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Imine Metathesis Catalyzed By A Silica-Supported Hafnium Imido Complex

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Supporting Information Placeholder

ABSTRACT: Well-defined single-site silica-supported hafniaaziridine complex $[(\equiv\text{Si}-\text{O})\text{Hf}(\eta^2\pi\text{-MeNCH}_2)(\eta^1\text{-NMe}_2)(\eta^1\text{-HNMe}_2)]$ was prepared using surface organometallic chemistry. Upon thermal treatment under high vacuum, the grafted species was converted into an unprecedented hafnium imido, bis-amido, complex $[(\equiv\text{Si}-\text{O})\text{Hf}(=\text{NMe})(\eta^1\text{-NMe}_2)]$. The surface complexes were characterized by elemental analysis and the following spectroscopic techniques: infrared, solid-state single and multiple quantum NMR, advanced DNP-SENS, and extended X-ray absorption fine structure. $[(\equiv\text{Si}-\text{O})\text{Hf}(=\text{NMe})(\eta^1\text{-NMe}_2)]$ catalyzed imine metathesis under mild conditions, and characterization of the reactivity showed that the imido exchange with N-(4-phenylbenzylidene)benzylamine yielded $[(\equiv\text{Si}-\text{O})\text{Hf}(=\text{NCH}_2\text{Ar})(\eta^1\text{-NMe}_2)]$, demonstrating a kind of 2+2 mechanism involving the imine and the imido, proposed reaction mechanism is also supported by DFT calculations.

KEYWORDS: heterogeneous catalysis, imine metathesis, SOMF, metalaziridine, and imido fragment.

INTRODUCTION

Understanding of a wide range of catalysts on surfaces has benefited from the fundamental approach referred to as “surface organometallic chemistry” (SOMC), whereby molecular organometallic compounds react with support surface functional groups to precisely synthesize surface species that are characterized in depth by spectroscopic methods.¹⁻² This approach has developed into “Catalysis by Design,” with surface organometallic fragments (SOMFs) selected to be intermediates in presumed catalytic cycles. Most of the well-documented SOMFs incorporate hydrocarbon ligands (M-R, M=C, M≡CR, etc.), but, recently, a similar level of understanding has emerged for metal-amide complexes

grafted on highly dehydroxylated silica surfaces as shown in (Scheme 1). A variety of examples of catalysis were observed with these complexes, including the hydroaminoalkylation of alkenes and the metathesis of imines, depending on the supported metal/nitrogen-containing-ligand combination, M- $\eta^2\text{NRCHR}$ or M=NR, respectively.³⁻⁴ The reported work on such catalysts is largely focused on imido or amido complexes (e.g., of molybdenum),⁵⁻⁶ and the nitrogen-containing ligands were generally found to be mere spectators. But recent evidence of Zr=N surface fragments³ performing imine metathesis catalysis triggered our interest in determining whether this reactivity is specific to zirconium or can be extended to other metal such as hafnium.

The imine metathesis reaction has been known since 1922, beginning with the report of Ingold and Piggott.⁷ Research reported 50 years later showed that an acid catalyst is required for this reaction, and the authors postulated the presence of an ionic intermediate.⁸ More recently Meyer et al.⁹ synthesized a Zr-containing 2,4-diazametallacyclobutane. A recent report by Di Stefano et al.¹⁰ showed that even minute amounts of primary amines can catalyze imine metathesis. Typically, the catalysts were applied at about 100°C in organic solvents.

Early transition metal catalysts supported on silica have been reported for imine metathesis catalysis (Zr,^{3, 11} Mo¹²) with some unprecedented catalytic surface intermediates being isolated.

Interest in olefin metathesis has been intense for decades, triggering continuing efforts to discover new and improved catalysts. Attention has been focused on reactions of molecules containing heteroatoms and on catalysts incorporating various transition metals. Particular interest has focused on molecules that incorporate a heteroatom in the double bond and not only an sp² C olefinic carbon.

The work reported herein extends the classes of M-N and M=N SOMFs as shown in (Scheme 1), by reported examples with hafnium using preparation strategy is akin to that employed for zirconium.³

Scheme 1. Schematic representation illustrating the conversion of the surface organometallic fragments (SOMF).¹

RESULTS AND DISCUSSION

Highly dehydroxylated silica (pretreated thermally under high vacuum at 700°C, SiO₂₋₇₀₀, and incorporating 0.3 mmol OH/g)¹³ was treated with an equivalent amount (0.33 mmol) of the precursor [Hf(NMe₂)₄] in pentane to afford silica-supported material **1** (see the Supporting Information (SI) for details). The volatile components of **1** were removed by evacuation under high vacuum to yield a white powder. Following thermal treatment of **1** at 200°C under dynamic vacuum (10⁻⁵ mbar) for 4 h, a new light-pink material **2** was generated. **1** and **2** were characterized by elemental analysis, infrared (IR) spectroscopy, and solid-state (SS) NMR spectroscopy. Further, **1** was characterized by dynamic nuclear polarization surface enhanced solid state (DNP SENS) and extended X-ray absorption fine structure (EXAFS) spectroscopy.

The IR spectra show that the isolated surface silanols on SiO₂₋₇₀₀ were nearly all consumed as the precursor [Hf(NMe₂)₄] was grafted, as evidenced by the disappearance of the 3747 cm⁻¹ band in the spectrum of **1** (Figure 1). Concomitantly, strong new bands appeared in the regions 2800–3000 cm⁻¹ (assigned to ν_{C-H} bands) and 1400–1500 cm⁻¹ (assigned to the δ_{C-H} bands). The elemental analysis (Table S1, SI) of **1** determined N/Hf and C/Hf ratios of 3.8 and 7.1, respectively. These values are higher than those expected for a monopodal surface species (the respective theoretical values are 3 and 6). The simplest explanation of the difference is that the dimethylamine evolved during the grafting reaction was partially retained on the silica surface, either by physisorption or by coordination to the metal center.¹⁴ A weak signal observed at 3294 cm⁻¹ (ν_{N-H} band) corroborates this inference. These IR results are consistent with the grafting of the amido hafnium complex to the silica via a protonolysis reaction of the amido ligand by surface silanols (with the formation of anchored ≡Si-O-Hf moieties). The elemental analysis of **2** (Table S1, SI) indicates N/Hf and C/Hf ratios of 2.5 and 4.6, respectively (theory: 2 and 4). The carbon and nitrogen contents declined after heat treatment

IR spectra of **2** (Figure 1) demonstrate a marked decrease in the intensity of the ν_{C-H} bands along with the appearance of a new

signal at 1595 cm⁻¹. These results suggest the presence of new functional groups (tentatively assigned as a symmetric ν_(M-N-C) band originating from the metal imido fragments)¹² concomitant with a partial loss of -C-H groups.

Figure 1. IR spectra of the support, SiO₂₋₇₀₀, and the anchored complexes, [(≡Si-O)-Hf(η²π-MeNCH₂)(η¹-NMe₂)(η¹-HNMe₂)] (**1**) and [(≡Si-O)-Hf(=NMe)(η¹-NMe₂)] (**2**).

Further insights into the coordination spheres of the supported hafnium complexes **1** and **2** were provided by advanced SS NMR spectroscopy and state-of-the-art DNP-SENS, and EXAFS spectroscopies. The ¹H NMR spectrum of **1** exhibits overlapping signals at 2.2 and 2.7 ppm, as expected from the various alkyl groups bonded to the nitrogen ligands (Figure S1, SI). The ¹³C CP MAS spectrum of **1** displays one intense signal at 37 ppm and a shoulder at 46 ppm, explained by the nonequivalent methyl groups in -N-(CH₃)₂. A low-field weak resonance at 81 ppm is also correlated with the proton resonance at 2.7 ppm in the HETCOR spectra. This result is consistent with a methylene (CH₂) group in a 3-membered metallacycle.¹⁵ Two-dimensional proton double- (DQ) and triple-quantum (TQ) correlation experiments were performed with **1**. A strong autocorrelation peak was observed for the signal at 2.2 ppm in both the DQ and TQ spectra (appearing at 4.4 and 6.6 ppm in the ω1 dimensions, respectively), indicative of methyl protons (Figure 2). However, the proton resonance at 2.7 ppm shows an autocorrelation only in the DQ spectrum and confirms the presence of a methylenic unit (-CH₂-) in the surface species.

EXAFS spectra of **1** were recorded at the Hf L_{III} edge, with the measurements made at liquid nitrogen temperature in a cell described elsewhere (details of the experiments and the data are shown in the SI).¹⁶ Various plausible models of the supported species were investigated in the data fitting, which is summarized in the SI. The number of statistically justified EXAFS fitting parameters was calculated on the basis of the Nyquist criterion to be 16, corresponding to at most four shells. Consequently, a combination of Hf-N, Hf-C, and Hf-O scattering paths was used to build models. The data in the SI include the best-fit parameters for each of several models that represent the data well and a discussion of how the recommended model was selected. We emphasize that, although the EXAFS data alone are not sufficient to determine the structure of **1**, the recommended model (Table 1) is

consistent with all the characterization data determined in this work and represented by the sketch shown in (Figure 2c).

The EXAFS data indicate one Hf–O shell with a coordination number of approximately 1.2 at a distance of 1.83 Å, which is much shorter than the bonding distances in the bulk compound HfO₂ (which range from 2.03 to 2.13 Å), as determined by X-ray diffraction crystallography (XRD)).^{16,17} A comparison of these distances indicates that hafnium is strongly bonded to the support. The result that this distance is less than the Hf–O distance characterizing HfO₂ is not surprising; there are examples of hafnium complexes with Hf–O distances determined by EXAFS spectroscopy that are similar to the value determined in our work and markedly less than the value characterizing bulk HfO₂.¹⁷ The coordination of the η¹-HNMe₂ ligand is indicated by a Hf–N shell with a coordination number of 1.3 at a distance of 2.24 Å. The recommended model based on our EXAFS data is consistent with the 3-membered metallacycle (η²π-MeNCH₂), as evidenced by (i) the Hf–C shell with a coordination number of 1.3 at a distance of 2.11 Å and (ii) an Hf–N shell at a distance of 2.04 Å. The latter Hf–N shell in the EXAFS fit has a coordination number of 2.0, because it accounts for both the N atom in the ring and the η¹-NMe₂ ligand; in the combined shell determined in the EXAFS fitting, these are represented with the same Hf–N distance, because the EXAFS data are not sufficient to distinguish these two shells. The lengths found for the Hf–N and Hf–C bonds are close to those observed by XRD for molecular complexes such as [N-[1,1-dimethyl-2-(ethylimino-κN)propyl]-2,6-bis(1-methylethyl)benzenaminato-κN]tri(methyl-D₃)hafnium¹⁸ (2.24 Å for Hf–C and 2.08 Å, 2.30 Å corresponding, respectively, to covalent and coordinate Hf–N bonds), [HfC₃₀H₅₈N₃Cl₃Si₄]¹⁹ (2.52–2.18 Å for Hf–N and 2.21 Å for Hf–C), and [(TC-3,3)HfN(Ar)C(CH₂Ph)₂]²⁰ (2.14–2.02 Å for Hf–N and 2.35–2.26 Å for Hf–C). Note that the calculated Hf–O and Hf–C distances are both shorter than the reported distances in pure molecular complexes. We tentatively attribute this trend as evidence of the bonding of the [Hf(NMe₂)₄] complex to the silica surface.

On the basis of these SS NMR, IR, and EXAFS data, we propose that the surface complex in **1** is [(≡Si–O)Hf(η²π-MeNCH₂)(η¹-NMe₂)(η¹-HNMe₂)] (Figure 2c).

Table 1. EXAFS structure parameters^a representing **1**.

Shell	<i>N</i>	<i>R</i> (Å)	10 ³ × Δσ ² (Å)	Δ <i>E</i> ₀ (eV)
Hf–(O–Si≡)	1. 2	1.83	2.1	-8.0
Hf– <u>N</u> HMe ₂	1. 3	2.24	0.2	-8.0
Hf– MeN <u>C</u> H ₂	1. 3	2.11	0.2	-1.0
{Hf– MeN <u>C</u> H ₂ and Hf– NMe ₂ }	2. 0	2.04	0.3	2.5

^aNotation: *N*, coordination number; *R*, distance between absorber and backscatterer atoms; Δσ², disorder term; Δ*E*₀, inner potential correction. Estimated error bounds: *N*, ±20%; *R*, ±0.02 Å; Δσ², ±20%; Δ*E*₀, ±20%. The backscatterers at distances greater than 2.7 Å from the absorber Hf atom are not fitted in this model. Model II is the recommended best-fit model (more details are presented in the SI).

Figure 2. a) 1D ¹³C CP MAS (top) and 2D ¹H–¹³C HETCOR (bottom) NMR spectra of [(≡Si–O)Hf(η²π-MeNCH₂)(η¹-NMe₂)(η¹-HNMe₂)] (**1**); b) 1D ¹H NMR spectrum (top) and ¹H–¹H DQ and ¹H–¹H TQ spectra (bottom) of **1**; c) proposed structure of surface hafnium complex in **1**.

In contrast to the 1D SS NMR spectra of **1**, those characterizing **2** include mainly a broad band at 2.2 ppm, in the ¹H NMR spectrum (the weak signal at 1.2 ppm is attributed to some minor impurities, possibly dimethyl amine), and two resonances, at 37

and 48 ppm, in the ^{13}C CP MAS NMR spectrum. Remarkably, no clear signal in the spectra was observed in the region that corresponds to the $(-\text{CH}_2-)$ group of a 3-membered metallacycle (Figure 3). Furthermore, we infer on the basis of multiple quantum experiments that the ^1H peaks appearing at 2.2 ppm originates exclusively from the $-\text{CH}_3$ groups.

Figure 3. a) 1D ^{13}C CP MAS (top) and 2D ^1H - ^{13}C HETCOR (bottom) NMR spectra of $[(\equiv\text{Si-O})\text{Hf}(\text{=NMe})(\eta^1\text{-NMe}_2)]$ (**2**); b) 1D ^1H NMR spectrum (top) and ^1H - ^1H DQ and ^1H - ^1H TQ spectra

(bottom) of **2**; c) proposed structure of surface hafnium complex in **2**.

^{15}N SS NMR spectroscopy experiments were carried out with **1** and **2** using the DNP-SENS technique (Figure 4). The spectrum obtained for **1** exhibits two resonances, centered at 7 and 32 ppm. On the basis of its relative abundance, we tentatively assign the intense signal shifted downfield at 32 ppm to the ^{15}N resonances corresponding to the tricoordinated nitrogen sites of the $(\eta^2\pi\text{-NMeCH}_2)$ and (-NMe_2) functionalities. The weak upfield-shifted signal at 7 ppm is compatible with an $\text{NH}(\text{CH}_3)_2$ moiety, even after heat treatment - HNMe_2 remains on the surface. The comparable spectrum of **2** includes an additional signal at 113 ppm along with a signal at 34 ppm that appears to be much less intense than its counterpart at 32 ppm in **1**. The 113 ppm peak is suggested to originate from the hafnium imido moieties, consistent with the 1595 cm^{-1} peak in the IR spectrum, *vide supra*.

These results are in agreement with the conversion of the hafnium metallacycle (M-NR-CH) surface fragment in **1** into a metal imido (M=N in **2**). In view of all the foregoing results, we propose $[(\equiv\text{Si-O})\text{Hf}(\text{=NMe})(\eta^1\text{-NMe}_2)]$ as the structure of **2** (Figure 3c). We assume that the coordinated sigma bonded amine $\eta^1\text{-HNMe}_2$ in $[(\equiv\text{Si-O})\text{Hf}(\eta^2\pi\text{-MeNCH}_2)(\eta^1\text{-NMe}_2)(\eta^1\text{-HNMe}_2)]$ **1** reacts with the coordinated CH_2 of the metallacycle to give $[(\equiv\text{Si-O})\text{Hf}(\text{=NMe})(\eta^1\text{-NMe}_2)]$ **2** with formation of Me_3N (observed by GC).

Figure 4. ^{15}N MAS DNP SENS spectra of a) $[(\equiv\text{Si-O})\text{Hf}(\eta^2\pi\text{-MeNCH}_2)(\eta^1\text{-NMe}_2)(\eta^1\text{-HNMe}_2)]$ (**1**) and b) $[(\equiv\text{Si-O})\text{Hf}(\text{=NMe})(\eta^1\text{-NMe}_2)]$ (**2**).

The catalytic performance of **2** was evaluated for imine metathesis under conditions similar to those reported:³ catalyst (0.0031 mmol, 4 mol% with respect to the imine substrate employed), in toluene (typically 400 μL), at 80°C (see Table 1 and SI for details). Three imine substrates were tested: N-(4-phenylbenzylidene)benzylamine (**a**), N-(4-fluorobenzylidene)-4-fluoroaniline (**b**), and N-benzylidene-tert-butylamine (**c**), (Figure 5).

Figure 5. 1) Catalyst **2** and imine substrates, 2) imine metathesis catalysis, and 3) imine metathesis mechanism.

Table 2. Results of catalytic imine metathesis testing for substrates N-(4-phenylbenzylidene)benzylamine (**a**), N-(4-fluorobenzylidene)-4-fluoroaniline (**b**), and N-benzylidene-*tert*-butylamine (**c**).*

Entry	Cat.	Time (h)	Substrate (Conversion %)	Substrate (Conversion %)
1	2	1	a (54)	c (54)
2	-	1	a (11)	c (11)
3	1	1	a (11)	c (15)
4	2	6	a (50)	b (55)
5	-	6	a (25)	b (20)
6	2	4	a (36)	b (30)

*Catalyst **2** (0.0031 mmol), in toluene (400 μL), at 80 $^{\circ}\text{C}$, both imine substrates (0.0783 mmol). Reaction solution diluted to give a volume of 1 mL; conversion determined by GC-FID.

Products consistent with imine metathesis were identified by GC-MS analyses, as expected, in all the catalytic reaction experiments. In the presence of catalyst **2**, substrates (**a**) and (**c**) reached maximum conversion in just 1 h (Entry 1, Table 2), resulting in two new products, **a'** (1-([1,1'-biphenyl]-4-yl)-N-(*tert*-butyl)methanimine) and **c'** (N,1-diphenylmethanimine). Control runs (Entry 2, Table 2, and Entry 2, Table S2) with only the substrates or with only SiO_{2-700} present in the reaction showed reduced reaction rates (giving about 10% conversion). Furthermore, a run using **1** as the catalyst (Entry 3, Table 2) showed a conversion as low as those observed in the other control runs. Taken together, these results indicate that **2** is active for imine metathesis, and that the presence of the hafnium imido group is correlated with this performance.

Similar experiments were done with substrates (**a**) and (**b**) instead of (**a**) and (**c**), and somewhat lower reaction rates were observed, with equilibrium attained in about 6 h (Entry 3, Table 1), leading to two new products, **a'** (1-([1,1'-biphenyl]-4-yl)-N-(3-fluorophenyl)methanimine) and **b'** (1-(4-fluorophenyl)-N-phenylmethanimine). These results show that the activities of our catalysts are high in comparison with those reported for this type of catalysis; for example, with a Mo-containing catalyst,¹² the reaction time was in the range of 6–50 h for attainment of equilibrium, and for a Zr-containing catalyst,¹¹ the time was 12 h.

Figure 6. a) 1D ^{13}C CP MAS (top) and 2D ^1H - ^{13}C HETCOR (bottom); NMR spectra of $[(\equiv\text{Si}-\text{O})-\text{Hf}(\text{=NCH}_2\text{Ar})(\eta^1\text{-NMe}_2)]$ (**3**); b) 1D ^1H NMR spectrum c) ^1H - ^1H DQ; d) proposed structure of surface hafnium complex in **3**.

The role of the $([\text{M}]=\text{NR})$ intermediate in the mechanism was further investigated by derivatizing **2** with one of the substrates to generate another fragment. Thus, **2** was treated in a batch reactor with N-(4-phenylbenzylidene)benzylamine (**a**) (detailed in SI) to

yield **3**, which was examined by IR and SS NMR spectroscopies and elemental analysis) (Figures 6, S3, and S4). Comparisons of the IR spectra of **2** and **3** show the appearance of several bands in the spectrum as **3** formed, in agreement with the presence of aromatic $\nu(\text{CH})$ (at 3050 cm^{-1}) and $\delta(\text{C}=\text{C})$ (at $1650\text{--}1609\text{ cm}^{-1}$). Further, elemental analysis showed an increase in the C/Hf ratio to 11.3, consistent with the exchange of a methyl group by a benzyl group (theory: 9 C per Hf atom). The SS NMR spectra of **3** clearly show the presence of aromatic $\delta\text{ CH}$ (6.9 ppm in ^1H and 126 ppm in ^{13}C). We thus propose the structure of $[(\equiv\text{Si-O})\text{Hf}(=\text{NCH}_2\text{Ar})(\eta^1\text{-NMe}_2)]$ (Figures 6, and S4) for **3**. The data clearly show that the imido ligand undergoes a 2 + 2 exchange with the imine substrates. They also confirm the reactivity of the surface fragment $([\text{M}]=\text{NR})$ toward imine substrates and its role in imine metathesis.

Density functional theory (DFT) based calculations were performed to further support the mechanism shown in (Figure 5) using the model species A, shown in (Figure 7). Coordination of the model Me-CH=N-Me imine to A is exergonic by 27.7 kcal/mol and leads to species B, having a single coordinated imine. Coordination of a second imine, leading to D, is exergonic by 11.4 kcal/mol only. Based on these considerations, we assumed B as reference structure at 0 kcal/mol, considering coordination of the second imine as the starting step along the metathesis event. Coordination of both imines occurs via the lone pair on the N atom, rather than using the $\text{C}=\text{N}$ double bond (Figure 7). The metathesis event from D, via transition state D-E, requires a reorientation of the imine, to assume a geometry consistent with the classic transition state geometry considered for olefin metathesis (Figure 7), and occurs with the low energy barrier of 10.9 kcal/mol. Evolution of transition state D-E towards the products converges into the metallacycle E, 19.1 kcal/mol lower in energy compared to D. For the sake of consistency, we also examined metathesis from the single imine coordinated intermediate B. The reaction occurs via transition state B-C, with an energy barrier of 5.0 kcal/mol, and would converge into the metallacycle C, 15.0 kcal/mol lower in energy than B. This indicates that coordination of the second imine has moderate impact on the energy barrier for the metathesis event. The most stable structure along the reaction profile is the metallacycle, indicating that liberation of the product might reveal as the rate limiting step along the reaction profile.

Figure 7. DFT energy profile for imine metathesis, with a 3D sketch of intermediates D and E, and transition state D-E. All calculations at the M06/SDD/TZVP//PBE1PBE/SDD/SVP level of theory. The emerging C-N bond in transition state D-E is colored in yellow.

CONCLUSIONS

We report the preparation of new silica-supported hafnium complexes **1**, **2**, and **3** complemented by their characterization by SS NMR and IR spectroscopies and elemental analysis. Further characterizations were carried out with EXAFS spectroscopy, giving structural information about **1**, and ^{15}N MAS DNP SENS data were obtained characterizing **1** and **2**. The data demonstrate the presence of surface fragments (MNC) in **1**, $[(\equiv\text{Si-O})\text{Hf}(\eta^2\pi\text{-MeNCH}_2)(\eta^1\text{-NMe}_2)(\eta^1\text{-HNMe}_2)]$, and $([\text{M}]=\text{N})$ in **2** and **3**, $[(\equiv\text{Si-O})\text{Hf}(=\text{NMe})(\eta^1\text{-NMe}_2)]$ and $[(\equiv\text{Si-O})\text{Hf}(=\text{NCH}_2\text{Ar})(\eta^1\text{-NMe}_2)]$, respectively. The pivotal role of $([\text{M}]=\text{NR})$ in metathesis of imine was demonstrated in catalyst testing with two pairs of substrates. The proposed reaction mechanism is also supported by DFT calculations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Elemental analysis, NMR Characterization, substrate analysis, and blank tests; Tables S1–S2; Figures S1–S6 (PDF).

EXAF data analysis details; Tables S3–S4; Figures S7 (PDF).

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Notes

The authors declare no competing financial interests.

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