of diphenylphosphine results in the formal insertion of the smallest ketene moiety O=C=CH_2 into the Ti–C_{exo} bond. Attempts of starting the reaction at -80 °C and/or changing the solvent to THF or toluene also resulted in the isolation of complex **Ti2**. In the high-field region, the ^{1}H NMR spectrum of **Ti2** shows the characteristic signals of the Cp* ligand at $\delta(^1H)$ = 1.81 ppm and the two signals for the diastereotopic methylene group of the OC_q=CH_2 unit at $\delta(^1H)$ = 4.19, 4.23 ($\delta(^{13}C\{^1H\})$ = 82.6 (OC_q=$\underline{C}H_2$) and 181.3 ($O\underline{C}_q$=CH_2) ppm). The four signals for the chemical inequivalent hydrogen atoms of the coordinated five-membered ring of the former pentafulvene ligand at $\delta(^1H)$ = 5.19, 5.49, 5.62, and 6.60 ppm and the chemical shift of the $C_{q,exo}$ atom at $\delta(^{13}C\{^1H\})$ = 52.7 ppm are all in good agreement to previously reported complexes.[11]
Ti2 was also characterized by single-crystal X-ray diffraction; suitable crystals were obtained from a saturated *n*-hexane/toluene solution. The molecular structure of **Ti2** is shown in Figure 1.

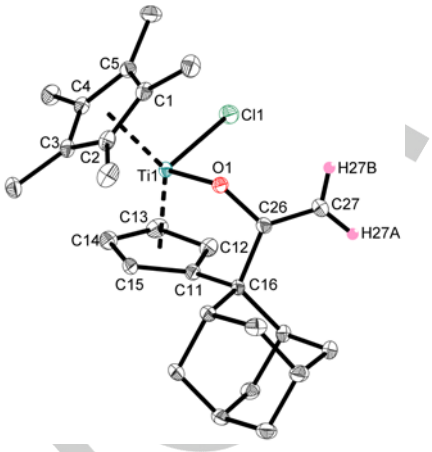
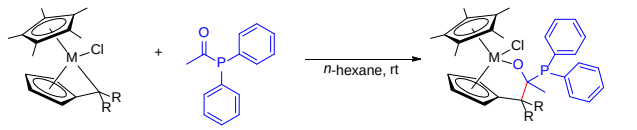


Figure 1. Molecular structure of **Ti2**. Hydrogen atoms (except H27A and H27B) are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–O1 1.9079(11), Ti1–Cl1 2.3690(5), O1–C26 1.3583(18), C11–C16 1.527(2), C16–C26 1.540(2), C26–C27 1.334(2), Cl1–Ti1–O1 98.42(4), Ct1–Ti1–Ct2 135.1, Σ∠C26 359.8 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

Complex **Ti2** crystallizes in the monoclinic space group $P2_1/c$. The molecular structure displays the expected pseudotetrahedral coordination environment at the titanium center (Cl1–Ti1–O1 98.42(2)°, Ct1–Ti1–Ct2 135.1°). The Ti1–Cl1 bond length of 2.3690(5) Å and the Ti1–O1 bond length of 1.9079(11) Å are typical of single bonds.[16,17] Compared to the starting material **Ti1** (C_{exo}–C_{ipso} 1.422(4) Å[9]) the C11–C16 bond length of 1.527(2) is elongated and now constitutes a C(sp^2)–C(sp^3) single bond.[18] The newly formed C16–C26 bond with a bond length of 1.540(2) Å is a typical C(sp^3)–C(sp^3) single bond[18], although for related complexes often significant elongations of this bond are observed.[11,12]
Surprisingly, the transfer of the reaction to the heavier congeners zirconium and hafnium by using the previously reported starting complexes **Zr1** and **Hf1**[8] yielded the desired products **Zr2** and **Hf2** in overall good yields, but the synthesis of **Zr2** ($\delta(^{31}P\{^1H\})$ = 25.0 ppm) also yielded a byproduct ($\delta(^{31}P\{^1H\})$ = -5.5 ppm) that could not be separated due to solubility properties similar to those of **Zr2**[15] (Scheme 5).



Zr1: M = Zr, CR_2 = Ad
Hf1: M = Hf, R = *p*-tolyl
L1
Zr2: M = Zr, CR_2 = Ad; + **byproduct**
Hf2: M = Hf, R = *p*-tolyl

Scheme 5. Synthesis of complexes **Zr2** and **Hf2**.

The first assumption of the byproduct being the analogous zirconium complex of **Ti2** was ruled out because no diphenylphosphine was formed during the reaction. Also, no evidence for the other diastereoisomer was found, which is

sometimes observed for related complexes[11,12] and also in this work (a discussion about the nature of the byproduct based on the NMR data are summarized in the Supporting Information[15]). Multiple attempts to crystallize the byproduct out of the product mixture failed, but crystals of **Zr2** which were suitable for single-crystal X-ray diffraction were obtained. The molecular structure of **Zr2** is shown in Figure 2.

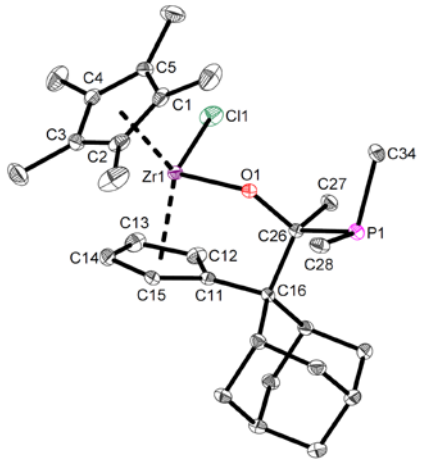
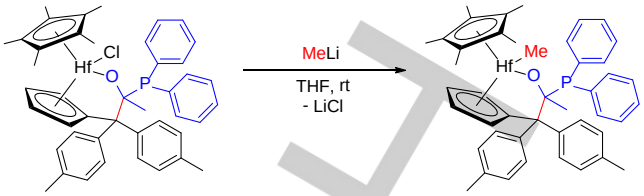


Figure 2. Molecular structure of **Zr2**. Hydrogen atoms, and phenyl groups of the phosphine moiety are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr1–O1 2.0018(9), Zr1–Cl1 2.48660(4), O1–C26 1.4280(15), P1–C26 1.9280(13), C11–C16 1.5271(18), C16–C26 1.6448(18), C26–C27 1.5433(18), Cl1–Zr1–O1 103.90(3), Ct1–Zr1–Ct2 133.1, Σ∠C26 (O1–C26–C27 + O1–C26–P1 + P1–C26–C27) 320.2, Σ∠P1 312.0 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

Zr2 crystallizes in the monoclinic space group $P2_1/n$ and the crystallographic features of this complex are all in the expected ranges. The Zr1–Cl1, O1–C26, P1–C26, and C11–C26 bond lengths constitute single bonds,[16-18] although as mentioned during the discussion of the structural data of **Ti2**, the newly formed C–C bond C16–C26 (1.6448(18) Å) is remarkably elongated, caused by the strong ring strain of the newly formed σ,π chelate ligand[19] and is comparable to those of extremely long C–C single bonds.[20] Despite this elongation, the former carbonyl carbon atom is sp^3-hybridized, as indicated by the sum of angles around C26 (320.2°).

Subsequent methylation of a mixture of **Zr2** and its byproduct with methyllithium resulted in a complex mixture of products with six different signals within the $^{31}P\{^1H\}$ NMR[15]. The hafnium complex **Hf2** reacts readily and cleanly with methyllithium to give the corresponding methylated complex **Hf3** (Scheme 6).



Hf2 **Hf3**

Scheme 6. Synthesis of the methylated hafnium complex **Hf3**.

Hf3 was fully characterized by multinuclear NMR analyses[15] ($\delta(^{31}P\{^1H\})$ = -16.0 ppm). Furthermore the molecular structure of **Hf3** was determined by single-crystal X-ray diffraction and is shown in Figure 3.

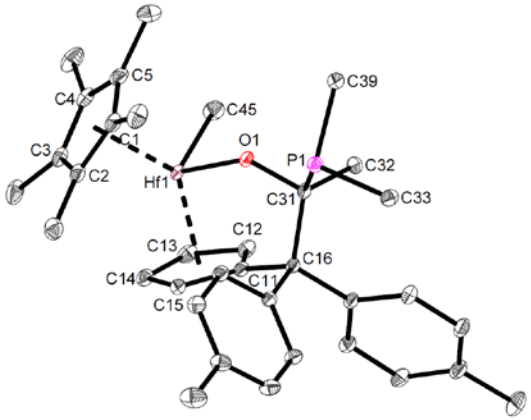


Figure 3. Molecular structure of **Hf3**. Hydrogen atoms, and phenyl groups of the phosphine moiety are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Hf1–O1 1.9744(7), Hf1–C45 2.2692(11), O1–C31 1.4275(12), P1–C31 1.9301(10), C11–C16 1.5330(14), C16–C31 1.6387(14), C31–C32 1.5295(14), C45–Hf1–O1 97.83(4), Ct1–Hf1–Ct2 134.3, Σ∠C31 (O1–C31–C32 + O1–C31–P1 + P1–C31–C32) 319.6, Σ∠P1 312.1 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

Complex **Hf3** crystallizes in the triclinic space group *P*-1. The crystallographic features of **Hf3** are quite similar to those of **Zr2**.[16] The Hf1–C45 bond length of 2.2692(11) Å is in the expected range for terminal hafnium–carbon single bonds.[17]

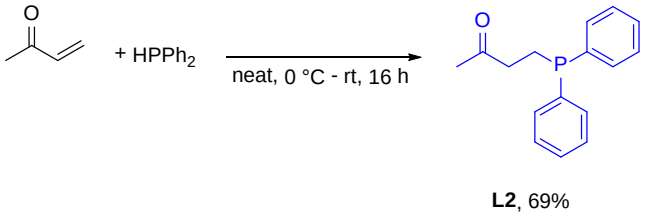
The activation of **Hf3** with the strong Lewis acid $B(C_6F_5)_3$ to yield its cationic counterpart resulted in a complex mixture of products. The only phosphorus containing species which forms during the reaction is diphenylphosphine ($\delta(^{31}P\{^1H\})$ = -40.8 ppm).[15] Additionally, the anion resulting of methyl abstraction $MeB(C_6F_5)_3^-$ could be identified by analysis of the NMR data, but additional signals in the $^{11}B\{^1H\}$ NMR and $^{19}F\{^1H\}$ NMR were also detected.[15]

Variations of the reaction conditions (different solvents, different temperatures) resulted in similar results.

Synthesis of Cationic Group 4 Metal Complexes with Six-Membered *M*,*O*,*C*,*C*,*C*,*P*-units

Due to the difficulties concerning the synthesis of cationic d^0 complexes with tridentate *Cp*,*O*,*P*-ligand frameworks, including a four-membered *M*,*O*,*C*,*P* ring section, further studies were focused on the synthesis of six-membered ring systems.

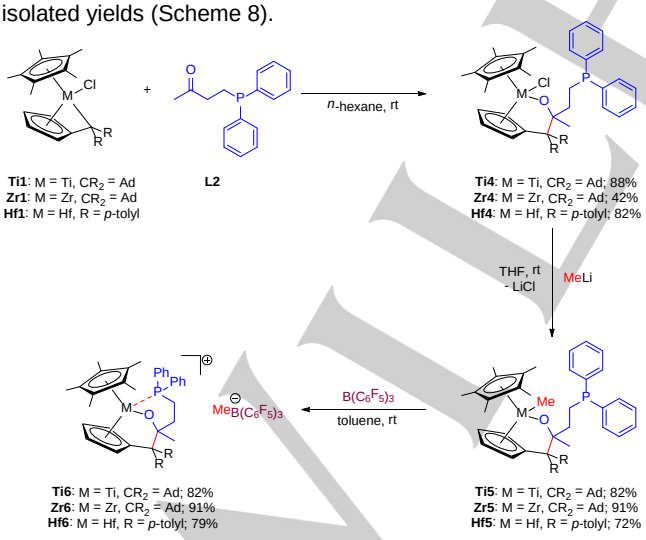
Yus and co-workers have previously described an elegant synthesis of compound **L2**, featuring a diphenylphosphine and a carbonyl functional group with two methylene groups as the linker, which we identified as an ideal bidentate *O*,*P*-ligand precursor for our attempted goal, and synthesized it according to a slightly modified literature procedure (Scheme 7).[21]



Scheme 7. Synthesis of the ligand precursor **L2**.

This regioselective, solvent- and catalyst-free hydrophosphanation of methyl vinyl ketone with diphenylphosphine yielded **L2** as a colorless oil in 69% isolated yield after column chromatography.

To our delight, the synthesis of the cationic complexes was successful by employing the established three-step synthetic pathway, starting from the monopentafulvene complexes **Ti1**, **Zr1**, **Hf1**, and **L2**, providing each complex in good to very good isolated yields (Scheme 8).



Scheme 8. Three-step synthesis of cationic group 4 metal complexes **Ti6**, **Zr6**, and **Hf6** by reacting monopentafulvene complexes **Ti1**, **Zr1**, and **Hf1** with **L2**, subsequent methylation and final activation with $B(C_6F_5)_3$.

Complexes **Ti4**, **Zr4**, **Hf4**, **Ti5**, **Zr5**, and **Hf5** are only slightly soluble in *n*-hexane and show good solubilities in benzene, toluene, and tetrahydrofuran, providing ideal purification purposes.

The molecular structures of complexes **Ti4**, **Ti5**, **Zr4**, and **Hf5** were determined by single-crystal X-ray diffraction and are shown in Figures 4 to 7 (the crystals were obtained either from saturated *n*-hexane or toluene solutions).

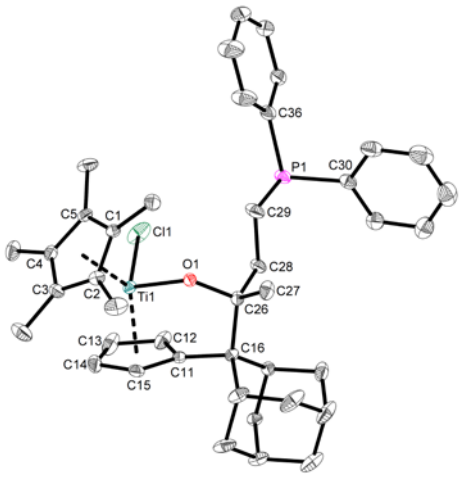


Figure 4. Molecular structure of **Ti4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–O1 1.8501(9), Ti1–Cl1 2.3965(4), O1–C26 1.4259(14), P1–C29 1.8454(14), C11–C16 1.5233(16), C16–C26 1.6200(16), C26–C27 1.5299(17), Cl1–Ti1–O1 101.09(3), Ct1–Ti1–Ct2 136.1, Σ∠C26 (O1–C26–C27 + O1–C26–C28 + C27–C26–C28) 320.5, Σ∠P1 314.6 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

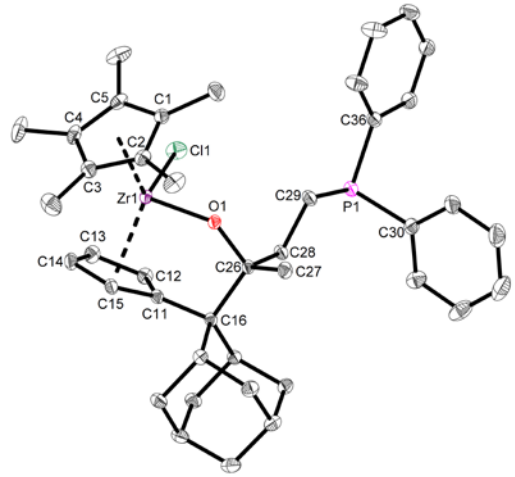


Figure 5. Molecular structure **Zr4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr1–O1 1.9586(5), Zr1–Cl1 2.4738(2), O1–C26 1.4260(9), P1–C29 1.8495(8), C11–C16 1.5312(10), C16–C26 1.6340(10), C26–C27 1.5276(10), Cl1–Zr1–O1 97.83(4), Ct1–Zr1–Ct2 133.5, Σ∠C26 (O1–C26–C27 + O1–C26–C28 + C27–C26–C28) 320.9, Σ∠P1 304.6 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

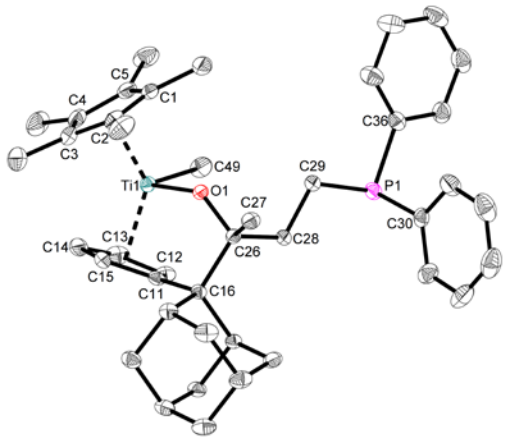


Figure 6. Molecular structure of **Ti5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–O1 1.8521(10), Ti1–C49 2.1876(15), O1–C26 1.4247(17), P1–C29 1.8479(15), C11–C16 1.5259(19), C16–C26 1.6259(19), C26–C27 1.5274(19), C49–Ti1–O1 97.93(5), Ct1–Ti1–Ct2 135.1, Σ∠C26 (O1–C26–C27 + O1–C26–C28 + C27–C26–C28) 321.0, Σ∠P1 303.5 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

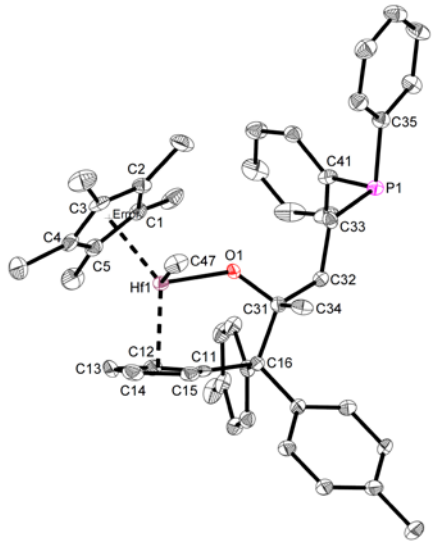


Figure 7. Molecular structure **Hf5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Hf1–O1 1.976(4), Hf1–C47 2.264(7), O1–C31 1.407(8), P1–C33 1.853(7), C11–C16 1.538(9), C16–C31 1.635(9), C31–C34 1.530(9), C47–Hf1–O1 99.2(2), Ct1–Hf1–Ct2 134.8, Σ∠C31 (O1–C31–C32 + O1–C31–C34 + C32–C31–C34) 324.3, Σ∠P1 302.5 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

Ti4, **Ti5**, **Zr4**, and **Hf5** all crystallize in monoclinic space groups, either $P2_1/n$ (**Ti4**), $P2_1/c$ (**Ti5**, **Zr4**), or $P2_1$ (**Hf5**). With regard to the crystallographic features of these complexes, expected similarities are found, and differences in the bond lengths and angles follow the tendency of increasing atomic radii within group 4.[16] Shortly summarized, the M–Cl and terminal M–CH_3 bond lengths are typical of single bonds, and the M–O bond lengths are shorter than typical single bonds between these atoms, due to M(d_π)–O(p_π) interactions. The former carbonyl C(sp^3)–O distances of 1.42 Å on average are now typical of C–O single bonds. Also, the remarkable elongation of the C–C bonds C16–C26 (**Ti4**, **Ti5**, **Zr4**) and C16–C31 (**Hf5**) of above 1.63 Å are present, together with the sp^3-hybridizations of the former carbonyl carbon atoms. The central metal atoms show consistently distorted-tetrahedral coordination environments.

The NMR data of all compounds are consistent with the X-ray structures. They are discussed for **Ti4** as an example Noteworthy, unlike the previously reported complexes[11,12] each was obtained as a diastereomerically pure compound.

The $^{31}P\{^1H\}$ NMR chemical shift of **Ti4** at $\delta(^{31}P\{^1H\})$ = -12.0 ppm is only marginal shifted toward lower field in comparison to the free ligand precursor **L2**, demonstrating same chemical environments at the phosphorus atoms. In the high-field region of the ^1H NMR spectrum at $\delta(^1H)$ = 1.39 ppm the methyl group of the quaternary carbon atom of the former carbonyl group is located with the corresponding ^{13}C resonance at $\delta(^{13}C\{^1H\})$ = 31.0 ppm. The ^{13}C NMR chemical shifts of the diastereotopic methylene groups of the $OC_qCH_2CH_2PPh_2$ moiety at $\delta(^{13}C\{^1H\})$ = 22.8 and 35.8 ppm show characteristic doublet coupling constants of $^1J_{C,P}$ = 11.6 Hz and $^2J_{C,P}$ = 20.7 Hz, respectively. Highly diagnostic is the ^{13}C chemical shift of the exocyclic carbon atom at $\delta(^{13}C\{^1H\})$ = 54.7 ppm, which is significantly shifted toward higher field compared to starting complex **Ti1**.[9] Four signals each for the C_5H_4 group are found in the ^1H and ^{13}C NMR spectra, ranging from $\delta(^1H)$ = 5.04 to 6.42 ppm and $\delta(^{13}C\{^1H\})$ = 104.5 to 120.1 ppm. These and the chemical shifts of the Cp^* and PPh_2 moieties are in the same characteristic ranges as for the previously reported complexes with the $OC_qCH_2PPh_2$ functionality.[11,12]

Activation of the methylated complexes **Ti5**, **Zr5**, and **Hf5** with the highly Lewis acidic borane $B(C_6F_5)_3$ in toluene at room temperature yielded the corresponding cationic group 4 metal complexes **Ti6**, **Zr6**, and **Hf6** as orange (**Ti6**) and colorless (**Zr6**, **Hf6**) solids, diastereomerically pure, and in yields of up to 91% after purification with the weakly coordinating borate anion $MeB(C_6F_5)_3^-$. As the result of the methyl group abstraction, the phosphorus coordinates to the metal center and the tridentate *Cp*,*O*,*P*-ligand frameworks are formed. These compounds are stable in the solid state, and, like their precursor complexes, can be stored for months under inert conditions without any decomposition.

The cationic complexes are insoluble in aliphatic hydrocarbons (e.g. *n*-pentane or *n*-hexane) and only marginally soluble in aromatic solvents such as benzene or toluene, which already indicates the formation of ionic species. Therefore NMR data were collected in deuterated dichloromethane, in which **Ti6**, **Zr6**, and **Hf6** proved to be stable. The NMR data for all compounds is summarized in table 1.

Table 1. Selected NMR parameters of complexes **Ti4-9**, **Zr4-6**, and **Hf4-6**[a].

Compd.	$\delta^{13}C\{^1H\}$ PCH_2CH_2 $^nJ_{C,P}(PCH_2CH_2)$	δ^1H / $\delta^{13}C\{^1H\}$ MCH_3/BCH_3	$\delta^{13}C\{^1H\}$ OC_q $^3J_{C,P}(OC_q)$	δ^1H / $\delta^{13}C\{^1H\}$ OC_qCH_3	$\delta^{13}C\{^1H\}$ $C_{q,exo}/C_{q,ipso}$	$\delta^{31}P\{^1H\}$
Ti4[d]	22.8 / 35.8 $^1J_{C,P}$ = 11.6 $^2J_{C,P}$ = 20.7	-	111.7 $^3J_{C,P}$ = 13.9	1.39 / 31.0	54.7 / 156.7	-12.0
Zr4[d]	22.8 / 36.7 $^1J_{C,P}$ = 11.5 $^2J_{C,P}$ = 20.2	-	106.9 $^3J_{C,P}$ = 13.3	1.41 / 31.1	55.1 / 154.9	-12.3
Hf4[d]	24.0 / 39.2 $^1J_{C,P}$ = 11.3 $^2J_{C,P}$ = 19.4	-	105.4 $^3J_{C,P}$ = 13.7	1.53 / 29.8	65.9 / 147.4	-13.9
Ti5[d]	22.6 / 36.6 $^1J_{C,P}$ = 10.8 $^2J_{C,P}$ = 19.8	0.26 / 35.3	107.4 $^3J_{C,P}$ = 12.9	1.32 / 30.8	54.9 / 151.4	-12.7
Zr5[d]	22.8 / 37.6 $^1J_{C,P}$ = 11.3 $^2J_{C,P}$ = 20.0	-0.07 / 23.0	104.3 $^3J_{C,P}$ = 13.0	1.36 / 31.0	55.3 / 150.3	-12.9
Hf5[d]	24.1 / 38.9 $^1J_{C,P}$ = 10.7 $^2J_{C,P}$ = n.o.	-0.08 / 27.8	103.4 $^3J_{C,P}$ = 13.2	1.31 / 30.4	66.1 / 143.9	-14.0
Ti6[d]*	28.7 / 39.1 $^1J_{C,P}$ = 28.7 $^2J_{C,P}$ = 48.1	0.48 / 12.8[b]	113.9 $^3J_{C,P}$ = n.o.	1.70 / 34.3	55.0 / 155.6	28.6
Zr6[d]*	25.1[b] /35.7 $^1J_{C,P}$ = n.o. $^2J_{C,P}$ = n.o.	0.49 /11.9[b]	109.5 $^3J_{C,P}$ = n.o.	1.67 / 36.2	55.8 / 155.5	14.4
Hf6[c]*	22.6 / 37.4 $^1J_{C,P}$ = 23.1 $^2J_{C,P}$ = n.o.	0.51 / 10.0[b]	106.4 $^3J_{C,P}$ = n.o.	1.86 / 32.2	66.1 / 150.8	16.6
Ti7[c],[e]	-	-	115.9 $^3J_{C,P}$ = 3.3	2.27 / 28.8	57.0 / 154.0	-4.0
Ti8[e]	-	0.62 / 35.0	114.6 $^3J_{C,P}$ = 2.8	2.24 / 32.7	58.1 / 149.4	-3.6
Ti9[e]*	-	0.49 / 9.7[b]	117.5 $^3J_{C,P}$ = n.o.	2.09 / 35.4	57.6 / 157.0	41.4

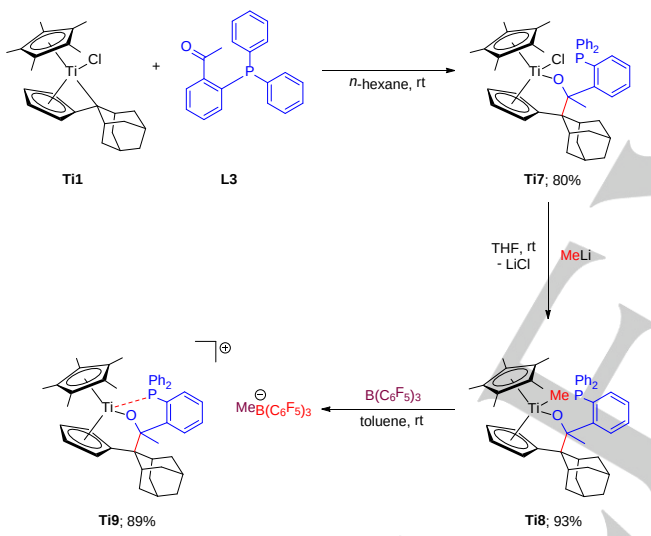
[a] Values are given in ppm and *J* values in Hz. Measurements were carried out in C_6D_6 or CD_2Cl_2 (marked with an asterisk) [b] assignment by $^1H/^{13}C$-HMQC spectra [c] only one signal given (1:1 mixture of diastereoisomers) [d] diphenylphosphine moieties, two methylene groups as the linker between OC_q and PPh_2 [e] diphenylphosphine moieties, aryl linker between OC_q and PPh_2

All chemical shifts in the ^1H and ^{13}C NMR spectra of the cationic complexes are in the expected range, also showing the expected characteristic coupling patterns for the nuclei close to the phosphorus (Table 1). The $^{31}P\{^1H\}$ resonances are shifted toward lower field, depending on the metal to a different extent, when compared to their methylated precursor complexes ($\Delta\delta^{31}P\{^1H\}$ = 41.3 (**Ti5**/**Ti6**), 27.3 (**Zr5**/**Zr6**), 30.6 (**Hf5**/**Hf6**) ppm). This indicates interactions between the Lewis basic phosphine groups and the Lewis acidic metal centers. For example, the cationic zirconium complex $[Cp_2ZrOC_6H_4P(^tBu_2)]^+[B(C_6F_5)_4]^-$ **I**, prepared by Wass et al., starting from the methylated precursor complex and the trityl salt $[Ph_3C]^+[B(C_6F_5)_4]^-$, showed a downfield shift of 44.4 ppm in the $^{31}P\{^1H\}$ NMR due to the coordination of the phosphorus to the metal center.[7] Similar downfield shifts were observed for the cationic complexes reported previously by our group[11], so that, in conclusion, the elongation of the *O*,*P*-subunit by one methylene group does not prevent coordination of the phosphorus to the metal center.

The NMR data clearly indicate the abstraction of the methyl group and the formation of the borate anion $MeB(C_6F_5)_3^-$ in all cases (e.g. for **Ti6**: $\delta(^{11}B\{^1H\})$ = -15.5 ppm; $\delta(^{19}F\{^1H\})$ = -167.9 (*m*-$F_{Ar}B$), -165.3 (*p*-$F_{Ar}B$), -133.1 (*o*-$F_{Ar}B$) ppm; $\delta(^1H/^{13}C\{^1H\}(BCH_3))$ = 0.48/12.8 ppm). The $\Delta\delta(m,p\text{-F})$ parameter introduced by Horton and co-workers to determine whether this anion shows a coordination to the d^0 metal centers in solution or

not, verify that the $MeB(C_6F_5)_3^-$ anions are noncoordinating in **Ti6**, **Zr6**, and **Hf6**.[22,23] The $\Delta\delta(m,p\text{-F})$ values of **Ti6** (2.6 ppm), **Zr6** (2.5 ppm), and **Hf6** (2.6 ppm) are in good accordance to other characterized cationic complexes, in which the $MeB(C_6F_5)_3^-$ anion is noncoordinating, e.g. $\Delta\delta(m,p\text{-F})$ = 2.6 ppm for the activation product of $Cp_2Zr(Me)OC_q(Fc)PCy_2$, $B(C_6F_5)_3$ and $[Pd(C_3H_5)Cl]_2$.[24] Furthermore, the M^+ signals of **Ti6**, **Zr6**, and **Hf6** were detected by high-resolution ESI mass spectrometry.

For further derivatization of the ligand-framework, we also wanted to test the potential of introducing an aryl linker between the oxygen and phosphorus donor sides and rest whether this leads to a metal phosphorus interaction or not. Therefore **Ti1** was reacted with the appropriate ligand precursor **L3**, which we synthesized according to a literature procedure.[25] Following the established three-step reaction pathway of insertion, subsequent methylation and final activation with $B(C_6F_5)_3$, the cationic titanium complex **Ti9** and its parent complexes **Ti7** (1:1 mixture of diastereoisomers) and **Ti8** were obtained in isolated yields between 80 and 93% (Scheme 9).



Scheme 9. Three-step synthesis of cationic titanium complex **Ti9** with an aryl linker between the oxygen and phosphorus donor sites.

Compounds **Ti7**, **Ti8**, and **Ti9** were thoroughly characterized by multinuclear NMR spectroscopy (most characteristic signals are summarized in Table 1) and the data agree well with the other cationic group 4 complexes derived from bidentate *O*,*P*-ligand precursors and monopentafulvene complexes.[11]

Most importantly, complex **Ti9** also shows a persistent connection between the Lewis acidic metal center and the Lewis basic phosphine moiety as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy ($\Delta\delta(^{31}P\{^1H\}$(**Ti8**/**Ti9**) = 45 ppm shift toward lower field). The $MeB(C_6F_5)_3^-$ anion is noncoordinating ($\Delta\delta(m,p\text{-F})$ = 2.6 ppm) and the M^+ signal of **Ti9** was detected by high-resolution ESI mass spectrometry.

In addition, we were able to determine the molecular structures of **Ti7** and **Ti8** by single-crystal X-ray diffraction, which are shown in Figures 8 and 9.

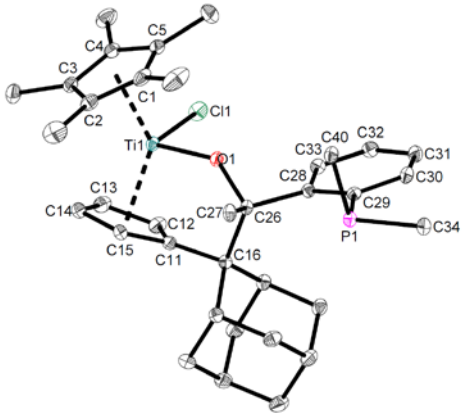


Figure 8. Molecular structure of **Ti7**. Hydrogen atoms, and the phenyl groups of the phosphine moieties are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–O1 1.8459(10), Ti1–Cl1 2.4099(5), O1–C26 1.4353(17), P1–C29 1.8555(14), C11–C16 1.5222(19), C16–C26 1.6486(19), C26–C27 1.5335(19), Cl1–Ti1–O1 96.88(3), Ti1–O1–C26 137.40(9), Ct1–Ti1–Ct2 134.1, Σ∠C26 (O1–C26–C27 + O1–C26–C28 + C27–C26–C28) 320.9, Σ∠P1 304.6 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

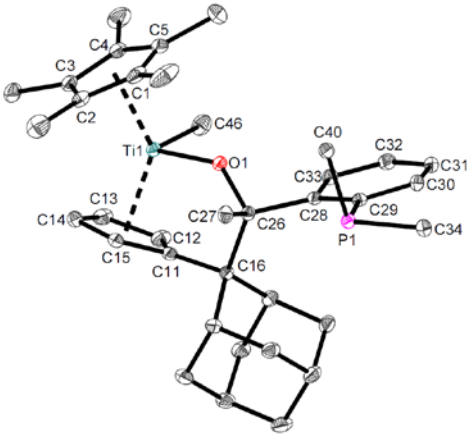


Figure 9. Molecular structure **Ti8**. Hydrogen atoms, and the phenyl groups of the phosphine moieties are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–O1 1.8501(11), Ti1–C46 2.2005(17), O1–C26 1.4301(18), P1–C29 1.8518(16), C11–C16 1.525(2), C16–C26 1.652(2), C26–C27 1.531(2), C46–Ti1–O1 95.84(6), Ti1–O1–C26 136.52(9), Ct1–Ti1–Ct2 134.9, Σ∠C26 (O1–C26–C27 + O1–C26–C28 + C27–C26–C28) 321.1, Σ∠P1 304.9 (Ct1 = centroid of C1–C5; Ct2 = centroid of C11–C15).

The structural data are in the same range as for the comprehensively discussed structures above, so that a more detailed discussion is omitted at this point.

Conclusions

In conclusion, we have presented the possibilities to modify the ancillary *Cp*,*O*,*P*-ligand framework of cationic group 4 complexes by employing a synthetic pathway of forming this tridentate ligand framework directly in the coordination sphere of the corresponding metal. Attempts to synthesize four-membered titanacycles within the ligand system proved to yield different products, mostly dependent on the nature of the metal. For titanium, the reaction of the starting complex **Ti1** with acetyldiphenylphosphine (**L1**) selectively results in the release of diphenylphosphine after the insertion reaction, forming complex **Ti2**, which is the product of the formal insertion of the carbonyl group of the smallest ketene ($H_2C{=}C{=}O$) into the Ti–C_{exo} bond. The zirconium congener **Zr1** reacts with **L1**, without the loss of diphenylphosphine to obtain **Zr2**, but this reaction is accompanied by the formation of a side product, which is assumingly a dimeric zirconium complex. The subsequent methylation of the product mixture showed the existence of a broad spectrum of products. In contrast, the hafnium complex **Hf1** as the initial point yielded both, the product **Hf2** of the insertion reaction and the subsequent methylation product **Hf3** in a selective manner. The attempted final activation with $B(C_6F_5)_3$ causes decomposition of the complex accompanied by release of diphenylphosphine. The use of monopentafulvene complexes **Ti1**, **Zr1**, and **Hf1** together with the readily accessible bidentate *O*,*P*-ligand precursor **L2** with two methylene groups as the linking moiety between the carbonyl functional group and the phosphine donor side, yielded the corresponding cationic complexes **Ti6**, **Zr6**, and **Hf6** in an efficient three-step synthetic protocol in good to excellent yields under mild reaction conditions. In addition, we have demonstrated, that an aryl group can successfully be introduced between the oxygen and the phosphorus starting from **Ti1** and the appropriate *P*,*O*-ligand precursor **L3**. As a consequence, the cationic group 4 metal complexes **Ti6**, **Zr6**, **Hf6**, and **Ti9** feature six-membered titanacycles because of a persistent interaction between the Lewis acidic metal center and the Lewis basic phosphine moiety. Further work in our group will focus on reactivity studies on the variety of cationic group 4 metal complexes reported herein and elsewhere with regard to tm-FLP chemistry.

Experimental Section

All air- and moisture-sensitive 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 and/or freeze-pump-thaw degassed three times prior to use. Solvents were distilled over Na/K alloy and benzophenone or CaH_2 under nitrogen atmosphere. Solid materials were stored and weighed in a glovebox or dried under high vacuum before use. The methyllithium was used as a 1.6 M solution in diethyl ether, and the *n*-butyllithium was used as a 1.6 M solution in *n*-hexane. Potassium diphenylphosphide was used as a 0.5 M solution in tetrahydrofuran. The pentafulvene complexes **Ti1**, **Zr1** and **Hf1** were synthesized according to literature procedures.[8,9] Methyl vinyl ketone, acetyl chloride, 2-fluoroacetophenone, and diphenyl phosphine were purchased from commercial sources. 2-Fluoroacetophenone was used as received. Methyl vinyl ketone, acetyl chloride, and diphenyl phosphine were distilled over $CaCl_2$ or CaH_2, freeze-pump-thaw degassed three times prior to use, and stored under nitrogen. Thin-layer chromatography was performed using commercial available Alugram SIL/G UV_{254} 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 referenced 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 $^{13}C\{^1H\}$ spectra were referenced 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 ($BF_3{\bullet}OEt_2$ ($\delta^{11}B\{^1H\}(BF_3{\bullet}OEt_2)$ = 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 higher, due to residual traces of solvents. Although in some cases satisfactory elemental analysis could not be obtained, the data is included to demonstrate the best results to date. The combustion analysis of group 4 organometallics is known to be difficult.[26] Melting points were determined using a "Mel-Temp" apparatus by Laboratory Devices, Cambridge, U.K..

Synthesis of L1: Compound **L1** was synthesized according to a slightly modified literature procedure.[14] To a solution of diphenylphosphine (2.3 mL, 13.43 mmol) and triethylamine (1.9 mL, 13.43 mmol) in 30 mL of diethyl ether, acetyl chloride (1.0 mL, 13.43 mmol) was added slowly, resulting in a colorless precipitate. The reaction mixture was stirred for 2 h at room temperature, followed by filtration of the suspension through celite and washing of the precipitate with diethyl ether (3×10 mL). Evaporation of all volatiles yielded **L1** as a colorless oil. Yield: 2.696 g (11.81 mmol, 88%). ^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 1.92 (d, 3H, $^3J_{P,H}$ = 6.1 Hz, CH_3), 7.00-7.07 (m, 6H, 4×*o*-CH_{Ph}P, 2×*p*-CH_{Ph}P), 7.43-7.47 (m, 4H, 4×*m*-CH_{Ph}P) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ = 32.5 (d, $^2J_{C,P}$ = 39.6 Hz, CH_3), 128.9 (d, $^2J_{C,P}$ = 7.5 Hz, 4×*o*-CH_{Ph}P), 129.6 (2×*p*-CH_{Ph}P), 133.5 (d, $^1J_{C,P}$ = 7.6 Hz, $C_{q,Ph}$P), 135.0 (d, $^3J_{C,P}$ = 18.3 Hz, 4×*m*-CH_{Ph}P), 219.1 (d, $^1J_{C,P}$ = 38.9 Hz, C=O) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 305 K): δ = 17.0 ppm.

Synthesis of L2: Compound **L2** was synthesized according to a slightly modified literature procedure.[21] Methyl vinyl ketone (1.5 mL, 17.76 mmol) was added slowly to diphenylphosphine (3.1 mL, 17.76 mmol) at 0 °C. The reaction mixture was stirred for 16 h at room temperature. The crude product was purified by column chromatography (SiO_2; PE:EE). The product **L2** was obtained as a colorless liquid. Yield: 3.121 g (12.18 mmol, 69%). R_f = 0.54 (SiO_2; PE:EE = 6:1). ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 1.49 (s, 3H, CH_3), 2.10-2.15 (m, 2H, PCH_2CH_2), 2.26-2.29 (m, 2H, PCH_2CH_2), 7.04-7.10 (m, 6H, 6×CH_{Ph}), 7.38-7.41 (m, 4H, 4×CH_{Ph}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 300 K): δ = 21.9 (d, $^1J_{C,P}$ = 11.7 Hz, PCH_2CH_2), 29.1 (CH_3), 39.6 (d, $^2J_{C,P}$ = 18.2 Hz,

$PCH_2\underline{C}H_2$), 128.8 (d, $^2J_{C,P}$ = 7.3 Hz, 4×*o*-CH_{Ph}P), 128.9 (2×*p*-CH_{Ph}P), 133.1 (d, $^3J_{C,P}$ = 18.8 Hz, 4×*m*-CH_{Ph}P), 139.2 (d, $^1J_{C,P}$ = 14.3 Hz, 2×$C_{q,Ph}$P), 205.1 (d, $^3J_{C,P}$ = 12.4 Hz, C=O) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 300 K): δ = -15.5 ppm.

Synthesis of L3: Compound **L3** was synthesized according to a slightly modified literature procedure.[24] To a solution of potassium diphenylphosphide (21.4 mL, 10.70 mmol; 0.5 M in THF) at reflux, was added a solution of 2-fluoroacetophenone (1.3 mL, 10.70 mmol) in THF. The resulting yellow suspension was stirred for 30 minutes at reflux, followed by addition of 50 mL of water and 50 mL of dichloromethane. The organic layer was collected and the aqueous phase was extracted with 2×50 mL of dichloromethane. The crude product was purified by column chromatography (SiO_2; DCM). The product **L2** was obtained as a yellow solid. Yield: 0.631 g (2.073 mmol, 19%). R_f = 0.56 (SiO_2; DCM). ^1H NMR (500 MHz, C_6D_6, 300 K): δ = 2.03 (d, 3H, $^{TS}J_{P,H}$ = 1.6 Hz, CH_3), 6.91-6.95 (m, 2H, 2×C_6H_4), 7.05-7.10 (m, 6H, 4× *o*-CH_{Ph}P, 2×*p*-CH_{Ph}P), 7.20-7.22 (m, 1H, C_6H_4), 7.33-7.35 (m, 1H, C_6H_4), 7.41-7.45 (m, 4H, 4×*m*-CH_{Ph}P) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 300 K): δ = 27.4 (CH_3), 128.0 (C_6H_4)*, 128.6 (2×*p*-CH_{Ph}P), 128.7 (d, $^2J_{C,P}$ = 7.0 Hz, 4×*o*-CH_{Ph}P), 130.3 (d, $^2J_{C,P}$ = 2.5 Hz, *o*-C_6H_4P), 131.6 (C_6H_4), 134.4 (d, $^3J_{C,P}$ = 20.7 Hz, 4×*m*-CH_{Ph}P), 135.2 (C_6H_4), 139.6 (d, $^1J_{C,P}$ = 11.8 Hz, 2×$C_{q,Ph}$P), 140.9 (d, $J_{C,P}$ = 29.1 Hz, $C_{q,C6H4}$C=O), 141.7 (d, $J_{C,P}$ = 17.2 Hz, $C_{q,C6H4}$P), 197.4 (C=O) ppm. * = overlap with C_6D_6 signal. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 300 K): δ = -2.5 ppm.

Synthesis of Ti2: In a glove box compound **L1** (0.383 g, 1.679 mmol) in *n*-hexane (3×5 mL) was added to a solution of complex **Ti1** (0.700 g, 1.679 mmol) in 10 mL of *n*-hexane. The suspension was stirred for 16 h at room temperature resulting in a yellow suspension. All volatiles were removed under vacuum to yield an oily orange mixture of complex **Ti2** and $HPPh_2$. Crystals suitable for single crystal X-ray diffraction of complex **Ti2** were obtained from a *n*-hexane/toluene (5:1) solution at -4 °C. Additionally, NMR data of crystalline **Ti2** were collected. Yield: 0.992 g (mixture of **Ti2** and $HPPh_2$). ^1H NMR (500 MHz, C_6D_6, 300 K): δ = 1.52-1.71 (m, 7H, $CH_{Ad}/CH_{2,Ad}$), 1.75-1.79 (m, 2H, $CH_{Ad}/CH_{2,Ad}$), 1.81 (s, 15H, C_5Me_5), 1.84-1.88 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.36-2.44 (m, 3H, $CH_{Ad}/CH_{2,Ad}$), 2.67-2.70 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 4.19 (s, 1H, OCq=CH2), 4.23 (s, 1H, OC_q=CH_2), 5.18-5.19 (m, 1H, C_5H_4), 5.48-5.50 (m, 1H, C_5H_4), 5.61-5.63 (m, 1H, C_5H_4), 6.59-6.61 (m, 1H, C_5H_4) ppm. HPh_2: δ = 5.20 (d, $^1J_{P,H}$ = 215.8 Hz, *H*PPh_2), 7.01-7.02 (m, 6H, 2×*p*-CH_{Ph}P, 4×*o*-CH_{Ph}P), 7.35-7.38 (m, 4H, 4×*m*-CH_{Ph}P) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 300 K): δ = 12.6 ($C_5\underline{Me}_5$), 28.0 (CH_{Ad}), 28.4 (CH_{Ad}), 31.8 (CH_{Ad}), 33.9 ($CH_{2,Ad}$), 34.1 ($CH_{2,Ad}$), 35.0 (CH_{Ad}), 35.02 ($CH_{2,Ad}$), 36.8 ($CH_{2,Ad}$), 38.8 ($CH_{2,Ad}$), 52.7 ($C_{q,exo}$), 82.6 (OC_q=$\underline{C}H_2$), 107.0 (C_5H_4), 113.7 (C_5H_4), 115.6 (C_5H_4), 123.3 (C_5H_4), 125.4 ($\underline{C}_5Me_5$), 148.4 ($C_{q,ipso}$), 181.3 ($O\underline{C}_q$=CH_2) ppm. $HPPh_2$: δ = 128.6 (2×*p*-CH_{Ph}P), 128.8 (d, $^2J_{C,P}$ = 6.2 Hz, 4×*o*-CH_{Ph}P), 134.3 (d, $^3J_{C,P}$ = 17.0 Hz, 4×*m*-CH_{Ph}P), 135.4 (d, $^1J_{C,P}$ = 10.8 Hz, 2×$C_{q,Ph}$P) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 300 K): δ = -40.8 ($HPPh_2$) ppm. HR/MS calculated: m/z = 455.2430 [M-Cl^-+MeOH]; measured (ESI): m/z = 455.2425.

Synthesis of Zr2: In a glove box compound **L1** (0.332 g, 1.456 mmol) in *n*-hexane (3×5 mL) was added to a solution of complex **Zr1** (0.670 g, 1.456 mmol) in 10 mL of *n*-hexane. The suspension was stirred for 16 h at room temperature resulting in a colorless suspension. All volatiles were removed under vacuum to yield a colorless solid, identified as a mixture of complex **Zr2** and an additional byproduct (ratio 3:1). Crystals suitable for single crystal X-ray diffraction of complex **Zr2** were obtained from an *n*-hexane/toluene (4:1) solution at -4 °C. Only the clearly assignable signals of **Zr2** are given in the analyses of the NMR data. We suppose, that the byproduct is some kind of dimeric species due to eight additional C_5H_4 signals in the ^1H NMR. Two other signals in the ^1H NMR might be assigned to two other pentamethylcyclopentadienyl groups ($\delta^{31}P\{^1H\}$ = -5.5 ppm; byproduct). Yield: 0.842 g (mixture of **Zr2** + byproduct). ^1H NMR (500 MHz, C_6D_6, 300 K): δ = 1.85 (s, 15H, C_5Me_5), 1.90 (d, $^3J_{P,H}$ = 12.7 Hz, OC_qCH_3), 5.46-5.47 (m, 1H, C_5H_4), 5.57-5.58 (m, 1H, C_5H_4), 5.83-5.84 (m, 1H, C_5H_4), 6.41-6.42 (m, 1H, C_5H_4) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 300 K): δ = 25.0 ppm.

Synthesis of Hf2: In a glove box compound **L1** (0.188 g, 0.823 mmol) in *n*-hexane (3×5 mL) was added to a solution of complex **Hf1** (0.500 g, 0.823 mmol) in 10 mL of *n*-hexane. The suspension was stirred for 16 h at room temperature resulting in a colorless suspension. All volatiles were removed under vacuum to yield **Hf2** a colorless solid. Yield: 0.481 g (0.576 mmol, 70%). Melting point: 216-218 °C (dec.). IR (ATR): $\tilde{\nu}$ = 2951, 2915, 2861, 1511, 1478, 1454, 1433, 1375, 1092, 1061, 1024, 923, 890, 867, 856, 831, 816, 798, 752, 739, 700, 664, 639, 601 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 305 K): δ = 2.02 (s, 15H, C_5Me_5), 2.04 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.25 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.32 (d, $^3J_{P,H}$ = 2.6 Hz, 3H, OC_qCH_3), 5.44-5.46 (m, 1H, C_5H_4), 5.52-5.54 (m, 1H, C_5H_4), 5.66-5.68 (m, 1H, C_5H_4), 6.19-6.21 (m, 1H, CH_{Aryl}), 6.60-6.62 (m, 1H, CH_{Aryl}), 6.68-6.70 (m, 1H, C_5H_4), 6.85-6.87 (m, 1H, CH_{Aryl}), 6.96-7.08 (m, 7H, 7×CH_{Aryl}), 7.14-7.17 (m, 2H, 2×CH_{Aryl})*, 7.25-7.32 (m, 4H, 4×CH_{Aryl}), 7.82-7.85 (m, 2H, 2×CH_{Aryl}) ppm. * = overlap with C_6D_6 signal. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 300 K): δ = 16.3 ppm. note: $^{13}C\{^1H\}$ NMR measurements only showed low intensities of the signals due to poor solubility.

Synthesis of Hf3: To a solution of complex **Hf2** (0.250 g, 0.299 mmol) in 10 mL of tetrahydrofuran was added a methyl lithium solution (0.2 mL, 0.299 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed under vacuum, and the residue was dissolved in 8 mL of toluene. The solution was filtered, and the residue was washed with toluene (2×5 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 an *n*-hexane solution at -26 °C. Yield: 0.186 g (0.228 mmol, 76%). Melting point: 202-204 °C (dec.). IR (ATR): $\tilde{\nu}$ = 3040, 2994, 2944, 2916, 2871, 1584, 1476, 1428, 1368, 1196, 1149, 1095, 1059, 1024, 923, 889, 870, 857, 811, 797, 751, 740, 697 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 305 K): δ = 0.11 (s, 3H, $HfCH_3$), 1.93 (s, 15H, C_5Me_5), 2.06 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.07 (d, $^3J_{P,H}$ = 3.2 Hz, 3H, OC_qCH_3), 2.25 (s, 3H, $CH_{3,p\text{-tolyl}}$), 5.07-5.08 (m, 1H, C_5H_4), 5.45-5.47 (m, 1H, C_5H_4), 5.59-5.61 (m, 1H, C_5H_4), 6.39-6.41 (m, 1H, $CH_{p\text{-tolyl}}$), 6.52-6.53 (m, 1H, C_5H_4), 6.66-6.68 (m, 1H, $CH_{p\text{-tolyl}}$), 6.91-6.93 (m, 1H, $CH_{p\text{-tolyl}}$), 6.96-7.14 (m, 10H, 10×CH_{Aryl}), 7.31-7.34 (m, 2H, 2×*m*-CH_{PhP}), 7.48-7.50 (m, 1H, $CH_{p\text{-tolyl}}$), 7.78-7.81 (m, 2H, 2×*m*-CH_{PhP}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ = 11.7 ($C_5\underline{Me}_5$), 20.8 ($CH_{3,p\text{-tolyl}}$), 21.2 ($CH_{3,p\text{-tolyl}}$), 27.7 ($OC_q\underline{C}H_3$), 28.4 ($HfCH_3$), 69.1 (d, $^2J_{C,P}$ = 20.7 Hz, $C_{q,exo}$), 106.2 (C_5H_4), 109.2 (C_5H_4), 110.0 (C_5H_4), 111.5 (d, $^1J_{C,P}$ = 20.2 Hz, $O\underline{C}_qCH_3$), 115.4 (C_5H_4), 117.6 ($\underline{C}_5Me_5$), 126.9 (2×*o*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 127.8 (d, $^2J_{C,P}$ = 4.1 Hz, 2×*o*-CH_{PhP}), 128.1 (2×*o*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 128.4 (*p*-$CH_{PhP}$), 128.5 (d, $^2J_{C,P}$ = 8.1 Hz, 2×*o*-CH_{PhP}), 129.4 (*p*-CH_{PhP}), 132.5 (d, $^4J_{C,P}$ = 5.6 Hz, 2×*m*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 132.9 (2×*m*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 135.0 (d, $^3J_{C,P}$ = 16.7 Hz, 2×*m*-CH_{PhP}), 135.7 ($\underline{C}_{q,p\text{-tolyl}}CH_3$), 136.6 ($\underline{C}_{q,p\text{-tolyl}}CH_3$), 137.5 (d, $^3J_{C,P}$ = 22.7 Hz, 2×*m*-CH_{PhP}), 140.0 (d, $^1J_{C,P}$ = 28.7 Hz, $C_{q,PhP}$), 141.18 (*p*-$\underline{C}_{q,p\text{-tolyl}}CH_3$), 141.2 (d, $^1J_{C,P}$ = 26.8 Hz, $C_{q,PhP}$), 142.5 (d, $^3J_{C,P}$ = 7.3 Hz, *p*-$\underline{C}_{q,p\text{-tolyl}}CH_3$), 145.7 ($C_{q,ipso}$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 305 K): δ = 16.0 ppm. HR/MS calculated: m/z = 815.2908 [M-H^+]; measured (ESI): m/z = 815.2905.

Synthesis of Ti4: In a glove box compound **L2** (0.500 g, 1.951 mmol) in *n*-hexane (3×5 mL) was added to a solution of complex **Ti1** (0.813 g, 1.951 mmol) in 10 mL of *n*-hexane. The suspension was stirred for 16 h at room temperature resulting in a yellow suspension. The supernatant was decanted, the residue was washed with *n*-hexane (3×5 mL) and dried under vacuum to yield **Ti4** as a yellow solid. Crystals suitable for single crystal X-ray diffraction of complex **Ti4** were obtained from a

saturated *n*-hexane solution at room temperature. Yield: 1.156 g (1.717 mmol, 88%). Melting point: 178-180 °C. IR (ATR): $\tilde{\nu}$ = 3079, 3017, 2955, 2899, 2854, 1480, 1461, 1452, 1434, 1414, 1384, 1366, 1333, 1315, 1262, 1213, 1201, 1173, 1149, 1096, 1062, 1025, 1000, 952, 917, 886, 874, 848, 832, 743, 694, 675, 658, 635, 565 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 299 K): δ = 1.28-1.35 (m, 2H, PCH_2), 1.39 (s, 3H, OC_qCH_3), 1.48-1.69 (m, 9H, PCH_2CH_2, $CH_{Ad}/CH_{2,Ad}$), 1.79 (s, 15H, C_5Me_5), 2.09-2.15 (m, 2H, $CH_{Ad}/CH_{2,Ad}$), 2.27-2.30 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.36-2.47 (m, 3H, $CH_{Ad}/CH_{2,Ad}$), 2.80-2.87 (m, 1H, PCH_2CH_2), 5.04-5.06 (m, 1H, C_5H_4), 5.40-5.42 (m, 1H, C_5H_4), 5.45-5.47 (m, 1H, C_5H_4), 6.40-6.42 (m, 1H, C_5H_4), 7.06-7.09 (m, 1H, *p*-CH_{Ph}P), 7.11-7.14 (m, 1H, *p*-CH_{Ph}P), 7.19-7.22 (m, 4H, 4×*o*-CH_{Ph}P), 7.71-7.74 (m, 4H, 4×*m*-CH_{Ph}P) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 299 K): δ = 12.6 ($C_5\underline{Me}_5$), 22.8 (d, $^1J_{C,P}$ = 11.6 Hz, PCH_2), 27.5 (CH_{Ad}), 28.0 (CH_{Ad}), 31.0 ($OC_q\underline{C}H_3$), 32.6 (CH_{Ad}), 33.0 (CH_{Ad}), 33.4 ($CH_{2,Ad}$), 34.8 ($CH_{2,Ad}$), 35.8 (d, $^2J_{C,P}$ = 20.7 Hz, $PCH_2\underline{C}H_2$), 37.2 ($CH_{2,Ad}$), 37.3 ($CH_{2,Ad}$), 39.4 ($CH_{2,Ad}$), 54.7 ($C_{q,exo}$), 104.5 (C_5H_4), 111.6 (C_5H_4), 111.7 (d, $^3J_{C,P}$ = 13.9 Hz, $O\underline{C}_qCH_3$), 112.7 (C_5H_4), 120.1 (C_5H_4), 123.7 ($\underline{C}_5Me_5$), 127.9 (*p*-CH_{Ph}P)*, 128.5 (d, $^2J_{C,P}$ = 5.7 Hz, 2×*o*-CH_{Ph}P), 128.77 (d, $^2J_{C,P}$ = 6.8 Hz, 2×*o*-CH_{Ph}P), 128.8 (*p*-CH_{Ph}P), 132.7 (d, $^3J_{C,P}$ = 17.1 Hz, 2×*m*-CH_{Ph}P), 133.9 (d, $^3J_{C,P}$ = 19.4 Hz, 2×*m*-CH_{Ph}P), 140.2 (d, $^1J_{C,P}$ = 16.9 Hz, $C_{q,Ph}$P), 142.1 (d, $^1J_{C,P}$ = 16.5 Hz, $C_{q,Ph}$P), 156.7 ($C_{q,ipso}$) ppm. * = overlap with C_6D_6 signal. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 299 K): δ = -12.0 ppm. EA: Anal. Calcd for $C_{41}H_{50}ClOPTi$: C, 73.16; H, 7.49. Found: C, 72.07; H, 7.66.

Synthesis of Zr4: In a glove box compound **L2** (0.476 g, 1.857 mmol) in *n*-hexane (3×5 mL) was added to a solution of complex **Zr1** (0.854 g, 1.857 mmol) in 10 mL of *n*-hexane. The suspension was stirred for 16 h at room temperature resulting in a colorless suspension. The supernatant was decanted, the residue was washed with *n*-hexane (3×5 mL) and dried under vacuum to yield **Zr4** as a colorless solid. Crystals suitable for single crystal X-ray diffraction of complex **Zr4** were obtained from a saturated toluene solution at room temperature. Yield: 0.558 g (0.779 mmol, 42%). Melting point: 190-192 °C. IR (ATR): $\tilde{\nu}$ = 3078, 3021, 2961, 2900, 2856, 1481, 1470, 1433, 1375, 1211, 1199, 1174, 1151, 1097, 1060, 1027, 999, 980, 960, 887, 872, 846, 820, 742, 696, 676, 657, 632, 563 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 299 K): δ = 1.27-1.35 (m, 2H, $CH_{Ad}/CH_{2,Ad}$), 1.41 (s, 3H, OC_qCH_3), 1.48-1.72 (m, 9H, PCH_2CH_2, $CH_{Ad}/CH_{2,Ad}$), 1.85 (s, 15H, C_5Me_5), 2.15-2.22 (m, 3H, PCH_2, $CH_{Ad}/CH_{2,Ad}$), 2.33-2.39 (m, 1H, PCH_2), 2.44-2.54 (m, 3H, $CH_{Ad}/CH_{2,Ad}$), 5.31-5.33 (m, 1H, C_5H_4), 5.51-5.53 (m, 1H, C_5H_4), 5.68-5.70 (m, 1H, C_5H_4), 6.18-6.20 (m, 1H, C_5H_4), 7.06-7.08 (m, 1H, *p*-CH_{Ph}P), 7.10-7.13 (m, 1H, *p*-CH_{Ph}P), 7.19-7.22 (m, 4H, 4×*o*-CH_{Ph}P), 7.68-7.72 (m, 4H, 4×*m*-CH_{Ph}P) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 299 K): δ = 11.8 ($C_5\underline{Me}_5$), 22.8 (d, $^1J_{C,P}$ = 11.5 Hz, PCH_2), 27.5 (CH_{Ad}), 28.0 (CH_{Ad}), 31.1 ($OC_q\underline{C}H_3$), 32.8 (CH_{Ad}), 33.1 (CH_{Ad}), 33.4 ($CH_{2,Ad}$), 34.9 ($CH_{2,Ad}$), 36.7 (d, $^2J_{C,P}$ = 20.2 Hz, $PCH_2\underline{C}H_2$), 37.2 ($CH_{2,Ad}$), 37.7 ($CH_{2,Ad}$), 39.6 ($CH_{2,Ad}$), 55.1 ($C_{q,exo}$), 105.4 (C_5H_4), 106.9 (d, $^3J_{C,P}$ = 13.3 Hz, $O\underline{C}_qCH_3$), 110.1 (2×C_5H_4), 115.1 (C_5H_4), 120.5 ($\underline{C}_5Me_5$), 128.0 (*p*-CH_{Ph}P)*, 128.6 (d, $^2J_{C,P}$ = 5.8 Hz, 2×*o*-CH_{Ph}P), 128.8 (d, $^2J_{C,P}$ = 7.8 Hz, 2×*o*-CH_{Ph}P, 128.9 (*p*-CH_{Ph}P), 132.7 (d, $^3J_{C,P}$ = 17.3 Hz, 2×*m*-CH_{Ph}P), 133.8 (d, $^3J_{C,P}$ = 19.4 Hz, 2×*m*-CH_{Ph}P), 139.9 (d, $^1J_{C,P}$ = 16.4 Hz, $C_{q,Ph}$P), 141.8 (d, $^1J_{C,P}$ = 16.2 Hz, $C_{q,Ph}$P), 154.9 ($C_{q,ipso}$) ppm. * = overlap with C_6D_6 signal. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 299 K): δ = -12.3 ppm. EA: Anal. Calcd for $C_{41}H_{50}ClOPZr$: C, 68.73; H, 7.03. Found: C, 69.32; H, 7.13.

Synthesis of Hf4: In a glove box compound **L2** (0.213 g, 0.831 mmol) in *n*-hexane (3×5 mL) was added to a solution of complex **Hf1** (0.505 g, 0.831 mmol) in 10 mL of *n*-hexane. The suspension was stirred for 16 h at room temperature resulting in a pale yellow suspension. The supernatant was decanted, the residue was washed with *n*-hexane (3×3 mL) and dried under vacuum to yield **Hf4** as a pale yellow solid. Yield: 0.591 g (0.684 mmol, 82%). Melting point: 175-177 °C. IR (ATR): $\tilde{\nu}$ = 2885, 2831, 1525, 1493, 1474, 1392, 1381, 1371, 1278, 1254, 1178, 1164, 1152, 990, 845, 835, 772, 759, 726, 711, 660 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 305 K): δ = 1.53 (s, 3H, OC_qCH_3), 1.94 (s, 15H, C_5Me_5), 1.97-1.98 (m, 1H, PCH_2CH_2), 2.11 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.17 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.24-2.29 (m, 1H, PCH_2), 2.66-2.71 (m, 1H, PCH_2), 2.93-3.00 (m, 1H, PCH_2CH_2), 4.94-4.95 (m, 1H, C_5H_4), 5.41-5.42 (m, 1H, C_5H_4), 5.68-5.69 (m, 1H, C_5H_4), 6.82-6.83 (m, 2H, C_5H_4, CH_{Aryl}), 6.90-6.97 (m, 3H, 3×CH_{Aryl}), 7.05-7.14 (m, 7H, 7×CH_{Aryl}), 7.38-7.41 (m, 1H, CH_{Aryl}), 7.47-7.59 (m, 5H, 4×*m*-CH_{Ph}P, CH_{Aryl}), 7.70-7.71 (m, 1H, CH_{Aryl}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ = 11.9 ($C_5\underline{Me}_5$), 20.9 ($CH_{3,p\text{-tolyl}}$), 21.0 ($CH_{3,p\text{-tolyl}}$), 24.0 (d, $^1J_{C,P}$ = 11.3 Hz, PCH_2), 29.8 ($OC_q\underline{C}H_3$), 39.2 (d, $^2J_{C,P}$ = 19.4 Hz, $PCH_2\underline{C}H_2$), 65.9 ($C_{q,exo}$), 105.4 (d, $^3J_{C,P}$ = 13.7 Hz, $O\underline{C}_qCH_3$), 109.3 (C_5H_4), 109.4 (C_5H_4), 110.4 (C_5H_4), 118.2 (C_5H_4), 119.8 ($\underline{C}_5Me_5$), 128.4 (*p*-CH_{Ph}P)*, 128.5 (*p*-CH_{Ph}P)*, 128.6 (d, $^2J_{C,P}$ = 6.9 Hz, 2×*o*-CH_{Ph}P), 128.68 (2×*o*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 128.7 (d, $^2J_{C,P}$ = 7.0 Hz, 2×*o*-CH_{Ph}P), 129.1 (2×*o*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 130.3 (2×*m*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 130.9 (2×*m*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 133.2 (d, $^3J_{C,P}$ = 18.2 Hz, 2×*m*-CH_{Ph}P), 133.5 (d, $^3J_{C,P}$ = 18.4 Hz, 2×*m*-CH_{Ph}P), 135.8 ($\underline{C}_{q,p\text{-tolyl}}CH_3$), 136.1 ($\underline{C}_{q,p\text{-tolyl}}CH_3$), 139.7 (d, $^1J_{C,P}$ = 14.3 Hz, $C_{q,Ph}$P), 140.7 (d, $^1J_{C,P}$ = 15.8 Hz, $C_{q,Ph}$P), 141.5 (*p*-$\underline{C}_{q,p\text{-tolyl}}CH_3$), 143.6 (*p*-$\underline{C}_{q,p\text{-tolyl}}CH_3$), 147.4 ($C_{q,ipso}$) ppm. * = overlap with C_6D_6 signal. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 305 K): δ = -13.9 ppm. EA: Anal. Calcd for $C_{46}H_{50}ClHfOP$: C, 63.96; H, 5.83. Found: C, 64.20; H, 6.17.

Synthesis of Ti5: To a solution of complex **Ti4** (0.500 g, 0.743 mmol) in 15 mL of tetrahydrofuran was added a methyllithium solution (0.5 mL, 0.743 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed under vacuum, and the residue was dissolved in 12 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 **Ti5** as a pale yellow solid. Crystals suitable for single crystal X-ray diffraction were obtained from a saturated toluene solution at -26 °C. Yield: 0.398 g (0.610 mmol, 82%). Melting point: 202-204 °C (dec.). IR (ATR): $\tilde{\nu}$ = 2903, 2857, 1480, 1462, 1432, 1373, 1173, 1146, 1098, 1060, 1025, 982, 955, 874, 849, 813, 746, 734, 695, 659, 635, 581 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 298 K): δ = 0.26 (s, 3H, $TiCH_3$), 1.32 (s, 3H, OC_qCH_3), 1.52-1.66 (m, 7H, $CH_{Ad}/CH_{2,Ad}$), 1.71 (s, 15H, C_5Me_5), 1.78-2.11 (m, 6H, PCH_2, PCH_2CH_2, $CH_{Ad}/CH_{2,Ad}$), 2.22-2.30 (m, 2H, $CH_{Ad}/CH_{2,Ad}$), 2.35-2.42 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.48-2.50 (m, 1H, PCH_2CH_2), 2.70-2.73 (m, 1H, $CH_{Ad}/CH_{2,Ad}$) 4.85-4.87 (m, 1H, C_5H_4), 5.07-5.09 (m, 1H, C_5H_4), 5.29-5.30 (m, 1H, C_5H_4), 6.14-6.15 (m, 1H, C_5H_4), 7.05-7.19 (m, 6H, 4×*o*-CH_{Ph}P, 2×*p*-CH_{Ph}P)*, 7.55-7.58 (m, 2H, 2×*m*-CH_{Ph}P), 7.63-7.66 (m, 2H, 2×*m*-CH_{Ph}P) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ = 12.0 ($C_5\underline{Me}_5$), 22.6 (d, $^1J_{C,P}$ = 10.8 Hz, PCH_2), 27.7 (CH_{Ad}), 28.2 (CH_{Ad}), 30.8 ($OC_q\underline{C}H_3$), 32.88 (CH_{Ad}), 32.9 (CH_{Ad}), 33.7 ($CH_{2,Ad}$), 35.0 ($CH_{2,Ad}$), 35.3 ($TiCH_3$), 36.6 (d, $^2J_{C,P}$ = 19.8 Hz, $PCH_2\underline{C}H_2$), 37.3 ($CH_{2,Ad}$), 37.4 ($CH_{2,Ad}$), 39.6 ($CH_{2,Ad}$), 54.9 ($C_{q,exo}$), 103.4 (C_5H_4), 107.4 (d, $^3J_{C,P}$ = 12.9 Hz, $O\underline{C}_qCH_3$), 107.9 (C_5H_4), 108.6 (C_5H_4), 116.3 (C_5H_4), 118.6 ($\underline{C}_5Me_5$), 128.1 (*p*-CH_{Ph}P)*, 128.6 (d, $^2J_{C,P}$ = 5.8 Hz, 2×*o*-CH_{Ph}P), 128.8 (d, $^2J_{C,P}$ = 6.7 Hz, 2×*o*-CH_{Ph}P), 128.9 (*p*-CH_{Ph}P), 132.6 (d, $^3J_{C,P}$ = 17.4 Hz, 2×*m*-CH_{Ph}P), 133.7 (d, $^3J_{C,P}$ = 19.2 Hz, 2×*m*-CH_{Ph}P), 139.9 (d, $^1J_{C,P}$ = 16.3 Hz, $C_{q,Ph}$P), 141.9 (d, $^1J_{C,P}$ = 15.6 Hz, $C_{q,Ph}$P), 151.4 ($C_{q,ipso}$) ppm. * = overlay with C_6D_6 signal. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K): δ = -12.7 ppm. EA: Anal. Calcd for $C_{42}H_{53}OPTi$: C, 77.29; H, 8.18. Found: C, 75.25; H, 8.34.

Synthesis of Zr5: To a solution of complex **Zr4** (0.500 g, 0.698 mmol) in 15 mL of tetrahydrofuran was added a methyllithium solution (0.4 mL, 0.698 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 (2×10 mL). All volatiles were removed under vacuum to give complex **Zr5** as a colorless solid. Yield: 0.442 g (0.635 mmol, 91%). Melting point: 167-169 °C (dec.). IR (ATR): $\tilde{\nu}$ = 2961, 2903, 2858, 1480, 1467, 1452, 1434, 1366, 1261, 1170, 1148,

1095, 1058, 1029, 999, 980, 963, 885, 871, 845, 803, 739, 695, 658, 632, 602, 559 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 298 K): δ = -0.07 (s, 3H, $ZrCH_3$), 1.36 (s, 3H, OC_qCH_3), 1.60-1.74 (m, 6H, $CH_{Ad}/CH_{2,Ad}$, PCH_2CH_2), 1.81 (s, 15H, C_5Me_5), 1.89-2.30 (m, 10H, $CH_{Ad}/CH_{2,Ad}$, PCH_2CH_2), 2.54-2.56 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.66-2.69 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 5.08-5.10 (m, 1H, C_5H_4), 5.43-5.45 (m, 1H, C_5H_4), 5.54-5.55 (m, 1H, C_5H_4), 6.06-6.08 (m, 1H, C_5H_4), 7.05-7.13 (m, 2H, 2×*p*-CH_{PhP}), 7.16-7.19 (m, 4H, 4×*o*-CH_{PhP})*, 7.56-7.59 (m, 2H, 2×*m*-CH_{PhP}), 7.63-7.66 (m, 2H, 2×*m*-CH_{PhP}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ = 11.4 ($C_5\underline{Me}_5$), 22.8 (d, $^1J_{C,P}$ = 11.3 Hz, PCH_2), 23.0 ($ZrCH_3$), 27.7 (CH_{Ad}), 28.2 (CH_{Ad}), 31.0 ($OC_q\underline{C}H_3$), 32.9 (CH_{Ad}), 33.1 (CH_{Ad}), 33.6 ($CH_{2,Ad}$), 35.0 ($CH_{2,Ad}$), 37.2 ($CH_{2,Ad}$), 37.6 (d, $^2J_{C,P}$ = 20.0 Hz, $PCH_2\underline{C}H_2$), 37.8 ($CH_{2,Ad}$), 39.8 ($CH_{2,Ad}$), 55.3 ($C_{q,exo}$), 104.3 (d, $^3J_{C,P}$ = 13.0 Hz, $O\underline{C}_qCH_3$), 104.8 (C_5H_4), 106.7 (C_5H_4), 107.6 (C_5H_4), 113.2 (C_5H_4), 117.2 ($\underline{C}_5Me_5$), 128.1 (*p*-CH_{PhP})*, 128.6 (d, $^2J_{C,P}$ = 5.9 Hz, 2×*o*-CH_{PhP}), 128.8 (d, $^2J_{C,P}$ = 6.6 Hz, 2×*o*-CH_{PhP}), 128.9 (*p*-CH_{PhP}), 132.6 (d, $^3J_{C,P}$ = 17.5 Hz, 2×*m*-CH_{PhP}), 133.7 (d, $^3J_{C,P}$ = 19.2 Hz, 2×*m*-CH_{PhP}), 139.8 (d, $^1J_{C,P}$ = 16.1 Hz, $C_{q,PhP}$), 141.7 (d, $^1J_{C,P}$ = 15.6 Hz, $C_{q,PhP}$), 150.3 ($C_{q,ipso}$) ppm. * = overlay with C_6D_6 signal. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K): δ = -12.9 ppm. EA: Anal. Calcd for $C_{42}H_{53}OPZr$: C, 72.47; H, 7.67. Found: C, 71.41; H, 7.92.

Synthesis of Hf5: To a solution of complex **Hf4** (0.200 g, 0.232 mmol) in 15 mL of tetrahydrofuran was added a methyllithium solution (0.2 mL, 0.698 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 8 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 **Hf5** as a colorless solid. Yield: 0.140 g (0.166 mmol, 72%). Melting point: 201-203 °C (dec.). IR (ATR): $\tilde{\nu}$ = 2916, 2870, 1645, 1584, 1509, 1475, 1435, 1377, 1369, 1261, 1196, 1149, 1093, 1060, 1024, 923, 889, 869, 857, 811, 798, 751, 740, 697, 664, 637 cm^{-1}. ^1H NMR (500 MHz, C_6D_6, 305 K): δ = -0.08 (s, 3H, $HfCH_3$), 1.31 (s, 3H, OC_qCH_3), 1.86 (s, 15H, C_5Me_5), 1.86-1.90 (m, 1H, PCH_2CH_2), 2.13 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.18-2.22 (m, 1H, PCH_2), 2.19 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.63-2.68 (m, 1H, PCH_2), 2.87-2.94 (m, 1H, PCH_2CH_2), 4.97-4.98 (m, 1H, C_5H_4), 5.14-5.15 (m, 1H, C_5H_4), 5.44-5.46 (m, 1H, C_5H_4), 6.68-6.69 (m, 1H, C_5H_4), 6.83-6.85 (m, 1H, CH_{Aryl}), 6.90-7.18 (m, 12H, 12×CH_{Aryl}), 7.49-7.56 (m, 4H, 4×*m*-CH_{PhP}), 7.84-7.86 (m, 1H, CH_{Aryl}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ = 11.5 ($C_5\underline{Me}_5$), 20.9 ($CH_{3,p\text{-tolyl}}$), 21.0 ($CH_{3,p\text{-tolyl}}$), 24.1 (d, $^1J_{C,P}$ = 10.7 Hz, PCH_2), 27.8 ($HfCH_3$), 30.4 ($OC_q\underline{C}H_3$), 38.9 ($PCH_2\underline{C}H_2$), 66.1 ($C_{q,exo}$), 103.4 (d, $^3J_{C,P}$ = 13.2 Hz, $O\underline{C}_qCH_3$), 106.0 (C_5H_4), 108.8 (C_5H_4), 109.0 (C_5H_4), 116.3 (C_5H_4), 116.7 ($\underline{C}_5Me_5$), 128.3 (2×*o*-$\underline{C}H_{p\text{-tolyl}}CH_3$)*, 128.4 (*p*-$CH_{PhP}$)*, 128.5 (*p*-$CH_{PhP}$), 128.6 (d, $^2J_{C,P}$ = 5.8 Hz, 2×*o*-CH_{PhP}), 128.7 (d, $^2J_{C,P}$ = 5.8 Hz, 2×*o*-CH_{PhP}), 129.0 (2×*o*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 130.5 (2×*m*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 131.1 (2×*m*-$\underline{C}H_{p\text{-tolyl}}CH_3$), 133.2 (d, $^3J_{C,P}$ = 18.2 Hz, 2×*m*-CH_{PhP}), 133.5 (d, $^3J_{C,P}$ = 18.6 Hz, 2×*m*-CH_{PhP}), 135.6 ($\underline{C}_{q,p\text{-tolyl}}CH_3$), 135.9 ($\underline{C}_{q,p\text{-tolyl}}CH_3$), 140.0 (d, $^1J_{C,P}$ = 14.5 Hz, $C_{q,PhP}$), 140.7 (d, $^1J_{C,P}$ = 16.2 Hz, $C_{q,PhP}$), 143.2 (*p*-$\underline{C}_{q,p\text{-tolyl}}CH_3$), 143.3 (*p*-$\underline{C}_{q,p\text{-tolyl}}CH_3$), 143.9 ($C_{q,ipso}$) ppm. * = overlay with C_6D_6 signal. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 305 K): δ = -14.0 ppm. **EA:** Anal. Calcd for $C_{47}H_{53}HfOP$: C, 66.93; H, 6.33. Found: C, 65.61; H, 6.61.

Synthesis of Ti6: A mixture of complex **Ti5** (0.400 g, 0.613 mmol) and $B(C_6F_5)_3$ (0.314 g, 0.613 mmol) was stirred in 10 mL of toluene. When the stirring process is stopped after a few minutes, the development of two phases can be observed due to the formation of complex **Ti6**. The solvent was decanted, the residue was washed with *n*-hexane (3×5 mL) and dried under vacuum to give complex **Ti6** as an orange solid. Yield: 0.603 g (0.505 mmol, 82%). Melting point: 92-94 °C. IR (ATR): $\tilde{\nu}$ = 2914, 2861, 1641, 1509, 1485, 1454, 1379, 1267, 1081, 977, 965, 947, 933, 830, 805, 784, 744, 697, 660, 649, 633, 604, 569 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 0.48 (s(br), 3H, BCH_3), 1.57-1.76 (m, 8H, $CH_{Ad}/CH_{2,Ad}$), 1.70 (s, 3H, OC_qCH_3), 1.89 (s, 15H, C_5Me_5), 1.95-2.02 (m, 2H, $CH_{Ad}/CH_{2,Ad}$), 2.08-2.20 (m, 3H, PCH_2CH_2, $CH_{Ad}/CH_{2,Ad}$), 2.37-2.38 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.55-2.58 (m, 1H, $CH_{Ad}/CH_{2,Ad}$), 2.68-2.82 (m, 2H, PCH_2), 3.00-1.11 (m, 1H, PCH_2CH_2), 4.81-4.82 (m, 1H, C_5H_4), 5.51-5.52 (m, 1H, C_5H_4), 5.83-5.87 (m, 1H, C_5H_4), 6.44-6.46 (m, 1H, C_5H_4), 7.02-7.03 (m, 2H, 2×CH_{Ph}), 7.21-7.26 (m, 2H, 2×CH_{Ph}), 7.37-7.41 (m, 2H, 2×CH_{Ph}), 7.47-7.50 (m, 1H, 2×CH_{Ph}), 7.60-7.64 (m, 2H, 2×CH_{Ph}), 7.66-7.69 (m, 1H, CH_{Ph}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ = 12.8 (BCH_3)*, 13.1 ($C_5\underline{Me}_5$), 27.0 (CH_{Ad}), 27.7 (CH_{Ad}), 28.7 (d, $^1J_{C,P}$ = 28.7 Hz, PCH_2), 33.8 (CH_{Ad}), 34.1 ($CH_{2,Ad}$), 34.3 ($OC_q\underline{C}H_3$), 34.6 ($CH_{2,Ad}$), 36.4 (CH_{Ad}), 36.6 ($CH_{2,Ad}$), 37.4 ($CH_{2,Ad}$), 38.9 ($CH_{2,Ad}$), 39.1 (d, $^2J_{C,P}$ = 48.1 Hz, $PCH_2\underline{C}H_2$), 55.0 ($C_{q,exo}$), 108.7 (C_5H_4), 111.1 (C_5H_4), 113.6 (C_5H_4), 113.9 ($O\underline{C}_qCH_3$), 118.7 (C_5H_4), 126.0 ($\underline{C}_5Me_5$), 128.8 ($C_{q,ArB}$)*, 129.1 (d, $^2J_{C,P}$ = 8.9 Hz, 4×*o*-CH_{PhP}), 130.9 (d, $^1J_{C,P}$ = 34.7 Hz, $C_{q,PhP}$), 131.5 (*p*-CH_{PhP}), 132.8 (*p*-CH_{PhP}), 132.9 (d, $^3J_{C,P}$ = 14.6 Hz, 4×*m*-CH_{PhP}), 133.8 (d, $^1J_{C,P}$ = 26.1 Hz, $C_{q,PhP}$), 136.8 (dm, $^1J_{C,F}$ = 256.0 Hz, $C_{q,Ar}F$), 137.9 (dm, $^1J_{C,F}$ = 242.5 Hz, $C_{q,Ar}F$), 148.7 (dm, $^1J_{C,F}$ = 239.1 Hz, $C_{q,Ar}F$), 155.6 ($C_{q,ipso}$) ppm. * = assignment by $^1H/^{13}C$-HMQC/HMBC spectra. $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 299 K): δ = -15.5 ppm. $^{19}F\{^1H\}$ NMR (470 MHz, CD_2Cl_2, 299 K): δ = -167.9 (m, 6F *m*-F_{ArB}), -165.3 (t, $^3J_{F,F}$ = 20.4 Hz, 3F, *p*-F_{ArB}), -133.1 (m, 6F, *o*-F_{ArB}) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 299 K): δ = 28.6 ppm. EA: Anal. Calcd for $C_{60}H_{53}BF_{15}OPTi$: C, 61.87; H, 4.59. Found: C, 61.67; H, 4.76. HR/MS calculated: m/z = 637.3079 [M^+]; measured (ESI): m/z = 637.3073.

Synthesis of Zr6: A mixture of complex **Zr5** (0.250 g, 0.359 mmol) and $B(C_6F_5)_3$ (0.184 g, 0.359 mmol) was stirred in 10 mL of toluene. When the stirring process is stopped after a few minutes, the development of two phases can be observed due to the formation of complex **Zr6**. The solvent was decanted, the residue was washed with *n*-hexane (3×5 mL) and dried under vacuum to give complex **Zr6** as a colorless solid. Yield: 0.393 g (0.325 mmol, 91%). Melting point: 85-87 °C. IR (ATR): $\tilde{\nu}$ = 2912, 2860, 1641, 1509, 1454, 1379, 1267, 1081, 965, 951, 935, 842, 805, 743, 694, 659, 644, 632, 605, 567 cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 296 K): δ = 0.49 (s(br), 3H, BCH_3), 1.52-1.59 (m, 2H, $CH_{Ad}/CH_{2,Ad}$), 1.67 (s, 3H, OC_qCH_3), 1.71-1.81 (m, 3H, $CH_{Ad}/CH_{2,Ad}$), 1.90 (s, 15H, C_5Me_5), 1.96-2.23 (m, 9H, PCH_2CH_2, $CH_{Ad}/CH_{2,Ad}$), 2.54-2.75 (m, 3H, PCH_2, $CH_{Ad}/CH_{2,Ad}$), 2.79-2.88 (m, 1H, PCH_2CH_2), 5.29-5.30 (m, 1H, C_5H_4), 5.75-5.76 (m, 1H, C_5H_4), 5.80-5.81 (m, 1H, C_5H_4), 6.43-6.44 (m, 1H, C_5H_4), 7.14-7.17 (m, 2H, 2×CH_{PhP}), 7.28-7.32 (m, 2H, 2×CH_{PhP}), 7.43-7.46 (m, 2H, 2×CH_{PhP}), 7.50-7.53 (m, 1H, CH_{PhP}), 7.63-7.66 (m, 2H, 2×CH_{PhP}), 7.69-7.71 (m, 1H, CH_{PhP}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 296 K): δ = 11.9 (BCH_3)*, 12.0 ($C_5\underline{Me}_5$), 25.1 (PCH_2)*, 27.2 (CH_{Ad}), 27.9 (CH_{Ad}), 33.4 (CH_{Ad}), 33.9 ($CH_{2,Ad}$), 34.3 (CH_{Ad}), 34.6 ($CH_{2,Ad}$), 35.7 ($PCH_2\underline{C}H_2$)*, 36.2 ($OC_q\underline{C}H_3$), 37.1 ($CH_{2,Ad}$), 37.4 ($CH_{2,Ad}$), 39.3 ($CH_{2,Ad}$), 55.8 ($C_{q,exo}$), 109.1 (C_5H_4), 109.5 ($O\underline{C}_qCH_3$), 111.9 (C_5H_4), 112.5 (C_5H_4), 115.6 (C_5H_4), 123.9 ($\underline{C}_5Me_5$), 129.2 (d, $^1J_{C,P}$ = 36.3 Hz, $C_{q,PhP}$), 129.4 ($C_{q,ArB}$)*, 129.7 (d, $^2J_{C,P}$ = 9.2 Hz, 2×*o*-CH_{PhP}), 130.7 (d, $^2J_{C,P}$ = 10.1 Hz, 2×*o*-CH_{PhP}), 130.8 (d, $^1J_{C,P}$ = 30.7 Hz, $C_{q,PhP}$), 131.7 (*p*-CH_{PhP}), 132.2 (d, $^3J_{C,P}$ = 13.2 Hz, 2×*m*-CH_{PhP}), 133.3 (*p*-CH_{PhP}), 133.4 (d, $^3J_{C,P}$ = 14.1 Hz, 2×*m*-CH_{PhP}), 136.8 (dm, $^1J_{C,F}$ = 247.7 Hz, $C_{q,Ar}F$), 138.0 (dm, $^1J_{C,F}$ = 250.7 Hz, $C_{q,Ar}F$), 148.7 (dm, $^1J_{C,F}$ = 250.2 Hz, $C_{q,Ar}F$), 155.5 ($C_{q,ipso}$) ppm. * = assignment by $^1H/^{13}C$-HMQC/HMBC spectra. $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 296 K): δ = -14.9 ppm. $^{19}F\{^1H\}$ NMR (470 MHz, CD_2Cl_2, 296 K): δ = -167.8 (m, 6F, *m*-F_{ArB}), -165.3 (t, $^3J_{F,F}$ = 20.4 Hz, 3F, *p*-F_{ArB}), -133.1 (m, 6F, *o*-F_{ArB}) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 296 K): δ = 14.4 ppm. EA: Anal. Calcd for $C_{60}H_{53}BF_{15}OPZr$: C, 59.65; H, 4.42. Found: C, 57.63; H, 4.86. HR/MS calculated: m/z = 679.2646 [M^+]; measured (ESI): m/z = 679.2620.

Synthesis of Hf6: A mixture of complex **Hf5** (0.100 g, 0.119 mmol) and $B(C_6F_5)_3$ (0.061 g, 0.119 mmol) was stirred in 10 mL of toluene. When the stirring process is stopped after a few minutes, the development of two phases can be observed due to the formation of complex **Hf6**. The solvent was decanted, the residue was washed with *n*-hexane (3×5 mL) and dried under vacuum to give complex **Hf6** as a colorless solid. Yield:

0.127 g (0.094 mmol, 79%). Melting point: 89-91 °C. IR (ATR): $\tilde{\nu}$ = 3031, 2917, 2861, 1641, 1589, 1509, 1455, 1380, 1266, 1082, 951, 935, 910, 814, 743, 688 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 305 K): δ = 0.51 (s, 3H, BCH_3)*, 1.67-1.69 (m, 1H, PCH_2CH_2), 1.86 (s, 3H, OC_qCH_3), 2.05 (s, 15H, C_5Me_5), 2.11 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.29-2.31 (m, 2H, PCH_2CH_2), 2.35 (s, 3H, $CH_{3,p\text{-tolyl}}$), 2.77-2.85 (m, 1H, PCH_2CH_2), 5.04-5.05 (m, 1H, C_5H_4), 5.33-5.35 (m, 1H, C_5H_4), 5.90-5.91 (m, 1H, C_5H_4), 6.35-6.36 (m, 1H, C_5H_4), 6.95-7.12 (m, 4H, 4×CH_{Aryl})**, 7.15-7.20 (m, 3H, 3×CH_{Aryl}), 7.35-7.44 (m, 4H, 4×CH_{Aryl}), 7.45-7.54 (m, 3H, 3×CH_{Aryl}), 7.62-7.69 (m, 4H, 4×CH_{Aryl}) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 305 K)***: δ = 10.0 (BCH_3)*, 12.2 ($C_5\underline{Me}_5$) 20.9 ($CH_{3,p\text{-tolyl}}$), 21.0 ($CH_{3,p\text{-tolyl}}$), 22.6 (d, $^{1}J_{C,P}$ = 23.1 Hz, PCH_2), 32.2 ($OC_q\underline{C}H_3$), 37.4 ($PCH_2\underline{C}H_2$), 66.1 ($C_{q,exo}$), 106.4 ($O\underline{C}_qCH_3$), 110.0 (C_5H_4), 113.5 (C_5H_4), 114.7 (C_5H_4), 115.9 (C_5H_4), 123.0 ($\underline{C}_5Me_5$), 129.1 ($C_{q,Ar}B$)*, 148.8 (dm, $^{1}J_{C,F}$ = 246.2 Hz, $C_{q,Ar}F$), 150.8 ($C_{q,ipso}$) ppm. * = assignment by ^{1}H/^{13}C-HMQC/HMBC spectra. ** = overlay with signals of toluene (residue).*** = only clearly assignable signals listed (residue of toluene and close position of signals in the range between 125 and 135 ppm). ^{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*-$F_{Ar}B$), -165.3 (t, $^{3}J_{F,F}$ = 20.4 Hz, 3F, *p*-$F_{Ar}B$), -133.2 (m, 6F, *o*-$F_{Ar}B$) ppm. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 305 K): δ = 16.6 ppm. EA: Anal. Calcd for $C_{65}H_{53}BF_{15}HfOP$: C, 57.60; H, 3.94. Found: C, 60.28; H, 4.21.

Synthesis of Ti7: Complex **Ti1** (0.250 g, 0.600 mmol) and the ligand precusor **L3** (0.183 g, 0.600 mmol) were suspended in 10 mL of *n*-hexane, resulting in a yellow 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 **Ti9** as a yellow solid (mixture of both diastereoisomers 1:1). NMR data is given for both diastereoisomers without exact assignment. Crystals suitable for single crystal X-ray diffraction were obtained from a saturated toluene solution at -4 °C. Yield: 0.345 g (0.478 mmol, 80%). Melting point: 160-162 °C (dec.). IR (ATR): $\tilde{\nu}$ = 2931, 2903, 2851, 1584, 1475, 1454, 1434, 1382, 1374, 1211, 1183, 1131, 1084, 1070, 1057, 1041, 1020, 996, 927, 914, 892, 880, 837, 826, 817, 782, 767, 747, 697, 680, 650, 640, 603 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ = 1.05-1.08 (m, 2H, 2×CH_{Ad}/$CH_{2,Ad}$), 1.20-1.27 (m, 2H, 2×CH_{Ad}/$CH_{2,Ad}$), 1.41-1.43 (m, 1H, CH_{Ad}/$CH_{2,Ad}$), 1.50-1.66 (m, 10H, 10×CH_{Ad}/$CH_{2,Ad}$), 1.70 (s, 15H, C_5Me_5), 1.78 (s, 15H, C_5Me_5), 1.81-1.94 (m, 4H, 4×CH_{Ad}/$CH_{2,Ad}$), 2.01-2.04 (m, 1H, CH_{Ad}/$CH_{2,Ad}$), 2.12-2.15 (m, 1H, CH_{Ad}/$CH_{2,Ad}$), 2.27 (s, 3H, OC_qCH_3), 2.43-2.44 (m, 2H, 2×CH_{Ad}/$CH_{2,Ad}$), 2.58-2.59 (m, 4H, OC_qCH_3, CH_{Ad}/$CH_{2,Ad}$), 2.78-2.81 (m, 2H, 2×CH_{Ad}/$CH_{2,Ad}$), 3.38-3.41 (m, 1H, CH_{Ad}/$CH_{2,Ad}$), 3.66-3.70 (m, 1H, CH_{Ad}/$CH_{2,Ad}$), 5.15-5.16 (m, 1H, C_5H_4), 5.18-5.19 (m, 1H, C_5H_4), 5.23-5.24 (m, 1H, C_5H_4), 5.27-5.28 (m, 1H, C_5H_4), 5.59-5.60 (m, 1H, C_5H_4), 5.75-5.76 (m, 1H, C_5H_4), 6.77-7.78 (m, 1H, C_5H_4), 6.88-6.96 (m, 2H, 2×CH_{Aryl}), 7.03-7.14 (m, 14H, C_5H_4, 13×CH_{Aryl}), 7.24-7.27 (m, 1H, CH_{Aryl}), 7.31-7.42 (m, 10H, 10×CH_{Aryl}), 7.74-7.77 (m, 1H, CH_{Aryl}), 8.53-8.56 (m, 1H, CH_{Aryl}) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K): δ = 12.9 ($C_5\underline{Me}_5$), 13.1 ($C_5\underline{Me}_5$), 27.4 (CH_{Ad}), 27.5 (CH_{Ad}), 27.52 (CH_{Ad}), 27.7 (CH_{Ad}), 28.8 (d, $^{4}J_{C,P}$ = 32.6 Hz, $OC_q\underline{C}H_3$), 32.0 (d, $^{4}J_{C,P}$ = 32.4 Hz, $OC_q\underline{C}H_3$), 33.1 (CH_{Ad}), 33.7 (CH_{Ad}), 34.3 ($CH_{2,Ad}$), 34.4($CH_{2,Ad}$), 34.7 ($CH_{2,Ad}$), 34.9 ($CH_{2,Ad}$), 35.1 (CH_{Ad}), 36.2 (CH_{Ad}), 37.0 ($CH_{2,Ad}$), 37.3 ($CH_{2,Ad}$), 37.5 ($CH_{2,Ad}$), 37.9 ($CH_{2,Ad}$), 38.9 ($CH_{2,Ad}$), 39.0 ($CH_{2,Ad}$), 57.0 ($C_{q,exo}$), 57.8 ($C_{q,exo}$), 104.2 (C_5H_4), 104.6 (C_5H_4), 104.9 (C_5H_4), 106.8 (C_5H_4), 114.8 (C_5H_4), 115.6 (C_5H_4), 115.9 (d, $^{3}J_{C,P}$ = 3.3 Hz, $OC_q\underline{C}H_3$), 120.0 (d, $^{3}J_{C,P}$ = 2.8 Hz, $OC_q\underline{C}H_3$), 123.9 ($\underline{C}_5Me_5$), 124.3 ($\underline{C}_5Me_5$), 125.2 (C_5H_4), 126.4 (C_5H_4), 130.7 (d, $^{1}J_{C,P}$ = 24.4 Hz, $C_{q,C6H4}P$), 131.5 (d, $^{1}J_{C,P}$ = 26.2 Hz, $C_{q,C6H4}P$), 138.4 (d, $^{1}J_{C,P}$ = 14.0 Hz, $C_{q,PhP}$), 138.9 (d, $^{1}J_{C,P}$ = 13.3 Hz, $C_{q,PhP}$), 140.5 (d, $^{1}J_{C,P}$ = 16.3 Hz, $C_{q,PhP}$), 140.9 (d, $^{1}J_{C,P}$ = 17.9 Hz, $C_{q,PhP}$), 154.0 ($C_{q,ipso}$), 154.7 ($C_{q,ipso}$), 155.7 (d, $^{2}J_{C,P}$ = 11.3 Hz, *o*-$C_{q,C6H4}P$), 155.9 (d, $^{2}J_{C,P}$ = 11.1 Hz, *o*-$C_{q,C6H4}P$) ppm. Signals of CH_{Aryl}: 126.8, 127.5, 127.9*, 128.4, 128.61, 128.66, 128.70, 128.72, 128.75, 128.77, 128.87, 128.92, 128.93, 128.98, 133.71, 133.74, 133.82, 133.86, 133.88, 133.90, 133.92, 134.0, 136.6, 137.0 ppm. * = overlap with C_6D_6 signal. ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 300 K): δ = -4.8, -4.0 ppm. HR/MS calculated: m/z = 727.2927 [M+Li^{+}]; measured (ESI): m/z = 727.2917.

Synthesis of Ti8: To a solution of complex **Ti7** (0.250 g, 0.347 mmol) in 10 mL of tetrahydrofuran was added a methyllithium solution (0.2 mL, 0.347 mmol; 1.6 M in diethyl ether). The reaction mixture was stirred for 16 h at room temperature. The solvent was completely removed under vacuum, and the residue was dissolved in 8 mL of toluene. The solution was filtered, and the residue was washed with toluene (2×6 mL). All volatiles were removed under vacuum to give complex **Ti8** as a yellow solid. Crystals suitable for single crystal X-ray diffraction were obtained from a saturated *n*-hexane solution at -4 °C. Yield: 0.226 g (0.323 mmol, 93%). Melting point: 206-208 °C (dec.). IR (ATR): $\tilde{\nu}$ = 2954, 2937, 2900, 2850, 1473, 1450, 1434, 1375, 1260, 1133, 1098, 1072, 1057, 1037, 1020, 995, 933, 838, 812, 779, 764, 745, 697, 679, 652, 639, 517, 601 cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 0.62 (s, 3H, $TiCH_3$), 1.09-1.18 (m, 2H, 2×CH_{Ad}/$CH_{2,Ad}$), 1.60 (s, 15H, C_5Me_5), 1.64-1.71 (m, 5H, 5×CH_{Ad}/$CH_{2,Ad}$), 1.89-1.95 (m, 2H, 2×CH_{Ad}/$CH_{2,Ad}$), 2.03-2.05 (m, 1H, CH_{Ad}/$CH_{2,Ad}$), 2.24 (s, 3H, OC_qCH_3), 2.61-2.71 (m, 3H, 3×CH_{Ad}/$CH_{2,Ad}$), 3.64-3.68 (m, 1H, CH_{Ad}/$CH_{2,Ad}$), 4.77-4.79 (m, 1H, C_5H_4), 5.02-5.04 (m, 1H, C_5H_4), 5.47-5.48 (m, 1H, C_5H_4), 6.67-6.68 (m, 1H, C_5H_4), 6.86-6.89 (m, 1H, C_6H_4), 7.01-7.19 (m, 7H, 7×CH_{Aryl})*, 7.25-7.27 (m, 1H, C_6H_4), 7.33-7.36 (m, 2H, 2×*m*-CH_{PhP}), 7.40-7.43 (m, 2H, 2×*m*-CH_{PhP}), 7.80-7.82 (m, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 12.1 ($C_5\underline{Me}_5$), 27.7 (CH_{Ad}), 27.9 (CH_{Ad}), 32.7 (d, $^{4}J_{C,P}$ = 32.8 Hz, $OC_q\underline{C}H_3$), 33.5 (CH_{Ad}), 34.8 ($CH_{2,Ad}$), 34.9 ($CH_{2,Ad}$), 35.0 ($TiCH_3$), 36.3 (CH_{Ad}), 37.5 ($CH_{2,Ad}$), 37.6 ($CH_{2,Ad}$), 39.3 ($CH_{2,Ad}$), 58.1 ($C_{q,exo}$), 103.1 (C_5H_4), 103.5 (C_5H_4), 110.2 (C_5H_4), 114.6 (d, $^{3}J_{C,P}$ = 2.8 Hz, $O\underline{C}_qCH_3$), 118.5 ($\underline{C}_5Me_5$), 121.4 (C_5H_4), 127.3 (C_6H_4), 127.9 (C_6H_4)*, 128.3 (*p*-CH_{PhP})*, 128.4 (*p*-CH_{PhP})*, 128.7 (d, $^{2}J_{C,P}$ = 6.4 Hz, 2×*o*-CH_{PhP}), 128.9 (d, $^{2}J_{C,P}$ = 5.7 Hz, 2×*o*-CH_{PhP}), 131.1 (d,$^{1}J_{C,P}$ = 24.7 Hz, $C_{q,C6H4}P$), 132.7 (d, $J_{C,P}$ =6.3 Hz, C_6H_4), 133.9 (d, $^{3}J_{C,P}$ = 19.6 Hz, 4×*m*-CH_{PhP}), 136.7 (C_6H_4), 139.1 (d, $^{1}J_{C,P}$ = 13.6 Hz, $C_{q,PhP}$), 140.7 (d, $^{1}J_{C,P}$ = 17.2 Hz, $C_{q,PhP}$), 149.4 ($C_{q,ispo}$), 156.5 (d, $^{2}J_{C,P}$ = 22.3 Hz, *o*-$C_{q,C6H4}P$) ppm. * = overlay with C_6D_6 signal. ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 305 K): δ = -3.6 ppm. HR/MS calculated: m/z = 707.3474 [M+Li^{+}]; measured (ESI): m/z = 707.3453.

Synthesis of Ti9: A mixture of complex **Ti8** (0.150 g, 0.214 mmol) and $B(C_6F_5)_3$ (0.110 g, 0.214 mmol) was stirred in 10 mL of toluene. When the stirring process is stopped after a few minutes, the development of two phases can be observed due to the formation of complex **Ti9**. The solvent was decanted, the residue was washed with *n*-hexane (3×5 mL) and dried under vacuum to give complex **Ti9** as an orange solid. Yield: 0.230 g (0.190 mmol, 89%). Melting point: 110-112 °C (dec.). IR (ATR): $\tilde{\nu}$ = 2961, 2910, 2855, 1639, 1509, 1454, 1380, 1265, 1175, 1119, 1082, 978, 965, 951, 830, 803, 749, 725, 696, 660, 643m 604 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 305 K): δ = 0.49 (s, 3H, BCH_3), 1.39-1.76 (m, 9H, 9×CH_{Ad}/$CH_{2,Ad}$), 1.88 (s, 15H, C_5Me_5), 2.05-2.06 (m, 1H, CH_{Ad}/$CH_{2,Ad}$), 2.09 (s, 3H, OC_qCH_3), 2.21-2.22 (m, 1H, CH_{Ad}/$CH_{2,Ad}$), 2.51-2.56 (m, 2H, 2×CH_{Ad}/$CH_{2,Ad}$), 2.72-2.75 (m, 1H, CH_{Ad}/$CH_{2,Ad}$), 3.68-3.70 (m, 1H, C_5H_4), 5.75-5.76 (m, 1H, C_5H_4), 5.87-5.91 (m, 1H, C_5H_4), 6.15-6.17 (m, 1H, C_5H_4), 7.13-7.47 (m, 7H, 7×CH_{Aryl}), 7.51-7.55 (m, 2H, 2×CH_{Aryl}), 7.57-7.60 (m, 1H, C_6H_4), 7.66-7.68 (m, 3H, 3×CH_{Aryl}), 8.08-8.11 (m, 1H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 305 K): δ = 9.7 (BCH_3)*, 12.9 ($C_5\underline{Me}_5$), 27.0 (CH_{Ad}), 28.0 (CH_{Ad}), 32.9 (CH_{Ad}), 33.6 ($CH_{2,Ad}$), 34.9 ($CH_{2,Ad}$), 35.4 ($OC_q\underline{C}H_3$), 35.9 (CH_{Ad}), 37.1 ($CH_{2,Ad}$), 37.5 ($CH_{2,Ad}$), 39.0 ($CH_{2,Ad}$), 57.6 ($C_{q,exo}$), 111.7 (C_5H_4), 112.8 (C_5H_4), 114.5 (d, $^{TS}J_{C,P}$ = 2.0 Hz, C_5H_4), 117.3 (C_5H_4), 117.5 ($O\underline{C}_qCH_3$), 126.2 ($\underline{C}_5Me_5$), 126.7 (d, $^{1}J_{C,P}$ = 39.9 Hz, $C_{q,PhP}$), 128.1 (*p*-CH_{PhP}), 128.2 (*p*-CH_{PhP}), 128.7 (d, $^{1}J_{C,P}$ = 17.9 Hz, $C_{q,C6H4}P$), 128.9 ($C_{q,ArB}$)*, 129.2 (d, $^{1}J_{C,P}$ = 49.9 Hz, $C_{q,PhP}$), 130.2 (d, $^{2}J_{C,P}$ = 9.6 Hz, 4×*o*-CH_{PhP}), 130.4 (d, $J_{C,P}$ = 8.6 Hz, C_6H_4), 131.3 (d, $J_{C,P}$ = 9.2 Hz, C_6H_4), 131.8 (C_6H_4), 132.7 (d, $^{3}J_{C,P}$ = 10.6 Hz, 4×*m*-CH_{PhP}), 137.0 (dm, $^{1}J_{C,F}$ = 244.5 Hz, $C_{q,Ar}F$),

138.0 (dm, $^{1}J_{C,F}$ = 236.8 Hz, $C_{q,Ar}F$), 139.2 (C_6H_4), 148.8 (dm, $^{1}J_{C,F}$ = 237.1 Hz, $C_{q,Ar}F$), 152.6 (d, $^{2}J_{C,P}$ = 11.0 Hz, *o*-$C_{q,C6H4}P$), 157.0 ($C_{q,ipso}$) ppm. * = 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*-$F_{Ar}B$), -165.3 (t, $^{3}J_{F,F}$ = 20.3 Hz, 3F, *p*-$F_{Ar}B$), -133.1 (m, 6F, *o*-$F_{Ar}B$) ppm. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 305 K): δ = 41.4 ppm. HR/MS calculated: m/z = 685.3079 [M^+]; measured (ESI): m/z = 685.3075.

Acknowledgements

Financial Support by the DFG Research Training Group 2226 is kindly acknowledged.

Accession Codes

CCDC 1860720-1860728 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.

Keywords: cations • metallacycles • titanium • zirconium • hafnium

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Entry for the Table of Contents

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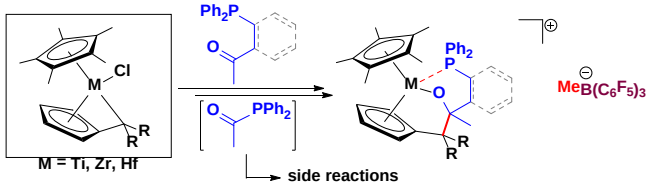

Reactions of π-η^5:σ-η^1-monopentafulvene complexes to cationic d^0 complexes of each group 4 metal with tridentate *Cp*,*O*,*P*-ligands by a convenient three-step synthetic pathway (insertion of bidentate *O*,*P*-ligand precursors, subsequent methylation, activation with $B(C_6F_5)_3$) are reported. Starting with acetylphosphine as the ligand precursor, side reactions are initiated, dependent on the group 4 metal.

Cationic group 4 complexes with tridentate *Cp*,*O*,*P*-ligands*

*Malte Fischer, Maximilian Jaugstetter, Raoul Schaper, Marc Schmidtmann, Rüdiger Beckhaus**

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Cationic group 4 complexes (M = Ti, Zr, Hf): Modifications and Limitations in the design of tridentate *Cp*,*O*,*P*-ligand frameworks built directly in the coordination sphere of the metal