Abstract: A series of hafnium complexes with a reduced arene of the general formula $[\text{K}(L)]\{\text{Hf}(\text{XY-N,N})(\text{arene})\}$ (XY-$N,N = \{(3,5-\text{Me},\text{C}_{5}H_{4})\text{NCH}_{2}CH_{2}\}^{N-}$), $L = \text{THF}$, 18-crown-6; arene $= \text{C}_{6}H_{5}^{2+}$, $\text{C}_{5}H_{4}^{2+}$) mimic the chemistry of hafnium in its formal oxidation state +II. All compounds were obtained upon reduction of the chlorido complex $[\text{HfCl}(\text{XY-N,N})(\text{thf})]$ with two equivalents of potassium naphthalenide or anthracenide. The reducing nature and the basicity of the reduced anthracene ligand were explored in the reaction of benzonitrile and azobenzene, and by deprotonation of tert-butylacetylene, respectively. The reduction of benzonitrile provides an initial double nitrile insertion product under kinetic control that rearranges after extrusion of one of the inserted nitriles to a hafnium imido complex as the thermodynamic product. The reduction of azobenzene resulted in a diphenylhydrazido(2–) complex. Treatment of terminal alkynes with the anthracene or naphthalene ligand provided a convenient source of low-valent transition metals.\(^{[4]}\) For example, the iron(II) reduced naphthalene complex $[\text{K}(18\text{-crown-6})]^{-}\{\text{Cp}^{+}\text{Fe}(\eta^{4}\text{-C}_{8}H_{8})\}$ (Cp$^{+} = \text{C}_{5}\text{Me}_{5}$) acts as a convenient “Cp$^{+}\text{Fe}^{2+}$ source in the activation of white phosphorus, where it mimics the chemistry of a formal Fe$^{0}$ complex.\(^{[5]}\) While a variety of reduced arene complexes were isolated for titanium\(^{[6]}\) and zirconium,\(^{[7]}\) corresponding complexes for the heavier congener hafnium are limited to their homoleptic homologue $[\text{K}(18\text{-crown-6})]^{-}\{\text{Hf}(\text{arene})\}$ (arene $= \text{C}_{6}H_{5}^{2+}$, $\text{C}_{5}H_{4}^{2+}$, cyclooctatetraenide ($\text{C}_{8}H_{8}^{2-}$)).\(^{[8]}\) These tris-(arene)hafnates with a formally Hf$^{2+}$ center were proposed as suitable precursors for studies on poorly explored low-valent hafnium chemistry. So far only five complexes of hafnium in the formal oxidation state of +II have been isolated, for example $[\text{Cp}^{+}\text{Hf}(\text{CO})]^{-}$, $[\text{Cp}^{+}\text{Hf}(\text{dmpe})(\text{CO})]^{-}$, $[\text{Hf}(\text{L}_{3}(\text{PM}_{3}\text{Ph})_{2}N(\eta^{2}\text{-arene}))]^{-}$ and $[\text{(Me}_{2}\text{cAAC})\text{Hf}(\text{X})(\text{N})]^{-}$ ($\text{X} = \text{Cl}$, $\text{CH}_{3}\text{Ph}$).\(^{[9]}\) Hence, a new class of hafnium(IV) complexes with a dianionic naphthalenide or anthracene ligand may open up an alternative route to explore the chemistry of reduced Hf complexes. Herein we report a series of hafnium complexes with reduced naphthalene and anthracene ligands supported by the ary1-substituted triamidoamine ligand ($\{(3,5-\text{Me},\text{C}_{5}H_{4})\text{NCH}_{2}CH_{2}\}^{N-}$).\(^{[10]}\) The strong reducing nature of these reduced arene complexes was shown by the reduction of benzonitrile and azobenzene, and the high basicity of the reduced arene ligands was demonstrated by the reaction with weak Brønsted acids, such as tert-butylacetylene.

Introduction

Metal complexes of reduced, polycyclic arene ligands constitute a special class of organometallic reagents that serve as soluble metal reductants owing to the lability of the arene ligands during reduction.\(^{[1]}\) The most common examples are alkali or alkaline earth metal naphthalenides and anthracenides.\(^{[2,3]}\) Recently, considerable interest was also shown towards the synthesis of reduced arene complexes of transition metals, driven by their potential use as a storable source of low-valent transition metals.\(^{[4]}\) For example, the iron(II) reduced naphthalene complex $[\text{K}(18\text{-crown-6})]^{-}\{\text{Cp}^{+}\text{Fe}(\eta^{4}\text{-C}_{8}H_{8})\}$ (Cp$^{+} = \text{C}_{5}\text{Me}_{5}$) acts as a convenient “Cp$^{+}\text{Fe}^{2+}$ source in the activation of white phosphorus, where it mimics the chemistry of a formal Fe$^{0}$ complex.\(^{[5]}\) While a variety of reduced arene complexes were isolated for titanium\(^{[6]}\) and zirconium,\(^{[7]}\) corresponding complexes for the heavier congener hafnium are limited to their homoleptic homologue $[\text{K}(18\text{-crown-6})]^{-}\{\text{Hf}(\text{arene})\}$ (arene $= \text{C}_{6}H_{5}^{2+}$, $\text{C}_{5}H_{4}^{2+}$, cyclooctatetraenide ($\text{C}_{8}H_{8}^{2-}$)).\(^{[8]}\) These tris-(arene)hafnates with a formally Hf$^{2+}$ center were proposed as suitable precursors for studies on poorly explored low-valent hafnium chemistry. So far only five complexes of hafnium in the formal oxidation state of +II have been isolated, for example $[\text{Cp}^{+}\text{Hf}(\text{CO})]^{-}$, $[\text{Cp}^{+}\text{Hf}(\text{dmpe})(\text{CO})]^{-}$, $[\text{Hf}(\text{L}_{3}(\text{PM}_{3}\text{Ph})_{2}N(\eta^{2}\text{-arene}))]^{-}$ and $[\text{(Me}_{2}\text{cAAC})\text{Hf}(\text{X})(\text{N})]^{-}$ ($\text{X} = \text{Cl}$, $\text{CH}_{3}\text{Ph}$).\(^{[9]}\) Hence, a new class of hafnium(IV) complexes with a dianionic naphthalenide or anthracene ligand may open up an alternative route to explore the chemistry of reduced Hf complexes. Herein we report a series of hafnium complexes with reduced naphthalene and anthracene ligands supported by the ary1-substituted triamidoamine ligand ($\{(3,5-\text{Me},\text{C}_{5}H_{4})\text{NCH}_{2}CH_{2}\}^{N-}$).\(^{[10]}\) The strong reducing nature of these reduced arene complexes was shown by the reduction of benzonitrile and azobenzene, and the high basicity of the reduced arene ligands was demonstrated by the reaction with weak Brønsted acids, such as tert-butylacetylene.

Results and Discussion

Synthesis and Structure of Reduced Arene Complexes

The starting material $[\text{HfCl}(\text{XY-N,N})(\text{thf})]$ (1-Cl: XY-$N,N = \{(3,5-\text{Me},\text{C}_{5}H_{4})\text{NCH}_{2}CH_{2}\}^{N-}$) was prepared from $\text{H}_{2}(\text{XY-N,N})$ and $[\text{H}(\text{NMe}_{2})]$ following a similar method used for $[\text{TiCl}(\text{XY-N,N})]$.$^{[11]}$ In the first step, a mixture of $\text{H}_{2}(\text{XY-N,N})$ and $[\text{H}(\text{NMe}_{2})]$ was stirred in toluene for 30 min at room temperature to obtain $[\text{Hf}(\text{NMe}_{2})(\text{XY-N,N})]$ (1-NMe$_{2}$), which after work-up was isolated as a colorless solid in 82% yield (see Supporting Information (SI), Sec. 2.1). Protonation of 1-NMe$_{2}$ with $[\text{NEt}_{3}\text{H}]^{+}$ in THF under ambient condition afforded the chlorido complex 1-Cl as a colorless solid in 96% yield (see SI, Sec. 2.2). When the protonation was carried out in CH$_{2}$Cl$_{2}$, the chlorido complex $[\text{HfCl}(\text{XY-N,N})(\text{NMe}_{2})\text{H}]$ was formed as a NMe$_{2}$H adduct.\(^{[12]}\) The higher coordination number for the hafnium chlorido...
complex compared to the corresponding titanium complex can be explained with the larger size of the hafnium ion. Both starting materials were fully characterized by multinuclear NMR spectroscopy and elemental analysis. In addition, the octahedral geometry of the hafnium center in 1-Cl was confirmed by single-crystal X-ray diffraction (see SI, Figure S29). Compound 1-Cl is the first example of a structurally characterized triamidoamine ligand-supported hafnium chloride.

Reduction of 1-Cl with two equivalents of potassium naphthalenide (Knaph) or anthracenide (Kanth) under an atmosphere of nitrogen or argon led to a distinct color change from colorless to dark brown (for Knaph) or dark red (for Kanth). 

\[ \text{H}^1 \text{NMR spectroscopy revealed the selective formation of the reduced arene complexes [K(thf)][Hf(Xy-N,N)(naph)] (2-naph) or [K(thf)][Hf(Xy-N,N)(anth)] (2-anth) along with one equivalent of free arene (Scheme 1).} \]

After work-up, the reduced arene complexes were isolated as bright brown and dark red solids in 82 and 91% yield, respectively (see SI, Sec 2.3 and 2.4). Unlike the previously reported scandium naphthalene complex \([\text{K}(\text{thf})][\text{Sc}(\text{N}(\text{Bu})(\text{Xy}))_{\text{naph}}]\), 2-naph does not reduce anthracene to form the corresponding reduced anthracene complex 2-anth, indicating a lower reduction potential of 2-naph as compared to that of the scandium complex. While 2-anth is a thermally stable solid, compound 2-naph decomposes simultaneously both in solution and in the solid state when stored at room temperature. However, 2-naph can be stored for several months at \(-40^\circ\text{C}\) under argon atmosphere. The arene complexes are highly soluble in THF and DME, moderately soluble in EtO and aromatic solvents, and insoluble in aliphatic solvents.

The reduction of 1-Cl resulted in a quite different outcome when compared to that of the corresponding titanium- (IV) complex \([\text{TiCl}(\text{Xy-N,N})]\). Whilst the reduction of \([\text{TiCl}(\text{Xy-N,N})]\) with two equivalents of potassium metal or potassium naphthalenide under dinitrogen afforded a stable titanium dinitrogen complex \(\text{K}_2\left[\text{Ti}(\text{Xy-N,N})_2\right]\)\(\text{N}_2\), the reduction of 1-Cl with potassium naphthalenide under dinitrogen atmosphere produced the reduced naphthalene hafnium complex instead of a dinitrogen complex \(\text{K}_2\left[\text{Hf}(\text{Xy-N,N})_2\right]\)\(\text{N}_2\). Such a difference in the outcome of the reduction of \([\text{MCl}(\text{Xy-N,N})(\text{thf})]\) \((\text{M} = \text{Ti}; n = 0; \text{M} = \text{Hf}; n = 1)\) is most likely due to the reluctance of hafnium to form complexes with low-valent hafnium that is required to activate dinitrogen.\(^{[13]}\)

Treatment of the reduced arene complexes 2-naph and 2-anth with one equivalent of 18-crown-6 in THF led to the corresponding crown ether complexes \([\text{K}(18\text{-crown-6})][\text{Hf}(\text{Xy-N,N})(\text{naph})] (2\text{-naph-C})\) and \([\text{K}(18\text{-crown-6})][\text{Hf}(\text{Xy-N,N})(\text{anth})] (2\text{-anth-C})\), Scheme 1, which were isolated in high yield as dark green and orange solids, respectively (see SI, Sec 2.4 and 2.6). These crown ether complexes are thermally more stable than their corresponding crown ether-free analogues.

The reduced arene complexes were characterized by multinuclear NMR spectroscopy and elemental analysis. In addition, the solid-state structure of 2-anth-C was confirmed by single-crystal X-ray diffraction (Figure 1). Several attempts to obtain crystal structures of other reduced arene complexes remained unsuccessful due to the instability of the crystals which seem to lose co-crystallized solvent molecules very fast. The molecular structure of 2-anth-C revealed a separated ion pair with the potassium cation located in a pocket formed by the 18-crown-6 and two THF molecules. The dianionic anthracene ligand binds the hafnium center in a \(\sigma^2\),\(\pi\)-coordination fashion with \(\text{Hf}1-\text{C}1-\text{C}4\) and \(\text{Hf}1-\text{C}1-\text{C}4\), which were isolated in 82 and 91% yield, respectively. The \(\text{Hf}1-\text{C}1-\text{C}4\) bonds are marginally longer than the \(\text{Hf}1-\text{C}1-\text{C}3\) bonds. This bonding pattern differs from those of the previously known reduced arene complexes with a \(\sigma^2\),\(\pi\)-coordination, where the \(\sigma\)-bonds are shorter than the \(\pi\)-bonds.\(^{[50]}\) However, the alternating bond lengths of \(\text{C}1-\text{C}2-\text{C}3\) bonds, as well as a large folding angle of 40.6(8)° between the planes defined by \(\text{C}1-\text{C}2-\text{C}3-\text{C}4\) and \(\text{C}1-\text{C}9\text{A}-\text{C}4\text{A}-\text{C}4\), indicate rather a \(\sigma^2\),\(\pi\)-coordination of the reduced anthracene ligand than a \(\pi\)-canonical structure. The \(\text{Hf}1-\text{C}1-\text{C}2\) bond lengths \((d(\text{Hf}1-\text{C}1-\text{C}2)_{\text{avg}} = 2.4685 \text{ Å})\) in 2-anth-C compare very well with that of the only known homoletic hafnium-reduced anthracene complex \([\text{K}(18\text{-crown-6})][\text{Hf}(\text{C}_8\text{H}_{10}\text{H}_3\text{})]\) \((d(\text{Hf}1-\text{C}1\text{H}3)_{\text{avg}} = 2.467 \text{ Å})\). As expected, the triamidoamine ligand binds the hafnium center in a trigonal monopyramidal geometry with the hafnium center residing 0.672(8) Å above the equatorial plane formed by the three amido nitrogen atoms.

Further structural information of the reduced arene complexes 2-naph/2-naph-C and 2-anth/2-anth-C in solution is provided by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy. In contrast to the pseudo \(\text{C}_2\)-symmetric
structure in the solid state, a single set of signals for the trimidoamine ligand shows an overall C$_3$-symmetric structure in [D$_7$]THF or [D$_3$]benzene (see SI, Figure S6–S13). This higher symmetry is not the only proof of a fluxional process on the NMR time scale. An addition of free anthracene to the anthracene complexes leads to very broad signals in the $^1$H NMR spectrum due to the fast exchange with the reduced anthracene ligand. A similar fluxional behavior was also observed for a reduced naphthalene complex of zirconium with a similar tetradenate, triamionic [O$_2$C] ligand.$^{[76]}$

The most characteristic signals in the $^1$H NMR spectra are those of the reduced naphthalene and anthracene ligands which appear markedly upfield shifted compared to those in the free ligands. For example, the $^1$H NMR spectrum of 2-naph displays four multiplets for the naphthalene ligand at $\delta = 2.60$ (C$_{4-5}$-H), 5.02 (C$_{3-2}$-H), 5.30 (C$_{8-7}$-H) and 5.82 ppm (C$_{6-5}$-H) (Figure S6), which appear at significantly higher field than in free naphthalene ($\delta = 7.45$ and 7.84 ppm, in [D$_7$]THF). Similarly, 2-anth shows five upfield shifted signals for the reduced anthracene ligand at $\delta = 2.63$ (C$_{1-2}$-H), 4.96 (C$_{2-3}$-H), 5.06 (C$_{3-4}$-H), 6.48 (C$_{4-5}$-H) and 6.55 ppm (C$_{5-6}$-H) (Figure S10). The most upfield shifted multiplet at $\delta = 2.63$ for 2-anth also confirms that the anthracene ligand coordinates via its terminal and not by its central ring, because in this case the C$_{6-5}$-H singlet signal should be most upfield shifted. The same coordination behavior in solution even at elevated temperature is shown by $^1$H NMR spectra between 298 K and 363 K, which do not show any significant alteration of the signal pattern of the anthracene ligand (Figure S14), except for a broadening of some signals at higher temperature.

In order to rationalize the coordination mode of the anthracene ligand in 2-Anth-C, DFT calculations (B3PW91 functional) were carried out.$^{[14]}$ In particular, the energy difference between the 1,4- vs. the 9,10-coordination of the anthracene dianion was investigated. First of all, the two coordination modes were found to be possible with a preference of 12.0 kcalmol$^{-1}$ for the 1,4-coordination in line with the experimental observation. The HOMO of the complex clearly describes the Hf–anthracene $\pi$ interaction (Figure 2). At the Natural Bonding Orbital level, two Hf–C $\sigma$ bonds are found and appear to be strongly polarized toward C (82.5 %) in line with a pronounced ionic interaction. This explains the low Wiberg Bond Indexes (ca. 0.1) for the Hf–C bonds. At the second-order donor–acceptor Natural Bonding Orbital (NBO) analysis, donation from the C$_{7-8}$ $\pi$ bond is also found (roughly 60 kcalmol$^{-1}$), in line with a $\sigma^*$-$\pi$-coordination mode. For the 9,10-coordination mode, the bonding analysis is quite similar (WBI of 0.1) but the Hf–C bonds are found to be purely of donor–acceptor type and therefore weaker, explaining the lower stability of this coordination mode.

**Reaction with Benzonitrile**

The strong reducing nature of the anthracene complexes was exploited in the C–C coupling reaction between organonitriles and the anthracene ligand. Addition of an excess of benzonitrile to a THF solution of 2-anth at $-36^\circ$C led to a rapid color change from bright red to greenish brown. Monitoring the reaction mixture by $^1$H NMR spectroscopy revealed an immediate formation of the unusual bis(iminyl) complex [K(thf)][Hf(anth)(Xy$_2$N$_2$)Ph$_3$]$_2$ (3) as the result of insertion of two equivalents of benzonitrile into the Hf–C$_{9-10}$ bonds (Scheme 2). Compound 3 was isolated as thermolabile, red crystals after diffusion of n-pentane into a concentrated THF solution of a mixture of 2-anth and benzonitrile at $-36^\circ$C (see SI, Sec. 2.7). Compound 3 is moderately soluble in THF, sparingly soluble in aromatic solvents and insoluble in aliphatic solvents. The solid-state structure of 3 was established by single-crystal X-ray diffraction and reveals that the C–C coupling reaction proceeds through the C9/C10 atoms of the anthracene ligand, although it is coordinated to the hafnium center through its terminal ring. The molecule crystallizes as a contact ion pair with the potassium cation located in...
the amine ligand. However, the equatorial Hf–N_average single bond length compares well with the other Hf–N_average single bond lengths (d(Hf1–N_average) = 2.191 Å). The nearly identical C=N double bond lengths of the iminyl groups (d(C11–N1) = 1.245(7) Å and d(C18–N2) = 1.235(7) Å) compare well with the C=N bond lengths in our recently reported mono(iminyl) anthracene complexes of scandium [Li(thf)][Sc(N-(Bu)Xy)3(anth)(R–C=N)] (R = C6H4-4-OMe; d(C–N) = 1.259(5) Å), rBu (d(C–N) = 1.264(4) Å; n = 0–2).[16] The anthracene ligand in 3 is more flat than that in the precursor 2-anth-C, as evident from the folding angle of 13.3(4)° (3) vs. 40.6(8)° (2-anth-C). To the best of our knowledge, such a double C–C coupling reaction of reduced nitrile groups by a reduced anthracene complex is unprecedented. The reduction of organonitriles with alkali metals or with reduced arene complexes of alkali metals commonly leads to the deamination of the nitriles and C–C coupling reactions of the reduced nitrile groups are a rarely observed pathway.[6,15] However, C–C coupling between two organonitriles at group 4 metal centers is a well-known reaction.[16]

In contrast to the C3-symmetric structure in the solid state, the 1H and 13C NMR spectra of compound 3 in [D2]THF reveal an overall more symmetric (C2) structure in solution, as evident from the two set of signals in a 1:2 ratio for the triamidoamine ligand (Figure S16 and S17). The most notable signals in the 1H NMR spectrum of 3 are those of the benzylic group (C6-H@O) signals in the 13C NMR spectrum, the most characteristic signals are those of the iminyl groups (Ph=C–N@) at δ = 167.0 and 176.0 ppm. Monitoring the decomposition of 3 in [D2]THF by 1H NMR spectroscopy revealed that the diminimyl anthracene complex selectively loses one equivalent of benzonitrile to form the hafnium imido complex [K(thf)][Hf(anth)(Xy)] after migration of a proton from C9 to C10 carbon atom of the anthracene ligand (Scheme 2). In fact, stirring a greenish brown solution of 2-anth and 1 equivalent of benzonitrile at room temperature for 48 h led to the selective formation of 4, which was isolated after work-up as an analytically pure, orange solid in 61% yield (see SI, Sec. 2.8). Unlike 3, compound 4 is thermally stable, but decomposes quickly upon exposure to air. The reason behind the extrusion of one benzonitrile from 3 to form compound 4 is not known yet, but most likely is due to the steric congestion around the hafnium center in 3.

Compound 4 was characterized by multinuclear NMR spectroscopy and elemental analysis. The molecular structure was confirmed by single-crystal X-ray diffraction, which reveals a contact ion pair with the potassium cation located between two molecular fragments through the coordination with one imido nitrogen atom and three xylyl groups of the two triamido ligands and forms a polymeric structure in the solid state (Figure 4 and Figure S30). The hafnium center adopts a distorted trigonal bipyramidal coordination geometry, with the imido and the amine nitrogens occupying the
two apical positions (\(\angle N_4-N_5-H_1 = 175.60(6)\)), leaving the other three amide nitrogens on the equatorial plane. The \(H_1-N_5\) double bond of 1.9093(17) Å is significantly shorter (11.6%) than the \(H_1-N_{\text{amide}}\) bonds (\(d(H_1-N_{\text{amide}})_{\text{eq}} = 2.1588\) Å), but compares well with the reported \(H-N\) bonds in the hafnium imido complexes (\(d(H_1-N_{\text{amide}})_{\text{eq}} = 1.963\) Å) \(^{[17]}\). The anthracene group is bonded to the benzonitrile group through a double bond as evident from the C9–C41 bond length of 1.377(3) Å and the planarity around C9 (\(\Sigma \angle C_9 = 359.89^{\circ}\)) and C41 (\(\Sigma \angle C_41 = 359.92^{\circ}\)) atoms.

The \(^1\)H and \(^{13}\)C NMR spectroscopic studies provide further structural information of 4 in solution. In contrast to the \(C_3\)-symmetric structure in the solid state, compound 4 displays a time-averaged \(C_3\)-symmetry in \([D_6] \text{THF}\) at 298 K, as indicated by a single set of signals for the triamidoamine ligand (Figure S18). The most characteristic signal in the \(^1\)H NMR spectrum is that of the CH2 proton of the anthracene group at \(\delta = 3.34\) ppm that appears markedly upfield shifted compared to that of the \(C=O\) of 3 (\(\delta = 6.24\) and 6.47 ppm). In the \(^{13}\)C NMR spectrum, the signals for the doubly bonded carbon atoms C9 and C41 appear at \(\delta = 116.1\) and 160.0 ppm, respectively. These spectroscopic features fully support the solid-state structure observed by single-crystal X-ray diffraction.

DFT calculations were carried out to understand the reaction mechanism for the reaction of 2-anth with benzonitrile (Figure 5). The reaction begins with the coordination of benzonitrile to the HF center, which is slightly endothermic (3.1 kcal mol\(^{-1}\)) and forms the intermediate Int1. The endothermic reaction is explained by the fact that the coordination of benzonitrile induces the switch from 1,4- to 3,4-coordination of the anthracene ligand to the hafnium center. From Int1, two possible insertions can occur either at C1 or at C10. Both were calculated and the insertion at C10 is preferred by 8.6 kcal mol\(^{-1}\) (see TS1 and TS1’ in Figure 5). The insertion barrier is 5.1 kcal mol\(^{-1}\) (only 2.0 kcal mol\(^{-1}\) from Int1), in line with a kinetically facile reaction. The height of the barrier is easily explained by the fact that the ring slippage induced by the benzonitrile coordination implies a delocalization of the C1 lone pair and especially at the C10 position. Following the Intrinsic Reaction Coordinate it yields the merely stable 3,4-insertion of benzaldehyde (Figure 5). The reaction begins with the coordination of PhCN (Int4, –8.1 kcal mol\(^{-1}\)). The associated barrier is 3.9 kcal mol\(^{-1}\), indicating a fast reaction. This yields the formation of complex 3 that is thermodynamically stable (–15.9 kcal mol\(^{-1}\)). In the absence of a second molecule of benzonitrile, Int2 can isomerize to form a more stable complex. Indeed, a direct 1,4-hydrogen shift (from C9 to C10) with an accessible barrier of 18.8 kcal mol\(^{-1}\), yields

**Figure 4.** Molecular structure of the anion of compound 4 in the crystal lattice of 4-(C\(_6\)H\(_5\)) in the solid state with displacement parameters at 30% probability level.\(^{[2]}\) Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (\(^{\circ}\)): H1–N1 2.1682(16), H1–N2 2.1710(17), H1–N3 2.1375(17), H1–N4 2.4137(17), H1–N5 1.9093(17), N5–C2 1.345(2), C1–N2 1.377(3); N1–H1–N2 104.05(6), N2–H1–N3 117.72(6), N1–H1–N3 111.18(5), N1–H1–N4 76.91(6), N2–H1–N4 75.70(6), N3–H1–N4 74.32(6), N4–H1–N5 175.60(6), N1–N5–C41 121.78(14), N5–C41–C2 124.73(18), N5–C41–C42 113.35(16), C9–C41–C42 121.84(18).

**Figure 5.** Calculated enthalpy profile for the reaction of 2-anth with PhCN at room temperature. In the profile, [Hf] represents [K(thf)][Hf(Xy–N,N,N)]. Formal charges are omitted for clarity.

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complex 4 that is the most stable complex (−27.3 kcal mol⁻¹). Therefore, one can conclude that complex 3 is formed under kinetic control, whereas complex 4 is the thermodynamic product.

**Reaction with Azobenzene**

The reducing as well as the labile nature of the anthracene ligand in 2-anth were further explored in the reduction of azobenzene. Treatment of 2-anth with one equivalent of azobenzene led to the diphenylhydrazido(2−) complex [K][Hf(η²-PhNNPh)(Xy−N,N,N)] (5) after elimination of anthracene. In this reaction, the dianionic anthracenyl group acts as a two-electron donor ligand. Compound 5 was isolated as an analytically pure, yellow powder in 77% yield (see SI, Sec. 2.9). Although diphenylhydrazido(2−) complexes of the group 4 metals Ti and Zr are known, a corresponding hafnium analogue remained elusive and compound 5 represents the first example of a structurally characterized hafnium diphenylhydrazido(2−) complex. As a solid it is thermally stable, but decomposes instantaneously upon exposure to air.

Single-crystal X-ray diffraction of compound 5 reveals a contact ion pair with the potassium cation bonded to three THF molecules, one amide nitrogen of azobenzene and two xylyl groups of the triamidoamine ligand (Figure 6). The six-coordinate hafnium center adopts a distorted trigonal prismatic geometry. The phenyl groups of the azobenzene ligand are oriented in a staggered conformation, as evident from the C₉₋N₁−N₂−C₉₈ torsion angle of −82.6(4)°. The dianionic nature of the azobenzene ligand is evident from the elongated N−N bond (d(N−N) = 1.463(4) Å) in 5 compared to free azobenzene (d(N−N) = 1.249(4) Å). In addition, the short Hf1−N1 and Hf1−N2 bond lengths of 2.190(3) and 2.082(3) Å, respectively, compare better with the other Hf−Namm bond lengths (d(Hf1−Namm) = 2.147 Å) than the Hf1−Namm bond length of 2.347(3) Å in compound 5.

Compound 5 was further characterized by multinuclear NMR spectroscopy and its composition was confirmed by elemental analysis. The ¹H and ¹³C NMR spectra in [D₈]THF display a single set of signals for the xylyl groups and the azobenzene ligand, indicating a C₃̃-symmetric structure in solution. The higher symmetry in solution compared to the pseudo C₃̃-symmetric structure in the solid state can be rationalized with a fluxional process on the NMR time scale, which is also evident from the broadening of several signals both in the ¹H and ¹³C NMR spectra (Figure S21 and S22).

Group 4 metal hydrazido(2−) complexes are known to react with alkynes via two different pathways, depending on the type of alkyne. While terminal alkynes with a weakly acidic proton preferably protonate one of the amide groups of the hydrazido(2−) ligand to form a hydrazido(1−) complex, internal alkynes undergo cyclodaddition to form metallacycles. When compound 5 was treated with one equivalent of terminal alkyne such as phenylacetylene, selective formation of the hydrazido(1−) complex [K][H(NHN(H)Ph)(Xy−N,N,N)(C=CPh)] (6) was observed at room temperature (Scheme 3). However, compound 5 does not react with internal alkynes such as diphenylacetylene or 4,4-dimethyl-2-pentyne, probably due to the steric congestion around the hafnium center. After work-up compound 6 was isolated as an analytically pure, yellow solid in 90% yield (see SI, Sec. 2.10). It is a thermally stable solid but sensitive towards air.

Along with single-crystal X-ray diffraction, compound 6 was fully characterized by multinuclear NMR and IR spectroscopy. The composition was confirmed by elemental analysis. The crystal structure shows a disordered structure with co-crystallized solvent molecules. However, the structure confirms the expected atomic connectivity with a terminal phenyl acetylide ligand (Figure S31). Due to the disordered structure, bonding parameters were not discussed further. As expected, the ¹H and ¹³C NMR spectra in [D₈]THF at room temperature confirm a C₃̃-symmetric structure in solution and show three sets of signals for the xylyl groups (Figure S23 and S24). The most notable signal in the ¹H NMR spectrum is that of the low field shifted N−H signal at 6.36 ppm. In the ¹³C NMR spectrum, the signals for the triply bonded carbons...
of the phenyl acetylide ligand appear at 128.1 (CCPh) and 149.6 (CCPh) ppm. The IR spectrum obtained in a KBr pellet displays a weak signal at 3214 cm\(^{-1}\), which is characteristic for a N–H stretching vibration. The signal appears at a slightly lower wavenumber than that corresponding to N–H stretching in a similar zirconium hydrazido(1-) complex \([\text{ArO}](\text{Zr}(\text{Me})[\text{η}^2-\text{NPhNHPh}])\) (ArO = 2,6-di-tert-butylphenoxide) which appears at 3254 cm\(^{-1}\).[30]

**Reaction with tert-Butylacetylene**

Attempts to protonate the reduced anthracene ligand with [NEt\(_3\)H][Cl] or [NEt\(_3\)H][BPh\(_4\)] led to an unsselective decomposition of the anthracene complex 2-anth. However, the protonation with a weak Brønsted acid such as tert-butylacetylene resulted in the selective protonation of the anthracene ligand affording the diacetylide complex [K][Hf(\text{C}(=\text{C}Bu)\_n)(X\_y–N\_N)] (7) along with 9,10-dihydroanthracene (Scheme 4). Compound 7 was isolated after work-up as a light green powder in 80% yield (see SI, Sec. 2.11). Treatment of 7 with one equivalent of 18-crown-6 in THF led to the corresponding crown ether complex [K(18-crown-6)][Hf(\text{C}(\text{C}Bu)\_n)(X\_y–N\_N)] (7-C) which was isolated as green crystals by diffusion of \(n\)-hexane into a concentrated THF solution of 7-C (see SI, Sec. 2.12). Both acetylide complexes are thermally stable solids, but decompose upon exposure to air.

The diacetylide complexes 7 and 7-C were characterized by multinuclear NMR spectroscopy and elemental analysis. In addition, the molecular structure of 7-C was determined by single-crystal X-ray diffraction (Figure 7). Complex 7-C represents the first example of a structurally characterized hafnium acetylide complex outside the cyclopentadienyl ligand system.[21] In spite of the encapsulation with 18-crown-6, the potassium cation is still coordinated to a xylyl group of the triamidoamine ligand \((d(K–C) = 3.361 \text{ Å})\) and forms a contact ion pair in the solid state. The hafnium center in 7-C adopts a distorted octahedral geometry formed by the tetradeinate triamidoamine and two acetylide ligands. While the three amido nitrogen atoms coordinate to the hafnium center in a meridional fashion, the two acetylide ligands adopt a cis orientation \((\pm C_1–Hf1–C7 = 99.5(2)\)). The Hf–C distances of 2.229(7) and 2.292(7) \(\AA\) to the linear acetylide ligands \((\pm C_1–Hf1–C2 = 168.0(6)\), Hf1–C7–C8 168.1(6)) are slightly higher than that found for terminally bound hafnium acetylide complexes (2.170(5)–2.220(1) \(\AA\)).[21,22] The observed elongation of the Hf–C bonds is most likely due to the strong trans influence of the amine and amido ligands. The short C=C triple bond lengths \((d(C1–C2) = 1.213(9) \text{ Å}, d(C7-C8) = 1.214(9) \text{ Å})\) of the acetylide ligands are in the expected range for a C=C triple bond. As expected, the average Hf–N\(_{\text{min}}\) bond (2.174 \(\text{ Å}\)) is much shorter than the Hf–N\(_{\text{max}}\) bond (2.405(5) \(\text{ Å}\)).

In contrast to the C\(_1\)-symmetric structure in the solid state, the \(^{1}\text{H}\) and \(^{13}\text{C}\) NMR spectra of 7 and 7-C in [\(\text{D}_2\)]THF at room temperature display a single set of signals both for the triamidoamine and two acetylide ligands, pointing towards a C\(_2\)-symmetric structure in solution. Such a higher symmetry of 7 and 7-C suggests a fluxional process on the NMR time scale. Apart from the expected signals for the triamido amine ligand, the \(^{1}\text{H}\) NMR spectra of 7 and 7-C show a singlet at 1.07 and 1.11 ppm, respectively, corresponding to the 18 protons for the tert-butyl groups of the acetylide ligands. The most characteristic signals of 7 and 7-C in the \(^{13}\text{C}\) NMR spectrum are those of the sp-hybridized carbon of the acetylide ligands at 119.0 and 115.1 ppm for the C\(_6\) carbon atoms, and 146.6 and 151.9 ppm for the C\(_8\) carbon atoms, respectively.

**Conclusion**

We have shown that the triamidoamine supported hafnium(IV)-chloride can be selectively reduced to give a series of hafnium naphthalene and anthracene complexes. These complexes can be viewed as \([\text{HfX}_3]^-\) -type “ate” complexes of hafnium with the formal oxidation state of...
Conflict of interest

The authors declare no conflict of interest.

Keywords: arene ligand · DFT calculation · hafnium · insertion · oxidation state

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