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Closely Related Benzylene-Linked Diamidophosphine Scaffolds and Their Zirconium and Hafnium Complexes: How Small Changes of the Ligand Result in Different Complex Stabilities and Reactivities

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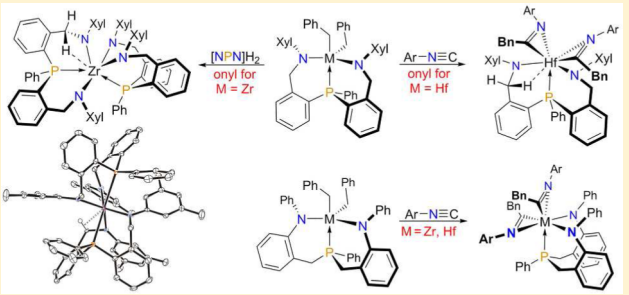
Supporting Information

ABSTRACT: The closely related benzylene-linked diaminophosphines PhP($CH_2C_6H_4$-*o*-NHPh)$_2$ ([^{Ph}**A**]H_2) and PhP(C_6H_4-*o*-CH_2NHXyl)$_2$ ([**B**]H_2) were prepared as robust alternatives to the previously reported *N*,*N*′-bis(trimethylsilyl)-substituted derivative PhP($CH_2C_6H_4$-*o*-NHSiMe_3)$_2$ ([^{Si}**A**]H_2). Upon reaction of [^{Ph}**A**]H_2 and [**B**]H_2 with M(NMe_2)$_4$ (M = Zr, Hf), the respective dimethylamido complexes [^{Ph}**A**]M(NMe_2)$_2$ and [**B**]M(NMe_2)$_2$ ([^{Ph}**A**]-**1-M** and [**B**]-**1-M**, M = Zr, Hf) were isolated in high yields and converted to the corresponding diiodo derivatives [^{Ph}**A**]MI_2 and [**B**]MI_2 ([^{Ph}**A**]-**2-M** and [**B**]-**2-M**, M = Zr, Hf). In contrast to [^{Si}**A**]ZrI_2, these thermally robust diiodo complexes were found to react cleanly with Bn_2MgL_2 (L = THF or Et_2O), resulting in the corresponding dibenzyl species [^{Ph}**A**]MBn_2 and [**B**]MBn_2 ([^{Ph}**A**]-**4-M** and [**B**]-**4-M**, M = Zr, Hf). Upon addition of [**B**]H_2 to [**B**]$ZrBn_2$, the related homoleptic species [**B**]$_2$Zr ([**B**]-**5-Zr**) was generated. Similar 2:1 complexes have not been observed for the hafnium homologue bearing the latter ligand or for [^{Si}**A**]- or [^{Ph}**A**]-coordinated complexes. The former dibenzyl complexes were reacted with 2,6-xylylisonitrile, and clean conversions to the bis-η^2-iminoacyl complexes [**B**]-**6-Hf** and [^{Ph}**A**]-**6-M** were observed for [**B**]-**4-Hf** and [^{Ph}**A**]-**4-M** (M = Zr, Hf). For [^{Si}**A**]$HfBn_2$ ([^{Si}**A**]-**4-Hf**) only one equivalent of the former isonitrile was inserted into one of the hafnium carbon bonds, which is in line with the steric differences between [^{Si}**A**] and [^{Ph}**A**].

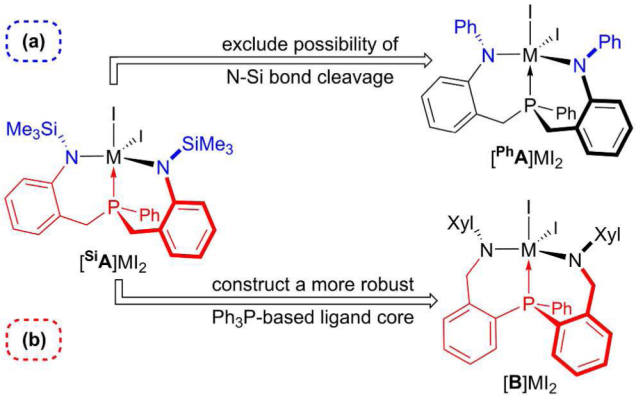


INTRODUCTION

Over the past decades, reduced zirconocene and hafnocene fragments (i.e., "Cp_2Zr" and "Cp_2Hf") and their tetra- and pentamethyl-cyclopentadienyl variants have been investigated in detail, especially in view of their reactivities toward alkynes and dinitrogen.[1] In both of these research fields, unanticipated dissimilarities between zirconium and hafnium were uncovered and ascribed to hafnium's propensity to form stronger σ-bonds, which in turn leads to an increased π-back-bonding.[2] That the formal substitution of pentamethyl-cyclopentadiene for tetramethyl-cyclopentadiene led to the discovery of even more astonishing differences with respect to the reactivity of the resulting zircono- and hafnocenes clearly demonstrated that seemingly minor changes at the ligand require a careful evaluation.[3] While these effects are nowadays well accepted in cyclopentadienyl chemistry,[4] little is known on the impact of small changes at Cp-free capping ligands. In the case of amidophosphines, which are frequently seen as adequate replacements for cyclopentadienyl moieties,[5] divergent reactivities have been found for homologous zirconium and hafnium complexes as well,[6] but systematic studies using comparable ligand backbone architectures are scare.[6b,c]

In a previous report, we have noted that the simple zirconium diiodo complex [^{Si}**A**]ZrI_2 shown in Chart 1 is fairly unstable at room temperature, while the hafnium homologue [^{Si}**A**]HfI_2 was found to exhibit a significantly enhanced thermal stability.[7] On the basis of this finding, we decided to systematically probe for differences between [NPN]-coordinated hafnium and zirconium derivatives[8] and the depend-

Chart 1. Strategies to Improve the Thermal Stability of [^{Si}A]MI_2 (M = Zr, Hf) via Replacement of the *N*-Trimethylsilyl Substituents (a) or via Inversion of the Benzylene Linker (b)



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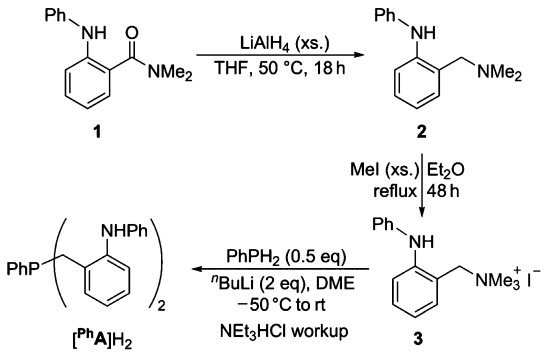
encies of these differences on subtle ligand alterations. To exclude that the dissimilar thermal stabilities of [^{Si}A]ZrI_2 and [^{Si}A]HfI_2 are solely due to a more or less pronounced ligand degradation reaction, robust analogues of the former benzylene-linked [NPN] ligand were required. At first glance, a formal exchange of the trimethylsilyl groups for *N*-phenyl substituents (see Chart 1) seemed reasonable in order to exclude possible decomposition pathways via silyl amide bond cleavage.[9] An inversion of the benzylene linker, however, was recognized as a plausible strategy as well, as this modification would result in a more robust triphenylphosphine-based ligand core (see Chart 1),[10] which might hamper decomposition pathways via phosphine-centered redox processes. In the latter case, *N*-xylyl substituents were chosen to circumvent solubility issues, which have been noted for related [PN_3] ligands.[11]

Anticipating that either one or even both of these strategies would lead to thermally stable group 4 diiodo complexes, which tolerate consecutive transformations and reactivity studies, a simultaneous exploration of [^{Ph}A]- and [**B**]-coordinated systems was pursued (see Chart 1). As detailed in the following, we have found that dibenzyl complexes incorporating these ligands can be accessed via their thermally stable diiodo derivatives. As an alternative route for the preparation of [^{Si}A]MBn_2 was discovered as well, a comparative analysis of all these dibenzyl derivatives was conducted, which revealed different complex stabilities and reactivities[12] toward isonitriles (mono- vs bis-insertion).

RESULTS AND DISCUSSION

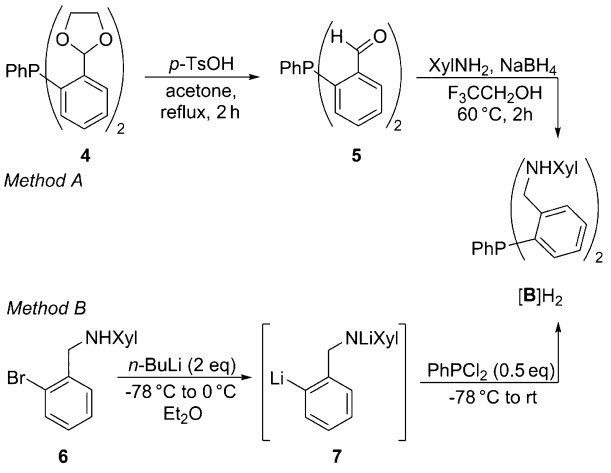
Ligand Synthesis. For the synthesis of [^{Ph}A]H_2, a retrosynthetic strategy that relied on the presence of the *N*-phenyl substituent prior to the introduction of the phosphine had to be developed, as numerous attempts to access the target molecule via Pd- or Cu-catalyzed coupling[13,8a] of the unsubstituted ligand backbone[7] ($PhP(CH_2C_6H_4$-*o*-$NH_2)_2$) were unsuccessful. Employing *N*-phenyl-substituted 2-aminobenzyl halides[14] or anthranilic chlorides[15] was found to be problematic as well, mainly due to the ease of 9,10-dihydroacridine and acridone formation via intramolecular electrophilic alkylation of the *N*-phenyl substituent.[16] To circumvent the former acridine formation process, the benzylic leaving group was modified in a trial and error approach and in one attempt replaced by a trimethylammonium group. Gratifyingly, this approach hampered intramolecular cyclization, but still allowed for nucleophilic substitution at the benzylic positon and thus for the introduction of the phenyl phosphine subunit in the last step.[17] Based on these observation, a large-scale synthesis for the trimethylammonium-substituted *N*-phenyl benzylamine **3** was developed starting from **1**[18] (see Scheme 1). After reduction of **1** with lithium aluminum hydride, the dimethylamine derivative **2** was obtained in high yields and directly converted to **3** via treatment with excess methyl iodide. An *N*-$SiMe_3$ protection of the NH group is possible, but not required, as no signs of methylation at that nitrogen atom were noticed. Upon addition of *n*-butyllithium to a cold 1:2 mixture of phenyl phosphine and **3** in DME, the dilithium salt of the target molecule was generated (see Scheme 1). After acidic workup with NEt_3HCl and separation of the iodide and chloride salts, the crude protioligand was obtained as a thick yellow oil. Further purification was achieved by protonation of the diaminophosphine with hydrogen chloride and recrystallization of the resulting bis-hydrochloride salt. After deprotonation with triethylamine and separation of triethylammonium hydrochloride, protioligand [^{Ph}A]H_2 was obtained as a thick oil in high purity as judged by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy ($\delta(^{31}P)$ = −24.3 ppm). Upon standing at room temperature, this oil solidified over a period of several days, but the preparation of stock solutions was more convenient, as it allowed for the direct use of [^{Ph}A]H_2.

Scheme 1. Synthesis of the Protioligand [^{Ph}A]H_2



For the preparation of the protioligand [**B**]H_2, reductive amination of the bis-formyl-substituted triphenylphosphine derivative **5** was attempted in a first approach (see Scheme 2, method A).[19] The required bis-aldehyde **5** was easily generated via deprotection of **4**[20] and directly reacted with 3,5-xylylamine.[11a] The resulting bis-imine was reduced *in situ* with sodium borohydride, and the target molecule then purified by column chromatography. Although pure [**B**]H_2 was obtained, poorly reproducible yields in the range 10−35% rendered this route rather unreliable. In the presence of water, bis-aldehyde **5** is known to undergo complex redox reactions that involve formyl coupling with concurrent transfer of an oxygen atom to the phosphine.[21] In the above-described reaction of **5** with 3,5-xylylamine, these formyl-coupled phosphine oxides were detected by ^{31}P{^{1}H} NMR spectroscopy. However, attempts to trap both equivalents of water, which are generated in the condensation reaction via addition of molecular sieves or sodium sulfate, did not result in higher yields or in an improved reproducibility.

Scheme 2. Synthesis of Protioligand [B]H_2 (Xyl = 3,5-Xylyl)



Therefore, a second method (method B, see Scheme 2) starting from *N*-xylyl-*ortho*-bromobenzylamine (**6**) was developed. Addition of two equivalents of *n*-butyllithium to a cold

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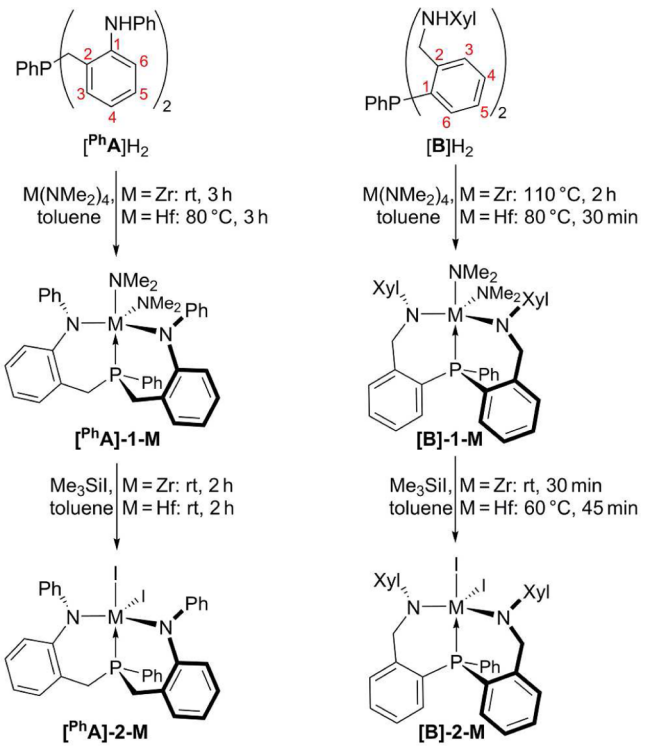
solution of **6** in diethyl ether resulted in amine deprotonation and bromine−lithium exchange. In a one-pot procedure, the dilithiated intermediate **7** was quenched with $PhPCl_2$ and pure $[\mathbf{B}]H_2$ isolated after recrystallization from ethanol. Using this method, the desired protioligand was obtained as an off-white powder in reproducible yields of approximately 50% ($\delta(^{31}P)$ = −26.3 ppm), and its molecular structure was ascertained by single-crystal X-ray diffraction (see Supporting Information). Due to its robust triphenylphosphine core, protioligand $[\mathbf{B}]H_2$ was found to be stable in air for weeks, while oxidative decomposition was observed for $[^{Ph}\mathbf{A}]H_2$ within a few hours after exposure to air.

Synthesis of $[^{Ph}\mathbf{A}]MI_2$ and $[\mathbf{B}]MI_2$ (M = Zr, Hf). With gram quantities of $[^{Ph}\mathbf{A}]H_2$ and $[\mathbf{B}]H_2$ available, the synthesis of the desired group 4 diiodo complexes was pursued via the corresponding dimethylamido complexes. Thus, $[^{Ph}\mathbf{A}]H_2$ and $[\mathbf{B}]H_2$ were reacted with $M(NMe_2)_4$ (M = Zr, Hf), and the resulting complexes $[^{Ph}\mathbf{A}]M(NMe_2)_2$ ($[^{Ph}\mathbf{A}]$-**1-M**) and $[\mathbf{B}]M(NMe_2)_2$ ($[\mathbf{B}]$-**1-M**) isolated in both cases (see Scheme 3).

Scheme 3. Synthesis of Complexes $[^{Ph}\mathbf{A}]$-1-M, [B]-1-M, $[^{Ph}\mathbf{A}]$-2-M, and [B]-2-M (M = Zr, Hf)[a]



[a]Arabic numbers printed in red are used in the Experimental Section for NMR signal assignments.

Each ^{1}H and ^{13}C NMR spectrum of these dimethylamido complexes exhibited only one set of signals for the two ligand side arms of the respective amidophosphine and two geminally coupled doublets for the methylene protons indicative of C_s-symmetric species in solution. However, NMR spectra measured at −80 °C showed a desymmetrization to C_1, indicative of an antiparallel alignment of both ligand side arms upon cooling.[7] Single crystals of $[^{Ph}\mathbf{A}]$-**1-Zr** (see Supporting Information for an ORTEP diagram) and $[\mathbf{B}]$-**1-Hf** (see Figure 1) were subjected to X-ray diffraction, and the expected trigonal bipyramidal coordination geometries around the central metals

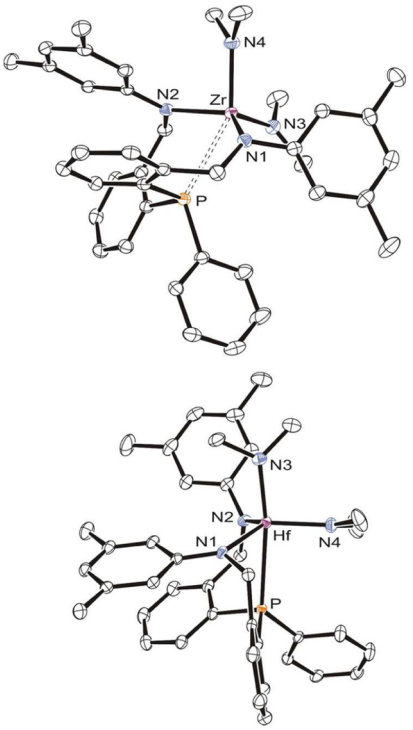


Figure 1. ORTEP diagrams of $[\mathbf{B}]$-**1-Zr** (top) and $[\mathbf{B}]$-**1-Hf** (bottom). Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity; thermal ellipsoids are set at 50% probability. Selected bond lengths and angles are summarized in Table 1 together with the corresponding values for $[^{Ph}\mathbf{A}]$-**1-Zr**.

were found in the refined C_1-symmetric molecular structures. In the case of $[\mathbf{B}]$-**1-Zr**, the main axis through P−Zr−N4 deviates significantly from 180° (P−Zr−N4 = 150.96(5)°) and allows for an alternative interpretation of the complex geometry as a tetrahedral zirconium ion with a loosely bound phosphine. This is corroborated by a rather long metal phosphorus distance of 2.8976(5) Å, which points to a relatively weak Zr···P interaction.[22] This observation is in line with the phosphine donor in $[\mathbf{B}]$ being less electron donating than the one in $[^{Ph}\mathbf{A}]$, which renders the zirconium phosphine interaction in $[\mathbf{B}]$-**1-Zr** weaker than in $[^{Ph}\mathbf{A}]$-**1-Zr**. For $[\mathbf{B}]$-**1-Hf**, the deviation from the expected trigonal bipyramidal geometry is by far less pronounced and interpreted as a consequence of hafnium's stronger σ-bond to the phosphine anchor (cf. Figure 1).[2c]

Complexes $[^{Ph}\mathbf{A}]$-**1-M** and $[\mathbf{B}]$-**1-M** (M = Zr, Hf) were found to react cleanly with Me_3SiI, affording the expected

Table 1. Selected Metrical Parameters and ^{31}P NMR Shifts (C_6D_6) of Complexes $[^{Ph}\mathbf{A}]$-1-Zr, [B]-1-Zr, and [B]-1-Hf

	$[^{Ph}\mathbf{A}]$-1-Zr	[B]-1-Zr	[B]-1-Hf
M−P (Å)	2.8305(9)	2.8976(5)	2.8114(8)
M−N (Å)	2.1601(11)	2.1293(15)	2.1223(15)
	2.1442(10)	2.1502(16)	2.0739(16)
M−(NMe_2) (Å)	2.0430(11)	2.0606(16)	2.0469(16)
	2.0488(13)	2.0510(16)	2.0426(16)
P−M−(NMe_2) (deg)	163.85(3)	150.96(5)	169.89(4)
	95.03(3)	97.34(5)	91.33(5)
N−M−N (deg)	125.31(4)	125.14(6)	113.86(6)
δ ^{31}P (ppm)	10.2	−28.0	−23.8

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diiodo complexes [^{Ph}A]MI$_2$ ([^{Ph}A]-2-M) and [B]MI$_2$ ([B]-2-M). In contrast to [^{Si}A]MI$_2$ ([^{Si}A]-2-M, M = Zr, Hf), these complexes were found to be thermally stable at room temperature and even at +70 °C. That the titanium derivatives could be prepared seems noteworthy as well, as this was not the case for [^{Si}A]H$_2$[7] (see Supporting Information for experimental procedures and the ORTEP plots of the molecular structures of [^{Ph}A]Ti(NMe)$_2$, [^{Ph}A]TiI$_2$, [B]Ti(NMe$_2$)$_2$, and [B]TiI$_2$).[23] In the ^{31}P{^{1}H} NMR spectra of complexes [^{Ph}A]-2-M and [B]-2-M (M = Zr, Hf), the expected singlet resonances were found in each case. On the NMR time scale, these species were found to exhibit averaged C_s-symmetries in solution as judged by ^{1}H NMR spectroscopy. On the basis of single-crystal X-ray diffraction analysis, the zirconium diiodo derivatives [^{Ph}A]-2-Zr and [B]-2-Zr were found to be C_1-symmetric in the solid state (see Figure 2), which is also the case for [^{Si}A]-2-Zr (see

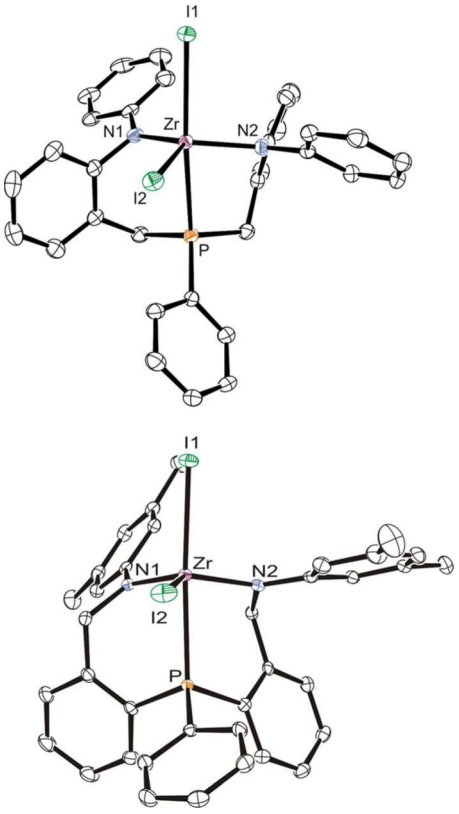


Figure 2. ORTEP diagrams of [^{Ph}A]-2-Zr (top) and [B]-2-Zr (bottom). Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity; thermal ellipsoids are set at 50% probability. Selected bond lengths and angles are summarized in Table 2 together with the corresponding values for [^{Si}A]-2-Zr.

Supporting Information for an ORTEP plot). For all three systems, similar slightly distorted trigonal bipyramidal coordination environments were found in the respective solid-state structures (see Table 2 for selected metrical parameters). That averaged C_s-symmetric solution structures were observed for complexes [^{Ph}A]-1-M, [^{Ph}A]-2-M, [B]-1-M, and [B]-2M was interpreted as a consequence of a twist-type rotational equilibration of both ligand side arms in solution, which agrees well with our previous study on group 4 complexes bearing the related propylene-linked ligand [PhP(CH$_2$CH$_2$CH$_2$NPh)$_2$]$^{2-}$.[7] For [^{Si}A]-1-M and [^{Si}A]-2-M, however, C_1-symmetries were observed not only in the solid state but also in solution,

Table 2. Selected Metrical Parameters and ^{31}P NMR Shifts (C_6D_6) of Complexes [^{Si}A]-2-Zr, [^{Ph}A]-2-Zr, and [B]-2-Zr

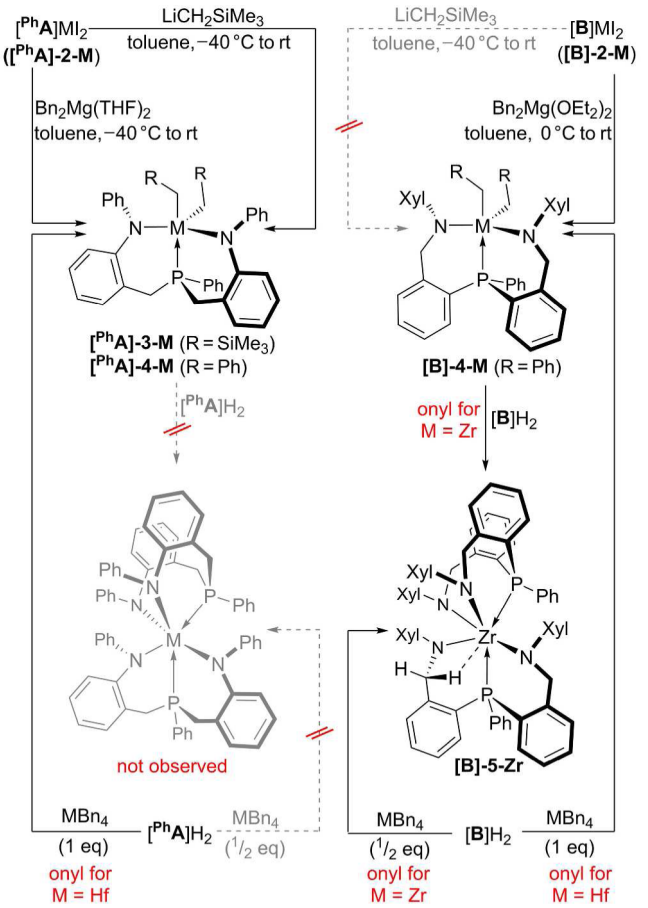
	[^{Si}A]-2-Zr	[^{Ph}A]-2-Zr	[B]-2-Zr
M–P (Å)	2.7875(7)	2.7671(7)	2.7646(11)
M–N (Å)	2.019(2)	2.046(2)	2.044(2)
	2.051(2)	2.059(2)	2.035(2)
M–I (Å)	2.8595(3)	2.8407(3)	2.8350(11)
	2.8356(3)	2.7765(3)	2.8116(12)
P–M–I (deg)	175.861	168.842(15)	174.443(15)
	82.774(15)	94.379(14)	84.59(3)
N–M–N (deg)	109.68(9)	121.06(8)	111.32(8)
δ ^{31}P (ppm)	8.5	0.7	−10.0

indicating that the sterically demanding *N*-trimethylsilyl groups effectively interfere with this equilibration process.[24]

Synthesis of Dibenzyl Complexes. In order to exploit hafnium's tendency to form stronger metal–carbon σ-bonds, the synthesis of dialkyl complexes was pursued. Therefore, the reactions of LiCH$_2$SiMe$_3$ and Bn$_2$MgL$_2$ (L = THF, Et$_2$O)[25] with [^{Ph}A]-2-M and [B]-2-M were examined. Upon reaction of [^{Ph}A]-2-M with LiCH$_2$SiMe$_3$, the expected alkyls [^{Ph}A]-3-M were isolated for both metals (see Scheme 4, see Supporting Information for the ORTEP plots of the corresponding molecular structures), which was not the case for complexes [^{Si}A]-2-M.[7]

Disappointingly, only mixtures of products were obtained upon reaction of [B]-2-M with LiCH$_2$SiMe$_3$. As a systematic

Scheme 4. Synthesis of [^{Ph}A]-3-M, [^{Ph}A]-4-M, [B]-4-M, and [B]-5-Zr (M = Zr, Hf) Starting from [^{Ph}A]-2-M and [B]-2-M



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comparison between analogous dialkyl complexes was desired, the dibenzyl derivatives were targeted, hoping that these species were accessible for both ligands. Gratifyingly, clean reactions between Bn_2MgL_2 and [^{Ph}**A**]-**2-Hf** (L = THF) and [**B**]-**2-Hf** (L = Et_2O) were observed, and the corresponding hafnium dibenzyl complexes [^{Ph}**A**]-**4-Hf** and [**B**]-**4-Hf** were isolated in good yields (see Scheme 4). For zirconium, [^{Ph}**A**]$ZrBn_2$ ([^{Ph}**A**]-**4-Zr**) was isolated readily as well, but its [**B**]$ZrBn_2$ counterpart ([**B**]-**4-Zr**) was found to be exceedingly heat and light sensitive. Nevertheless, an *in situ* characterization of [**B**]-**4-Zr** by NMR spectroscopy undoubtedly showed that this product was formed cleanly. For both of the zirconium complexes, [^{Ph}**A**]-**4-Zr** and [**B**]-**4-Zr**, similar averaged C_s-symmetric structures were found in solution, which is also the case for the hafnium derivatives. Although solid samples of [**B**]-**4-Zr** could not be obtained due to decomposition upon solvent removal, solutions of the four derivatives [NPN]MBn_2 (M = Zr, Hf; [NPN] = [^{Ph}**A**], [**B**]) were made available, which brought a comparative analysis within reach. Single crystals of [^{Ph}**A**]-**4-Zr**, [^{Ph}**A**]-**4-Hf**, and [**B**]-**4-Hf** were subjected to X-ray diffraction, and C_1-symmetric structures similar to [^{Ph}**A**]-**2-Zr** and [**B**]-**2-Zr** were found to be present in the solid state (see Figure 3 and Supporting Information, cf. Table 3). In all three cases, trigonal bipyramidal coordination polyhedra around the respective central metals were found with the axial positions in each case occupied by the phosphine and one of the benzyl ligands. For [**B**]-**4-Hf**, an additional agostic interaction between the central metal and H7B with d(Hf···H7B) = 2.49(4) Å seems to be present (see Figure 3),[26] although doubts remain due to the (refined) positional disorder of one benzyl and one *N*-xylyl group. In agreement with these molecular structures, inequivalent benzyl ligands (*cis* and *trans* to P) were detected in the respective proton NMR spectra, which is also the case for their zirconium counterparts. Given that three steps were required to prepare each dibenzyl complex starting from the respective protioligands, alternative synthetic routes employing $ZrBn_4$[27] (*vide infra*) and $HfBn_4$[28] were pursued and found to be effective in the case of hafnium (see Scheme 4). Using a simple protonolysis approach, both hafnium dibenzyl complexes [^{Ph}**A**]-**4-Hf** and [**B**]-**4-Hf** were obtained from the corresponding protioligands in 78% and 81% yield, respectively. This procedure was also successful for the *N*-trimethylsilyl-substituted protioligand [^{Si}**A**]H_2, which led to the isolation of [^{Si}**A**]$HfBn_2$ ([^{Si}**A**]-**4-Hf**) in 71% yield (see Scheme 5).

According to NMR and X-ray diffraction analysis, [^{Si}**A**]-**4-Hf** was found to adopt a C_1-symmetric structure in solution and in the solid state. Two ^{1}H NMR signals for two inequivalent trimethylsilyl groups were detected for [^{Si}**A**]-**4-Hf**, and the complex was judged to be configurationally stable at room temperature by EXSY NMR spectroscopy. At 80 °C (i.e., under the conditions of complex formation; cf. Scheme 5) a minor species (approximately 7%) with $\delta(^{31}P\{^1H\})$ = −4.6 ppm was detected in addition to [^{Si}**A**]-**4-Hf** ($\delta(^{31}P\{^1H\})$ = 8.2 ppm) and identified as the corresponding C_s-symmetric isomer (an ORTEP plot of the corresponding molecular structure is provided in the Supporting Information). Prolonged heating, however, resulted in decomposition prior to an enrichment of this C_s-symmetric product. These observations exposed significant differences between [^{Si}**A**]-**4-Hf** and [^{Ph}**A**]-**4-Hf** despite their similar metrical parameters in the solid state (cf. Table 3).

Interestingly, the zirconium derivative [^{Si}**A**]$ZrBn_2$ could not be obtained from [^{Si}**A**]H_2 and $ZrBn_4$ or from [^{Si}**A**]ZrI_2 and

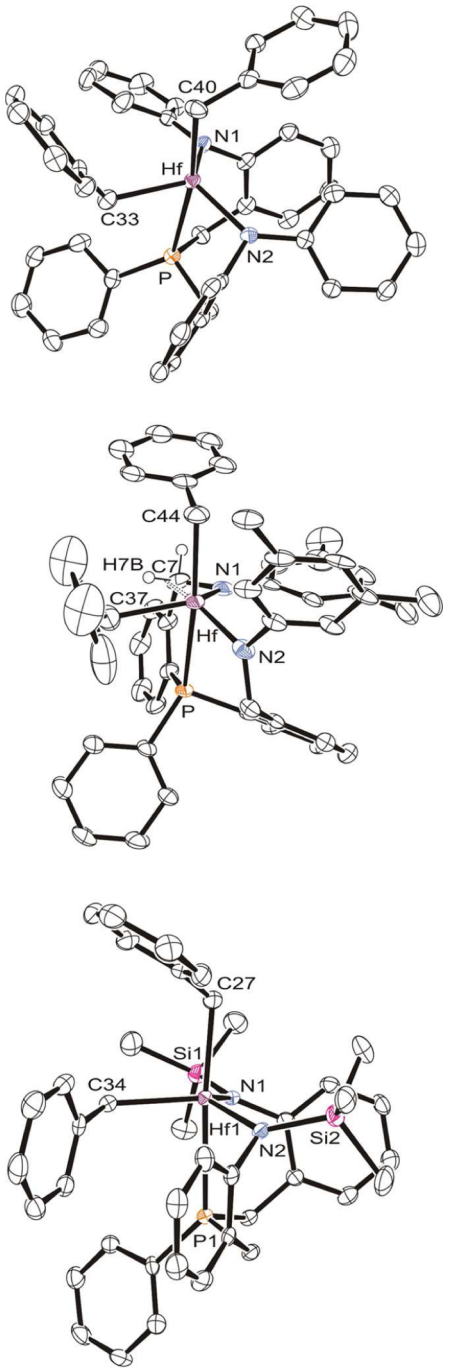

Figure 3. ORTEP diagrams of [^{Ph}**A**]-**4-Hf** (top), [**B**]-**4-Hf** (middle), and [^{Si}**A**]-**4-Hf** (C_1-symmetric isomer, bottom). Hydrogen atoms are omitted for clarity; thermal ellipsoids are set at 50% probability; disordered Bn and *N*-Xyl positions in [**B**]-**4-Hf** are omitted for clarity. Selected metrical parameters are summarized in Table 3.

$Bn_2Mg(L)_2$ (L = THF, Et_2O),[25] but was readily prepared via salt metathesis. After deprotonation of [^{Si}**A**]H_2 with *n*-BuLi at −40 °C, the dilithium salt of the ligand was reacted with $Bn_2ZrCl_2(OEt_2)$,[29] affording the desired dibenzyl complex [^{Si}**A**]-**4-Zr** in 41% yield (see Scheme 5). In contrast to [^{Si}**A**]H_2 and [^{Ph}**A**]H_2, [**B**]H_2 was found to react cleanly with $ZrBn_4$, resulting in the formation of a new zirconium complex. In contrast to the expected dibenzyl species [**B**]-**4-Zr**, which exhibits a single $^{31}P\{^1H\}$ NMR signal at −15.6 ppm, two broad and equally intense $^{31}P\{^1H\}$ NMR resonances at −18.7 and

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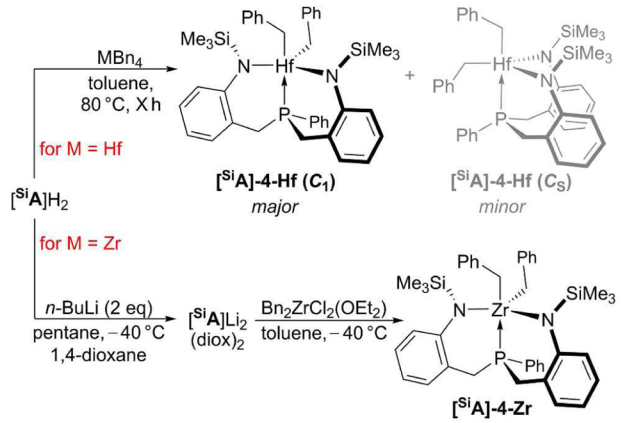
Table 3. Selected Metrical Parameters and ^{31}P NMR Shifts (C_6D_6) of Complexes [^{Si}A]-4-Hf (C_1), [^{Ph}A]-4-Hf, and [B]-4-Hf

	[^{Si}A]-4-Hf (C_1)[a]	[^{Ph}A]-4-Hf	[B]-4-Hf
M–P (Å)	2.8676(9)	2.7858(12)	2.8412(13)
M–N (Å)	2.058(3)	2.070(4)	2.056(3)
	2.070(3)	2.076(4)	2.031(3)
M–C (Å)	2.281(3)	2.276(5)	2.274(4)
	2.264(3)	2.270(5)	2.272(4)
P–M–C (deg)	172.42(9)	171.04(13)	163.07(10)
	88.66(9)	81.76(12)	84.32(11)
N–M–N (deg)	119.01(10)	117.13(14)	112.21(12)
δ ^{31}P (ppm)	8.2	4.6	−19.3

[a]Metrical parameters for a second fairly similar independent molecule in the unit cell are provided in the Supporting Information together with the corresponding values for the C_s-symmetric isomer of [^{Si}A]-4-Hf.

Scheme 5. Synthesis of [^{Si}A]-4-M (M = Zr, Hf)



−21.3 ppm were found for this new complex (the $^{31}P\{^1H\}$ NMR spectrum recorded at room temperature is shown on the left-hand side in Figure 4).

The latter product was then isolated and identified as the homoleptic 2:1 complex [B]$_2$Zr ([B]-5-Zr), which was formed exclusively even when [B]H_2 and $ZrBn_4$[27] (or Zr-$(CH_2SiMe_3)_4$)[30] were employed in equimolar amounts (half of the $ZrBn_4$ or $Zr(CH_2SiMe_3)_4$ precursors remained unreacted in these cases). Addition of [B]H_2 to [B]-4-Zr led to the isolation of [B]-5-Zr as well (see Scheme 4). For hafnium, however, the formation of a similar homoleptic 2:1 complex was neither observed upon reaction of [B]-4-Hf with [B]H_2 nor via direct protonolysis of $HfBn_4$[28] with two equivalents of [B]H_2. To confirm the molecular structure of [B]-5-Zr, single crystals were grown from a concentrated *n*-pentane/Et_2O solution at −40 °C and subjected to X-ray diffraction analysis (see Figure 5). In agreement with the $^{31}P\{^1H\}$ and ^1H NMR

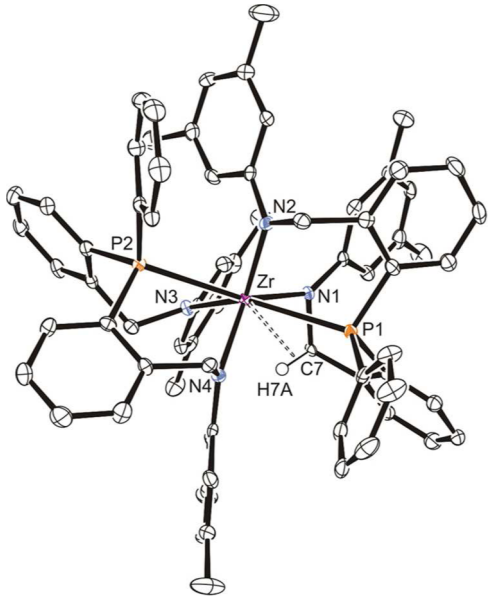


Figure 5. ORTEP diagram of [B]-5-Zr. Hydrogen atoms are omitted for clarity; thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (deg): Zr–P1 2.8580(11), Zr–P2 2.9456(11), Zr–N1 2.120(3), Zr–N2 2.157(3), Zr–N3 2.161(3), Zr–N4 2.139(3), Zr–C7 2.745(4), Zr···H7A 2.39(4), P1–Zr–P2 129.90(3), P1–Zr–H7A 72.1(10), P2–Zr–H7A 141.9(11), N1–Zr–P1 68.47(9), N1–Zr–N2 95.48(13), N2–Zr–P1 79.32(9), N3–Zr–P2 77.92(9), N4–Zr–P2 77.95(9), N4–Zr–N3 92.54(13), H7A–Zr–C7 20.2(11).

data, inequivalent ligands were found upon inspection of the solid-state molecular structure of [B]-5-Zr. As indicated by the short Zr···H7A contact (2.39(4) Å) and the narrow Zr–N1–C7 angle of 98.4(2)°,[26] an agostic interaction between the metal center and one methylene group of one of the ligands seems to be present. Whether crystal-packing effects or the metal's compact coordination environment plays a role in this agostic contact cannot be excluded, as broad ^1H NMR signals at or below room temperature (−60 to 25 °C) interfered with the NMR signal assignment at these temperatures (*vide infra*). Despite the presence of six donors around zirconium, the

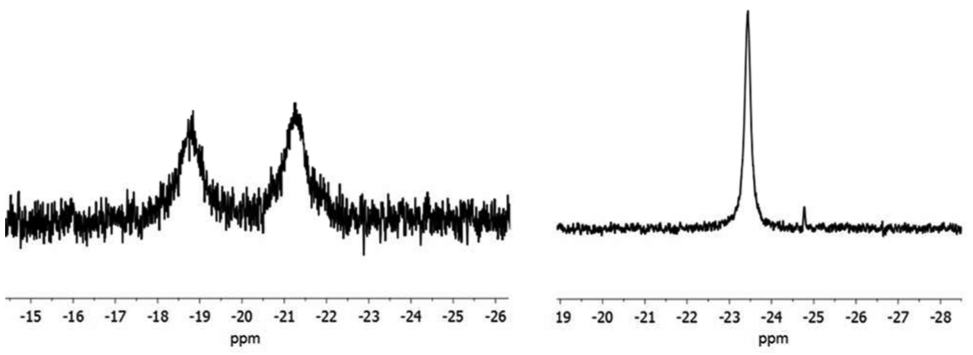


Figure 4. $^{31}P\{^1H\}$ NMR spectra (162 MHz, toluene-d_8) of [B]-5-Zr recorded at room temperature (left) and at +100 °C (right).

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metal's coordination polyhedron is derived neither from a regular octahedral nor from a trigonal prismatic geometry. Instead, it is best described as a tetrahedral assembly, which is distorted by two zirconium−phosphine interactions and the agostic contact. The zirconium−nitrogen bond lengths are found within the expected range for zirconium amides, but the Zr−P1 (2.8580(11) Å) and Zr−P2 (2.9456(11) Å) distances are at the upper end of similar zirconium amidophosphine complexes, suggesting these interactions to be rather weak.[22]

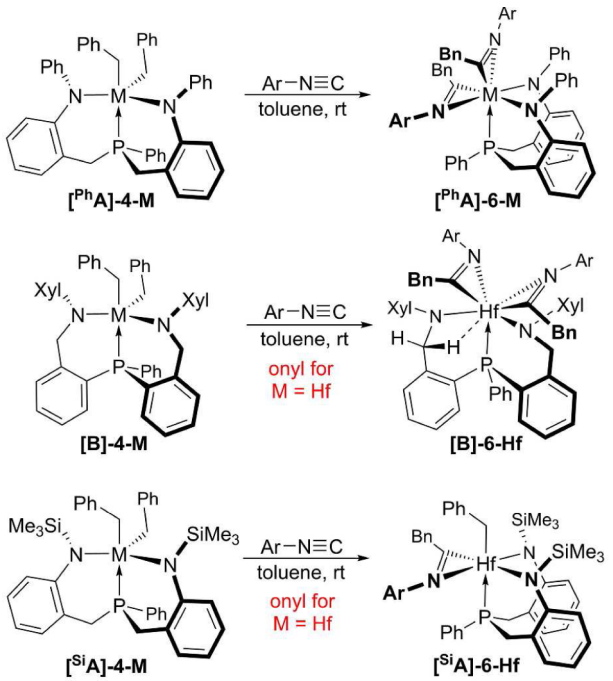
At +100 °C only one $^{31}P\{^{1}H\}$ NMR signal was detected for [**B**]-**5-Zr** (see Figure 4), and reasonably sharp signals were observed in the ^{1}H NMR spectrum (see Supporting Information), which is in line with a highly symmetric species bearing two equivalent diamidophosphine ligands, assumingly with no agostic interactions present at this temperature. So far, similar homoleptic 2:1 complexes bearing [^{Ph}**A**] remained elusive, although all of the possible routes shown in Scheme 4 have been probed carefully. Therefore, the three-step routes starting from the diiodo complexes were required for the preparation of both zirconium dibenzyl complexes [^{Ph}**A**]-**4-Zr** and [**B**]-**4-Zr**.

Reactivities of [NPN]MBn$_2$ (M = Zr, Hf) toward Isonitriles. To further elucidate the different stabilities of the dibenzyl zirconium and hafnium complexes, reactivity studies seemed to be required and insertion reactions were targeted in this study. Upon treatment of [^{Ph}**A**]-**4-M** (M = Zr, Hf) with 2,6-xylylisonitrile, clean insertion reactions[31] affording the bis(η^2-iminoacyl) complexes [^{Ph}**A**]-**6-M** were observed, as judged by NMR spectroscopy (see Scheme 6).

Both products were isolated without difficulties and found to be stable at room temperature. Gentle heating led to decomposition rather than C−C coupling, which was found to occur cleanly for tropocoronand-,[32] guanidinate-,[33] amidinate-,[34] aryloxide-[35] and Cp-coordinated[36] bis(η^2-iminoacyl) group 4 complexes. This thermal degradation is even more pronounced for the corresponding ^{t}BuNC insertion products, which were found to be unstable even below room temperature, thus impeding their purification and isolation. In the proton NMR spectra of both complexes [^{Ph}**A**]-**6-M**, two sets of signals were detected for the η^2-iminoacyl ligands, indicating that these groups are situated in *cis*- and *trans*-position to the phosphine. In the case of [**B**]-**4-Hf**, a similar insertion of 2,6-xylylisonitrile into both Hf−C bonds affording [**B**]-**6-Hf** was observed, but only mixtures of products were obtained for [**B**]-**4-Zr** (see Scheme 6). To further elucidate this observations, single crystals for X-ray diffraction were grown for [^{Ph}**A**]-**6-Zr** and [**B**]-**6-Hf** by cooling saturated solutions of the complexes in Et_2O to −40 °C (see Figure 6). In both cases, the η^2-iminoacyl ligands were found in the expected positions, i.e., *cis* and *trans* to the phosphine, with the two N=C vectors of the η^2-iminoacyl groups aligned nearly collinear (see Figure 6, cf. Table 4). Interestingly, these N=C vectors are pointing in opposite directions (*anti*) in the case of [^{Ph}**A**]-**6-Zr**, but in the same direction (*syn*) in the case of [**B**]-**6-Hf**, which has been observed in other bis(η^2-iminoacyl) complexes as well.[37,33b] For the latter complex, an agostic interaction between H22B and the central hafnium ion seems to be present, as judged by the narrow H22A−C22−H22B angle (100.1(17)°).[26] The question why a clean reaction of 2,6-xylylisonitrile with [**B**]-**4-M** was only observed for M = Hf cannot be answered with certainty, as this observation might not solely depend on the stability of the anticipated zirconium complex [**B**]-**6-Zr**, but also on the stability of the starting material [**B**]-**4-Zr**, whose thermal decomposition *might* be accelerated in the presence of isonitrile ligands. Nevertheless, the finding agrees well with previous reports on zirconium's higher reactivity,[2c] for example in zirconocen-catalyzed silane dehydrocoupling reactions.[38] In the case of complexes [^{Si}**A**]-**4-M** (M = Zr, Hf), a clean conversion with respect to insertion of 2,6-xylylisonitrile was found for the hafnium derivative only, while at least four different species were observed in the corresponding reaction of [^{Si}**A**]-**4-Zr**. Upon addition of two equivalents of 2,6-xylylisonitrile to [^{Si}**A**]-**4-Hf**, a new species ([^{Si}**A**]-**6-Hf**) was formed cleanly according to $^{31}P\{^{1}H\}$ NMR spectroscopy. Inspection of the corresponding ^{1}H NMR revealed that only half of the isonitrile was consumed and that one hafnium benzyl moiety was left unreacted. A comparison of the benzylic methylene resonances in the starting material (δ(*cis*-CH_2^{Bn}) = 2.18 and 2.25 ppm with $^{3}J_{H,P}$ = 8.0 and 6.8 Hz, δ(*trans*-CH_2^{Bn}) = 2.58 and 2.62 ppm with $^{3}J_{H,P}$ = 2.5 and 2.2 Hz) and the product ($\delta(CH_2^{Bn})$ = 2.44 and 2.75 ppm, unresolved $^{3}J_{H,P}$) revealed that the *trans*-positioned benzyl group remained in place, while the *cis*-positioned one underwent insertion.[24] To confirm this finding, the molecular structure of [^{Si}**A**]-**6-Hf** was acquired by single-crystal X-ray diffraction and found to exhibit the expected stereochemistry (see Figure 6).

Upon heating [^{Si}**A**]-**6-Hf** with 2,6-xylylisonitrile, extensive decomposition was observed instead of a second insertion into the remaining hafnium benzyl unit. Assuming that the electronic structures of [^{Ph}**A**]-**4-Hf** and [^{Si}**A**]-**4-Hf** are fairly similar, the preference for monoinsertion in the case of [^{Si}**A**]-**4-Hf** is thought to be a consequence of the sterically more demanding *N*-trimethylsilyl substituents. That the benzyl−hafnium bond in [^{Si}**A**]-**6-Hf** is indeed shielded by both flanking trimethylsilyl groups is not obvious from the ORTEP plot of the molecular structure shown in Figure 6, but seen in the corresponding space-filling representation (see Supporting Information). Thus, the different insertion chemistry of [^{Si}**A**]-

Scheme 6. Reactions of [^{Ph}A]-4-M, [B]-4-M, and [^{Si}A]-4-M with Ar−NC (M = Zr, Hf; Ar = 2,6-Me$_2$C$_6$H$_3$)



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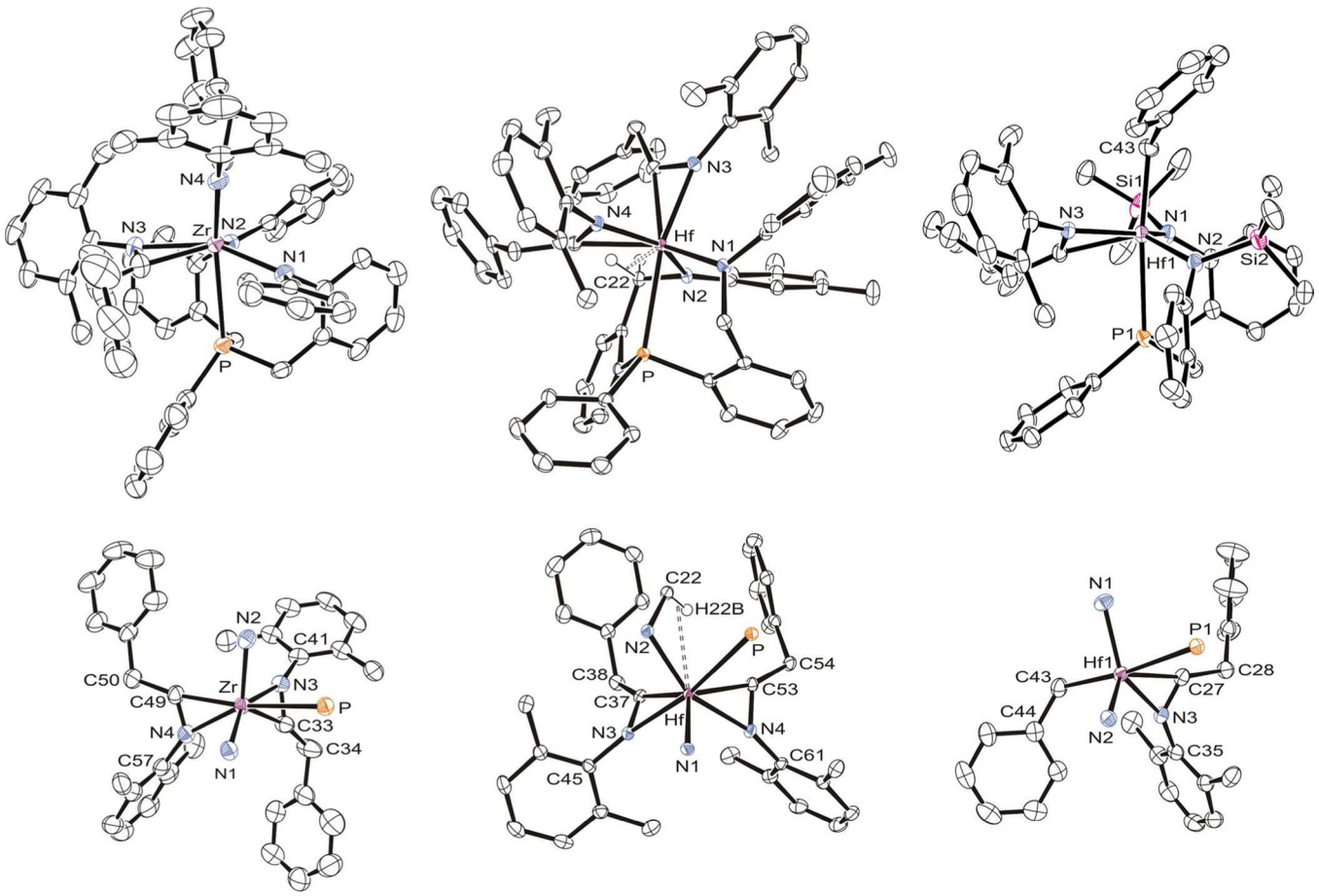

Figure 6. ORTEP diagrams of [^{Ph}A]-**6-Zr** (left), [**B**]-**6-Hf** (middle), and [^{Si}A]-**6-Hf** (right). Hydrogen atoms are omitted for clarity; thermal ellipsoids are set at 50% probability. Carbon atoms of the diamidophosphine ligands (except C22 in the case of [**B**]-**6-Hf**) are omitted in the truncated views depicted in the second row. Selected bond lengths and angles are summarized in Table 4. In addition to the shown molecule of [^{Si}A]-**6-Hf**, a second independent molecule with fairly similar metrical parameters is present in the unit cell (for details see Supporting Information).

Table 4. Selected Metrical Parameters and ^{31}P NMR Shifts (C_6D_6) of Complexes [^{Ph}A]-6-Zr, [B]-6-Hf, and [^{Si}A]-6-Hf

	[^{Ph}A]-6-Zr	[B]-6-Hf	[^{Si}A]-6-Hf[a]
M−P (Å)	2.9422(10)	2.8184(4)	2.8674(7)
M−N (Å)	2.193(3)	2.1313(14)	2.110(2)
	2.186(3)	2.1130(14)	2.078(2)
M−N$^{(ArN=CBn)}$ (Å)	2.274(3)	2.2302(15)	2.227(2)
	2.212(3)	2.3019(14)	
M−C (Å)	2.253(4)	2.2237(18)	2.242(3)[b]
	2.271(4)	2.2548(17)	2.313(3)[c]
P−M−N$^{(ArN=CBn)}$ (deg)	155.98(8)	165.38(4)	99.21(6)
	89.54(8)	97.66(4)	
P−M−C (deg)	122.54(13)	148.38(5)	78.72(7)[b]
	104.00(12)	82.23(4)	172.37(8)[c]
N−M−N (deg)	103.38(11)	103.94(6)	112.87(9)
C=N$^{(ArN=CBn)}$	1.289(4)	1.294(2)	1.294(4)
	1.274(5)	1.298(2)	
δ ^{31}P (ppm)	7.4	−13.7	6.8

[a]Metrical parameters for a second fairly similar independent molecule in the unit cell are provided in the Supporting Information. [b]η^2-Iminoacyl carbon (C27). [c]Benzylic carbon (C43).

4-Hf and [^{Ph}A]-**4-Hf** seems to originate from the different spatial demands of both these ligands. However, the most pronounced and therefore most unpredictable differences between zirconium and hafnium have been found for ligand [**B**] (e.g., formation of the 2:1 complex [**B**]-**5-Zr**), which might in part stem from the ligand's propensity to support agostic interactions with the central metals. While the latter point certainly requires further clarification, it was clearly shown that the silyl-free ligand [^{Ph}A] is superior to [^{Si}A] and that both these ligands are distinct from [**B**], although it is just an inverted benzylene linker differentiating [^{Ph}A] and [^{Si}A] from [**B**].

CONCLUSIONS

To this end, the conclusion to be drawn from this study is that the diamidophosphine-coordinated zirconium complexes prepared herein are less robust (i.e., more reactive) than their hafnium counterparts, which is in line with the observations made for zirconocenes.[2c] Accordingly, the dibenzyl hafnium complexes [^{Si}A]-**4-Hf**, [^{Ph}A]-**4-Hf**, and [**B**]-**4-Hf** could be prepared via direct reaction of the respective protioligands with $HfBn_4$, while decomposition or formation of the homoleptic species [**B**]-**5-Zr** was observed with $ZrBn_4$. In the case of ligand [**B**], the dibenzyl zirconium species [**B**]-**4-Zr** was found to be exceedingly sensitive, which disallowed for an isolation of solid samples. The related dibenzyl zirconium complexes of [^{Ph}A] and [^{Si}A], however, were isolated without difficulties, although significantly different synthetic routes had to be chosen. Despite the latter dissimilarity between [^{Ph}A] and [^{Si}A], the

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differences between zirconium and hafnium seem to be most pronounced for ligand [**B**]. This was supported by probing the reactivities of the six dibenzyl complexes [^{Ph}**A**]-**4-M**, [**B**]-**4-M**, and [^{Si}**A**]-**4-M** (M = Zr, Hf) with respect to insertion of 2,6-xylylisonitrile. Stable η^2-iminoacyl products were isolated for both metals in the case of ligand [^{Ph}**A**], but only the hafnium bis(η^2-iminoacyl) complex [**B**]-**6-Hf** was obtained for ligand [**B**]. For [^{Si}**A**]-**4-Hf**, the mono-(η^2-iminoacyl) complex [^{Si}**A**]-**6-Hf** was isolated, indicating that the metal−carbon bonds are less accessible for this sterically more demanding ligand. Whether the benzylic positions within these complexes, in particular within the [**B**]-coordinated derivatives, are prone to cyclometalations[39] and whether such processes induce a more pronounced discrimination of one metal over the other is currently being explored in our laboratory.

EXPERIMENTAL SECTION

All manipulations were performed under an atmosphere of dry and oxygen-free argon by means of standard Schlenk or glovebox techniques. Toluene, THF, pentanes, hexanes, diethyl ether, and dimethoxyethane (DME) were purified by passing the solvents through activated alumina columns (MBraun solvent purification system). Toluene-d_8, THF-d_8, benzene-d_6, and 1,4-dioxane were refluxed over sodium and purified by distillation. DMSO-d_6, CD_2Cl_2-d_2, $Me_3SiOSiMe_3$, NEt_3, and dichloromethane were dried over CaH_2 and distilled prior to use. NMR spectra were recorded on a Bruker Avance II 400 MHz or a Bruker Avance III 600 MHz spectrometer at room temperature unless noted otherwise. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to residual proton signals of the lock solvent. ^{31}P{^{1}H} NMR spectra were referenced to external $P(OMe)_3$ (141.0 ppm with respect to 85% H_3PO_4 at 0.0 ppm). Microanalyses (C, H, N) were performed at the Department of Chemistry at the University of Heidelberg. Solutions of *n*-butyllithium (2.5 M in hexanes), solutions of HCl (1.0 M in Et_2O), $M(NMe_2)_4$ (M = Zr, Hf), Me_3SiX (X = Cl, OTf, I), methyl iodide, phenyl phosphine, NEt_3HCl, $LiAlH_4$, and 2,6-(dimethylphenyl)isonitrile were purchased from commercial suppliers and used as received. A purchased solution of (trimethylsilylmethyl)lithium (1.0 m solution in pentane) was condensed to half of its volume, and $LiCH_2SiMe_3$ crystallized at −40 °C and was isolated as a white powder. Commercially available solutions of BnMgCl (1.0 M in Et_2O) were used for the preparation of MBn_4 (M = Zr, Hf),[27,28] $Bn_2ZrCl_2(OEt_2)$,[29] and $Bn_2Mg(L)_2$ (L = THF, Et_2O).[25] Compounds **1**,[18] **4**,[20] **5**,[20] [^{Si}**A**]H_2,[7] [^{Si}**A**]-**1-M**,[7] and [^{Si}**A**]-**2-M** (M = Zr, Hf)[7] were synthesized according to the literature. Experimental procedures for the preparation of compounds **2**, **3**, and **6** are provided in the Supporting Information.

[^{Ph}A]H_2. Neat phenylphosphine (240 μL, 2.18 mmol, 1.00 equiv) was added in one portion to a stirred suspension of **3** (1.80 g, 4.89 mmol, 2.24 equiv) in DME (100 mL) at −78 °C. After 5 min, *n*-BuLi (2.50 M in hexanes, 4.00 mL, 9.60 mmol, 4.40 equiv) was added dropwise at this temperature. Stirring was continued for 1 h at −78 °C, and the reaction flask then placed in an ice bath. After stirring for 30 min at 0 °C, the reaction mixture was allowed to warm to room temperature and stirred for another 2 h. Subsequently, all volatiles were removed under vacuum, and the residue was extracted with toluene (40 mL). Solid $HNEt_3Cl$ (1.22 g, 3.60 mmol, 3.50 equiv) was added to the toluene extract, and the resulting suspension was stirred for 2 h. The liberated NEt_3 was removed in part by concentrating the reaction mixture to a volume of approximately 30 mL. Lithium iodide was then precipitated by addition of 1,4-dioxane (5 mL), and the yellow suspension was filtered over Celite. The Celite pad was washed with toluene (2 × 5 mL), and the combined filtrate was concentrated to approximately 5 mL, diluted with Et_2O (20 mL), and then cooled to 0 °C. A solution of HCl (2.0 M in Et_2O, 5.40 mL, 10.8 mmol, 2.20 equiv) was added dropwise, resulting in the formation of a white precipitate. Stirring was continued for 30 min at 0 °C. The solids were collected on a sinter glass frit, washed with Et_2O (2 × 10 mL), and dried under vacuum to afford the bis(hydrochloride) salt of the title compound as a white solid (0.95 g, 1.74 mmol, 80%). ^{1}H NMR (600 MHz, THF-d_8): δ [ppm] = 8.02−7.47 (m, 4 H, R_2NH_2Cl), 7.68−7.61 (m, 2 H, *o*-PPh), 7.41 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, *p*-PPh), 7.29 (t, $^3J_{H,H}$ = 6.9 Hz, 2 H, *m*-PPh), 7.18 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 6-ArH), 7.09 (t, $^3J_{H,H}$ = 7.8 Hz, 4 H, *m*-NPh), 6.98 (d, $^3J_{H,H}$ = 7.7 Hz, 6 H, *o*-NPh), 6.93 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, 3-ArH), 6.75 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, *p*-NPh), 6.64 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, 4-ArH), 4.31−4.21 (m, 2 H, PCH_2), 4.01−3.91 (m, 2 H, PCH_2). ^{13}C{^{1}H} NMR (151 MHz, THF-d_8): δ [ppm] = 145.4 (s, *ipso*-NPh), 143.4 (d, $^3J_{P,C}$ = 4.3 Hz, 1-ArC), 134.5 (d, $^2J_{P,C}$ = 13.8 Hz, *o*-PPh), 132.7 (s, *p*-PPh), 132.4 (d, $^3J_{P,C}$ = 7.1 Hz, 3-ArC), 129.6 (s, *m*-NPh), (s, *ipso*-PPh), 129.4 (s, *m*-PPh), 128.5 (s, 5-ArC), 124.9 (s, 2-ArC), 122.2 (s, 4-ArC), 120.6 (s, *p*-NPh), 120.3 (s, 6-ArC), 118.4 (s, *m*-NPh), 29.5 (d, $^1J_{P,C}$ = 17.9 Hz, PCH_2). ^{31}P{^{1}H} NMR (243 MHz, THF-d_8): δ [ppm] = 4.06 (s). HR-MS (FAB$^+$): observed *m*/*z* = 473.2148, calcd *m*/*z* for $C_{32}H_{30}N_2P$ ([M − 2 Cl − H]$^+$) = 473.2141. To a stirred suspension of the bis(hydrochloride) salt (0.95 g, 1.74 mmol) in dichloromethane (30 mL) at 0 °C was added neat NEt_3 (1.00 mL, 7.18 mmol, 4.13 equiv with respect to the bis(hydrochloride) salt) over the course of 15 min. The resulting reaction mixture was stirred for 15 min at 0 °C and then allowed to warm to room temperature. The solvent was removed under reduced pressure, and Et_2O (30 mL) was added to the residue. The precipitate (NEt_3HCl) was removed via filtration over Celite, and the Celite pad was washed carefully with Et_2O (3 × 10 mL). The combined extracts and washings were condensed under reduced pressure, and the title compound was obtained as a pale yellow, viscous oil (544 mg, 1.15 mmol, 53% with respect to $PhPH_2$). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.32−7.26 (m, 2 H, ArH), 7.24−7.19 (m, 2 H, ArH), 7.13−7.05 (m, 5 H, ArH), 7.01 (td, $^4J_{H,H}$ = 1.1 Hz, $^3J_{H,H}$ = 8.4 Hz, 3 H, ArH), 6.97−6.90 (m, 3 H, ArH), 6.79 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, ArH), 6.75 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, ArH), 5.46 (d, $^3J_{H,H}$ = 3.7 Hz, 2 H, NH), 2.97 (s, 4 H, PCH_2). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ [ppm] = 144.9 (s, ArC), 141.7 (d, $J_{P,C}$ = 3.0 Hz, ArC), 137.3 (d, $J_{P,C}$ = 17.6 Hz, ArC), 133.2 (d, $J_{P,C}$ = 19.1 Hz, ArC), 131.4 (d, $J_{P,C}$ = 5.9 Hz, ArC), 129.8 (s, ArC), 129.6 (d, $J_{P,C}$ = 2.6 Hz, ArC), 128.8 (d, $J_{P,C}$ = 7.1 Hz, ArC), 127.5 (d, $J_{P,C}$ = 2.5 Hz, ArC), 123.0 (d, $J_{P,C}$ = 1.8 Hz, ArC), 121.5 (d, $J_{P,C}$ = 1.0 Hz, ArC), 120.4 (s, ArC), 117.6 (s, ArC), 117.3 (s, ArC), 32.31 (d, $^1J_{P,C}$ = 15.1 Hz, PCH_2). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ [ppm] = −24.3 (s). Anal. Calcd for $C_{32}H_{29}N_2P$: C 81.33 H 6.19, N 5.93. Found: C 81.59, H 6.34, N 6.16.

[B]H_2. *Method A.* To a solution of **5** (7.50 g, 23.6 mmol, 1.00 equiv) in trifluoroethanol (150 mL) was added 3,5-dimethylaniline (5.90 mL, 5.72 g, 47.2 mmol, 2.00 equiv), and the stirred reaction mixture was heated to 60 °C for 1 h. Sodium borohydride (2.14 g, 56.6 mmol, 2.40 equiv) was added, and the mixture was stirred for 1 h at that temperature. After removal of the solvent under reduced pressure, the residue was dried thoroughly under vacuum, and dichloromethane (100 mL) was added. After filtration, the solution was condensed to dryness and the crude product subjected to column chromatography (petroleum ether/ethyl acetate = 10:1, R_f = 0.38). The title compound was obtained as a colorless solid in varying yields (1.25−4.38 g, 2.37−8.29 mmol, 10−35%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.44−7.48 (m, 2 H, 3-ArH), 7.32−7.39 (m, 5 $H_{overlapping}$, 4-ArH, PPh-H), 7.20−7.26 (m, 4 $H_{overlapping}$, 5-ArH, PPh-H), 6.94 (dd, $^3J_{H,H}$ = 7.5 Hz, $^3J_{P,H}$ = 4.3 Hz, 2 H, 6-ArH), 6.38 (s, 2 H, *p*-Xyl), 5.99 (s, 4 H, *o*-Xyl), 4.53 (dd, $^2J_{H,H}$ = 13.8 Hz, $^4J_{P,H}$ = 4.0 Hz, 2 H, CH_2), 4.39 (dd, $^2J_{H,H}$ = 13.8 Hz, $^4J_{P,H}$ = 5.3 Hz, 2 H, CH_2), 3.49 (bs, 2 H, NH), 2.13 (s, 12 H, Xyl-CH_3). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ [ppm] = 148.3 (s, *ipso*-Xyl), 144.3 (d, $^2J_{P,C}$ = 24.5 Hz, 2-ArC), 139.0 (s, *m*-Xyl), 136.5 (d, $J_{P,C}$ = 9.7 Hz, PPh-C), 136.0 (d, $^2J_{P,C}$ = 14.2 Hz, 6-ArC), 134.6 (d, $^1J_{P,C}$ = 20.2 Hz, 1-ArC), 134.4 (s, 4-ArC), 129.6 (s, 5-ArC), 129.4 (s, PPh-C), 129.1−129.2 (overlapping signals, 3-ArC, PPh-C), 128.0 (s, Ph-C), 119.9 (s, *p*- Xyl), 111.2 (s, *o*-Xyl, PPh−C), 47.4 (d, $^3J_{P,C}$ = 23.1 Hz, CH_2), 21.6 (s, Xyl-CH_3). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ [ppm] = −26.3 (s). Anal. Calcd for $C_{36}H_{37}N_2P$: C 81.79, H 7.05, N 5.30. Found: C 81.79, H 7.21, N 5.06. HR-MS (FAB): *m*/*z* = 529.2799, calcd *m*/*z* for $C_{36}H_{38}N_2P$ ([M]$^+$) = 529.2773 (Δ = 4.9 ppm).

Method B. A solution of **6** (10.0 g, 34.4 mmol, 0.50 equiv) in dry diethyl ether (350 mL) was cooled to −78 °C, and *n*-BuLi (28.0 mL, 2.5 M in hexanes, 70.0 mmol, 2.00 equiv) was added dropwise. The

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reaction mixture was briefly warmed to 0 °C and recooled to −78 °C. A solution of $PhPCl_2$ (2.30 mL, 17.2 mmol, 1.00 equiv) in diethyl ether (350 mL) was then added over the course of 2 h. The reaction mixture was allowed to warm to room temperature, and stirring was continued overnight. The reaction was quenched by addition of distilled H_2O (200 mL), and the phases were separated. The organic phase was washed with distilled H_2O (2 × 100 mL), dried over sodium sulfate, and concentrated under reduced pressure. The pale yellow residue was recrystallized from ethanol, and the product obtained as a colorless solid (4.60 g, 8.69 mmol, 51%). Analytical data were found to be identical to those obtained for the product prepared via method A.

[^{Ph}A]Zr(NMe$_2$)$_2$ ([^{Ph}A]-1-Zr). A solution of $Zr(NMe_2)_4$ (154 mg, 583 μmol, 1.10 equiv) in toluene (10 mL) was added slowly to a stirred solution of [^{Ph}A]H_2 (250 mg, 530 μmol, 1.00 equiv) in toluene (10 mL). An immediately color change to yellow was observed, and the solution was stirred 3 h at room temperature. Subsequently, all volatiles were removed under vacuum, and the residue was washed with Et_2O (2 × 5 mL). The product was obtained as a pale yellow solid (254 mg, 391 μmol, 67%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.36 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, 4-ArH), 7.26 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, *o*-PPh), 7.14−7.09 (m, 6 H$_{overlapping}$, 5-ArH, *m*-NPh), 6.97 (ddd, *J* = 1.4 Hz, *J* = 5.2 Hz, *J* = 8.8 Hz, 2 H, *m*-PPh), 6.95−6.91 (m, 1 H, *p*-PPh), 6.86−6.83 (m, 2 H, 3-ArH), 6.83−6.80 (m, 2 H, 6-ArH), 6.72 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, *p*-NPh), 6.59 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, *o*-NPh), 3.32 (s, 6 H, NMe_2), 2.83 (dd, *J* = 7.1 Hz, *J* = 13.4 Hz, 2 H, PCH_2), 2.74 (s, 6 H, NMe_2), 2.51 (dd, *J* = 8.7 Hz, *J* = 13.4 Hz, 2 H, PCH_2). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ [ppm] = 153.3 (s, *ipso*-NPh), 144.1 (s, 1-ArC), 136.9 (s, 2-ArC), 133.3 (s, 4-ArC), 132.7 (s, *ipso*-PPh), 131.4 (d, $^3J_{P,C}$ = 13.5 Hz, *o*-PPh), 131.2 (d, $^3J_{P,C}$ = 4.9 Hz, 6-ArC), 129.8 (d, $^4J_{P,C}$ = 0.9 Hz, *p*-PPh), 129.6−129.5 (overlapping signals, *m*-NPh, 5-ArC), 129.0 (d, $^3J_{P,C}$ = 7.5 Hz, *m*-PPh), 126.7 (s, 3-ArC), 117.6 (s, *p*-NPh), 115.4 (s, *m*-NPh), 45.1 (d, $^3J_{P,C}$ = 3.9 Hz, NMe_2), 43.0 (s, NMe_2), 30.6 (s, PCH_2). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ [ppm] = 10.2 (s). Anal. Calcd for $C_{36}H_{39}N_4PZr$: C 66.53, H 6.05, N 8.62. Found: C 65.91, H 6.36, N 8.79. Note that low carbon values have been found, despite numerous attempts using recrystallized and carefully dried, finely ground samples.

[^{Ph}A]Hf(NMe$_2$)$_2$ ([^{Ph}A]-1-Hf). A solution of $Hf(NMe_2)_4$ (197 mg, 555 μmol, 1.04 equiv) in toluene (10 mL) was added slowly to a stirred solution of [^{Ph}A]H_2 (250 mg, 530 μmol, 1.00 equiv) in toluene (10 mL). An immediately color change to yellow was observed, and the solution was stirred 6 h at 80 °C. Subsequently, all volatiles were removed under vacuum, and the residue was washed with Et_2O (2 × 5 mL). The product was obtained as a pale yellow solid (258 mg, 345 μmol, 63%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.41 (d, $^3J_{H,H}$ = 5.4 Hz, 2 H, 4-ArH), 7.28 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, *o*-PPh), 7.16−7.12 (m, 6 H$_{overlapping}$, 5-ArH,/*m*-NPh), 6.99−6.94 (m, 2 H, *m*-PPh), 6.94−6.90 (m, 1 H, *p*-PPh), 6.88−6.85 (m, 2 H, 3-ArH), 6.85−6.82 (m, 2 H, 6-ArH), 6.72 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, *p*-NPh), 6.63 (d, $^3J_{H,H}$ = 5.4 Hz, 4 H, *o*-NPh), 3.39 (s, 6 H, NMe_2), 2.87 (dd, *J* = 7.8 Hz, *J* = 13.4 Hz, 2 H, PCH_2), 2.73 (s, 6 H, NMe_2), 2.56 (dd, *J* = 8.8 Hz, *J* = 13.5 Hz, 2 H, PCH_2). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ [ppm] = 153.5 (s, *ipso*-NPh), 143.7 (s, 1-ArC), 136.8 (s, 2-ArC), 133.6 (s, 4-ArC), 132.3 (s, *ipso*-PPh), 131.4 (d, $^2J_{P,C}$ = 13.3 Hz, *o*-PPh), 131.1 (d, $^4J_{P,C}$ = 4.7 Hz, 6-ArC), 129.9 (s, *p*-PPh) 129.7−129.6 (overlapping signals, 5-ArC, *m*-NPh), 129.1 (d, $^3J_{P,C}$ = 7.6 Hz,, *m*-PPh), 126.7 (s, 3-ArC), 117.6 (s, *p*-NPh), 115.7 (s, *o*-NPh), 44.9 (s, NMe_2), 42.7 (s, NMe_2), 30.4 (s, PCH_2). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ [ppm] = 16.0 (s). Anal. Calcd for $C_{36}H_{39}N_4PHf$: C 58.65, H 5.33, N 7.60. Found: C 58.66, H 5.36, N 7.64.

[B]Zr(NMe$_2$)$_2$ ([B]-1-Zr). A solution of $Zr(NMe_2)_4$ (278 mg, 10.4 mmol, 1.10 equiv) in toluene (5 mL) was added to a stirred solution of [**B**]H_2 (500 mg, 9.46 mmol, 1.00 equiv) in toluene (10 mL), and the reaction mixture was heated to 110 °C for 2 h. After cooling to room temperature, all volatiles were removed under reduced pressure and the residue was washed with *n*-pentane (2 × 2 mL). After drying under vacuum, the product was obtained as a pale yellow powder (528 mg, 7.47 mmol, 79%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.24 (t, *J* = 6.2 Hz, 2 H, 3-ArH), 7.09 (t, *J* = 7.4 Hz, 2 H, *o*-PPh), 7.03 (t, *J* = 8.4 Hz, 2 H, 4-ArH), 6.99 (t, *J* = 7.5 Hz, 2 H, *m*-PPh), 6.91 (t, *J* = 7.6 Hz, 1 H, *p*-PPh), 6.86 (t, *J* = 7.3 Hz, 2 H, 6-ArH), 6.78 (t, *J* = 7.5 Hz, 2 H, 5-ArH), 6.61 (s, 4 H, *o*-Xyl), 6.45 (s, 2 H, *p*-Xyl), 5.01 (d, *J* = 15.5 Hz, 2 H, CH_2), 4.70 (d, *J* = 15.5 Hz, 2 H, CH_2), 3.18 (s, 6 H, NMe_2), 2.97 (s, 6 H, NMe_2), 2.25 (s, 12 H, Xyl-CH_3). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ [ppm] = 153.4 (s, *ipso*-Xyl), 147.4 (d, *J* = 18.8 Hz, 1-ArC), 138.0 (s, *m*-Xyl), 135.6 (d, *J* = 1.3 Hz, 6-ArC), 134.2 (d, *J* = 13.8 Hz, 2-ArC), 133.3 (d, *J* = 14.3 Hz, PPh-C), 130.6 (d, *J* = 8.4 Hz, PPh-C), 130.5 (d, *J* = 15.9 Hz, 3-ArC), 130.0 (d, *J* = 1.2 Hz, 5-ArC), 129.2 (s, PPh-C), 128.7 (d, *J* = 7.5 Hz, 4-ArC), 128.4 (s, PPh-C), 119.9 (s, *p*-Xyl), 114.4 (s, *o*-Xyl), 52.2 (d, *J* = 11.1 Hz, CH_2), 43.7 (s, NMe_2), 42.9 (d, *J* = 1.9 Hz, NMe_2), 22.2 (s, Xyl-CH_3). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ [ppm] = −28.0 (s). Anal. Calcd for $C_{40}H_{47}N_4PZr$: C 68.05, H 6.71, N 7.94. Found: C 67.77, H 6.70, N 7.55.

[B]Hf(NMe$_2$)$_2$ ([B]-1-Hf). Following the procedure provided for the zirconium derivative [**B**]-**1-Zr**, the title compound was prepared starting from $Hf(NMe_2)_4$ (369 mg, 10.4 mmol, 1.10 equiv) and [**B**]H_2 (500 mg, 9.46 mmol, 1.00 equiv) in toluene (15 mL). The resulting reaction mixture was heated to 80 °C for 30 min, and the product isolated as a pale yellow powder (623 mg, 7.85 mmol, 83%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.25 (t, *J* = 5.7 Hz, 2 H, 3-ArH), 7.00−7.07 (m, 4 H$_{overlapping}$, 4-ArH, *o*-PPh), 6.97 (t, *J* = 7.5 Hz, 2 H, *m*-PPh), 6.91 (t, *J* = 6.8 Hz, 1 H, *p*-PPh), 6.85 (t, *J* = 7.6 Hz, 2 H, 6-ArH), 6.78 (t, *J* = 7.5 Hz, 2 H, 5-ArH), 6.71 (s, 4 H, *o*-Xyl), 6.45 (s, 2 H, *p*-Xyl), 4.95 (d, *J* = 15.5 Hz, 2 H, CH_2), 4.71 (d, *J* = 15.5 Hz, 2 H, CH_2), 3.20 (s, 6 H, NMe_2), 3.02 (s, 6 H, NMe_2), 2.27 (s, 12 H, Xyl-CH_3). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ [ppm] = 151.1 (s, *ipso*-Xyl), 145.3 (d, *J* = 17.8 Hz, 1-ArC), 140.1 (s, *m*-Xyl), 135.4 (d, *J* = 1.5 Hz, 6-ArC), 132.9 (d, *J* = 13.8 Hz, 2-ArC), 130.2 (d, *J* = 8.4 Hz, PPh-C), 129.7 (d, *J* = 1.3 Hz, PPh-C), 129.0 (s, PPh-C), 128.8 (d, *J* = 14.9 Hz, 3-ArC), 128.3 (s, PPh-C), 128.2 (s, 5-ArC), 127.5 (d, *J* = 3.7 Hz, 4-ArC), 119.7 (s, *p*-Xyl), 114.8 (s, *o*-Xyl), 50.6 (d, *J* = 11.8 Hz, CH_2), 23.2 (s, NMe_2), 21.4 (s, NMe_2), 21.8 (s, Xyl-CH_3). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ [ppm] = −23.8 (s). Anal. Calcd for $C_{40}H_{47}HfN_4P$: C 60.56, H 5.97, N 7.06. Found: C 60.93, H 6.32, N 6.85.

[^{Ph}A]ZrI$_2$ ([^{Ph}A]-2-Zr). A solution of trimethylsilyl iodide (105 mg, 527 μmol, 2.10 equiv) in toluene (5 mL) was added slowly to a stirred solution of [^{Ph}A]-**1-Zr** (163 mg, 251 μmol, 1.00 equiv) in toluene (10 mL), and the reaction mixture was stirred for 2 h at room temperature. Subsequently, all volatiles were removed under vacuum, and the residue was washed with toluene (2 × 5 mL). The product was obtained as an orange solid (248 mg, 149 μmol, 73%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 7.49−7.43 (m, 3 H, ArH), 7.43−7.38 (m, 4 H, ArH), 7.38−7.33 (m, 2 H, ArH), 7.26−7.21 (m, 4 H, ArH), 7.16−7.12 (m, 4 H, *m*-NPh), 6.94−6.90 (m, 2 H, *p*-NPh,), 6.83 (dd, $^3J_{H,H}$ = 0.9 Hz, $^3J_{H,H}$ = 8.6 Hz, 4 H, *o*-NPh), 3.22 (dd, *J* = 9.1 Hz, *J* = 13.9 Hz, 2 H, PCH_2), 3.09 (dd, *J* = 10.3 Hz, *J* = 13.9 Hz, PCH_2, 2 H). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2): δ [ppm] = 150.9 (s, ArC), 144.8 (s, ArC), 136.9 (s, ArC), 134.5 (d, $J_{P,C}$ = 3.0 Hz, ArC), 132.0 (d, $J_{P,C}$ = 9.6 Hz, ArC), 131.6−131.4 (m, ArC), 131.0 (d, $J_{P,C}$ = 2.8 Hz, ArC), 129.7 (s, ArC), 129.6 (d, $J_{P,C}$ = 1.6 Hz, ArC), 129.4 (d, $J_{P,C}$ = 8.7 Hz, *m*-NPh), 129.3 (s, ArC), 122.3 (s, *p*-NPh), 118.5 (s, *m*-NPh), 117.3 (s, ArC), 29.4 (d, *J* = 12.2 Hz, PCH_2). ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2): δ [ppm] = 1.1 (s). Anal. Calcd for $C_{32}H_{27}I_2N_2PZr$: C 47.13, H 3.34, N 3.43. Found: C 47.35, H 3.34, N 3.54.

[^{Ph}A]HfI$_2$ ([^{Ph}A]-2-Hf). A solution of trimethylsilyl iodide (91.0 mg, 456 μmol, 2.10 equiv) in toluene (5 mL) was added slowly to a stirred solution of [^{Ph}A]**1-Hf** (160 mg, 217 μmol, 1.00 equiv) in toluene (10 mL), and the reaction mixture was stirred for 2 h at room temperature. Following the workup procedure provided for the zirconium derivative, the title compound was obtained as a yellow solid (248 mg, 149 μmol, 73%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 7.48−7.39 (m, 7 H, ArH), 7.32−7.32 (m, 2 H, ArH), 7.25 (dd, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,H}$ = 14.8 Hz, 4 H, ArH), 7.12 (t, $^3J_{H,H}$ = 7.9 Hz, 4 H, *m*-NPh), 6.85 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, *p*-NPh), 6.81 (t, $^3J_{H,H}$ = 6.6 Hz, 4 H, *o*-NPh), 3.32 (dd, *J* = 9.4 Hz, *J* = 13.9 Hz, 2 H, PCH_2), 3.20−3.14 (m, 2 H, PCH_2). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2): δ [ppm] = 151.0 (s, ArC), 144.8 (s, ArC), 134.5 (s, ArC), 133.5 (d, $J_{P,C}$ = 19.2 Hz, ArC), 132.0 (d, $J_{P,C}$ = 9.6 Hz, ArC), 131.5 (d, $J_{P,C}$ = 5.4 Hz, ArC), 131.0 (s, ArC), 129.7 (s, ArC), 129.5 (d, $J_{P,C}$ = 3.4 Hz, ArC), 129.4 (d, $J_{P,C}$ = 8.8

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Hz, ArC), 129.3 (s, *m*-NPh), 122.3 (s, *p*-NPh), 118.5 (s, *m*-NPh), 117.3 (s, ArC), 29.4 (d, $^{1}J_{P,C}$ = 12.3 Hz, PCH_2). $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2): δ [ppm] = 9.1 (s). Anal. Calcd for $C_{32}H_{27}HfI_2N_2P$: C 42.57, 3.01, N 3.10. Found: C 42.92, H 3.29, N 3.14.

[B]ZrI$_2$ ([B]-2-Zr). A solution of trimethylsilyl iodide (0.16 mL, 240 mg, 1.20 mmol, 2.10 equiv) in toluene (5 mL) was added dropwise to a stirred solution of [**B**]-**1-Zr** (400 mg, 0.57 mmol, 1.00 equiv) in toluene (15 mL), and the resulting reaction mixture was stirred for 30 min at room temperature. All volatiles were removed under vacuum, and the residue was washed with a mixture (50 vol % each) of diethyl ether and pentane (2 × 3 mL). After drying under vacuum, the title compound was obtained as a yellow powder (402 mg, 0.46 mmol, 81%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.34−7.38 (m, 2 H, 3-ArH), 6.88−6.96 (m, 7 $H_{overlapping}$, 4-ArH, 6-ArH, PPh-H), 6.85 (t, J = 7.5 Hz, 2 H, 5-ArH), 6.80 (s, 4 H, *o*-Xyl), 6.36 (t, J = 7.5 Hz, 2 H, PPh-H), 6.48 (s, 2 H, *p*-Xyl), 5.39 (d, J = 16.8 Hz, 2 H, CH_2), 4.37 (d, J = 16.8 Hz, 2 H, CH_2), 2.08 (s, 12 H, Xyl-CH_3). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 145.0 (s, *ipso*-Xyl), 145.1 (d, J = 16.5 Hz, 1-ArC), 140.0 (s, *m*-Xyl), 135.2 (d, J = 10.7 Hz, 3-ArC), 134.0 (d, J = 10.7 Hz, PPh-C), 131.0 (s, 6-ArC), 130.3 (s, PPh-C), 129.8 (d, J = 8.9 Hz, 2-ArC), 128.7 (d, J = 8.7 Hz, PPh-C), 118.6 (s, 5-ArC), 128.3 (s, 4-ArC), 128.0 (d, J = 5.0 Hz, PPh-C), 126.2 (s, *p*-Xyl), 118.2 (s, *o*-Xyl), 50.8 (d, J = 9.0 Hz, CH_2), 21.6 (s, Xyl-CH_3). $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = −10.0 (s). Anal. Calcd for $C_{36}H_{35}I_2N_2PZr$: C 49.60, H 4.05, N 3.21. Found: C 49.60, H 4.34, N 3.40.

[B]HfI$_2$ ([B]-2-Hf). A solution of trimethylsilyl iodide (0.15 mL, 222 mg, 1.06 mmol, 2.10 equiv) in toluene (1 mL) was added dropwise to a stirred solution of [**B**]-**1-Hf** (400 mg, 0.50 mmol, 1.00 equiv) in toluene (15 mL), and the resulting pale yellow solution was heated at 60 °C for 45 min. The reaction mixture was allowed to cool to room temperature and condensed to dryness. Following the workup procedure provided for the zirconium derivative, the title compound was obtained as a yellow solid (422 g, 0.44 mmol, 88%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.15−7.20 (m, 2 H, 3-ArH), 7.07 (t, J = 6.4 Hz, 2 H, 4-ArH), 6.99 (s, 4 H, *o*-Xyl), 6.88−6.93 (m, 5 $H_{overlapping}$, 6-ArH, PPh-H), 6.85 (t, J = 7.5 Hz, 2 H, 5-ArH), 6.67 (t, J = 7.5 Hz, 2 H, PPh-H), 6.48 (s, 2 H, *p*-Xyl), 5.37 (d, J = 16.8 Hz, 2 H, CH_2), 4.43 (d, J = 16.8 Hz, 2 H, CH_2), 2.11 (s, 12 H, Xyl-CH_3). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 148.3 (s, *ipso*-Xyl), 146.0 (d, J = 16.1 Hz, 1-ArC), 139.0 (s, *m*-Xyl), 135.7 (s, 4-ArC), 133.9 (d, J = 10.7 Hz, 3-ArC), 131.8 (d, J = 21.6 Hz, PPh-C), 131.0 (d, J = 1.8 Hz, 5-ArC), 130.3 (d, J = 2.1 Hz, 6-ArC), 130.0 (d, J = 9.0 Hz, 2-ArC), 129.3 (s, PPh-C), 128.7 (d, J = 9.0 Hz, PPh-C), 128.6 (s, PPh-C), 125.4 (s, *p*-Xyl), 118.5 (s, *o*-Xyl), 49.4 (d, J = 8.7 Hz, CH_2), 21.6 (s, Xyl-CH_3). $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = −6.0 (s). Anal. Calcd for $C_{36}H_{35}HfI_2N_2P$: C 45.09, H 3.68, N 2.92. Found: C 44.55, H 3.69, N 3.07. Note that low carbon values have been found, despite numerous attempts using recrystallized and carefully dried, finely ground samples.

[^{Ph}A]Zr(CH$_2$SiMe$_3$)$_2$ ([^{Ph}A]-3-Zr). A precooled solution (−40 °C) of $LiCH_2TMS$ (23.0 mg, 244 μmol, 2.22 equiv) in toluene (10 mL) was slowly added to a cold suspension (−40 °C) of [^{Ph}**A**]-**2-Zr** (90.0 mg, 110 μmol, 1.00 equiv) in toluene (20 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. A few drops of 1,4-dioxane were added to precipitate MgI_2 in the form of its 1,4-dioxane adduct. The resulting suspension was filtered using a micropore syringe filter, and the solvent was removed under vacuum. The residue was washed with pentane (2 × 5 mL) and then dried under vacuum to afford the product as a pale yellow solid (51.8 mg, 70.4 μmol, 64%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.36 (d, $^{3}J_{H,H}$ = 7.1 Hz, 2 H, ArH), 7.08−6.99 (m, 8 H, ArH), 6.98−6.92 (m, 3 H, ArH), 6.80−6.70 (m, 10 H, ArH), 2.77 (dd, $J_{H,H}$ = 6.6 Hz, $J_{H,H}$ = 13.2 Hz, 2 H, PCH_2), 2.53 (dd, $J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 13.3 Hz, 2 H, PCH_2), 1.44 (d, $^{3}J_{H,H}$ = 2.5 Hz, 2 H, CH_2SiMe_3), 1.35 (d, $^{3}J_{H,H}$ = 7.1 Hz, 2 H, CH_2SiMe_3), 0.45 (s, 9 H, $SiMe_3$), −0.01 (s, 9 H, $SiMe_3$). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 152.4 (s, ArC), 142.7 (s, ArC), 136.0 (s, ArC), 133.2 (s, ArC), 131.4 (d, J = 4.9 Hz, ArC), 131.1 (d, $J_{P,C}$ = 11.8 Hz, ArC), 130.7 (s, ArC), 129.7 (d, J = 2.6 Hz, ArC), 129.4 (s, ArC), 129.3 (s, ArC), 128.9 (d, $J_{P,C}$ = 7.0 Hz, ArC), 125.7 (s, ArC), 120.0 (s, ArC), 116.2 (s, ArC), 29.8 (s, PCH_2), 3.9 (s, CH_2SiMe_3), 2.6 (s, CH_2SiMe_3), 1.4 (s, $SiMe_3$), 0.0 (s, $SiMe_3$). $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = 1.0 (s). Anal. Calcd for $C_{40}H_{49}N_2PSi_2Zr$: C 65.26, H 6.71, N 3.81. Found: C 65.63, H 6.60, N 4.06.

[^{Ph}A]Hf(CH$_2$SiMe$_3$)$_2$ ([^{Ph}A]-3-Hf). A precooled solution (−40 °C) of $LiCH_2TMS$ (14.8 mg, 157 μmol, 2.22 equiv) in toluene (10 mL) was slowly added to cold suspension (−40 °C) of [^{Ph}**A**]-**2-Hf** (64.0 mg, 70.9 μmol, 1.00 equiv) in toluene (10 mL). The reaction mixture was allowed to warm to room temperature, and stirring was continued for 2 h. Following the workup procedure provided for the zirconium derivative, the title compound was obtained as a pale yellow solid (44.7 mg, 54.3 μmol, 77%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.38 (d, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, ArH), 7.09−7.00 (m, 8 H, ArH), 6.96−6.94 (m, 3 H, ArH), 6.84 (t, $^{3}J_{H,H}$ = 7.4 Hz, 2 H, ArH), 6.81−6.76 (m, 6 H, ArH), 6.71 (t, $^{3}J_{H,H}$ = 7.3 Hz, 2 H, ArH), 2.81 (dd, J = 7.0 Hz, J = 13.2 Hz, 2 H, PCH_2), 2.59 (dd, J = 8.2 Hz, J = 13.3 Hz, 2 H, PCH_2), 0.99 (d, $^{3}J_{P,H}$ = 2.4 Hz, 2 H, CH_2SiMe_3), 0.73 (d, $^{3}J_{P,H}$ = 7.4 Hz, 2 H, CH_2SiMe_3), 0.44 (s, 9 H, $SiMe_3$), −0.02 (s, 9 H, $SiMe_3$). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 152.6 (s, ArC), 142.7 (s, ArC), 136.0 (s, ArC), 133.6 (d, $J_{P,C}$ = 2.1 Hz, ArC), 133.1 (s, ArC), 131.5 (d, $J_{P,C}$ = 4.9 Hz, ArC), 131.1 (d, $J_{P,C}$ = 11.4 Hz, ArC), 129.9 (d, $J_{P,C}$ = 1.1 Hz, ArC), 129.8 (d, $J_{P,C}$ = 2.6 Hz, ArC), 129.3 (s, ArC), 128.4 (s, ArC), 127.1 (d, $J_{P,C}$ = 1.4 Hz, ArC), 119.6 (s, ArC), 116.5 (s, ArC), 29.7 (s, PCH_2), 22.7 (s, CH_2SiMe_3), 14.3 (s, CH_2SiMe_3), 4.2 (s, $SiMe_3$), 2.9 (s, $SiMe_3$). $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = 5.5 (s). Anal. Calcd for $C_{40}H_{49}HfN_2PSi_2$: C 58.34, H 6.00, N 3.40. Found: C 58.91, H 6.05, N 3.45. Note that low carbon values have been found, despite numerous attempts using recrystallized and carefully dried, finely ground samples.

[^{Ph}A]ZrBn$_2$ ([^{Ph}A]-4-Zr). A precooled solution (−40 °C) of $Bn_2Mg(THF)_2$ (34.3 mg, 98.5 μmol, 1.10 equiv) in toluene (10 mL) was slowly added to a precooled suspension (−40 °C) of [^{Ph}**A**]-**2-Zr** (73 mg, 89.5 μmol, 1.00 equiv) in toluene (10 mL). The vigorously stirred reaction mixture was allowed to warm to room temperature, and stirring then continued for 2 h. Subsequently, a few drops of 1,4-dioxane were added to precipitate the magnesium salt biproducts. The resulting suspension was filtered using a syringe filter, and the solvent was removed under vacuum. The residue was washed with pentane (2 × 5 mL) to afford the title compound as a pale yellow solid (55.3 mg, 74.3 μmol, 83%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.25 (d, $^{3}J_{H,H}$ = 7.4 Hz, 2 H, ArH), 7.16−7.15 (m, 2 H, ArH), 7.07 (d, $^{3}J_{H,H}$ = 7.2 Hz, 2 H, ArH), 7.03−6.94 (m, 9 H, ArH), 6.94−6.86 (m, 4 H, ArH), 6.81 (t, $^{3}J_{H,H}$ = 7.4 Hz, 4 H, ArH), 6.77−6.70 (m, 5 H, ArH), 6.58 (d, $^{3}J_{H,H}$ = 7.4 Hz, 2 H, ArH), 6.52 (d, $^{3}J_{H,H}$ = 7.7 Hz, 4 H, ArH), 3.02 (s, 2 H, CH_2Ar), 2.54−2.49 (m, 2 H, PCH_2), 2.58−2.47 (m, 4 H, PCH_2/CH_2Ar). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 151.3 (s, ArC), 147.4 (s, ArC), 147.3 (d, $J_{P,C}$ = 3.2 Hz, ArC), 141.4 (d, $J_{P,C}$ = 5.7 Hz, ArC), 136.3 (s, ArC), 133.4 (d, $J_{P,C}$ = 2.4 Hz, ArC), 132.4 (d, $J_{P,C}$ = 4.2 Hz, ArC), 131.2 (d, $J_{P,C}$ = 5.1 Hz, ArC), 130.9 (s, ArC), 130.8 (s, ArC), 130.0 (d, $J_{P,C}$ = 2.6 Hz, ArC), 129.9 (s, ArC), 129.6 (s, ArC), 129.3 (s, ArC), 129.1 (s, ArC), 129.0 (d, $J_{P,C}$ = 1.9 Hz, ArC), 128.6 (s, ArC), 127.6 (s, ArC), 127.3 (s, ArC), 126.5 (s, ArC), 122.0 (s, ArC), 121.5 (s, ArC), 120.4 (s, ArC), 116.9 (s, ArC), 80.9 (s, CH_2Ar), 73.4 (d, $^{2}J_{P,C}$ = 25.5 Hz, CH_2Ar), 30.1 (d, $^{1}J_{P,C}$ = 3.5 Hz, PCH_2). $^{31}P\{^{1}H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = 1.4 (s). Anal. Calcd for $C_{46}H_{41}N_2PZr$: C 74.26, H 5.55, N 3.77. Found: C 73.42, H 5.93, N 3.23. Note that low carbon values have been found, despite numerous attempts using recrystallized and carefully dried, finely ground samples.

[^{Ph}A]HfBn$_2$ ([^{Ph}A]-4-Hf). *Method A.* A precooled solution (−40 °C) of $Bn_2Mg(THF)_2$ (28.9 mg, 82.8 μmol, 1.10 equiv) in toluene (10 mL) was slowly added to a precooled suspension (−40 °C) of [^{Ph}**A**]-**2-Hf** (68 mg, 75.3 μmol, 1.00 equiv) in toluene (10 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Following the workup procedure provided for the zirconium derivative, the title compound was obtained as a pale yellow solid (51.9 mg, 62.5 μmol, 83%). Analytical data were found to be identical to those obtained for the product prepared via method B.

Method B. A solution of $HfBn_4$ (302 mg, 556 μmol, 1.05 equiv) in toluene (2 mL) was added to a stirred solution of [^{Ph}**A**]H_2 (250 mg,

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530 μmol, 1.00 equiv) in toluene (5 mL), and the resulting pale yellow solution was heated to 70 °C overnight. The reaction mixture was allowed to cool to room temperature and condensed to dryness under reduced pressure. The residue was washed with *n*-pentane (2 × 2 mL) and dried under vacuum to afford the title compound as a pale yellow solid (340 mg, 406 μmol, 78%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.25 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, ArH), 7.21−7.17 (m, 3 H, ArH), 7.11 (d, $^3J_{H,H}$ = 7.6 Hz, 3 H, ArH), 7.02−6.93 (m, 9 H, ArH), 6.92−6.85 (m, 4 H, ArH), 6.82 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, ArH), 6.78−6.70 (m, 4 H, ArH), 6.67 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, ArH), 6.58 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, ArH), 6.52 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, ArH), 2.80−2.74 (m, 4 $H_{overlapping}$, PCH_2, CH_2Ar), 2.57 (dd, *J* = 8.7 Hz, *J* = 13.7 Hz, 2 H, PCH_2), 2.24 (d, *J* = 6.2 Hz, 2 H, CH_2Ar). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 151.3 (s, ArC), 148.4 (s, ArC), 146.9 (s, ArC), 144.7 (s, ArC), 142.3 (s, ArC), 140.9 (s, ArC), 136.4 (s, ArC), 134.0 (s, ArC), 131.1 (d, $J_{P,C}$ = 5.2 Hz, ArC), 130.9 (s, ArC), 130.8 (s, ArC), 130.2 (d, $J_{P,C}$ = 2.3 Hz, ArC), 129.9 (s, ArC), 129.5 (s, ArC), 129.3 (s, ArC), 129.1 (d, $J_{P,C}$ = 7.5 Hz, ArC), 128.4 (s, ArC) 127.5 (d, $J_{P,C}$ = 1.2 Hz, ArC), 127.5 (s, ArC), 127.1 (s, ArC), 122.3 (s, ArC), 121.6 (s, ArC), 120.2 (s, ArC), 117.0 (s, ArC), 89.3 (d, $^2J_{P,C}$ = 7.8 Hz, CH_2Ar), 80.5 (s, CH_2Ar), 29.9 (s PCH_2). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = 4.6 (s). Anal. Calcd for $C_{46}H_{41}HfN_2P$: C 66.46, H 4.97, N 3.37. Found: C 66.17, H 5.03, N 3.16.

[B]ZrBn$_2$ ([B]-4-Zr). To a stirred solution of [**B**]-**2-Zr** (200 mg, 0.25 mmol, 1.00 equiv) in toluene (10 mL) was added $Bn_2Mg(OEt_2)_2$ (98 mg, 0.28 mmol, 1.10 equiv), and the resulting suspension was stirred for 15 min at room temperature. After filtration, the title compound was detected in the filtrate and used immediately for further reactions. All attempts to isolate the pure compound were hampered due to decomposition upon removal of the solvent. NMR data were recorded after reaction of 20 mg of [**B**]-**2-Zr** with 9.8 mg of $Bn_2Mg(OEt_2)_2$ in deuterated benzene (0.7 mL). The resulting suspension in C_6D_6 was filtered into an NMR tube using a micropore syringe filter, and the spectra were acquired immediately after filtration. ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.21 (t, *J* = 7.7 Hz, 2 H, 3-ArH), 6.96−7.09 (m, 5 $H_{overlapping}$, Bn-H, PPh-H), 6.89−6.95 (m, 8 $H_{overlapping}$, Bn-H, PPh-H), 6.84 (t, *J* = 7.2 Hz, 2 H, 5-ArH), 6.76 (t, *J* = 7.5 Hz, 4 $H_{overlapping}$, Bn-H, PPh-H), 6.63 (t, *J* = 7.5 Hz, 2 H, Bn-H), 6.41 (s, 2 H, *p*-Xyl), 6.27 (s, 4 H, *o*-Xyl), 5.08 (d, *J* = 15.7 Hz, 2 H, CH_2), 4.09 (d, *J* = 15.7 Hz, 2 H, CH_2), 3.08 (d, *J* = 9.0 Hz, 2 H, Zr-CH_2), 2.56 (s, 2 H, Zr-CH_2), 2.12 (s, 12 H, Xyl-CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 141.7 (s, *ipso*-Xyl), 137.1 (d, *J* = 16.9 Hz, 1-ArC), 135.0 (d, *J* = 1.6 Hz, PPh-C), 134.3 (s, *m*-Xyl), 132.2 (d, *J* = 10.3 Hz, 3-ArC), 131.8 (s, Bn-C/PPh-C), 129.2 (s, 6-ArC), 128.8 (d, *J* = 2.9 Hz, PPh-C), 128.1 (s, Bn-C/PPh-C), 127.8 (d, *J* = 3.3 Hz, PPh-C), 127.4 (s, Bn-C/PPh-C), 126.6 (s, Bn-C/PPh-C), 125.5 (s, Bn-C/PPh-C), 124.5 (s, Bn-C/PPh-C), 122.1 (s, *p*-Xyl), 121.0 (s, Bn-C), 119.3 (s, Bn-C), 115.0 (s, *o*-Xyl), 68.5 (d, *J* = 20.3 Hz, Zr-CH_2), 62.0 (d, *J* = 4.8 Hz, Zr-CH_2), 49.2 (s_{br}, CH_2), 20.6 (s, Xyl-CH_3). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = −15.6 (s).

[B]HfBn$_2$ ([B]-4-Hf). *Method A.* To a stirred solution of [**B**]-**2-Hf** (200 mg, 0.30 mmol, 1.00 equiv) in toluene (10 mL) was added $Bn_2Mg(OEt_2)_2$ (118 mg, 0.33 mmol, 1.10 equiv) in one portion, and the resulting suspension was stirred for 15 min at room temperature. The reaction mixture was filtered and condensed to dryness under reduced pressure. The residue was washed with *n*-pentane (2 × 2 mL) and dried under vacuum to afford the product as a white powder (200 mg, 0.23 mmol, 75%). Analytical data were found to be identical to those obtained for the product prepared via method B.

Method B. A solution of $HfBn_4$ (205 mg, 0.38 mmol, 1.00 equiv) in toluene (2 mL) was added to a stirred solution of [**B**]H_2 (200 mg, 0.38 mmol, 1.00 equiv) in toluene (5 mL), and the resulting pale yellow solution was heated to 80 °C for 30 min. The reaction mixture was allowed to cool to room temperature and condensed to dryness under reduced pressure. The residue was washed with *n*-pentane (2 × 2 mL) and dried under vacuum to afford the title compound as a white powder (272 mg, 0.31 mmol, 81%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.19 (t, *J* = 7.5 Hz, 4 $H_{overlapping}$, 3-ArH, PPh-H), 6.92−7.08 (m, 11 $H_{overlapping}$, 4-ArH, 6-ArH, Bn-H, PPh-H), 6.90 (t, *J* = 7.6 Hz, 4 $H_{overlapping}$, Bn-H, PPh-H), 6.86 (t, *J* = 7.3 Hz, 2 H, 5-ArH), 6.67 (t, *J* = 7.5 Hz, 2 H, Bn-H/PPh-H), 6.57 (s, 4 H, *o*-Xyl), 6.47 (s, 2 H, *p*-Xyl), 4.93 (d, *J* = 15.8 Hz, 2 H, CH_2), 4.22 (d, *J* = 15.7 Hz, 2 H, CH_2), 2.76 (d, *J* = 8.2 Hz, 2 H, CH_2-Ph), 2.39 (d, *J* = 2.2 Hz, 2 H, CH_2-Ph), 2.16 (s, 12 H, Xyl-CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 146.1 (s, *ipso*-Xyl), 143.5 (d, *J* = 18.3 Hz, 1-ArC), 135.4 (s, *m*-Xyl), 132.7 (d, *J* = 12.7 Hz, 3-ArC), 130.0 (d, *J* = 1.3 Hz, PPh-C), 129.8 (d, *J* = 8.4 Hz, 2-ArC), 129.3 (s, Bn-C/PPh-C), 129.0 (s, Bn-C/PPh-C), 128.7 (d, *J* = 7.5 Hz, 6-ArC), 128.2 (s, Bn-C/ArC), 128.0 (s, Bn-C/ArC), 127.8 (s, 4-ArC), 127.6 (d, *J* = 3.9 Hz, 5-ArC), 127.2 (s, Bn-C/PPh-C), 127.1 (s, Bn-C/PPh-C), 126.8 (s, Bn-C/PPh-C), 122.9 (s, *p*-Xyl), 121.9 (s, Bn-C), 120.7 (s, Bn-C), 117.3 (s, *o*-Xyl), 80.2 (d, *J* = 22.2 Hz, CH_2-Ph), 73.3 (d, *J* = 7.4 Hz, CH_2-Ph), 49.5 (d, *J* = 12.5 Hz, CH_2), 21.1 (s, Xyl-CH_3). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = −19.3 (s). Anal. Calcd for $C_{50}H_{49}HfN_2P$: C 67.67, H 5.57, N 3.16. Found: C 67.44, H 5.34, N 3.33.

[B]$_2$Zr ([B]-5-Zr). A solution of $ZrBn_4$ (43.1 mg, 0.09 mmol, 0.50 equiv) in toluene (2 mL) was added to a stirred solution of [**B**]H_2 (100 mg, 0.19 mmol, 1.00 equiv) in toluene (5 mL), and the resulting yellow solution was heated to 80 °C for 30 min. The reaction mixture was allowed to cool to room temperature, and all volatiles were removed under reduced pressure. The crude product was washed with *n*-pentane (2 × 3 mL) and subsequently dried under vacuum to afford the product as a pale yellow powder (98.5 mg, 0.14 mmol, 72%). ^{1}H NMR (600 MHz, tol-d_8, 383 K): δ [ppm] = 7.36−728 (m, 3 H, ArH), 6.20−7.12 (m, 3 H, ArH), 7.10−6.94 (m, >14 H due to overlapping residual proton signals of tol-d_8, ArH), 6.91−6.87 (m, 2 H, ArH), 6.86 (s, 4 H, *o*-Xyl), 6.85−6.70 (m, 4 H, ArH), 6.33 and 6.32 (two overlapping s, 6 H, *o*-Xyl and *p*-Xyl), 6.24 (s, 2 H, *p*-Xyl), 5.41 (d, *J* = 15.4 Hz, 2 H, CH_2), 5.19 (d, *J* = 15.4 Hz, 2 H, CH_2), 5.73 (d, *J* = 15.0 Hz, 2 H, CH_2), 4.58 (d, *J* = 14.4 Hz, 2 H, CH_2), 1.93 (s, 24 H, Xyl-CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, tol-d_8, 383 K): δ [ppm] = 144.1 (s, ArC), 144.0 (s, ArC), 147.3 (d, *J* = 19.0 Hz, ArC), 146.8 (d, *J* = 20.9 Hz, ArC), 138.1 (d, *J* = 12.0 Hz, ArC), 136.9 (s, ArC), 135.5 (s, ArC), 135.1 (s, ArC), 133.4 (d, *J* = 12.8 Hz, ArC), 129.8 (s, ArC), 129.8 (s, ArC), 129.7 (s, ArC), 129.6 (s, ArC), 129.4 (s, ArC), 128.6 (s, ArC), 128.6 (s, ArC), 127.1 (d, *J* = 3.2 Hz, ArC), 125.8 (s, ArC), 121.9 (s, ArC), 120.9 (s, ArC), 120.0 (s, ArC), 117.5 (s, ArC), 21.8 (s, Ar-CH_3), 21.4 (s, Ar-CH_3). $^{31}P\{^1H\}$ NMR (243 MHz, tol-d_8, 383 K): δ [ppm] = −23.4 (s). Anal. Calcd for $C_{72}H_{70}N_4P_2Zr$: C 75.56, H 6.16, N 4.90. Found: C 75.46, H 6.24, N 4.80.

[^{Si}A]ZrBn$_2$ ([^{Si}A]-4-Zr). A solution of [^{Si}**A**]H_2 (583 mg, 1.25 mmol, 1.00 equiv) in pentane (40 mL) was cooled to −40 °C, and *n*-BuLi (1.05 mL, 2.5 M solution in hexane, 2.63 mmol, 2.10 equiv) was added dropwise within 10 min. The pale yellow reaction mixture was stirred at −40 °C for 2 h, and dioxane (859 μL, 10.0 mmol, 8.00 equiv) was added, resulting in the formation of a yellowish precipitate. After filtration at 0 °C, the solids collected on the frit were washed with *n*-pentane (30 mL) and dried under vacuum. The dilithium salt [^{Si}**A**]$Li_2(diox)_2$ was obtained as a pale beige solid (459 mg, 813 μmol) and used directly for the preparation of the title compound. A solution of $Bn_2ZrCl_2(OEt_2)$ (340 mg, 813 μmol, 1.00 equiv) in toluene (20 mL) was slowly added to a solution of [^{Si}**A**]$Li_2(diox)_2$ (459 mg, 813 μmol, 1.00 equiv) in toluene at −40 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 2 h. The yellow suspension was filtered through Celite, and the filtrate condensed to dryness. The residue was washed with hexamethyldisiloxane and recrystallized from *n*-pentane (10 mL) at −40 °C to afford the product as a pale yellow solid (245 mg, 333 μmol, 41%). ^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 7.35−7.29 (m, 6 H, ArH), 7.14−7.11 (m, 1 H, ArH), 7.10−7.07 (m, 1 H, ArH), 7.06−7.03 (m, 2 H, ArH), 7.03−7.00 (m, 1 H, ArH), 6.98 (d, $J_{H,H}$ = 7.9 Hz, 2 H, ArH), 6.93−6.87 (m, 4 H, ArH), 6.87−6.83 (m, 2 H, ArH), 6.76 (t, $J_{H,H}$ = 7.4 Hz, 1 H, ArH), 6.66 (t, $J_{H,H}$ = 7.3 Hz, 1 H, ArH), 6.37 (d, $J_{H,H}$ = 7.1 Hz, 2 H, ArH), 3.16 (dd, $^2J_{H,H}/^3J_{P,H}$ = 2.9 Hz, $^2J_{H,H}/^3J_{P,H}$ = 13.6 Hz, 1 H, $PhCH_2$), 2.91 (dd, $^2J_{H,H}/^3J_{P,H}$ = 2.4 Hz, $^2J_{H,H}/^3J_{P,H}$ = 11.2 Hz, 1 H, $PhCH_2$), 2.83 (dd, $^2J_{H,H}/^3J_{P,H}$ = 2.5 Hz, $^2J_{H,H}/^3J_{P,H}$ = 11.2 Hz, 1 H, $PhCH_2$), 2.79 (dd, $^2J_{H,H}/^3J_{P,H}$ = 3.9 Hz, $^2J_{H,H}/^3J_{P,H}$ = 13.2 Hz, 1 H, PCH_2), 2.65−2.59 (m, 2 $H_{overlapping}$, PCH_2, $PhCH_2$), 2.57 (dd, $^2J_{H,H/P,H}$ = 8.3 Hz, $^2J_{H,H/P,H}$ = 10.5 Hz, 1 H, PCH_2) 2.50 (dd, $^2J_{H,H/P,H}$ = 10.8 Hz, $^2J_{H,H/P,H}$ = 13.2 Hz, 1 H, PCH_2), 0.28 (s, 9 H, $SiMe_3$), −0.14 (s, 9

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H, $SiMe_3$). $^1H\{^{31}P\}$ NMR (600 MHz, C_6D_6, selected peaks only): δ [ppm] = 3.16 (d, $^2J_{H,H}$ = 13.6 Hz, 1 H, $PhCH_2$), 2.91 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, $PhCH_2$), 2.83 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, $PhCH_2$), 2.79 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, PCH_2), 2.65−2.59 (m, 2 $H_{overlapping}$, PCH_2, $PhCH_2$), 2.57 (d, $^2J_{H,H}$ = 11.5 Hz, 2 H, PCH_2), 2.50 (d, $^2J_{H,H}$ = 13.3 Hz, 1 H, PCH_2). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 150.2 (d, $J_{C,P}$ = 0.7 Hz, ArC), 148.6 (d, $J_{C,P}$ = 3.0 Hz, ArC), 146.8 (d, $J_{C,P}$ = 2.7 Hz, ArC), 145.9 (d, $J_{C,P}$ = 9.6 Hz, ArC), 134.7 (d, $J_{C,P}$ = 1.8 Hz, ArC), 133.4 (d, $J_{C,P}$ = 2.4 Hz, ArC), 132.8 (d, $J_{C,P}$ = 2.9 Hz, ArC), 131.7 (d, $J_{C,P}$ = 4.6 Hz, ArC), 131.1 (d, $J_{C,P}$ = 1.1 Hz, ArC), 131.1 (s, ArC), 131.0 (s, ArC), 130.8 (d, $J_{C,P}$ = 1.8 Hz, ArC), 129.9 (d, $J_{C,P}$ = 5.3 Hz, ArC), 129.9 (d, $J_{C,P}$ = 1.3 Hz, ArC), 129.2 (d, $J_{C,P}$ = 7.0 Hz, ArC), 129.0 (d, $J_{C,P}$ = 3.1 Hz, ArC), 128.81 (s, ArC), 128.5 (d, $J_{C,P}$ = 2.0 Hz, ArC), 126.7 (s, ArC), 126.4 (s, ArC), 124.6 (d, $J_{C,P}$ = 1.9 Hz, ArC), 124.2 (s, ArC), 121.6 (s, ArC), 120.9 (s, ArC), 77.9 (d, $^2J_{C,P}$ = 4.5 Hz, PCH_2), 70.9 (d, $^2J_{C,P}$ = 28.7 Hz, PCH_2), 35.1 (d, $^2J_{C,P}$ = 2.8 Hz, $PhCH_2$), 27.7 (d, $^2J_{C,P}$ = 4.9 Hz, $PhCH_2$), 2.1 (s, $SiMe_3$), 1.6 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = 4.3 (s). Anal. Calcd for $C_{40}H_{49}N_2PSi_2Zr$: C 65.26, H 6.71, N 3.81. Found: C 65.20 H 6.73 N 3.56.

[^{Si}A]HfBn$_2$ ([^{Si}A]-4-Hf). A solution of $Hf(Bn)_4$ (586 mg, 1.08 mmol, 1.00 equiv) in toluene (10 mL) was added to a stirred solution of [^{Si}A]H_2 (500 mg, 1.08 mmol, 1.00 equiv) in toluene (20 mL) at room temperature. The resulting pale yellow solution was heated to 80 °C for 48 h and then allowed to cool to room temperature. All volatiles were removed under reduced pressure, and the residue was washed with hexamethyldisiloxane (2 × 5 mL). After drying under vacuum and recrystallization from *n*-pentane (10 mL) at −40 °C the title compound was obtained as a pale yellow solid (632 mg, 767 μmol, 71%). ^1H NMR (600 MHz, C_6D_6): δ [ppm] = 7.35 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, ArH), 7.30 (dd, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 14.4 Hz, 4 H, ArH), 7.11 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, ArH), 7.06−6.99 (m, 3 H, ArH), 6.97 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, ArH), 6.93−6.89 (m, 4 H, ArH), 6.87 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, ArH), 6.76 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, ArH), 6.60 (dd, $J_{H,H}$ = 13.9 Hz, $J_{H,H}$ = 21.2 Hz, 1 H, ArH), 6.32 (d, $J_{H,H}$ = 7.5 Hz, 2 H, ArH), 3.25 (dd, $^2J_{H,H/P,H}$ = 3.5 Hz, $^2J_{H,H/P,H}$ = 13.6 Hz, 1 H, PCH_2), 2.88 (dd, $^2J_{H,H/P,H}$ = 4.0 Hz, $^2J_{H,H/P,H}$ = 13.2 Hz, 1 H, PCH_2), 2.69−2.64 (m, 1 H, PCH_2), 2.64−2.52 (m, 3 $H_{overlapping}$, PCH_2, $PhCH_2$), 2.25 (dd, $^2J_{H,H}/^3J_{P,H}$ = 6.8 Hz, $^2J_{H,H}/^3J_{P,H}$ = 11.6 Hz, 1 H, $PhCH_2$), 2.18 (dd, $^2J_{H,H}/^3J_{P,H}$ = 8.0 Hz, $^2J_{H,H}/^3J_{P,H}$ = 11.6 Hz, 1 H, $PhCH_2$), 0.26 (s, 9 H, $SiMe_3$), −0.13 (s, 9 H, $SiMe_3$). $^1H\{^{31}P\}$ NMR (600 MHz, C_6D_6, selected peaks only): δ [ppm] = 3.25 (d, $^2J_{H,H}$ = 13.6 Hz, 1 H, PCH_2), 2.88 (d, $^2J_{H,H}$ = 13.2 Hz, 1 H, PCH_2), 2.66 (d, $^2J_{H,H}$ = 13.7 Hz, 1 H, PCH_2), 2.64−2.52 (m, 3 $H_{overlapping}$, PCH_2, $PhCH_2$), 2.25 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, $PhCH_2$), 2.18 (d, $^2J_{H,H}$ = 11.7 Hz, 1 H, $PhCH_2$). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 149.9 (s, ArC), 148.6 (d, $J_{C,P}$ = 3.4 Hz, ArC), 146.2 (d, $J_{C,P}$ = 2.7 Hz, ArC), 145.3 (d, $J_{C,P}$ = 9.7 Hz, ArC), 134.5 (s, ArC), 133.3 (d, $J_{C,P}$ = 3.8 Hz, ArC), 133.2 (d, $J_{C,P}$ = 2.8 Hz, ArC), 131.6 (d, $J_{C,P}$ = 4.7 Hz, ArC), 131.5 (d, $J_{C,P}$ = 1.7 Hz, ArC), 131.4 (d, $J_{C,P}$ = 1.6 Hz, ArC), 131.1 (s, ArC), 131.0 (s, ArC), 123.0 (d, $J_{C,P}$ = 5.3 Hz, ArC), 129.8 (d, $J_{C,P}$ = 1.2 Hz, ArC), 129.2 (d, $J_{C,P}$ = 7.1 Hz, ArC), 128.8 (d, $J_{C,P}$ = 3.2 Hz, ArC), 128.6 (s, ArC), 128.5 (d, $J_{C,P}$ = 2.0 Hz, ArC), 127.3 (s, ArC), 126.9 (s, ArC), 124.4 (d, $J_{C,P}$ = 1.9 Hz, ArC), 124.2 (s, ArC), 121.8 (s, ArC), 121.4 (s, ArC), 85.2 (d, $^2J_{C,P}$ = 8.0 Hz, $PhCH_2$), 79.2 (d, $^2J_{C,P}$ = 28.5 Hz, $PhCH_2$), 35.1 (d, $^1J_{C,P}$ = 4.4 Hz, PCH_2), 27.5 (d, $^1J_{C,P}$ = 6.4 Hz, $PhCH_2$), 2.3 (s, $SiMe_3$), 1.6 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ [ppm] = 8.2 (s). Anal. Calcd for $C_{40}H_{49}HfN_2PSi_2$: C 58.34, H 6.00, N 3.40. Found: C 58.30, H 5.93, N 3.44.

[^{Ph}A]Zr(C(=NXyl)Bn)$_2$ ([^{Ph}A]-6-Zr). A solution of 2,6-(dimethylphenyl)isonitrile (37.0 mg, 282 μmol, 2.10 equiv) in toluene (5 mL) was added slowly to a stirred solution of [^{Ph}A]-**4-Zr** (100 mg, 134 μmol, 1.00 equiv) in toluene (10 mL), and the reaction mixture was stirred for 20 min at room temperature. Subsequently, all volatiles were removed under vacuum, and the residue was washed with pentane (2 × 5 mL). The product was obtained as a yellow solid (85.0 mg, 84.3 μmol, 63%). ^1H NMR (600 MHz, C_6D_6): δ [ppm] = 7.35−7.28 (m, 3 H, ArH), 7.07−6.86 (m, 23 H, ArH), 6.84−6.76 (m, 9 H, ArH), 6.68−6.61 (m, 2 H, ArH), 6.58 (d, $^3J_{H,H}$ = 6.1 Hz, 2 H, ArH), 3.84 (s, 2 H, CH_2Ph), 3.70 (s, 2 H, CH_2Ph), 2.95 (s_{br}, 2 H, PCH_2), 2.67−2.50 (m, 2 H, PCH_2), 2.01 (s, 6 H, CH_3-Xyl), 1.04 (s_{br}, 6 H, CH_3-Xyl). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 155.3 (s, ArC), 149.0 (s, ArC), 145.3 (s, ArC), 137.3 (s, ArC), 136.6 (s, ArC), 136.2 (s, ArC), 134.3 (s, ArC), 132.6 (d, $J_{C,P}$ = 3.4 Hz, ArC), 131.0 (s, ArC), 130.9 (s, ArC), 130.8 (s, ArC), 130.4 (s, ArC), 130.2 (s, ArC), 129.8 (s, ArC), 129.3 (s, ArC), 129.2 (s, ArC), 129.1 (s, ArC), 128.7 (s, ArC), 128.6 (s, ArC), 128.6 (s, ArC), 128.4 (s, ArC), 128.4 (s, ArC), 128.2 (s, ArC), 127.7 (s, ArC), 126.6 (s, ArC), 125.7 (s, ArC), 125.1 (s, ArC), 124.7 (s, ArC), 117.6 (s, ArC), 117.3 (s, ArC), 46.6 (s, CH_2Ph), 45.4 (s, CH_2Ph), 34.4 (s, BnC=N), 22.7 (s, BnC=N), 19.5 (s, CH_3-Xyl), 19.4 (s, CH_3-Xyl), 14.3 (s, PCH_2). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ [ppm] = 7.4 (s). Anal. Calcd for $C_{64}H_{61}N_4PZr$: C 76.23, H 6.10 N 5.56. Found: C 75.68, H 6.26, N 5.55. Note that low carbon values have been found, despite numerous attempts using recrystallized and carefully dried, finely ground samples.

[^{Ph}A]Hf(C(=NXyl)Bn)$_2$ ([^{Ph}A]-6-Hf). This compound was prepared in analogy to the zirconium derivative. After reaction of 2,6-(dimethylphenyl)isonitrile (33.5 mg, 255 μmol, 2.10 equiv) with [^{Ph}A]-**4-Hf** (100 mg, 122 μmol, 1.00 equiv) in toluene, the title compound was obtained as a pale yellow solid (82.0 mg, 74.4 μmol, 61%). ^1H NMR (400 MHz, C_6D_6): δ [ppm] = 7.32−7.26 (m, 2 H, ArH), 7.10−7.01 (m, 8 H, ArH), 7.00−6.85 (m, 18 H, ArH), 6.82 (d, $^3J_{H,H}$ = 9.7 Hz, 5 H, ArH), 6.77 (dd, $J_{H,H}$ = 14.1 Hz, $J_{H,H}$ = 6.6 Hz, 2 H, ArH), 6.63 (t, $^3J_{H,H}$ = 7.0 Hz, 2 H, ArH), 6.57 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, ArH), 3.95 (s, 2 H, CH_2Ph), 3.78 (s, 2 H, CH_2Ph), 3.04 (s_{br}, 2 H, PCH_2), 2.67 (s_{br}, 2 H, PCH_2), 2.02 (s, 6 H, CH_3-Xyl), 1.04 (s, 6 H, CH_3-Xyl). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 155.4 (s, ArC), 148.6 (s, ArC), 144.9 (s, ArC), 137.5 (s, ArC), 136.8 (d, $J_{C,P}$ = 1.6 Hz, ArC), 136.4 (s, ArC), 136.3 (s, ArC), 134.4 (s, ArC), 132.8 (s, ArC), 130.9 (s, ArC), 130.8 (s, ArC), 130.8 (s, ArC), 130.3 (s, ArC), 130.1 (s, ArC), 129.8 (s, ArC), 129.7 (s, ArC), 129.1 (s, ArC), 128.6 (s, ArC), 128.5 (s, ArC), 128.5 (s, ArC), 128.5 (s, ArC), 127.7 (s, ArC), 127.6 (s, ArC), 126.6 (s, ArC), 126.5 (s, ArC), 125.7 (s, ArC), 125.2 (s, ArC), 124.7 (s, ArC), 118.2 (s, ArC), 117.4 (s, ArC), 46.8 (s, CH_2Ph), 45.8 (s, CH_2Ph), 34.4 (s, BnC=N), 22.7 (s, BnC=N), 19.4 (s, CH_3-Xyl), 19.4 (s, CH_3-Xyl), 14.3 (s, PCH_2). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ [ppm] = 8.2 (s). Anal. Calcd for $C_{64}H_{61}HfN_4P$: C 70.16, H 5.16, N 5.11. Found: C 69.19 H 5.53, N 5.06. Note that low carbon values have been found, despite numerous attempts using recrystallized and carefully dried, finely ground samples.

[B]Hf(C(=NXyl)Bn)$_2$ ([B]-6-Hf). A solution of 2,6-(dimethylphenyl)isonitrile (70.4 mg, 536 μmol, 2.00 equiv) in toluene (5 mL) was added to a stirred solution of [B]-**4-Hf** (238 mg, 268 μmol, 1.00 equiv) in toluene (5 mL) at room temperature. The resulting reaction mixture was stirred for 2 h, and all volatiles were removed under reduced pressure subsequently. The solid brown residue was washed with *n*-pentane (2 mL) and dried under vacuum to afford the title compound as a beige powder (213 mg, 185 μmol, 69%). ^1H NMR (600 MHz, C_6D_6): δ [ppm] = 7.29 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, 3-ArH), 7.22−7.18 (m, 4 H, 5-ArH and 6-ArH), 7.10 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, ArH), 7.03 (d, $^3J_{H,H}$ = 7.3 Hz, 4 H, ArH), 6.99 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, 4-ArH overlapping with ArH), 6.93 (dd, $J_{H,H}$ = 9.1 Hz, $J_{H,H}$ = 5.7 Hz, 4 H, ArH), 6.86−6.83 (m, 3 H, ArH), 6.75 (dd, $J_{H,H}$ = 7.0 Hz, $J_{H,H}$ = 4.8 Hz, 4 H, ArH), 6.70 (d, $J_{H,H}$ = 7.5 Hz, 2 H, ArH), 6.67 (s, 4 H, *o*-Xyl), 6.27 (s, 2 H, *p*-Xyl), 5.43 (d, $^2J_{H,H}$ = 15.5 Hz, 2 H, CH_2), 4.51 (d, $^2J_{H,H}$ = 13.1 Hz, 2 H, CH_2), 3.68 (s, 2 H, BnC=N), 3.50 (s, 2 H, BnC=N), 2.09 (s, 12 H, *m*-Xyl-CH_3), 1.71 (s, 6 H, H_3C-XylN=C), 1.66 (s, 6 H, H_3C-XylN=C). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 156.8 (s_{br}, XylC=N) 148.2 (d, $^3J_{C,P}$ = 22.1 Hz, *ipso*-Xyl), 148.0 (s, XylC=N), 145.8 (s, XylC=N), 138.6 (s, ArC), 138.4 (s, ArC), 136.9 (s, XylC), 135.5 (d, $J_{C,P}$ = 8.2 Hz, ArC), 133.2 (d, $J_{C,P}$ = 12.0 Hz, ArC), 130.5 (d, $J_{C,P}$ = 22.0 Hz, ArC), 130.2 (s, ArC), 130.0 (s, ArC), 129.9 (s, 4-ArC), 129.7 (s, 3-ArC), 129.2 (d, $J_{C,P}$ = 7.7 Hz, ArC), 128.8 (s, 5-ArC), 128.7 (s, ArC), 128.6 (s, ArC), 128.5 (d, $J_{C,P}$ = 5.3 Hz, ArC), 128.1−127.9 (signals overlapping with residual proton signals of benzene-d_6, ArC, XylC=N), 127.2 (d, $J_{C,P}$ = 3.9 Hz, XylC=N), 126.4 (d, $J_{C,P}$ = 21.8 Hz, ArC), 125.0 (d, $J_{C,P}$ = 1.9 Hz, *o*-Xyl), 119.9 (s, *p*-Xyl), 47.4 (d, $^3J_{C,P}$ = 23.6 Hz, CH_2), 47.0 (s, $PhCH_2$), 45.3 (s, $PhCH_2$), 21.8 (s, *m*-Xyl-CH_3), 19.4 (s, H_3C-XylC=N), 18.7

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(s, H_3C-XylC═N). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): [ppm] = −13.7 (s). Anal. Calcd for $C_{68}H_{67}N_4PHf$: C 71.04; H 5.87; N 4.87. Found: C 70.96, H 5.96, N 4.60.

[^{Si}A]Hf(C(═NXyl)Bn)(Bn) ([^{Si}A]-6-Hf). A solution of 2,6-(dimethylphenyl)isonitrile (20.1 mg, 153 μmol, 2.10 equiv) in toluene (5 mL) was added slowly to a stirred solution of [^{Si}A]-**4-Hf** (60.0 mg, 72.9 μmol, 1.00 equiv) in toluene (10 mL), and the reaction mixture was stirred for 20 min at room temperature. Subsequently, all volatiles were removed under vacuum, and the residue was washed with pentane (2 × 5 mL). The product was obtained as a pale yellow solid (50.0 mg, 51.8 μmol, 61%). ^1H NMR (600 MHz, C_6D_6): δ [ppm] = 7.58 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, ArH), 7.40 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, ArH), 7.33 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, ArH), 7.26 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, ArH), 7.05−7.01 (m, 6 H, ArH), 7.00−6.96 (m, 2 H, ArH), 6.94 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, ArH), 6.90−6.84 (m, 4 H, ArH), 6.74 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, ArH), 6.70 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, ArH), 6.65 (dd, J = 7.4 Hz, 11.5 Hz, 2 H, ArH), 3.73 (d, J = 14.8 Hz, 1 H, CH_2PhC═N), 3.69 (d, J = 14.8 Hz, 1 H, CH_2PhC═N), 3.44 (dd, J = 3.6 Hz, J = 13.1 Hz, 1 H, PCH_2), 3.01 (dd, J = 4.0 Hz, J = 13.0 Hz, 1 H, PCH_2), 2.75 (d, J = 12.1 Hz, 1 H, Hf-CH_2Ph), 2.69 (t, J = 12.7 Hz, 1 H, PCH_2), 2.62−2.54 (m, 1 H, PCH_2), 2.44 (d, J = 12.2 Hz, 1 H, Hf-CH_2Ph), 1.58 (s, 3 H, CH_3-Xyl), 1.17 (s, 3 H, CH_3-Xyl), 0.17 (s, 9 H, $SiMe_3$), − 0.07 (s, 9 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ [ppm] = 151.3 (d, $J_{C,P}$ = 0.8 Hz, ArC), 150.1 (d, $J_{C,P}$ = 10.4 Hz, ArC), 149.2 (d, $J_{C,P}$ = 3.1 Hz, ArC), 147.0 (s, ArC), 135.96 (s, ArC), 135.8 (d, $J_{C,P}$ = 1.2 Hz, ArC), 134.1 (s, ArC), 132.8 (d, $J_{C,P}$ = 2.3 Hz, ArC), 132.7 (d, $J_{C,P}$ = 1.7 Hz, ArC), 131.5 (d, $J_{C,P}$ = 2.4 Hz, ArC), 131.4 (s, ArC), 131.3 (s, ArC), 131.2 (d, $J_{C,P}$ = 4.7 Hz, ArC), 130.3 (s, ArC), 130.1 (s, ArC), 129.7 (d, $J_{C,P}$ = 5.3 Hz, ArC), 129.5 (s, ArC), 129.0 (s, ArC), 128.7 (d, $J_{C,P}$ = 2.2 Hz, ArC), 128.6 (s, ArC), 128.6 (s, ArC), 128.5 (d, $J_{C,P}$ = 3.8 Hz, ArC), 127.6 (d, $J_{C,P}$ = 2.9 Hz, ArC), 126.7 (s, ArC), 125.9 (s, ArC), 123.6 (s, ArC), 122.7 (d, $J_{C,P}$ = 1.6 Hz), 121.6 (s). 72.1 (d, $J_{C,P}$ = 28.7 Hz, Hf-CH_2Ph), 45.5 (s, CH_2PhC═N), 35.5 (d, $J_{C,P}$ = 4.2 Hz, PCH_2), 34.4 (s, BnC═N), 28.1 (d, J = 5.8 Hz, PCH_2), 19.4 (s, CH_3Xyl), 19.0 (s, CH_3Xyl), 3.2 (s, $SiMe_3$), 2.6 (s, $SiMe_3$). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ [ppm] = 6.8 (s). Anal. Calcd for $C_{49}H_{58}HfN_3PSi_2$: C 61.65, H 6.12, N 4.40. Found: C 61.86, H 6.07, N 4.37.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00384.

Additional ORTEP diagrams, selected NMR spectra and details of the structure determinations for [**B**]H_2, [^{Ph}**A**]-**1-Ti**, [^{Ph}**A**]-**1-Zr**, [**B**]-**1-Ti**, [**B**]-**1-Zr**, [**B**]-**1Hf**, [^{Ph}**A**]-**2-Ti**, [^{Ph}**A**]-**2-Zr**, [^{Si}**A**]-**2-Zr**, [**B**]-**2-Ti**, [**B**]-**2-Zr**, [**B**]-**2-Hf**, [^{Ph}**A**]-**3-Zr**, [^{Ph}**A**]-**3-Hf**, [^{Ph}**A**]-**4-Zr**, [^{Ph}**A**]-**4-Hf**, [^{Si}**A**]-**4-Hf** (C_1), [^{Si}**A**]-**4-Hf** (C_S), [**B**]-**4-Hf**, [**B**]-**5-Zr**, [^{Ph}**A**]-**6-Zr**, [^{Si}**A**]-**6-Hf**, and [**B**]-**6-Hf** (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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(12) The differences between Zr and Hf described in this article are in line with the commonly observed higher kinetic reactivity of zirconocenes (compared to hafnocenes). Whether hafnium reacts more sluggish in general, however, is currently under debate (see ref 2c), underlining the necessity to systematically probe for such differences.

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