

Benzimidazolin-2-iminato Hafnium Complexes: Synthesis, Characterization, and Catalytic Addition of Alcohols to Carbodiimides

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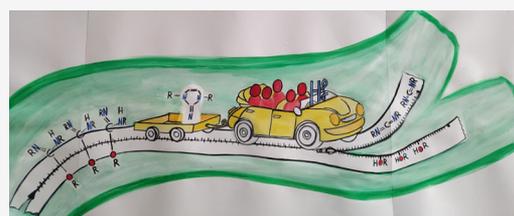
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ABSTRACT: A series of asymmetric imidazolin-2-iminato and benzimidazolin-2-iminato hafnium(IV) complexes were synthesized and fully characterized including single-crystal X-ray diffraction. The asymmetric imidazolin-2-iminato hafnium complex exhibits a shorter Hf–N bond length as compared with the corresponding benzimidazolin-2-iminato hafnium complex. These complexes were successfully utilized as catalysts for the addition of alcohols to carbodiimides. The synthesis of several active intermediates and kinetics, thermodynamics, and stoichiometric reaction studies allowed us to propose a mechanism for the reaction. The X-ray crystal structure of the monomeric $\text{Hf}(\text{O}^t\text{Bu})_4$ is presented.



INTRODUCTION

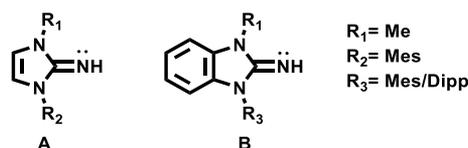
Hafnium complexes have mainly been used for the catalytic homo- and copolymerization of α -olefins^{1–18} and as Lewis acid catalysts in various organic transformations including the polymerization of cyclic esters.^{19–46} More recently, Hf–MOF complexes have been utilized in the catalytic activation of small molecules.^{47–51} Among the group-IV metals, hafnium is considered to be the most oxophilic metal when compared with zirconium and titanium, as illustrated by their corresponding metal–oxygen bond dissociation energies (Ti–O = 666 kJ/mol, Zr–O = 766 kJ/mol, and Hf–O = 801 kJ/mol).⁵² Hence, the strong metal–oxygen bond and the high electrophilicity of the metal have precluded the use of organometallic complexes of hafnium in processes involving oxygen-containing moieties with acidic protons.^{53–56} We have postulated that if, during a stoichiometric or a catalytic process, we start with a metal–oxygen bond and after the transformation we end up with a different metal–oxygen bond, then, theoretically, we are not paying thermodynamically for the M–O bond; however, we need to have the energy of activation to be able to execute the process.^{57–64}

An additional challenge is encountered when comparing the hafnium and zirconium sizes. Because of the lanthanide contraction, both metals have virtually the same covalent radii,^{52,65,66} and hence we can expect the same behavior as related to coordination numbers. Therefore, when designing a catalytic complex that will operate with oxygen-containing substrates, fine-tuning of the electronic and steric properties of the ligands is imperative to avoid the formation of strong and nonactive Hf–O bonds.

During the past decade, our group has been interested in non-Cp ancillary ligands. In particular, we have been attracted by chelating amido-type benzamidinate ligands.^{7,14,17,18,67–83}

Benzamidinate ligands can be deemed steric equivalents of Cp or Cp* (Cp = C₅H₅; Cp* = C₅Me₅) moieties; however, they retain distinctive electronic properties.^{16,84,93,85–92} The activation of the complexes containing these systems has provided crucial insights into the tailoring of new ancillary ligands, which are isolobal to the cyclopentadienyl ligands yet possess a higher level of steric control. Imidazolin-2-iminato ligands are among the leading fascinating examples of such non-Cp ancillary ligands, as presented in Scheme 1A.^{94–96} A

Scheme 1. (A) Imidazolin-2-imine and (B) Benzimidazolin-2-imine Neutral Ligands



simple and general method for the synthesis of this class of 2-iminoimidazolin-2-imine *N*-heterocyclic *N*-donor ligands, which behave as 2 σ , 4 π -electron donors, has been already introduced in the literature.^{97–103}

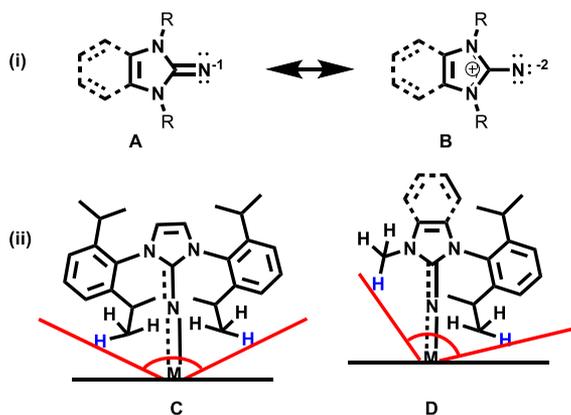
Catalytic additions of E–H (NH, PH, SH, $\equiv\text{CH}$, etc.) moieties to carbodiimides have received substantial interest in recent years, and various types of catalysts have been used such

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as main-group metal centers,¹⁰⁴ copper,¹⁰⁵ lanthanides,¹⁰⁶ actinides,^{57,61,63,64,107} and titanium.¹⁰⁸ Inspired by the observation that hafnium–oxygen moieties can be an active motif in catalytic processes,^{19,20,25–28,30,35–37,43,44,109–115} we started to design our ligands toward the synthesis of hafnium complexes. On the one hand, we need a ligand that is highly nucleophilic to allow the stabilization of the metal complex and to ensure that the ligand will remain attached to the metal after the catalytic process. On the other hand, a less sterically demanding ligand (i.e., smaller cone angle, *vide infra*) will allow us to achieve the unprecedented hafnium-catalyzed addition of alcohols to carbodiimides. We integrate a phenyl ring to the backbone of the imidazolin-2-iminato moiety to tailor its electronic and steric properties and synthesized a number of benzimidazolin-2-iminato ligands, as shown in Scheme 1B.

These imidazolin-2-iminato ligands can be represented by the two mesomeric structures shown in Scheme 2i, which, in

Scheme 2. (i) Mesomeric Structures (A and B) in Imidazolin-2-iminato Ligands; (ii) Different Cone Angles of the (C) Symmetric and (D) Asymmetric Ligands as a Consequence of the Different Substitution Groups



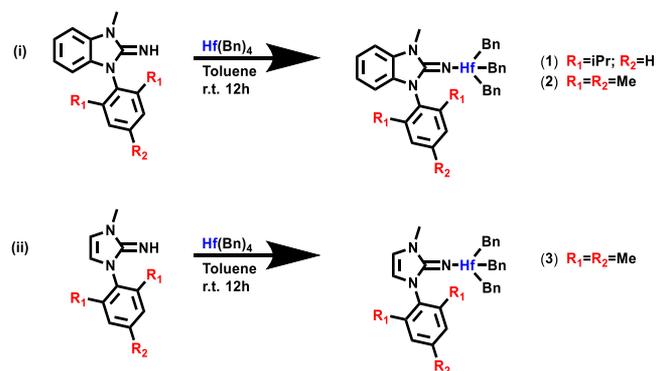
turn, should endow the highly basic ligands with a strong electron-donating capacity. Moreover, to create more accessible, less sterically encumbered metal atoms, a nonsymmetric ligand was designed to allow the incorporation of a reduced cone angle, resulting in a more open coordination sphere as compared with the symmetric imidazolin-2-iminato ligand; see Scheme 2ii.^{57,116,117}

In addition, to examine the electronic effect of the phenyl moiety on the nonsymmetric benzimidazolin-2-iminato complexes, we have also synthesized the nonsymmetric imidazolin-2-iminato ligand, as presented in Scheme 1A. In a previous work from our group, we have shown that the incorporation of the highly basic and nucleophilic ligands such as the benzimidazolin-2-iminato moiety helps to stabilize highly oxophilic uranium and thorium complexes (U–O: 758 kJ/mol; Th–O: 854 kJ/mol).^{57,61} Hence, in this work, we present the synthesis of three new hafnium complexes, with two of these complexes bearing the benzimidazolin-2-iminato ligand and three benzyl groups and an additional complex that contains an asymmetric imidazolin-2-iminato ligand and three benzyl groups for comparison. We have decided to tackle the question of whether these highly oxophilic hafnium complexes are able to operate as catalysts in the presence of alcohols, as required for the addition of alcohols to carbodiimides.

RESULTS AND DISCUSSION

The synthesis of complexes 1, 2, and 3 was carried out by reacting a solution of the homoleptic hafnium tetrabenzyl complex with one equivalent of the corresponding benzimidazolin-2-imine or imidazolin-2-imine ligand precursor (Scheme 3). The reaction mixture was allowed to stir overnight at room

Scheme 3. Synthesis of Complexes 1–3



temperature, followed by solvent evaporation under vacuum. Crystalline materials were obtained by recrystallization of the crude solids from a mixture of toluene and hexane at $-30\text{ }^{\circ}\text{C}$ (1:3, respectively).

The solid-state structures of all complexes were established by X-ray diffraction analyses (Figure 1). All three complexes showed shorter Hf–N_{C=N} bond lengths as compared with the corresponding Hf–N_{amido} bonds as well as a near-linearity for the Hf–N–C angles, corroborating a higher bond order for the Hf–N_{C=N} bonds. With respect to the Hf–N_{C=N} bond distances, complexes 1 and 2 displayed values of 1.915(4) and 1.917(4) Å, whereas complex 3 displayed a shorter metal–nitrogen bond of 1.818(12) Å, which is ~ 0.1 Å shorter as compared with complexes 1 and 2, respectively, and among the shortest bonds known in the literature to date (Hf=N bonds are between 1.82 and 1.86 Å),¹¹⁸ due to the stronger nucleophilicity of the imidazolin-2-iminato ligand as compared with that of the benzimidazolin-2-iminato motif. In regards to the imine C=N double-bond lengths, all complexes 1–3 have very similar values of 1.293(6), 1.293(6), and 1.288(19) Å and Hf–N–C angles close to linearity, with values of 176.7(3), 174.9(4), and 169.5(11) $^{\circ}$, respectively, indicating that the double-bond character of the C=N bond is maintained regardless of what ligand is being utilized.^{19,20,43} These differences allowed us to conclude that the existence of the phenyl ring on the backbone has a large influence on the electronic structure of the ligand attached to the metal.

Despite the electronic structural differences, a comparison of the cone angles, which allows us to assess the proximity of the ligand substituents to the metal center,^{48,49} was performed. When compared with the cone angles of ca. 248 $^{\circ}$ in the symmetric [(Im^{Dipp}N)TiMe₃]¹¹⁹ and 262 $^{\circ}$ in the symmetric [(Im^{Dipp}N)HfBn₃],¹²⁰ considerably smaller cone angle values were displayed for the hafnium complexes (160, 120, and 125 $^{\circ}$ for 1, 2, and 3, respectively). It can be inferred that these new hafnium complexes exhibited a more open coordination sphere that will be available to the metal toward the incoming substrates.^{121–124}

On the basis of our hypothesis, we strived to explore the intermolecular addition of alcohols to 1,3-di-*p*-tolylcarbodi-

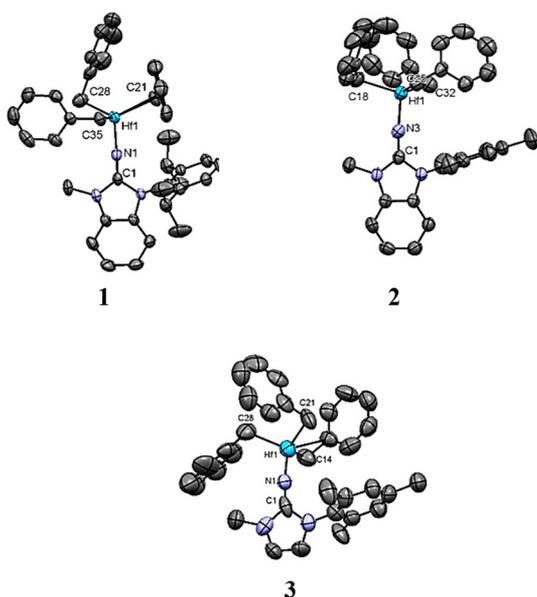


Figure 1. ORTEP drawings of complexes 1–3 are presented with thermal displacement parameters at 50% probability. Hydrogen atoms are omitted for clarity. Bond lengths for complex 1 (Å): Hf–N₁ = 1.917(4), Hf–C₂₈ = 2.233(6), Hf–C₂₁ = 2.273(5), Hf–C₃₅ = 2.275(5), and C₁–N₁ = 1.293(6). Bond angles (deg): Hf–N₁–C₁ = 176.6(4), N₁–Hf–C₂₈ = 105.4(2), N₁–Hf–C₂₁ = 105.85(19), and N₁–Hf–C₃₅ = 103.14(18). Cone angle (deg): 160. Bond lengths for complex 2 (Å): Hf–N₃ = 1.915(4), Hf–C₁₈ = 2.285(6), Hf–C₂₅ = 2.265(6), Hf–C₃₂ = 2.259(5), and C₁–N₁ = 1.293(6). Bond angles (deg): Hf–N₃–C₁ = 174.9(4), N₃–Hf–C₁₈ = 103.7(2), N₃–Hf–C₂₅ = 103.9(2), and N₁–Hf–C₃₂ = 103.6(2). Cone angle (deg): 120. Bond lengths for complex 3 (Å): Hf–N₁ = 1.818(12), Hf–C₁₄ = 2.238(16), Hf–C₂₁ = 2.288(15), Hf–C₂₈ = 2.233(17), and C₁–N₁ = 1.288(19). Bond angles (deg): Hf–N₁–C₁ = 169.5(11), N₁–Hf–C₁₄ = 105.1(6), N₁–Hf–C₂₁ = 109.5(6), and N₁–Hf–C₂₈ = 110.3(6). Cone angle (deg): 125.

amide (DTC) (Table 1). To our delight, all hafnium complexes proved active in this addition reaction, affording the respective

Table 1. Addition Reaction of ROH and DTC Mediated by Complexes 1–3^a

entry	cat	R = CH ₃ (%)	R = C(CH ₃) ₃ (%)
1	1	90	90
2	2	48	77
3	3	99	75

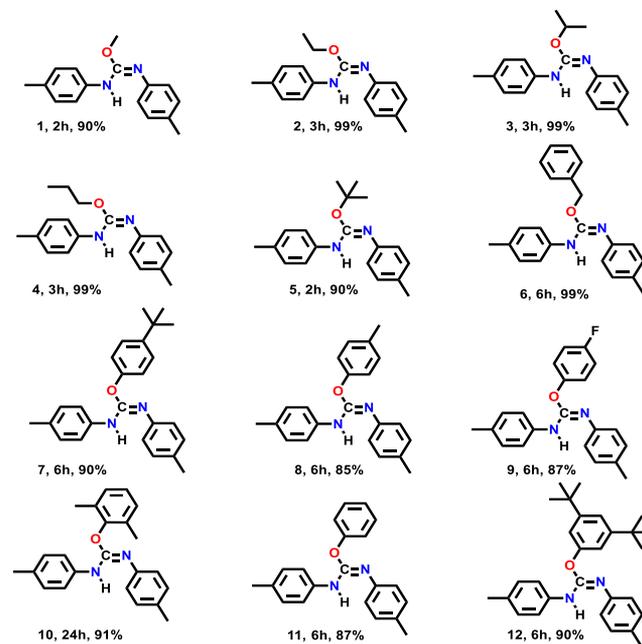
^aReaction conditions: catalyst 5.8 μmol, Cat/ROH/DTC 1:50:50, the solvent is C₆D₆, the total volume is 600 μL, 2 h, at RT. The yield was determined by ¹H NMR spectroscopy of the crude reaction mixture.

isourea products in moderate to very high yields. It is important to point out that no reaction was observed in the absence of the hafnium complexes. Moreover, the free ligands alone do not induce the addition reaction, and freshly recrystallized complexes were used in all catalytic studies.

Because the thermal stability and the reactivity of complex 1 were found to be the best for both methanol and *tert*-butanol

substrates, we continued our studies with complex 1. The scope of the reaction with regards to the alcohol substrate was studied by varying the steric demand and the acidity of the alcohol (Table 2). The catalytic addition of the less sterically

Table 2. Insertion Reaction of Alcohol and DTC Mediated by Complex 1^a



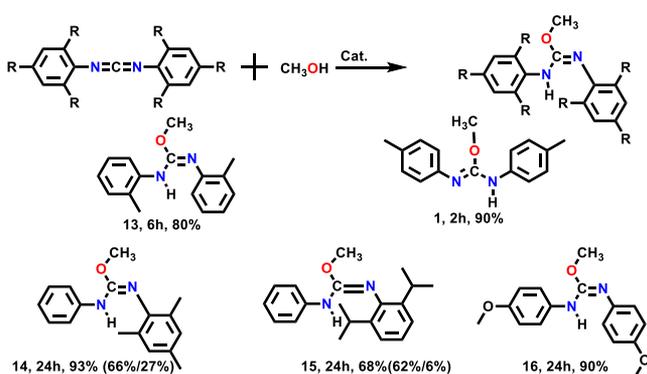
^aReaction conditions: catalyst 5.8 μmol, Cat/MeOH/DTC 1:50:50, the solvent is C₆D₆, the total volume is 600 μL, RT. The yield was determined by ¹H NMR spectroscopy of the crude reaction mixture.

encumbered alcohols, that is, MeOH, to diisopropylcarbohydrazide (DIC) and dicyclohexylcarbohydrazide (DCC) by precatalysts 1 did not lead to any turnovers. The reaction of more acidic alcohols (phenols) with DIC even proceeded without any catalysts. Nevertheless, this reaction did not operate when DTC was employed, and the aid of the hafnium complexes was needed for the fast formation of the isourea products. Similar to the aliphatic alcohols, changing the size of the phenol substrates has an important impact on this intermolecular addition reaction.

The scope of the reaction with regards to the alcohol substrate was studied by the variation of the steric demand and the acidity of the alcohols. One of the more surprising results encountered is that the aliphatic alcohols were added much faster than the corresponding aromatic ones. This result indicates the need for a higher electron density at the alkoxy moiety to induce efficient addition (entries 1–5). Moreover, the bulkiness of the aliphatic chain was found to have no major effect on the addition, as can be expected for a four-centered transition state. For aromatic phenols, the reaction time to reach ~90% yield was 6 h, unless a bulky phenol was utilized, as with 2,6-dimethylphenol, which needed 24 h (entry 10). The use of the sterically hindered 3,5-*t*Bu₂C₆H₃OH (entry 12) resulted in lower activities as compared with 2,6-Me₂C₆H₃OH (entry 10). The use of aromatic phenols induces a drop in the catalytic activity of the complexes, presumably due to the displacement of the ancillary ligand (see later) from the active metal site (complexes 6 and 7).

A stronger steric effect was found for different carbodiimides (Table 3). Larger NR substituents at the carbodiimide (RN=C=NR) resulted in lower reaction rates. For example, in a comparison of the *ortho*- and *para*-carbodiimides (entries 14 and 15, respectively), methanol added to the *ortho*-substituted carbodiimides much slower than to the corresponding DTC. In addition, the use of sterically hindered, nonsymmetrical carbodiimides (entries 16 and 17) induced a larger inhibition of the reactivity of the catalyst, and two isomers were obtained. The main product was the one formed from the more kinetically stable amido intermediate precursor, whereas the less steric amido moiety attached to the metal center before the protonolysis (*vide infra*).

Table 3. Insertion Reaction of Methanol and Carbodiimides Mediated by Complex 1^a



^aReaction conditions: catalyst 5.8 μmol , cat/MeOH/carbodiimide 1:50:50, the solvent is C_6D_6 , the total volume is 600 μL , at RT. The yield was determined by ^1H NMR spectroscopy of the crude reaction mixture.

To investigate the fate of complex 1 in the presence of alcohols and to identify possible reaction intermediates, 1 was treated with 20 equiv of $t\text{BuOH}$. Upon the addition, a release of three benzyl groups was monitored by ^1H NMR spectroscopy. The reaction mixture was set for crystallization at $-30\text{ }^\circ\text{C}$ in toluene overnight, leading to the formation of white crystals. The X-ray diffraction analysis of complex 4 (Figure 2) indicated the formation of a trigonal-bipyramidal complex with the protonated benzimidazolin-2-imine ligand in an axial position in addition to four more *tert*-butoxide groups, as can be seen in Scheme 4.

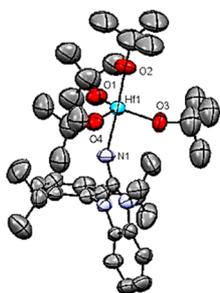
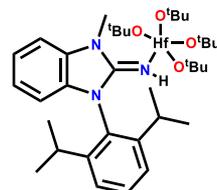


Figure 2. ORTEP drawings of complex 4, with thermal displacement parameters at 50% probability. Hydrogen atoms are omitted for clarity. Bond lengths for complex 4 (\AA): Hf–N₁ = 2.385(7), Hf–O₁ = 1.950(6), Hf–O₂ = 1.933(6), Hf–O₃ = 1.935(5), Hf–O₄ = 1.934(6), and N₁–C₁ = 1.305(10). Hf–N₁–C₁ = 145.0(5) $^\circ$.

Scheme 4. Schematic Drawing of Complex 4



The imidazolin-2-imine ligand exhibits an elongated Hf–N bond length of 2.385(7) \AA , whereas the N–C_{ipso} is 1.305(10) \AA , similar to that found for the other Hf complexes.¹²⁵ This elongation is clearly the result of the protonation of the ligand (the imido is more basic than the alkoxo); however, even in the presence of a large excess of alcohol, the ligand remains attached to the metal atom, influencing the catalytic reaction (Figure 2). As a result of the protonolysis, the ligand changes from a linear to a bent orientation toward the metal with a Hf–N–C_{ipso} angle of 145.0(5) $^\circ$, as can be seen in Scheme 4; the NH hydrogen atom is involved in hydrogen bonding with one of the oxo moieties in the equatorial plane of the complex.

To further assess the hydrogen bonding in 4, IR studies were performed. Complex 4 shows the N–H stretching vibration at 3328 cm^{-1} , which is shifted from the corresponding free ligand N–H vibration that appears at 3316 cm^{-1} . To confirm the N–H signal/interaction on the IR measurements, a reaction between complex 1 and $t\text{BuOD}$ was performed. The corresponding reaction product showed a sharp band at 2464 cm^{-1} , attributed to bridged N–D–O (2487 cm^{-1}) moiety.^{126,127}

To check the influence of the benzimidazolin-2-imino moiety on the geometry of complex 4 (Figure 2), we decided to examine the resulting geometry of the homoleptic *tert*-butoxide hafnium complex. The reaction of hafnium tetrabenzyl with 4 and 5 equiv of $t\text{BuOH}$ resulted in the consistent trimer 5a. Complex 5a has been reported in the literature in the synthesis of the evasive $\text{Hf}(\text{O}^t\text{Bu})_4$. In complex 5a, three hafnium atoms are bridged by a $\mu_3\text{-O}^t\text{Bu}$ and by a $\mu_3\text{-O}$ moiety. In addition, the hafnium atoms are bridged by a $\mu_2\text{-O}^t\text{Bu}$ unit, and each hafnium has two additional O^tBu motifs.^{128,129} The formation of the oxo species is always due to a ubiquitous amount of water found in the crystallizing solvent.¹²⁹ Hence, to avoid trace amounts of water, the crystallization was performed inside a glovebox having a maximum of 0.1 ppm of water. Under these conditions, in the crystallization process, a cocrystalline mixture of 5a and the evasive homoleptic $\text{Hf}(\text{O}^t\text{Bu})_4$ (5b) was obtained (Figure 3). The trimer part (5a) in the cocrystal is like that reported in the literature; however, the homoleptic $\text{Hf}(\text{O}^t\text{Bu})_4$ shows a hafnium in a distorted tetrahedral geometry. A simplified schematic drawing of the cocrystals 5a and 5b can be found in Scheme 5.

The slightly distorted tetrahedral structure of 5b displays angles of 108.9(8) ($\text{O}_{12}\text{-Hf}_4\text{-O}_{12}^8$, $\text{O}_{12}\text{-Hf}_4\text{-O}_{12}^3$, $\text{O}_{12}^2\text{-Hf}_4\text{-O}_{12}^3$, and $\text{O}_{12}^1\text{-Hf}_4\text{-O}_{12}^2$) and 110.7(17) $^\circ$ ($\text{O}_{12}\text{-Hf}_4\text{-O}_{12}^2$ and $\text{O}_{12}^1\text{-Hf}_4\text{-O}_{12}^3$) and bond lengths of 1.92(3) \AA for all Hf₄–O₁₂ bonds. A comparison of the Hf–O^tBu bond lengths (not bridging moieties) between structures 5a and 5b shows alike bond distances, Hf₁–O₆ = 1.937(13) and Hf₁–O₇ = 1.92(2) \AA , in 5a. Interestingly, when comparing other bond lengths of Hf–O^tBu in different complexes bearing different ancillary ligands and recrystallized in different solvents, similar

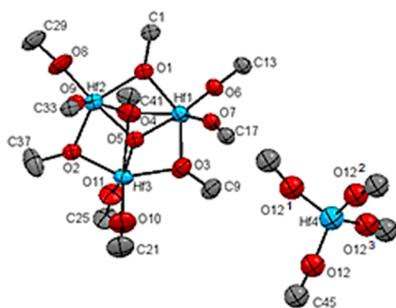
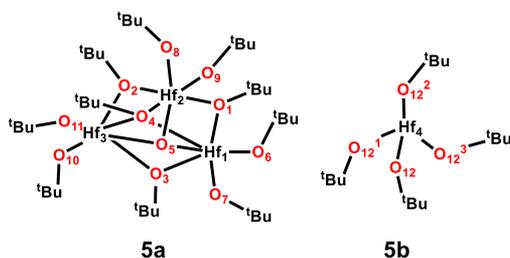


Figure 3. ORTEP drawings of complexes **5a** and **5b**, with thermal displacement parameters at 50% probability. Hydrogen and carbon atoms are omitted for clarity. Bond lengths for complex **5a** (Å): Hf₁–O₁ = 2.162(19), Hf₁–O₃ = 2.20(2), Hf₁–O₄ = 2.42(2), Hf₁–O₅ = 2.03(2), Hf₁–O₆ = 1.937(13), and Hf₁–O₇ = 1.92(2). Bond lengths for complex **5b** (Å): Hf₄–O₁₂ = 1.92(3).

Scheme 5. Schematic Drawing of Complexes **5a** and **5b**

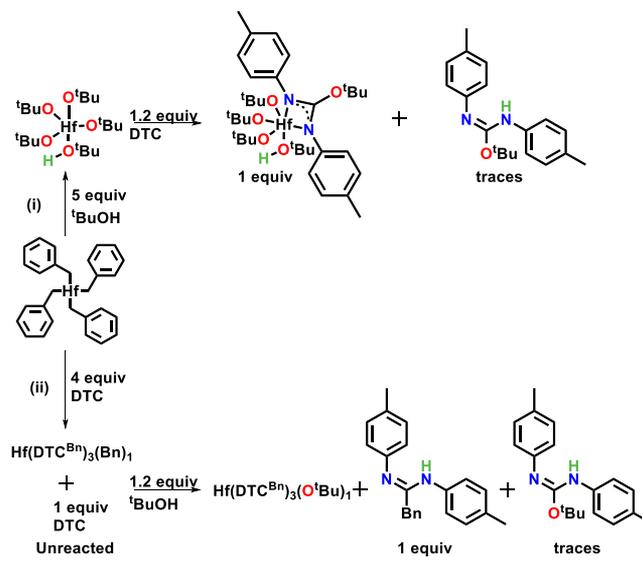


Hf–O^tBu bond lengths between 1.92 and 1.94 (Å) are always obtained.¹³⁰

Complex **5** shows that the hafnium complexes in the presence of the *tert*-butoxide moiety form clusters and bridges that might cause a less reactive/available metal center/complex due to a compact closed protective shell of the metal center. To test this hypothesis, we used complex **5** in the addition reaction of ^tBuOH toward DTC. This reaction was slower by 50% compared with that when using complex **4**. This result indicates the importance of incorporating a highly nucleophilic ligand in this type of complex to achieve better reactive catalytic complexes.

To understand the formation of some of the active species using hafnium tetrabenzyl as the starting material, various stoichiometric reactions were studied. It is clear that the formation of complexes **5a** and **5b** takes place in the solid state, however, in the solution, we were interested in studying how many molecules of ^tBuOH react with the hafnium tetrabenzyl. Hence, we have found that 5 equiv of ^tBuOH reacts with Hf(CH₂Ph)₄ to form, in solution, the pentacoordinate complex Hf(O^tBu)₄(^tBuOH), presenting only one signal for the ^tBu groups on the NMR, indicating that the additional proton is rapidly scrambled among all of the butoxide groups. The addition of 1.2 equiv of DTC produces the monoisourea trialkoxo hafnium complex with a molecule of ^tBuOH still attached to the hafnium center and a small amount of the free isourea product (Scheme 6, pathway i). However, the stoichiometric reaction between hafnium tetrabenzyl and 4 equiv of DTC (Scheme 6, pathway ii) proceeds, allowing three benzyl groups to add to the corresponding DTC to form the corresponding benzyl tris(amidinate) hafnium complex, and 1 equiv of DTC remains unreacted. The consecutive addition of 1.2 equiv of ^tBuOH to the “*in situ*” formed complex produces the corresponding mono *tert*-butoxide tris(carbodiimide)

Scheme 6. Reactivity Permutation of the Reaction of Hf(Bn)₄ with ^tBuOH and DTC



hafnium complex and allows the formation of the two amidinates, as shown in Scheme 6.

Interestingly, the structure of complex **1** changes when reacted with an excess of phenol or 2,6-xyleneol. In these cases, it resulted in a dimerized complex **6** for the less steric phenol; however, for the bulky phenol, the monomeric complex **7** was obtained. Amazingly, even when an excess of the aromatic alcohols is used, in both complexes, the ligand is present in the crystal structure! (See Figure 4 for complexes **6** and **7**.) In

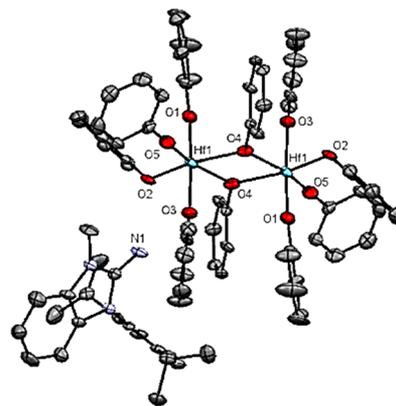
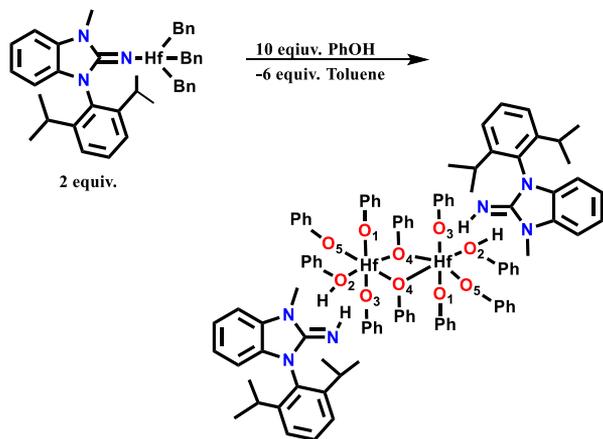


Figure 4. ORTEP drawing of complex **6**, with thermal displacement parameters at 50% probability. Hydrogen atoms are omitted for clarity. Bond lengths for complex **6** (Å): Hf–O₁ = 1.962(6), Hf–O₂ = 2.071(5), Hf–O₃ = 2.007(5), Hf–O₄ = 2.175(5), and Hf–O₅ = 1.942(5).

complex **6**, each hafnium is coordinated to three phenoxy groups and two bridging phenoxide moieties (Scheme 7), closing the charge balance. In addition, each hafnium is also attached to a bent phenol moiety, giving rise to a distorted octahedral coordination for each metal center. The two neutral phenol moieties are disposed in an anti-configuration on different sides of the plane of the hafnium moieties.

Complex **6** (Figure 4) crystallized in a dimeric distorted octahedral structure. The complex exhibits two hafnium metal centers, where each hafnium center is bonded to four phenols

Scheme 7. Schematic Drawing to Obtain Complex 6



and two bridging phenol units in addition to two benzimidazolin-2-iminato ligands in the peripheral sphere. The angle between Hf–O₂–C₂₇ showed a bent angle of 128.3° (Figure 5) as compared with the other Hf–O bonds (not the

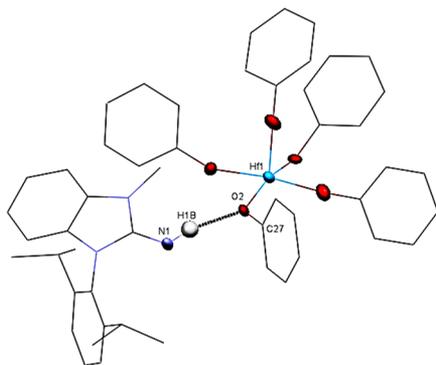


Figure 5. Hydrogen bonding between N₁–H–O₂ in part of the molecule of complex 6. The ORTEP drawing is presented with thermal displacement parameters at 50% probability. Hydrogen atoms are omitted for clarity, except for H_{1B}. Hydrogen bond length in complex 6 (Å): H_{1B}–O₁ = 1.875 Å.

bridging moieties). This bent angle suggested a hydrogen bonding with the N–H of the ligand and O₂. In addition, we can see the displacement of the ligand not bonded to the metal center producing the hydrogen bonding (Figure 5) with a bond length of 1.875 Å. This displacement could imply the lower catalytic activity using the phenols (entries 10 and 11). Thus, to understand the role of the ligand, an additional reaction was performed to obtain complex 7.

Complex 7 (Figure 6) crystallized in the distorted trigonal bipyramidal configuration. The structure exhibits a hafnium center, surrounded by four molecules of 2,6-xyleneol and one neutral 2,6-xyleneol molecule, as can be seen in Scheme 8. The bond length of Hf–O₄ (neutral ligand) was the longest compared with the other Hf–O bonds, as expected. The angle of Hf₁–O₄–C₄₅ is bent (137.3(3)), implying a hydrogen-bonding N₁–H_{1A}–O₄ with the benzimidazolin-2-imine ligand moiety stabilizing the complex structure (Figure 7).

Furthermore, to elaborate on our understanding regarding the role of the benzimidazolin-2-iminato ligand in the active species of complex 1, the complex was reacted with 5 equiv of ^tBuOH. This reaction resulted in the formation of 3 equiv of

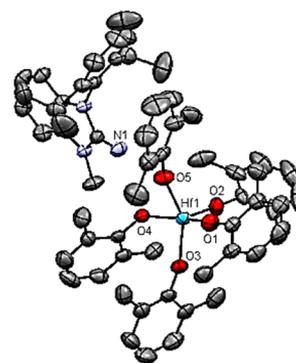


Figure 6. ORTEP drawing of complex 7, with thermal displacement parameters at 50% probability. Hydrogen atoms are omitted for clarity. Bond lengths for complex 7 (Å): Hf–O₁ = 1.989(5), Hf–O₂ = 1.922(4), Hf–O₃ = 1.983(3), Hf–O₄ = 2.072(4), and Hf–O₅ = 2.002(3).

Scheme 8. Schematic Drawing to Obtain Complex 7

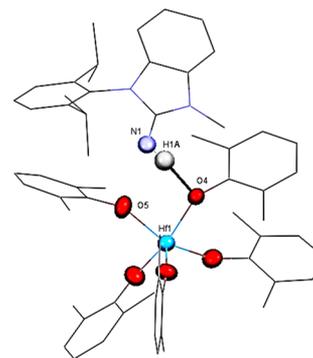
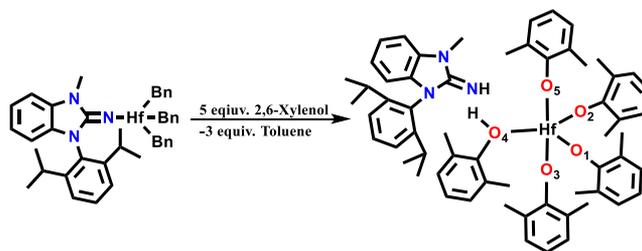
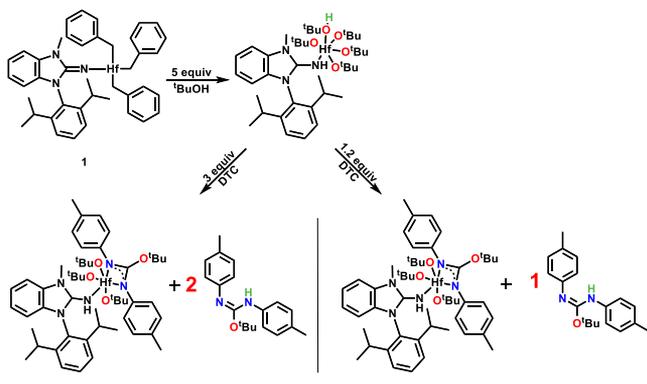


Figure 7. Hydrogen bonding in N₁–H–O₄. ORTEP drawing of complex 7, with thermal displacement parameters at 50% probability. Hydrogen atoms are omitted for clarity, except for the relevant hydrogen H_{1A}. Hydrogen bond length for complex 7 (Å): H_{1A}–O₄ = 2.048.

toluene and a benzimidazolin-2-imine penta(*tert*-butoxide) hafnium complex (Scheme 9). Then, we added 1.2 equiv of DTC, and the reaction was monitored by ¹H NMR spectroscopy, revealing the full consumption of the free DTC (the disappearance of the signal at 1.94 ppm and the appearance of the product signal at 5.79 ppm (N–H) as opposed to the NH of the ligand, which is located at the 5.29 ppm).

In addition, the ¹H NMR analysis revealed the appearance of the benzimidazolin-2-iminato monoisourea (DTC^{tBuO}) trialkoxo hafnium species (BenzIm^(DIPP,Me)NH)Hf–(O^tBu)₃(DTC^{O^tBu}). The integration of the *tert*-butoxide moieties corresponded to three *tert*-butoxide groups attached to the metal, one *tert*-butoxide moiety attached to the carbodiimide and additional *tert*-butoxide group from the

Scheme 9. Reaction of Complex 1 with ^tBuOH and DTC

amidinate product. Furthermore, when reacting the obtained complex from the reaction of complex 1 and 5 equiv of complex ^tBuOH (a similar complex to that of complex 4) with 3 equiv of DTC, the same products were obtained; however, 2 equiv of the amidinate product was obtained.

Kinetic studies on the addition of methanol to DTC using the precatalyst 1 were conducted by changing the concentration of one of the substrates or the catalyst (one order of magnitude) while keeping the other substrates constant, and the progress of the reaction was monitored by *in situ* ¹H NMR spectroscopy. The initial rate of the reaction was found to fit a linear dependence on the concentrations, revealing that the reactions display a first-order dependence on MeOH, DTC, and complex 1, following the kinetic rate law according to eq 1. (See the SI.)

$$\frac{dP}{dt} = k_{\text{obs}}[\text{cat}][\text{DTC}][\text{MeOH}] \quad (1)$$

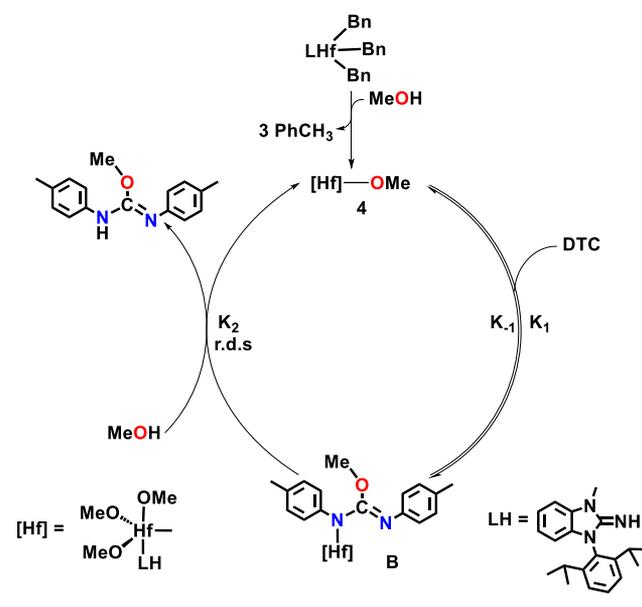
The activation parameters were determined from the Arrhenius and Eyring plots, affording the values of $E_a = 9.62(4)$ kcal/mol, $\Delta H^\ddagger = 9.02(4)$ kcal/mol, and $\Delta S^\ddagger = -44.3(4)$ e.u. The large negative entropy value supports a highly ordered transition state at the rate-determining step. When performing the reaction with MeOD, a primary kinetic isotope effect (KIE) of 2.78(5) was observed, suggesting that the protonolysis is the rate-determining step. Interestingly, for ^tBuOD, a smaller KIE of 1.31(6) was measured, as expected, when the steric influence started to be operative. A plausible mechanism is presented in Scheme 10 for the addition of methanol to DTC.

Complex 1 reacts with an excess of methanol to form complex 4. DTC inserts into complex 4 in a rapid equilibrium, forming the intermediate B. The protonolysis of the product from complex B, by methanol, is the rate-determining step, regenerating the active species 4.

CONCLUSIONS

We have synthesized and characterized seven new hafnium complexes bearing benzimidazolin-2-iminato and imidazolin-2-iminato ligands. Their X-ray crystal structures revealed short Hf–N bond lengths and a linear Hf–N–C angle, implying high bond orders. These complexes were utilized for the successful catalytic addition of alcohol to carbodiimides. This reaction showed the ability of the highly electrophilic hafnium complexes to participate in catalytic reactions involving different aliphatic and aromatic phenols due to the integration of the highly nucleophilic imidazolin-2-iminato ligands.

Scheme 10. Plausible Mechanism for Catalytic Insertion of Methanol into DTC



EXPERIMENTAL SECTION

General Considerations. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a high vacuum line (10^{-5} Torr) or in nitrogen-filled MBraun and Vacuum Atmospheres gloveboxes with a medium capacity recirculator (1 to 2 ppm oxygen). Argon and nitrogen were purified by passage through an MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Analytically pure solvents were dried and stored with Na/K alloy and degassed by three freeze–pump–thaw cycles prior to use (hexane, toluene, benzene-*d*₆, toluene-*d*₈). BenzImDippNH, BenzImMesNH, ImMesNH, and the metal complex precursor, hafnium tetrabenzyl, were synthesized according to published literature procedures.^{61,131,132} 1,3-Diisopropylcarbodiimide (Sigma-Aldrich) was dried by vacuum transfer. MeOH, EtOH, *i*PrOH, and ^tBuOH were distilled under CaH₂ and stored over 4 Å molecular sieves. PhOH, 2,6-Me₂PhOH, 2,4-^tBu₂PhOH, and 1,3-di-*p*-tolylcarbodiimide (Sigma-Aldrich) were dried for 12 h on a high vacuum line (10^{-5} Torr) and stored in a glovebox prior to use. MeOD and ^tBuOD were purchased from Sigma-Aldrich. NMR spectra were recorded on Avance 200, Avance 300, Avance II 400, Avance 500, and Avance II 600 Bruker spectrometers. Chemical shifts for ¹H NMR and ¹³C NMR measurements are reported in ppm and referenced using residual proton or carbon signals of the deuterated solvent relative to tetramethylsilane. For all complexes, the formation of the corresponding carbides precludes the elemental analysis (with or without V₂O₅). HRMS experiments were performed at 200 °C (source temperature) on a Maxis Impact (Bruker) mass spectrometer using an atmospheric pressure chemical ionization (APCI) solid-probe methodology. For X-ray crystallographic measurements, the single-crystalline material was immersed in perfluoropolyalkylether oil and was quickly fished with a glass rod and mounted on a Kappa charge-coupled device (CCD) diffractometer under a cold stream of nitrogen. Data collection was performed using monochromated Mo K α radiation using φ and ω scans to cover the Ewald sphere. The structure was solved by SHELXS-97 direct methods and refined by the SHELXL-97 program package.^{133–135}

Synthesis of Mono(benzimidazolin-2-iminato) Hafnium(IV) Complexes 1 and 2. A toluene solution of the respective benz(imidazolin-2-imine) Im^RNH (56.5 mg, 0.184 mmol) in 5 mL of toluene was added dropwise to a preprepared solution of hafnium tetrabenzyl (100 mg 0.184 mmol) in toluene (5 mL) at room temperature. The reaction mixture was stirred overnight at room

temperature. The solvent was removed under vacuum to afford the crude complexes **1** and **2**. In each case, the product was recrystallized from a concentrated toluene solution at $-35\text{ }^{\circ}\text{C}$ to yield compounds **1** and **2** as crystalline materials.

1-(2,6-Diisopropylphenyl)-3-methylbenzimidazolin-2-imine hafnium tribenzyl [(BenzIm^{DippN})HfBn₃], (Complex **1**): Yield: 0.128 g, 0.168 mmol, 92%. ¹H NMR (600 MHz, C₆D₆) δ 7.27 (t, 1H, H-Ar), 7.18 (m, 9H, H-Ph), 7.15 (m, 3H, H-Ph), 6.97 (m, 6H, H-Ph), 6.85 (s, 1H, H-Ar), 6.75 (s, 1H, H-Ar), 6.60 (d, $J = 7.6$ Hz, 1H, H-Ar), 6.38 (d, $J = 7.4$ Hz, 1H, H-Ar), 2.97 (s, 3H, CH₃), 2.72 (m, 2H, CH(CH₃)₂), 1.61 (s, 6H, CH₂Ph), 1.24 (d, $J = 6.9$ Hz, 6H, CH(CH₃)₂), 0.92 (d, $J = 6.9$ Hz, 6H, CH(CH₃)₂). ¹³C NMR (151 MHz, C₆D₆) δ 148.1, 145.5, 142.7, 131.0, 130.3, 129.4, 128.8, 124.2, 122.3, 108.7, 108.0, 72.3, 28.6, 27.5, 24.1, 23.6. MS (APCI) for C₄₁H₄₅HfN₃ = 759.742.

1-(2,4,6-Trimethylphenyl)-3-methylbenzimidazolin-2-imine hafnium tribenzyl [(BenzIm^{MesN})HfBn₃], (Complex **2**): Yield: 0.114 g, 0.160 mmol, 87%. ¹H NMR (500 MHz, C₆D₆) δ 7.31 (d, 1H, H-Ar), 7.13–6.99 (m, 15H, H-Ar), 6.79 (d, 1H, H-Ar), 6.63 (d, 1H, H-Ar), 6.36 (d, 1H, H-Ar), 2.88 (s, 3H, CH₃), 2.10 (s, 9H, CH₃-Ar), 2.00 (s, 6H, CH₂-Ph). ¹³C NMR (126 MHz, C₆D₆) δ 146.10, 142.5, 139.0, 137.5, 130.4, 129.2, 125.4, 122.3, 107.9, 71.2, 27.3, 20.6, 17.3. MS (APCI) for C₃₈H₃₉HfN₃ + H (M + H) – C₆H₅ = 642.3962

Synthesis of Mono 1-(2,4,6-Trimethylphenyl)-3-methylimidazolin-2-imine-hafnium Tribenzyl [(Im^{MesN})HfBn₃] (Complex **3**). A toluene solution of the respective (imidazolin-2-imine) Im^{MesN}NH (19.79 mg, 0.092 mmol) in 5 mL of toluene was added dropwise to a preprepared solution of hafnium tetrabenzyl (50 mg 0.092 mmol) in toluene (5 mL) at room temperature. The solvent was removed under vacuum to afford crude compound **3**. Complex **3** was recrystallized from a concentrated toluene solution at $-35\text{ }^{\circ}\text{C}$ to yield 0.049 g, 0.0736 mmol, and 80% yield of the crystalline materials. ¹H NMR (300 MHz, Tol) δ 7.07 (m, 7H, H-Ph), 6.89 (t, 3H, H-Ar), 6.75 (s, 3H, H-Ar), 6.54 (d, 6H, H-Ph), 5.58 (s, 1H, CH), 5.51 (s, 1H, CH), 2.74 (s, 3H, CH₃), 2.10 (s, 3H, CH₃-Ar), 2.01 (s, 6H, CH₃-Ar), 1.48 (s, 6H, CH₂-Ph). ¹³C NMR (75 MHz, Tol) δ 145.1, 143.4, 138.4, 137.0, 136.5, 133.2, 129.0, 128.7, 128.4, 128.0, 127.8, 127.4, 127.2, 127.1, 121.7, 112.3, 110.6, 69.6, 31.5, 30.9, 17.5. MS (APCI) for C₃₄H₃₇HfN₃ + N (from the APCI) (M + N) = 680.4198.

Synthesis of 1-(2,6-Diisopropylphenyl)-3-methylbenzimidazolin-2-imine Hafnium Tetra ^tBuO [(BenzIm^{DippN})Hf(^tBuO)₄] (Complex **4**). A solution of ^tBuOH (25 μL , 0.26 mmol) in 5 mL of toluene was added to a preprepared solution of complex **1** (50 mg, 0.06 mmol) in toluene (5 mL) at room temperature, and the reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum to afford crude compound **4**. The crude product of **4** was recrystallized from a concentrated toluene solution at $-35\text{ }^{\circ}\text{C}$ to yield compound **4** as a crystalline material. Yield: 0.048 g, 0.056 mmol, 94%. ¹H NMR (300 MHz, C₆D₆) δ 7.10 (m, 3H, H-Ph), 6.82 (t, 1H, H-Ar), 6.70 (t, 1H, H-Ar), 6.50 (d, $J = 7.4$ Hz, 1H, H-Ar), 6.17 (d, $J = 7.7$ Hz, 1H, H-Ar), 5.22 (s, 1H, NH), 3.62 (s, 3H, CH₃), 2.66 (m, 2H, CH(CH₃)₂), 1.36 (s, 36H, CH₃), 1.17 (d, $J = 6.8$ Hz, 6H, CH(CH₃)₂), 0.84 (d, $J = 6.9$ Hz, 6H, CH(CH₃)₂). ¹³C NMR (126 MHz, C₆D₆) δ 149.1, 132.3, 130.3, 128.9, 125.2, 124.9, 120.8, 107.0, 33.3, 28.1, 23.9. MS (APCI): C₃₆H₆₁HfN₃O₄ (M) = 778.6758.

Synthesis of Hafnium Tetra(tert-butoxide) [(HfO^tBu)₄] (Complex **5)**.¹²⁹ A solution of ^tBuOH (35 μL , 0.37 mmol) in 5 mL of toluene was added to a preprepared solution of hafnium tetrabenzyl (50 mg, 0.06 mmol) in toluene (5 mL) at room temperature, and the reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum to afford the crude compound **5** (a mixture of **5A** and **5B**). The crude product was recrystallized from a concentrated hexane solution at $-35\text{ }^{\circ}\text{C}$ to yield complex **5** as a cocrystalline material of **5A** and **5B**. In solution, the crystalline **5A** was not observed, and only signals for **5B** were present. Yield: 0.35 mg, 83%. ¹H NMR (200 MHz, C₆D₆) δ 7.25–7.09 (m, 5H, Ar), 2.21 (s, 3H, CH₃-Ph), 1.42 (s, 9H, C(CH₃)₃). ¹³C NMR (50 MHz, C₆D₆) δ 129.1, 125.4, 91.4, 32.7, 21.2.

Synthesis of 1-(2,6-Diisopropylphenyl)-3-methylbenzimidazolin-2-imine Hafnium Tetra(phenoxy) Phenol [(BenzIm^{DippN})Hf(PhO)₄(PhOH)] (Complex **6)**. A solution of phenol (24.8 mg, 0.263 mmol) in toluene (5 mL) was added to a prepared solution of the respective complex **1** (40 mg, 0.052 mmol) in 5 mL of toluene at room temperature. The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum to afford crude compound **6**. The crude product of **6** was recrystallized from a concentrated toluene solution at $-35\text{ }^{\circ}\text{C}$ to yield compound **6** as a crystalline material. Yield: 0.045 g, 0.042 mmol, 90%. ¹H NMR (500 MHz, C₆D₆) δ 7.19, 6.97 (m, 20H, H-Ph), 6.75–6.57 (m, 5H, H-Ar), 6.12 (d, 1H, H-Ar), 6.03 (d, 1H, H-Ar), 3.03 (s, 3H, CH₃), 2.03 (m, 2H, CH(CH₃)₂), 1.02 (d, 6H, CH₃), 0.68 (d, 6H, CH₃). ¹³C NMR (126 MHz, C₆D₆) δ 156.2, 147.7, 132.0, 129.0, 125.4, 119.9, 115.2, 31.4, 28.6, 23.7, 23.4, 22.6, 13.8. MS(APCI) for C₅₀H₅₁HfN₃O₅ + H + N (from the APCI) (M + H + N) – C₆H₅ = 890.8096.

Synthesis of 1-(2,6-Diisopropylphenyl)-3-methylbenzimidazolin-2-imine Hafnium Penta-2,6-xyleneol [(BenzIm^{DippN})Hf(2,6-dimethylphenoxy)₄(2,6-dimethylphOH)] (Complex **7)**. A solution of 2,6-xyleneol (32.1 mg, 0.263 mmol) in toluene (5 mL) was added to a prepared solution of the respective complex **1** (40 mg, 0.052 mmol) in 5 mL of toluene at room temperature. The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum to afford crude compound **7**. The crude product of **7** was recrystallized from a concentrated toluene solution at $-35\text{ }^{\circ}\text{C}$ to yield compound **7** as a crystalline material. Yield: 0.050 g, 0.04 mmol, 87%. ¹H NMR (300 MHz, C₆D₆) δ 6.96 (d, 10H, H_{Ar}), 6.90–6.86 (t, 5H, H_{Ar}), 6.76–6.65 (m, 5H, H_{Ar}), 6.17 (dd, 2H, H_{Ar}), 5.68 (s, 1H, NH), 4.02 (s, 1H, OH), 3.35 (s, 3H, CH₃), 2.39 (s, 3H, CH₃), 2.32 (m, 2H, CH(CH₃)₂), 1.96 (s, 6H, CH₃), 0.95 (d, $J = 6.7$ Hz, 6H, CH₃), 0.76 (d, $J = 6.8$ Hz, 6H, CH₃). ¹³C NMR (75 MHz, C₆D₆) δ 159.6, 155.8, 148.2, 131.5, 131.3, 130.9, 129.4, 128.2, 126.3, 125.2, 125.1, 120.0, 119.2, 115.2, 108.8, 107.0, 28.0, 24.4, 22.8, 17.4, 15.4. MS (APCI) for C₆₀H₇₀HfN₃O₅ (low-intensity signal: 1093.9998).

Kinetic Studies on the Addition of MeOH into DTC Using Complex **1**. All of the kinetic experiments were performed in the following manner. A J. Young NMR tube was charged with a measured amount of a preprepared solution of DTC, MeOH, and catalyst in C₆D₆, and additional solvent was added to reach a total volume of 0.6 mL. The solution was added to the glovebox, and the tube was sealed. The NMR tube was taken out of the glovebox, and the ¹H NMR experiment began at 25 $^{\circ}\text{C}$. All of the experiments were performed by changing only one of the substrates (0.11 to 1.1 mM) or the catalyst (0.55 to 5.5 μM) while the other reagents were constant. The product concentrations were measured by the area ratio of the methyl groups at 3.00 and 3.68 ppm, which were assigned to the starting material and the product, respectively. Reaction rates were determined by the least-squares fit of the initial product concentration versus time, and the plots are shown in Figures S34–S36. Activation parameters (ΔH^{\ddagger}), (ΔS^{\ddagger}), and (E_a) were calculated from the kinetic data using the Eyring and the Arrhenius plots (Figures S37 and S38).

Labeling Experiment. All KIE experiments were performed by charging a J. Young NMR tube with catalyst **1**, DTC, MeOH, or MeOD and ^tBuOH or ^tBuOD. For MeOH, the product concentration was measured by the area ratio of the methyl group at 3.00 and 3.68 ppm, assigned to the starting material and product, respectively. For ^tBuOH, the product concentration was measured by the area ratios of the ^tBuOH group at 1.03 and 1.55 ppm, assigned to the starting material and product, respectively. Reaction rates were determined by the least-squares fit of the initial product concentration versus time, and the plots are shown in Figures S40 and S41. The KIE values were calculated from the ratio of the two slopes: KIE_{MeOH} = 2.78(5) and KIE_{tBuOH} = 1.31(6).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00384>.

Synthesis of complexes, NMR spectra, kinetic studies, stoichiometric experiments, deuterium labeling studies, and crystallographic data for complexes 1–7. (PDF)

Accession Codes

CCDC 1945241–1945246 and 1945362 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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