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Hafnium imido complexes containing silyl ligands

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

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Abstract

The hafnium imido dichloride (2,6-*i*-$Pr_2C_6H_3$)N=Hf$(THF)_2Cl_2$ (**1**) reacts with two equivalents of $Ph_3SiLi(THF)_3$ to yield the corresponding disilyl complex (2,6-*i*-$Pr_2C_6H_3$)N=Hf$(THF)_2(SiPh_3)_2$ (**2**) in low yield. Compound **2** was crystallographically characterized. The hafnium monosilyl complex (2,6-*i*-$Pr_2C_6H_3$)N=Hf(4-*t*-$BuC_5H_4N)_2$Cl[Si$(SiMe_3)_3$] (**4**) was synthesized in a similar manner from (2,6-*i*-$Pr_2C_6H_3$)N=Hf(4-*t*-$BuC_5H_4N)_2Cl_2$ (**3**) and one equivalent of $(Me_3Si)_3SiK$ in good yield. The Cp*-containing hafnium imido complex {Cp*HfCl[μ-N(2,6-*i*-$Pr_2C_6H_3$)]}$_2$ (**5**) was prepared by thermolysis of Cp*Hf[Si$(SiMe_3)_3$][NH(2,6-*i*-$Pr_2C_6H_3$)]Cl via loss of $(Me_3Si)_3SiH$. Complex **5** was crystallographically characterized. Attempts to prepared derivatives of **5** with reactive σ-bonds resulted in the formation of Cp*-cyclometallated species. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hafnium imido complexes; Silyl ligands; Thermolysis

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1. Introduction

The chemistry of early transition and f-metal complexes in catalytic processes has developed dramatically in recent years. Olefin polymerization [1], hydrogenation [2], hydrosilylation [3], silane dehydropolymerization [4], and alkane activation [5] are among the transformations that have been accomplished with such species. Most of the research to date has focused on the use of metallocene-derived systems. Although several researchers have undertaken the investigation of non-metallocene-based systems [6], much remains to be learned about the role played by non-cyclopentadienyl ancillary ligands in early transition and f-metal complex reactivity.

Investigations in our group have focused on silane dehydropolymerizations with Group 4 metallocene catalysts, among which CpCp*Zr[Si$(SiMe_3)$]Me is the most active to date (Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5) [7d]. Altering the silyl, alkyl, or hydride ligands in the ‘mixed ring’ systems CpCp*M(SiR_3)X (M = Zr, Hf; R = H, alkyl, aryl; X = H, alkyl, aryl, Cl) [7] has not led to significant improvements in catalytic activity. Therefore, we expect a new generation of more active silane dehydropolymerization catalysts to feature ancillary ligands other than cyclopentadienyl [8].

Ancillary ligand set modifications might create a more electrophilic environment at the metal center, which may lead to more active catalysts for σ-bond metathesis reactions. For example, Basset and co-workers have recently described catalytic C–H and C–C bond activations under mild conditions [9]. The remarkable reactivity of the silica- and alumina-supported zirconium and tantalum centers used in the Basset systems is believed to be derived from the enhanced electrophilicity conferred by the silica and alumina surfaces, which act as hard ligands. In addition, the coordinatively unsaturated single-site metal hydride species generated on the solid supports are immobilized to prevent dimerization, which could inhibit catalytic activity.

We believe that replacement of soft cyclopentadienyl ligands with hard, bulky imido ligands [10] will enhance the electrophilicity of transition metal centers, while sterically protecting them from dimerization. Within this context, recent efforts in our laboratories have focused on the synthesis of Group 5 and 6 metal complexes with imido ancillary ligands [11]. Thus far,

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the activity of such complexes towards σ-bonds has remained limited to hydrogenations [11c] and phenylsilane activations [11a]. It is expected that more electrophilic Group 4 metals may display enhanced σ-bond metathesis reactivity in d^0 complexes that incorporate imido ancillary ligands. Herein, we report our syntheses of hafnium imido complexes that feature reactive σ-bonds for element–element and element–hydrogen bond activations.

2. Results and discussion

2.1. Synthesis and characterization of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}Hf(THF)_2(SiPh_3)_2$ (2)

Our initial approach to the synthesis of Group 4 imido complexes featuring reactive σ-bonds focused on the known hafnium compound $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}Hf(THF)_2Cl_2$ (**1**) [10e] (THF = tetrahydrofuran). However, addition of lithium silyl reagents $R_3SiLi(THF)_3$ [$R_3 = (SiMe_3)_3$, $t\text{-}BuPh_2$, Mes_2H] [12] to solutions of **1** at low temperatures in a variety of solvents resulted in the formation of intractable mixtures of products, which contained large amounts of the corresponding silane R_3SiH, and $(2,6\text{-}i\text{-}Pr_2C_6H_3)NH_2$. Identical results were obtained whether one or two equivalents of the lithium silyl reagents were used. The analogous reaction between two equivalents of $Ph_3SiLi(THF)_3$ [12d] and **1** in diethyl ether at −80 °C led to the isolation of low yields (≤ 10%) of the hafnium disilyl derivative $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}Hf(THF)_2(SiPh_3)_2$ (**2**, Eq. (1)). To our knowledge, complex **2** represents the first example of a Group 4 metal complex featuring imido and silyl ligands. Although **2** was fully characterized by spectroscopic methods and single crystal X-ray crystallography, attempts to optimize its yield, even in the dark, were unsuccessful. This prevented a detailed study of the reactivity of the Hf–Si bond of **2**.

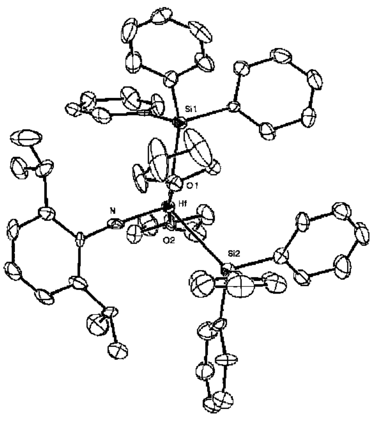
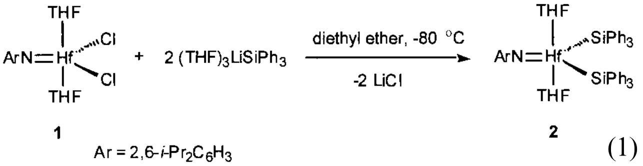


Fig. 1. ORTEP diagram of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}Hf(THF)_2(SiPh_3)_2$ (**2**).



(1)

The most prominent ^1H-NMR features of **2** include a doublet at δ 1.12, which corresponds to the *i*-Pr groups of the imido ligand, and the associated methine septet at δ 4.48. The aromatic resonances in the ^1H-NMR spectrum integrate to 33 H, in agreement with the presence of six phenyl groups and one $(2,6\text{-}i\text{-}Pr_2C_6H_3)N$ ligand. The ^{29}Si-NMR spectrum contains a single resonance at δ 35.1, confirming the presence of equivalent silyl ligands.

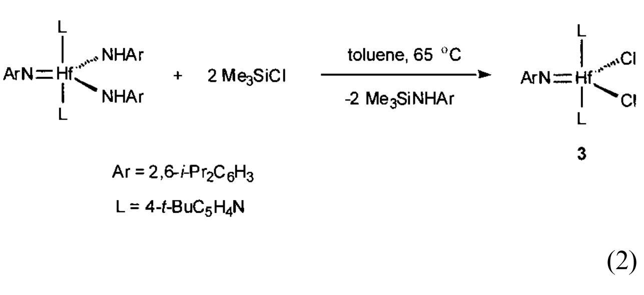
The solid-state structure of **2** was determined by X-ray crystallography. Yellow cubic crystals of **2** were obtained from a cold, concentrated pentane solution. The coordination environment around the Hf atom is that of a pseudo-trigonal bipyramid, with the two THF ligands in the axial positions. The O–Hf–O angle of 169.9° is close to linear as expected for the axial ligands of a trigonal bipyramid, with Hf–O bond lengths of 2.17 and 2.18 Å to O(1) and O(2), respectively. The imido and triphenylsilyl ligands occupy the equatorial positions, likely due to steric constraints. The short Hf–N bond length of 1.82 Å is characteristic of hafnium imido complexes [10f], as is the C_{ipso}–N–Hf angle of 162.4°, which is indicative of multiple bonding between hafnium and nitrogen [10f]. Complex **2** possesses nearly identical Hf–Si bond lengths of 2.87 and 2.85 Å to Si(1) and Si(2), respectively. The Hf–Si distances are almost identical to that of $CpCp^*Hf[Si(SiMe_3)_3]Cl$ (2.88 Å) [7c]. The sum of the angles between the ligands in the equatorial plane is very close to 360°, as expected for a planar trigonal geometry. Notably, the angle between the two silyl ligands of 129.7° is the largest of all three, indicative of the large steric demand of such groups. An ORTEP diagram of **2** is presented in Fig. 1.

Unfortunately, the reactivity of **2** and analogous hafnium disilyl complexes could not be explored due to its low yield, and the lack of success in preparing related compounds with other silyl ligands. Since all reactions of **1** with lithium silyl reagents led to the formation of large amounts of the corresponding silane and diisopropyl aniline, regardless of the solvent used in such reactions, we believe that the THF ligands might be acting as a source of hydrogen atoms. Thus, we devised the synthesis of hafnium imido complexes of the type $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}HfL_2Cl_2$ (L = two-electron donor), featuring the potentially more inert pyridine ligands.

2.2. Preparation of $(2,6\text{-}i\text{-}Pr_2C_6H_3)N{=}Hf(4\text{-}t\text{-}BuC_5H_4N)_2Cl_2$ (3)

Rothwell and co-workers have previously reported the preparation of hafnium imido compounds of the type (2,6-i-$Pr_2C_6H_3$)N=Hf(py′)$_2$[HN(2,6-i-$Pr_2C_6H_3$)]$_2$ (py′ = 4-pyrrolidinopyridine) [10f], which are potential precursors to the corresponding hafnium imido dichlorides. Initial efforts focused on the treatment of (2,6-i-$Pr_2C_6H_3$)N=Hf(py)$_2$[HN(2,6-i-$Pr_2C_6H_3$)]$_2$ (py = pyridine, which was prepared by addition of two equivalents of pyridine to pentane solutions of Hf[HN(2,6-i-$Pr_2C_6H_3$)]$_4$ [10f]) with two equivalents of Me_3SiCl, to replace the amido ligands with chlorides. Heating orange solutions of (2,6-i-$Pr_2C_6H_3$)N=Hf(py)$_2$[HN(2,6-i-$Pr_2C_6H_3$)]$_2$ in the presence of two equivalents of Me_3SiCl led to the precipitation of a pale yellow powder, which was assigned as impure (2,6-i-$Pr_2C_6H_3$)N=Hf(py)$_2Cl_2$ (by comparing its IR spectrum with that of its fully characterized analogue **3**, vide infra). Unfortunately, this compound could not be obtained in analytically pure form, as its solubility in polar (pyridine, acetonitrile, methylene chloride, chloroform) and non-polar (pentane, toluene, benzene, diethyl ether) solvents is negligible. Washing the solid with several portions of pentane and diethyl ether did not provide material that could be identified as (2,6-i-$Pr_2C_6H_3$)N=Hf(py)$_2Cl_2$ by combustion analysis. Formation of insoluble species is likely responsible for incomplete reaction of (2,6-i-$Pr_2C_6H_3$)N=Hf(py)$_2$[HN(2,6-i-$Pr_2C_6H_3$)]$_2$ with Me_3SiCl, which results in the isolation of mixtures of products as the pale yellow powder described above.

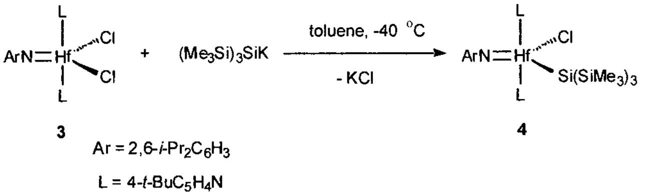
Replacing pyridine with 4-t-Bu-pyridine as a ligand in the preparation of (2,6-i-$Pr_2C_6H_3$)N=Hf(4-t-BuC_5H_4N)$_2$[HN(2,6-i-$Pr_2C_6H_3$)]$_2$ afforded a product that is considerably more soluble in aliphatic solvents than its pyridine counterpart. Treatment of toluene solutions of (2,6-i-$Pr_2C_6H_3$)N=Hf(4-t-BuC_5H_4N)$_2$[HN-(2,6-i-$Pr_2C_6H_3$)]$_2$ with two equivalents of Me_3SiCl at elevated temperatures resulted in the formation of the desired hafnium imido complex (2,6-i-$Pr_2C_6H_3$)N=Hf(4-t-BuC_5H_4N)$_2Cl_2$ (**3**, Eq. (2)), which is soluble in both benzene and toluene. Analytically pure samples of **3** were obtained by recrystallization from cold, concentrated toluene solutions. The spectroscopic data for **3** is consistent with a trigonal bipyramidal structure similar to that of **1**, with the two t-Bu-pyridine ligands in equivalent axial positions, giving rise to one set of resonances for the t-Bu and aromatic protons in the ^{1}H-NMR spectrum at δ 0.79, 6.67, and 8.80, respectively, in a 9:2:2 ratio.



(2)

2.3. Synthesis and reactivity of (2,6-i-$Pr_2C_6H_3$)N=Hf(4-t-BuC_5H_4N)$_2$Cl[Si(SiMe$_3$)$_3$] (4)

As in the case of **1**, no hafnium silyl complexes were isolated from reactions with either one or two equivalents of lithium silyls. Although many solvents and reaction temperatures were investigated, complex mixtures of products were obtained in all cases. As mentioned above, we reasoned that the formation of silanes and aniline in these reactions was related to the presence of THF in the reaction mixtures. Since lithium silyl reagents typically have THF associated with them, we decided to explore the reactivity of THF-free silyl anions. The potassium silyl compound $(Me_3Si)_3SiK$ [13] represents a source of the base-free silyl anion $(Me_3Si)_3Si^-$. Thus, treatment of **3** with one equivalent of $(Me_3Si)_3SiK$ resulted in quantitative formation (by ^{1}H-NMR spectroscopy in benzene-d_6) of (2,6-i-$Pr_2C_6H_3$)N=Hf(4-t-BuC_5H_4N)$_2$Cl[Si(SiMe$_3$)$_3$] (**4**, Eq. (3)), which represents the second example of a hafnium complex featuring imido and silyl ligands.



(3)

Compound **4** was identified by its ^{1}H-NMR spectrum, which includes a resonance at δ 0.29, corresponding to the silyl ligand. Likewise, the t-Bu resonance of the pyridine ligands appears at δ 0.81, and integrates in a ratio of 2:3 relative to that of the silyl group. The i-Pr groups of the imido ligand give rise to broad resonances at δ 1.49 for the methyl groups, and δ 4.72 for the methine protons. This broadening is likely due to hindered rotation about the C_{ipso}–N bond of the imido ligand, which is slow on the NMR time scale at ambient temperature. This hindered rotation can be attributed to the steric bulk of the –Si(SiMe$_3$)$_3$ group. Variable temperature ^{1}H-NMR spectroscopy studies of toluene-d_8 solutions of **4** revealed the presence of two well resolved sets of isopropyl resonances at − 80 °C, which correspond to a rate constant $k = 1410\ s^{-1}$ at the coalescence temperature of 22 °C. This yields a value for the free energy of activation $\Delta G^{\ddagger} = 13$ kcal mol^{-1} [14]. Unfortunately, we have not been able to analyze the solid state structure of **4**, since attempts to obtain X-ray quality crystals have so far resulted in formation of small, stacked flakes.

Preliminary reactivity studies revealed that the Hf center of **4** is sterically encumbered due to the presence of the bulky imido and silyl ligands. Thus, exposure of benzene-d_6 solutions of **4** to an atmosphere of dihydrogen at ambient temperature and up to 60 °C for 4 h

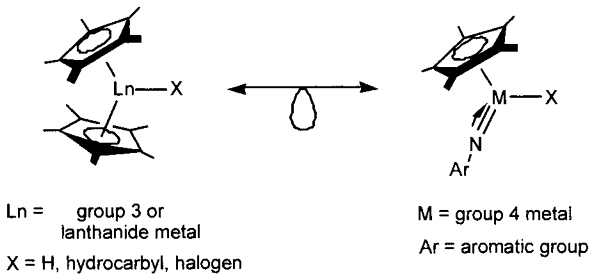
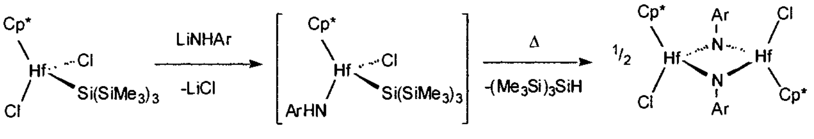


Chart 1.

resulted in no changes in the ^{1}H-NMR spectrum. Likewise, addition of one equivalent of $PhSiH_3$ to benzene-d_6 solutions of **4** led to no reaction after 4 h at room temperature, or upon heating to 80 °C for 2 h, as evidenced by ^{1}H-NMR spectroscopy. Upon heating to 100 °C for 2 h, an intractable mixture of hafnium-containing products was obtained, but $PhSiH_3$ remained intact.

*2.4. Synthesis of Cp*Hf(=NAr) derivatives ($Cp^* = C_5Me_5$, $Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$)*

In addition to the cyclopentadienyl-free imido complexes, we are interested in mixed cyclopentadienyl imido derivatives of the Group 4 metals. Such cyclopentadienyl-imido complexes are interesting in that they are isolobal with the Group 3 and lanthanide metallocenes (Chart 1). Given the rich σ-bond metathesis chemistry of the metallocene complexes of the Group 3 and lanthanide metals, preparation of hafnium cyclopentadienyl imido compounds presents an attractive alternative that would be amenable to comparisons of σ-bond metathesis reactivity.



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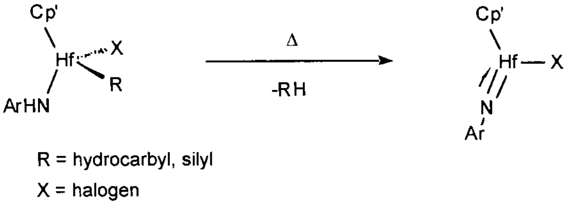
(5)

Examples of Group 4 cyclopentadienyl imido complexes exist in the literature [10e,12,17], but all of them possess additional donors that render them less electrophilic than their lanthanide metallocene analogues. In addition, there are no examples of such complexes with reactive σ-bonds.

In the examples of known Cp*M(=NAr) complexes, generation of the Group 4 metal–nitrogen multiple bond was achieved by base-induced α-H abstraction from a metal amide [10e,15]. This method led to the formation of base adducts of the metal imido complexes. We devised a synthesis of coordinatively unsaturated Cp*Hf(=NAr) complexes that circumvents the use of bases or ethereal solvents that could coordinate to Hf. This involves the *thermolytic* α-H abstraction from the metal-bound amide by a hydrocarbyl or silyl group (Eq. (4)).



(4)

The hafnium silyl complex $Cp^*Hf[Si(SiMe_3)_3]Cl_2$ [16] is a convenient starting material for the preparation of compounds with amide and silyl ligands. Addition of solid LiNHAr ($Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$) to benzene-$d_6$ or toluene solutions of $Cp^*Hf[Si(SiMe_3)_3]Cl_2$ likely resulted in generation of the desired complex $Cp^*Hf[Si(SiMe_3)_3](NHAr)Cl$. Although this compound was not isolated, heating the solutions to 65 °C for 12 h resulted in quantitative formation of $(Me_3Si)_3SiH$ (by ^{1}H-NMR spectroscopy in benzene-d_6) and a new hafnium-based product. While the new hafnium product $\{Cp^*HfCl[\mu\text{-}N(2,6\text{-}i\text{-}Pr_2C_6H_3)]\}_2$ (**5**) is associated with a single Cp* resonance at δ 1.83 in the ^{1}H-NMR spectrum, no resonance that could be attributed to a NH group was detected. Likewise, no ν_{NH} stretching band was observed in the IR spectrum of **5**. The structure of compound **5** appears to be that of a dimeric hafnium μ-imido complex (Eq. (5)), based on the presence of two sets of doublets at δ 1.29 and 1.51 in its ^{1}H-NMR spectrum, corresponding to diastereotopic –CHMe_2 groups on each of the imido ligands.

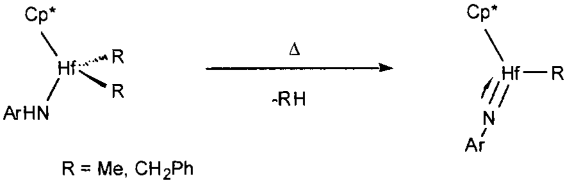
The solid state structure of **5** confirms the bridging nature of the imido ligands, which likely arises from the electron deficient nature of the hafnium center. Apparently, the coordination of two σ-type donors better satisfies the electrophilicity of Hf than one non-bridging, $\sigma + \pi$ imido donor [17]. The low intensity of the reflections in the X-ray data set collected did not allow anisotropic refinement of the carbon and nitrogen atoms, and only the hafnium and chlorine atoms were refined anisotropically. Nonetheless, the connectivity of **5** was firmly established, and the metric parameters obtained are consistent with those of known hafnium compounds [17]. The asymmetric unit consists of one half of the molecule, which is related to the other half by an inversion center. Complex **5** is characterized by unequal Hf–N distances of 2.05 and 2.11 Å, as well as bond lengths of 2.41 (Hf–Cl), and 2.22 Å (Hf-centroid).

The N(1)–Hf(1)–N(1)* angle of 84.9° is complemented by the Hf(1)–N(1)–Hf(1)* angle of 95.1°, giving rise to a nearly square planar Hf_2N_2 core. An ORTEP diagram of **5** is presented in Fig. 2.

Complex **5** can also be prepared by thermolysis of Cp*Hf(NHAr)MeCl (synthesized by addition of one equivalent of $ArNH_2$ to cold solutions of Cp*HfMe$_2$Cl [18] and identified by ^{1}H-NMR spectroscopy), which proceeds via the clean elimination of methane (by ^{1}H-NMR spectroscopy in benzene-d_6). This method avoids the use of (THF)$_3$LiSi(SiMe$_3$)$_3$, which is more difficult to obtain than the MeLi or MeMgCl employed in the preparation of Cp*HfMe$_2$Cl.

Attempts to prepare derivatives of **5** that incorporate reactive σ-bonds (Hf–C, Hf–Si, or Hf–H) have proven unsuccessful, pressumably due to the hindered nature of the Hf center of **5**. No reaction was observed upon addition of the afforementioned lithium and potassium silyl reagents to benzene-d_6 solutions of **5** (by ^{1}H-NMR spectroscopy). While the use of THF has been precluded by its potential to coordinate to the hafnium center, addition of the silyl reagents to solutions of **5** in diethyl ether or hydrocarbon solvents has resulted in isolation of **5**. Complex mixtures of products were obtained upon heating, likely due to the thermal decomposition of the silyl anions. Similar results were observed when Grignard (MeMgCl, PhCH$_2$MgCl, NpMgCl; Np = neopentyl) and lithium alkyl [NpLi, Me$_3$SiCH$_2$Li, (Me$_3$Si)$_2$CHLi] reagents were used in attempts to prepare compounds with Hf–C bonds.

Due to the lack of success in preparing derivatives of **5** that contain silyl, hydrocarbyl, or hydride ligands, a different route to the synthesis of such compounds was undertaken. Thus, Cp*HfMe$_2$[NH(2,6-i-Pr$_2$C$_6$H$_3$)] (**6**) and Cp*Hf(CH$_2$Ph)$_2$[NH(2,6-i-Pr$_2$C$_6$H$_3$)] (**7**) were prepared from Cp*HfMe$_3$ [19] and Cp*Hf(CH$_2$Ph)$_3$ [20], respectively, by protonation of one of the hydrocarbyl ligands with one equivalent of diisopropyl aniline at −80 °C. We hypothesized that the presence of two reactive Hf–C bonds would lead to imido complexes with a pre-formed Hf–Me or Hf–CH$_2$Ph bond upon thermolysis (Eq. (6)).



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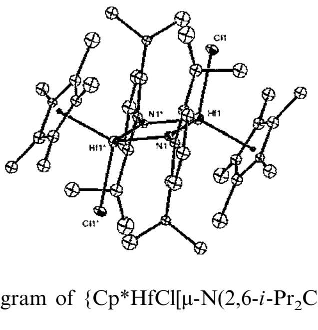
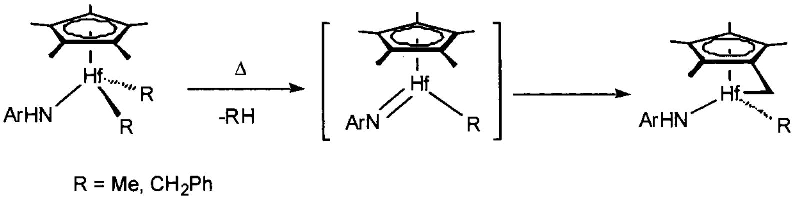


Fig. 2. ORTEP diagram of {Cp*HfCl[μ-N(2,6-i-Pr$_2$C$_6$H$_3$)]}$_2$ (**5**).

Heating benzene-d_6 solutions of **6** and **7** to 75 °C resulted in the elimination of methane and toluene, respectively (by ^{1}H-NMR spectroscopy). Both reactions required long reaction times of 48 h to proceed to completion, and led to the formation of several hafnium-containing products (by ^{1}H-NMR spectroscopy). The main products obtained in both cases were assigned as hafnium amide species, based on the observed ^{1}H-NMR resonances corresponding to NH hydrogens (at δ 5.46 and 5.39, respectively). In addition, the appearance of four major resonances in a 1:1:1:1 ratio in the Cp* region of the spectra indicates the formation of cyclometallated complexes of hafnium with η^1,η^5-CH$_2$C$_5$Me$_4$ ligands. Thermolytic hydrogen atom abstraction from a Cp* ligand has previously been observed in Group 4 metallocene chemistry [21]. Although preparative scale themolyses of **6** and **7** in benzene did not yield crystalline products that could be completely characterized, the tentative structure of the themolysis products is shown in Eq. (7).



(7)

Formation of the Cp* metallated complexes could proceed through initial α-abstraction to generate a transient hafnium imido species. Such imido species would then rearrange to the proposed metallated cyclopentadienyl derivatives by intramolecular addition of a Cp* C–H bond across the Hf=N bond [21,22]. Precedent for this type of reactivity exists in the conversion of Cp$_2^*$Hf(CH$_2$Ph)$_2$ to toluene and $Cp_2^*\overline{HfCH_2\text{-}o\text{-}C_6H_4}$, which is proposed to proceed by initial α-H abstraction [21b]. The transiently generated hafnium benzylidene complex undergoes Cp* ring hydrogen abstraction to produce the isolated cyclometallated intermediate Cp*(η^1,η^5-CH$_2$C$_5$Me$_4$)HfCH$_2$Ph.

3. Conclusions

The first hafnium complexes that incorporate imido and silyl ligands have been prepared. Although the poor synthetic yields of the disilyl complex (2,6-*i*-$Pr_2C_6H_3$)N=Hf$(THF)_2(SiPh_3)_2$ (**2**) did not allow us to examine its reactivity, its solid state structure confirmed the presence of Hf–Si bonds. The σ-bond metathesis reactivity of the silyl complex (2,6-*i*-$Pr_2C_6H_3$)N=Hf(4-*t*-$BuC_5H_4N)_2Cl[Si(SiMe_3)_3]$ (**4**) appears to be low, since it does not react with $PhSiH_3$ even at elevated temperatures. The low reactivity is likely due to the steric congestion around the Hf center.

During our attempts to synthesize coordinatively unsaturated Cp*Hf(=NAr) derivatives, we discovered that the aromatic group (2,6-*i*-$Pr_2C_6H_3$) is not large enough to prevent dimerization to a μ-imido species {Cp*HfCl[μ-N(2,6-*i*-$Pr_2C_6H_3$)]}$_2$ (**5**). The dimeric nature of **5** prevented its derivatization to complexes containing reactive Hf–Si, Hf–C, or Hf–H bonds.

The thermolyses of Cp*$HfMe_2$(NHAr) (**6**) and Cp*Hf$(CH_2Ph)_2$(NHAr) (**7**, Ar = 2,6-*i*-$Pr_2C_6H_3$) [which we expected to lead to the formation of complexes of the type Cp*Hf(=NAr)Me and Cp*Hf(=NAr)(CH_2Ph), respectively] led to the formation of hafnium amide specie. It appears that the Cp* ligand is deleterious in theses systems, since it is prone to intramolecular C–H activations, which yield cyclometallated complexes of the type Cp*(η^1,η^5-$CH_2C_5Me_4$)HfR (R = Me, CH_2Ph).

4. Experimental

4.1. General

Unless otherwise specified, all manipulations were performed under a N_2 or Ar atmosphere using standard Schlenk techniques or an inert atmosphere dry box. Dry, oxygen-free solvents were employed throughout. Olefin free C_5H_{12} was obtained by treatment with concentrated H_2SO_4, then 0.5 N $KMnO_4$ in 3 M H_2SO_4, followed by $NaHCO_3$, and finally $MgSO_4$. Thiophene-free benzene and $C_6H_5CH_3$ were obtained by pretreating the solvents with concentrated H_2SO_4, followed by Na_2CO_3, and $CaCl_2$. C_5H_{12}, C_6H_6, $C_6H_5CH_3$, THF, and Et_2O were distilled from sodium/benzophenone and stored under nitrogen prior to use, whereas benzene-d_6 and toluene-d_8 were vacuum distilled from Na–K alloy. Pyridine was distilled from Na and stored under nitrogen. 4-*t*-BuC_5H_4N was dried over CaH_2 and distilled under nitrogen. Me_3SiCl was distilled under nitrogen prior to use. Reagents were purchased from commercial suppliers and used without further purification unless otherwise specified. (2,6-*i*-$Pr_2C_6H_3$)N=Hf$(THF)_2Cl_2$ [10e], Hf[HN(2,6-*i*-$Pr_2C_6H_3$)]$_4$ [10f], Cp*Hf[Si$(SiMe_3)_3$]Cl_2 [16], Cp*$HfMe_2$Cl [18], Cp*$HfMe_3$ [19], Cp*Hf$(CH_2Ph)_3$ [20], $(THF)_3LiSi(SiMe_3)_3$ [12a], $(THF)_3$LiSi-*t*-$BuPh_2$ [12b], $(THF)_3LiSiHMes_2$ [12c], $(THF)_3LiSiPh_3$ [12d], and $KSi(SiMe_3)_3$ [13] were prepared by literature methods. NMR spectra were recorded on Bruker AMX-300, AMX-400, or DRX-500 spectrometers at ambient temperature unless otherwise noted. Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. Infrared spectra were recorded on a Mattson Infinity 60 FTIR instrument. Samples were prepared as KBr pellets unless otherwise noted, and data are reported in units of cm^{-1}.

4.2. Synthesis of (2,6-i-$Pr_2C_6H_3$)N=Hf$(THF)_2(SiPh_3)_2$ (2)

A Schlenk tube equipped with a stirbar was charged with (2,6-*i*-$Pr_2C_6H_3$)N=Hf$(THF)_2Cl_2$ (**1**) (0.50 g, 0.88 mmol) and $Ph_3SiLi(THF)_3$ (0.94 g, 1.80 mmol). Toluene (ca. 50 ml) was added at − 80 °C via cannula while stirring. The mixture was allowed to warm to room temperature (r.t.) overnight. Volatile materials were evaporated under vacuum. The products were extracted with 50 ml of C_5H_{12} and cannula filtered into another Schlenk flask. The yellow solution was then concentrated to a volume of ca. 10 ml and cooled to − 35 °C. Yellow crystals of **2** were obtained in a low yield of 10% (80 mg, 0.08 mmol). m.p. 137–142 °C. IR. 3050 (m), 2957 (s), 2868 (s), 1619 (m), 1459 (m, sh), 1427 (w), 1336 (m), 1260 (w, sh), 1188 (s), 1113 (m), 833 (w, br), 803 (w), 733 (m), 699 (m, sh), 484 (w). ^{1}H-NMR (500 MHz, benzene-d_6): δ 0.89 (m, 8H, β-THF), 1.12 (d, 12H, CH*Me*$_2$), 4.26 (m, 8H, α-THF), 4.48 (sept, 2H, C*H*Me$_2$), 7.18 (m, 9H, Ar), 7.24 (m, 12H, Ar), 7.64 (m, 12H, Ar). $^{13}C\{^1H\}$-NMR (126 MHz): δ 24.64 (β-THF), 24.97 (CH*Me*$_2$), 27.56 (*C*HMe$_2$), 76.31 (α-THF), 122.22, 127.21, 127.42, 129.65, 135.81, 136.56, 141.64, 146.48 (aromatics). ^{29}Si-NMR (99 MHz): δ 35.13. Anal. Calc. for $C_{56}H_{63}HfNO_2Si_2$: C, 66.15; H, 6.24; N, 1.38. Found: C, 65.55; H, 6.19; N, 1.10%.

4.3. Synthesis of (2,6-i-$Pr_2C_6H_3$)N=Hf(4-t-$BuC_5H_4N)_2Cl_2$ (3)

To a stirred orange solution of Hf[HN(2,6-*i*-$Pr_2C_6H_3$)]$_4$ (6.60 g, 7.47 mmol) in 200 ml of C_5H_{12} was added 4-*t*-Bu-pyridine (2.30 ml, 15.7 mmol) via syringe. A yellow solid crashed out of solution upon addition. After stirring the mixture for 1 h, the volume was reduced to ca. 50 ml under vacuum, and then the supernatant solution was discarded. Traces of C_5H_{12} were removed from the yellow solid under vacuum. The yellow product was then dissolved in a minimum amount of $C_6H_5CH_3$, and chilled to − 35 °C. Yellow crystals of (2,6-*i*-$Pr_2C_6H_3$)N=Hf(4-*t*-$BuC_5H_4N)_2$[NH-(2,6-*i*-$Pr_2C_6H_3$)]$_2$ were obtained in 88% yield (6.42 g, 6.57 mmol). Part of this material (3.00 g, 3.07 mmol) was placed in a Schlenk tube and dissolved in ca. 30 ml of $C_6H_5CH_3$. To this solution was added Me_3SiCl (0.80 ml, 6.14 mmol) via syringe. The orange mixture was heated to 65 °C under an atmosphere of nitrogen for ca. 18 h. A yellow solution was obtained, which was cannula filtered into another Schlenk flask. This solution was concentrated under vacuum until small yellow crystals could be seen on the sides of the flask. Cooling to −80 °C resulted in formation of yellow crystals, which were isolated and washed twice with ca. 10 ml of C_5H_{12}. Removal of residual solvents in vacuo afforded **3** in 87% yield (1.88 g, 2.44 mmol). m.p. 240–242 °C. IR 3047 (m), 2965 (s), 2925 (s), 2867 (m), 1937 (w), 1842 (w), 1793 (w), 1614 (s), 1542 (w, sh), 1501 (m, sh), 1460 (m), 1421 (s), 1366 (m), 1318 (m), 1274 (m), 1232 (m, sh), 1181 (s), 1102 (m), 1069 (m), 1017 (m, sh), 926 (w, br), 889 (w, sh), 828 (s), 800 (m, br), 753 (s), 724 (w, sh), 569 (s), 541 (w), 508 (m), 413 (w, sh). ^{1}H-NMR (300 MHz, benzene-d_6) δ 0.79 (s, 18H, *t*-Bu), 1.35 (d, 12H, CH*Me*$_2$), 5.62 (sept, 2H, C*H*Me$_2$), 6.67 (d, 4H, 3-C$_5$*H*$_4$N), 6.95 (t, 1H, Ar), 7.20 (d, 2H, Ar), 8.80 (d, 4H, 2-C$_5$*H*$_4$N). ^{13}C{^{1}H}-NMR (126 MHz) δ 27.53 (*C*Me$_3$), 27.63 (C*Me*$_3$), 30.18 (CH*Me*$_2$), 34.97 (*C*HMe$_2$), 119.26, 120.86, 122.75, 123.46, 125.11, 142.82, 152.20 (Aromatics). Anal. Calc. for $C_{36}H_{43}Cl_2HfN_3$: C, 51.84; H, 6.24; N, 6.05. Found: C, 51.90; H, 6.24; N, 5.94%.

4.4. Synthesis of (2,6-i-Pr$_2$C$_6$H$_3$)N=Hf(4-t-BuC$_5$H$_4$N)$_2$Cl[Si(SiMe$_3$)$_3$] (4)

In a Schlenk tube equipped with a stirbar were mixed **3** (0.50 g, 0.72 mmol) and $(Me_3Si)_3SiK$ (0.21 g, 0.72 mmol). The solid mixture was stirred and cooled to −40 °C, and 50 ml of cold toluene were added slowly via cannula. Upon warming to ambient temperature, a yellow–orange solution formed. After further stirring for 1 h, volatile materials were removed under vacuum. The remaining yellow–orange solid was extracted with ca. 60 ml of C_5H_{12}, and the orange solution obtained was cannula filtered into another Schlenk tube. Concentrating the solution to a volume of ca. 15 ml and cooling to −35 °C afforded orange microcrystals of **4** in 66% yield (0.43 g, 0.48 mmol). m.p. 149–153 °C (dec.). IR: 2961 (s), 2892 (s), 2869 (s), 1953 (w, br), 1854 (w), 1795 (w, br), 1616 (s), 1586 (m), 1544 (w, sh), 1498 (m, sh), 1461 (m), 1423 (s), 1343 (s), 1275 (m), 1258 (s), 1240 (s), 1202 (w), 1156 (w, br), 1100 (m), 1068 (m), 1022 (s), 961 (m), 834 (s, br), 752 (m), 728 (m), 679 (m), 622 (m, sh), 570 (m, sh), 543 (w, sh), 452 (w, br). ^{1}H-NMR (500 MHz, benzene-d_6): δ 0.29 (s, 27H, Si*Me*$_3$), 0.81 (s, 18H, *t*-Bu), 1.49 (d, 12H, CH*Me*$_2$), 4.72 (br, 2H, C*H*Me$_2$), 6.69 (d, 4H, 3-C$_5$*H*$_4$N), 7.00 (t, 1H, Ar), 7.39 (d, 2H, Ar), 9.28 (d, 4H, 2-C$_5$*H*$_4$N). ^{13}C{^{1}H}-NMR (126 MHz): δ 5.54 (Si*Me*$_3$), 25.60 (C*Me*$_3$), 28.47 (*C*HMe$_2$), 30.12 (CH*Me*$_2$), 35.42 (*C*Me$_3$), 120.60, 122.48, 123.01, 126.03, 129.66, 152.72, 165.45 (aromatics). ^{29}Si-NMR (99 MHz): δ −98.76 (*Si*(SiMe$_3$)$_3$), −4.35 (Si(*Si*Me$_3$)$_3$). Anal. Calc. for $C_{39}H_{70}ClHfN_3Si_4$: C, 51.63; H, 7.78; N, 4.63. Found: C, 52.11; H, 7.60; N, 4.37%.

*4.5. Synthesis of {Cp*HfCl[μ-N(2,6-i-Pr$_2$C$_6$H$_3$)]}$_2$ (5)*

To stirred $C_6H_5CH_3$ (ca. 15 ml) solution of Cp*HfCl$_2$[Si(SiMe$_3$)$_3$] (0.50 g, 0.80 mmol) in a Schlenk tube was added solid LiNH(2,6-*i*-Pr$_2$C$_6$H$_3$) (0.15 g, 0.80 mmol). The yellow solution obtained changed color to orange upon heating to 65 °C overnight. After cooling the reaction mixture to r.t., volatile materials were evaporated in vacuo. The orange solid obtained was washed with ca. 5 ml of C_5H_{12} and redissolved in ca. 10 ml of $C_6H_5CH_3$. Cooling the concentrated $C_6H_5CH_3$ solution to −35 °C afforded yellow–orange crystals of **5** in 72% yield (0.30 g, 0.29 mmol). m.p. 137–142 °C. IR: 3033 (m), 2958 (s), 2866 (s), 1619 (m), 1425 (w), 1336 (m), 1296 (m), 1265 (w, sh), 1190 (s), 1114 (m), 833 (w, br), 821 (w), 733 (m), 700 (m, br), 612 (w), 484 (w). ^{1}H-NMR (500 MHz, benzene-d_6) δ 1.29 (d, 6H, CH*Me*$_2$), 1.51 (d, 6H, CH*Me*$_2$), 1.83 (s, 15H, Cp*), 4.36 (sept, 2H, C*H*Me$_2$), 6.92 (t, 1H, Ar), 7.13 (d, 2H, Ar). ^{13}C{^{1}H}-NMR (126 MHz): δ 19.98 (CH*Me*$_2$), 23.55 (CH*Me*$_2$), 26.73 (C$_5$*Me*$_5$), 37.27 (*C*HMe$_2$), 118.96 (*C*$_5$Me$_5$), 123.33, 125.85, 132.12, 145.07 (aromatics). Anal. Calc. for $C_{22}H_{32}ClHfN$: C, 50.39; H, 6.15; N, 2.67. Found: C, 49.95; H, 6.12; N, 2.54%.

*4.6. Synthesis of Cp*HfMe$_2$[NH(2,6-i-Pr$_2$C$_6$H$_3$)] (6)*

To a stirred, cold (−80 °C) solution of Cp*HfMe$_3$ (0.59 g, 1.64 mmol) in ca. 20 ml of C_5H_{12} was added (2,6-*i*-Pr$_2$C$_6$H$_3$)NH$_2$ (0.31 ml, 1.64 mmol) dropwise via syringe. The mixture was slowly allowed to reach ambient temperature, and at that point the volatile materials were removed under vacuum until the solution reached a volume of ca. 5 ml. Cooling to −35 °C afforded tan crystalline **6** in 72% yield (0.61 g, 1.17 mmol). m.p. 43–45 °C. IR: 3063 (m, ν_{NH}), 3018 (m), 2959 (s), 2913 (s), 2867 (s), 2760 (m), 1898 (w), 1848 (w, br), 1793 (w), 1618 (m, sh), 1590 (m, sh), 1459 (s), 1434 (s), 1380 (m), 1360 (m), 1337 (m), 1302 (m, sh), 1259 (s), 1227 (m), 1203 (m), 1140 (m), 1116 (m), 1042 (m, sh), 1026 (m, sh), 955 (w), 890 (m, sh), 865 (m), 793 (m, br), 745 (s, sh), 696 (s, sh), 624 (w, br), 577 (w, sh), 554 (w, br), 474 (s, br). ^{1}H-NMR (300 MHz, benzene-d_6): δ 0.08 (s, 6H, Hf*Me*$_2$), 1.26 (d, 12H, CH*Me*$_2$), 1.82 (s, 15H, Cp*), 2.94 (sept, 2H, C*H*Me$_2$), 5.14 (s, 1H, N*H*), 6.97 (t, 1H, Ar), 7.13 (d, 2H, Ar). ^{13}C{^{1}H}-NMR (126 MHz): δ 11.18 (Hf*Me*$_2$), 23.85 (C$_5$*Me*$_5$), 30.40 (CH*Me*$_2$), 48.17 (*C*HMe$_2$), 119.18 (*C*$_5$Me$_5$), 121.89, 123.33, 138.88, 147.88 (aromatics). Anal. Calc. for $C_{24}H_{39}HfN$: C, 55.43; H, 7.56; N, 2.69. Found: C, 55.56; H, 7.38; N, 2.82%.

4.7. Synthesis of $Cp^*Hf(CH_2Ph)_2[NH(2,6\text{-}i\text{-}Pr_2C_6H_3)]$ (7)

To a stirred, cold (− 80 °C) solution of $Cp^*Hf(CH_2Ph)_3$ (1.07 g, 1.83 mmol) in ca. 25 ml of C_5H_{12} was added $(2,6\text{-}i\text{-}Pr_2C_6H_3)NH_2$ (0.35 ml, 1.83 mmol) dropwise via syringe. The solution was allowed to warm to r.t., and it was further stirred for 1 h. The volume of the solution was then reduced to ca. 10 ml in vacuo. Cooling to − 35 °C afforded off-white crystals of **7** in 78% yield (0.96 g, 1.43 mmol). m.p. 144–147 °C (dec.). IR: 3056 (m, ν_{NH}), 3014 (m), 2957 (s), 2921 (s), 2868 (s), 1928 (w, br), 1845 (w), 1791 (w, br), 1719 (w), 1593 (s), 1485 (s), 1435 (s), 1381 (m), 1357 (w), 1324 (m), 1254 (s), 1232 (m), 1201 (s), 1178 (w), 1148 (w, br), 1111 (m, br), 1029 (s), 993 (m, sh), 931 (w, sh), 890 (w), 864 (m, sh), 794 (m, sh), 745 (s, sh), 694 (s, sh), 584 (w, br), 554 (w, sh), 518 (w, sh), 414 (w). ^{1}H-NMR (300 MHz, benzene-d_6): δ 1.28 (d, 12H, $CHMe_2$), 1.80 (d, 2H, CH_2Ph), 1.86 (s, 15H, Cp*), 2.20 (d, 2H, CH_2Ph), 2.84 (sept, 2H, $CHMe_2$), 5.64 (s, 1H, NH), 6.10–7.36 (13H, aromatics). $^{13}C\{^1H\}$-NMR (126 MHz): δ 11.24 ($CHMe_2$), 24.59 (C_5Me_5), 29.24 (CH_2Ph), 75.46 ($CHMe_2$), 120.27 (C_5Me_5), 122.86, 122.97, 123.17, 127.75, 129.31, 140.40, 147.35, 149.60 (aromatics). Anal. Calc. for $C_{36}H_{47}HfN$: C, 64.32; H, 7.05; N, 2.08. Found: C, 63.95; H, 6.98; N, 1.94%.

4.8. X-ray single crystal structure determination of 2 and 5

4.8.1. X-ray crystal structure determination of 2

A yellow, block-like crystal was mounted on a glass capillary using Paratone N hydrocarbon oil and placed under a stream of cold nitrogen on a Siemens SMART diffractometer with a CCD area detector (Mo–K_α radiation, $\lambda = 0.71073$ Å). Preliminary orientation matrix and unit cell parameters were determined by collecting 60 10-s frames. A hemisphere of data was collected at a temperature of 160 K using ω scans of 0.30° and a collection time of 20 s per frame. Frame data were integrated using SAINT. An absorption correction was applied using SADABS. No correction for decay was necessary. The structure was solved using direct methods (SIR92) and all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions but were not refined.

4.8.2. Crystal data for 2

($C_{56}H_{63}HfNO_2Si_2$; 1016.78 g mol^{-1}; yellow block of 0.28 × 0.16 × 0.16 mm dimension; air sensitive): the hafnium disilyl complex crystallizes in the monoclinc system ($P2_1/c$) with the following unit cell: $a =$ 19.1425(3), $b = 12.7530(2)$, $c = 20.1801(4)$ Å, $\beta =$ 95.572(1)°. The cell volume is 4903.2(1) Å^3 with $Z = 4$, $D_{calc} = 1.377$ g cm^{-3}, and an absorption coefficient of 2.214 mm^{-1}. The max and min transmission were in the range of 0.977–0.619. A absorption correction from equivalents was applied. $F(000) = 2088$; 23 296 reflections were collected of which 9078 ($R_{int} = 0.078$) were independent. The data were refined by a full-matrix least-squares on F^2. The ratio of data/parameters was 4589/559, while the goodness-of-fit on F^2 is 1.17. $R[I > 3\sigma(I)]$: R 0.047, R_w 0.051, R_{all} 0.106. The largest difference peak and hole: 2.78 and − 2.19 e Å^{-3}.

4.8.3. X-ray crystal structure determination of 5

A yellow, cubic crystal was mounted on a glass capillary using Paratone N hydrocarbon oil and placed under a stream of cold nitrogen on a Siemens SMART diffractometer with a CCD area detector (Mo–K_α radiation, $\lambda = 0.71073$ Å). Preliminary orientation matrix and unit cell parameters were determined by collecting 60 10-s frames. A hemisphere of data was collected at a temperature of 127 K using ω scans of 0.30° and a collection time of 20 s per frame. Frame data were integrated using SAINT. An absorption correction was applied using SADABS. No correction for decay was necessary. The structure was solved using direct methods (SIR92) and the hafnium and chlorine atoms were refined anisotropically. The carbon and nitrogen atoms were refined isotropically. Hydrogen atoms were included in idealized positions but were not refined.

4.8.4. Crystal data for 5

($C_{22}H_{32}Cl_2Hf_2N_2$; 1048.89 g mol^{-1}; yellow cube of 0.03 × 0.04 × 0.07 mm dimension): the hafnium imido chloride complex crystallizes in the monoclinc system ($C2/c$) with the following unit cell: $a = 21.3765(7)$, $b =$ 17.8103(5), $c = 10.9785(4)$ Å, $\beta = 94.762(1)$°. The cell volume is 4165.3(2) Å^3 with $Z = 4$, $D_{calc} = 1.680$ g cm^{-3}, and an absorption coefficient of 5.156 mm^{-1}. The max and min transmission were in the range of 0.894–0.743. A absorption correction from equivalents was applied. $F(000) = 2080$; 9755 reflections were collected of which 3602 ($R_{int} = 0.101$) were independent. The data were refined by a full-matrix least-squares on F^2. The ratio of data/parameters was 1636/111, while the goodness-of-fit on F^2 0.99. $R[I > 3\sigma(I)]$: R 0.041, R_w 0.042, R_{all} 0.127. The largest difference peak and hole: 1.03 and − 0.93 e Å^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 168426 and 168427 for compounds **2** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428;
(b) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143;
(c) P.C. Möhring, N.J.J. Coville, J. Organomet. Chem. 479 (1994) 1.

[2] (a) A.H. Hoveyda, J.P. Morken, Angew. Chem. Int. Ed. Engl. 35 (1996) 1262;
(b) Z. Lin, T.J. Marks, J. Am. Chem. Soc. 109 (1987) 7979;
(c) N.E. Lee, S.L. Buchwald, J. Am. Chem. Soc. 116 (1994) 5985.

[3] (a) T.I. Gountchev, T.D. Tilley, Organometallics 18 (1999) 5661;
(b) G.A. Molander, E.D. Dowdy, B.C. Noll, Organometallics 17 (1998) 3754;
(c) P.-F. Fu, L. Brard, Y. Li, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 7157;
(d) M.B. Carter, B. Schiott, A. Gutierrez, S.L. Buchwald, J. Am. Chem. Soc. 116 (1994) 11667;
(e) G.A. Molander, M. Julius, J. Org. Chem. 57 (1992) 6347.

[4] (a) F. Gauvin, J.F. Harrod, H.-G. Woo, Adv. Organomet. Chem. 42 (1998) 363;
(b) T.D. Tilley, Acc. Chem. Res. 26 (1993) 22;
(c) J. Corey, in: G. Larson (Ed.), Advances in Silicon Chemistry, vol. 1, JAI Press, Greenwich, CT, 1991, p. 327;
(d) C.M. Forsyth, S.P. Nolan, T.J. Marks, Organometallics 10 (1991) 2543;
(e) T. Sakakura, H.J. Lautenschlager, M. Nakajima, M. Tanaka, Chem. Lett. (1991) 913.

[5] (a) T.J. Marks, Acc. Chem. Res. 25 (1992) 57;
(b) in: J.A. Davis, P.L. Watson, J.F. Liebman, A. Greenberg (Eds.), Selective Hydrocarbon Activation, VCH Publishers, New York, 1990;
(c) J.E. Bercaw, Pure Appl. Chem. 62 (1990) 1151;
(d) P.L. Watson, G.W. Parshall, Acc. Chem. Res. 18 (1985) 51;
(e) I.P. Rothwell, Polyhedron 4 (1985) 177;
(f) P.L. Watson, J. Am. Chem. Soc. 105 (1983) 6491;
(g) J.W. Bruno, G.M. Smith, T.J. Marks, C.K. Fair, A.J. Schultz, J.M. Williams, J. Am. Chem. Soc. 108 (1986) 40;
(h) M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.

[6] For recent reviews see: (a) A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587;
(b) F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 34 (1995) 2466.

[7] (a) H.-G. Woo, T.D. Tilley, J. Am. Chem. Soc. 111 (1989) 8043;
(b) T.D. Tilley, Comments Inorg. Chem. 10 (1990) 37;
(c) H.-G. Woo, R.H. Heyn, T.D. Tilley, J. Am. Chem. Soc. 114 (1992) 5698;
(d) H.-G. Woo, J.F. Walzer, T.D. Tilley, J. Am. Chem. Soc. 114 (1992) 7047.

[8] T. Imori, T.D. Tilley, Polyhedron 13 (1994) 2231.

[9] For example: (a) C. Lecuyer, F. Quignard, A. Choplin, D. Olivier, J.-M. Basset, Angew. Chem. Int. Ed. Engl. 30 (1991) 1660;
(b) C. Rosier, G.P. Niccolai, J.-M. Basset, J. Am. Chem. Soc. 119 (1997) 12408;
(c) O. Maury, L. Lefort, V. Vidal, J. Thivolle-Cazat, J.-M. Basset, Angew. Chem. Int. Ed. Engl. 38 (1999) 1952;
(d) M. Chabanas, V. Vidal, C. Copéret, J. Thivolle-Cazat, J.-M. Basset, Angew. Chem. Int. Ed. Engl. 39 (2000) 1962.

[10] For example: (a) C.C. Cummins, S.M. Baxter, P.T. Wolczanski, J. Am. Chem. Soc. 110 (1988) 8731;
(b) R.D. Profilet, C.H. Zambrano, P.E. Fanwick, J.J. Nash, I.P. Rothwell, Inorg. Chem. 29 (1990) 4362;
(c) C.C. Cummins, C.P. Schaller, G.D. Van Duyne, P.T. Wolczanski, A.W.E. Chan, R. Hoffman, J. Am. Chem. Soc. 113 (1991) 2985;
(d) R. Duchateau, A.J. Williams, S. Gambarotta, M.Y. Chiang, Inorg. Chem. 30 (1991) 4863;
(e) D.J. Arney, M.A. Bruck, S.R. Huber, D.E. Wigley, Inorg. Chem. 31 (1992) 3749;
(f) C.H. Zambrano, R.D. Profilet, J.E. Hill, P.E. Fanwick, I.P. Rothwell, Polyhedron 12 (1993) 689;
(g) J.L. Bennett, P.T. Wolczanski, J. Am. Chem. Soc. 116 (1994) 2179;
(h) D.E. Wigley, in: K.D. Karlin (Ed.), Advances in Inorganic Chemistry, vol. 42, John Wiley, New York, 1994, p. 239, and references therein.

[11] (a) U. Burckhardt, G.L. Casty, T.D. Tilley, T.K. Woo, U. Rothlisberger, Organometallics 19 (2000) 3830;
(b) U. Burckhardt, T.D. Tilley, J. Am. Chem. Soc. 121 (1999) 6328;
(c) G.L. Casty, T.D. Tilley, G.P.A. Yap, A.L. Rheingold, Organometallics 16 (1997) 4746.

[12] (a) G. Gutekunst, A.G. Brook, J. Organomet. Chem. 225 (1982) 1;
(b) B.K. Campion, R.H. Heyn, T.D. Tilley, Organometallics 12 (1993) 2584;
(c) D.M. Roddick, R.H. Heyn, T.D. Tilley, Organometallics 8 (1989) 324;
(d) M.V. George, D.J. Peterson, H. Gilman, J. Am. Chem. Soc. 82 (1960) 404.

[13] C. Kayser, C. Marschner, Monatsh. Chem. 130 (1999) 203.

[14] H. Friebolin, Basic One and Two-Dimensional NMR Spectroscopy, 2nd ed., VCH, New York, 1993.

[15] (a) Y. Bai, M. Noltemeyer, H.W. Roesky, Z. Naturforsch. B: Chem. Sci. 46B (1991) 1357;
(b) Y. Bai, H.W. Roesky, M. Noltemeyer, M. Witt, Chem. Ber. 125 (1992) 825.

[16] J. Arnold, D.M. Roddick, T.D. Tilley, A.L. Rheingold, S.J. Geib, Inorg. Chem. 27 (1988) 3510.

[17] (a) W.A. Nugent, B.L. Haymore, Coord. Chem. Rev. 31 (1980) 123;
(b) M.H. Chisholm, I.P. Rothwell, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987, p. 161 and references therein.

[18] D.M. Roddick, B.D. Santarsiero, J.E. Bercaw, J. Am. Chem. Soc. 107 (1985) 4670.

[19] L.E. Schock, T.J. Marks, J. Am. Chem. Soc. 110 (1988) 7701.

[20] D.C. Swenson, Z. Guo, D.J. Crowther, N.C. Baenziger, R.F. Jordan, Acta Crystallogr. Sect. C C56 (2000) E313.

[21] (a) C. McDade, J.C. Green, J.E. Bercaw, Organometallics 1 (1982) 1629;
(b) A.R. Bulls, W.P. Schaefer, M. Serfas, J.E. Bercaw, Organometallics 6 (1987) 1219;
(c) L.E. Schock, C.P. Brock, T.J. Marks, Organometallics 6 (1987) 232.

[22] L. Chamberlain, I.P. Rothwell, J.C. Huffman, J. Am. Chem. Soc. 104 (1982) 7338.