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## COMMUNICATION

# “Decarbonization” of an imino N-heterocyclic carbene ligand via triple benzyl migration from hafnium†‡

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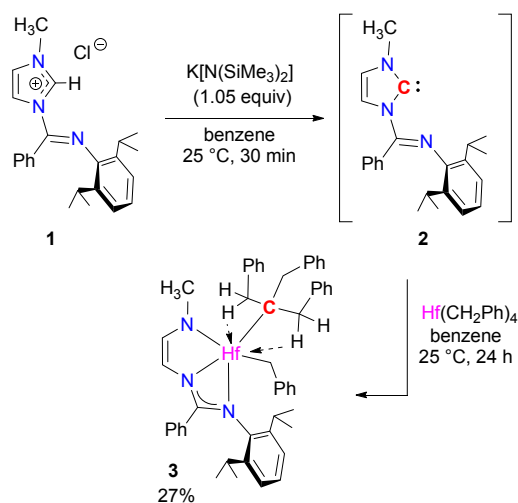
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**An imino N-heterocyclic carbene underwent three sequential benzyl migrations upon reaction with tetrabenzylhafnium, resulting in complete removal of the carbene carbon from the ligand. The resulting enamido-amidinato hafnium complex showed alkene polymerization activity comparable to that of a precatalyst containing the intact iminocarbene ligand.**

N-heterocyclic carbenes (NHCs) have attained status as one of the most versatile classes of ancillary ligands for transition metals due to their strong donor ability, ease of modification, and chemical robustness.<sup>1</sup> Their high donicity arises from a  $\sigma$ -type HOMO, which functions as a strongly Lewis basic “lone pair” centered on carbon.<sup>2</sup> Equally important is the high energy of the  $\pi$ -type LUMO,<sup>3</sup> which renders the NHC donor carbon generally unreactive toward nucleophiles, in contrast to related Fischer carbenes.<sup>4</sup> However, a growing number of reports indicate that the carbene carbon of a coordinated NHC is prone to various types of reactions under some circumstances.<sup>5–12</sup> Several of these processes result in modified ligands in which the former carbene carbon remains metal-bound. These include 1,2-migration of a single methyl<sup>7</sup> or benzyl<sup>8</sup> ligand to form an N-heterocyclic alkyl ligand which may undergo ring-opening,<sup>7b</sup> C-C reductive elimination to form an  $\eta^2$ -bound imidazolidinium cation,<sup>9</sup> and ring-expansion via insertion of the metal into a C-N bond.<sup>10–12</sup> It is important to delineate and understand such processes, as they represent potential catalyst degradation—or activation—pathways. Herein we report an unprecedented metal-induced transformation of an NHC that proceeds further than in previous examples, resulting in complete removal of the carbene carbon from the ligand upon triple benzyl migration. The resulting chelate complex is a competent precatalyst for alkene polymerization.

Imino-N-heterocyclic carbenes are an appealing class of chelate ligands that combine the soft-donor properties of an NHC with a hard-donor imine group.<sup>13,14</sup> Bidentate imino-NHCs, and related tridentate chelates,<sup>15</sup> have been investigated as ancillary ligands in several catalytic reactions involving late metals<sup>13b,15a,16</sup> and have recently shown merit in alkene polymerizations with early transition metals.<sup>15c,15d,17</sup> Notably,

reactions of imine-containing *N,N*-chelate ligands with early metal alkyl or benzyl complexes sometimes lead to 1,2-insertion reactions, affording modified chelates in which a neutral imine has been converted to an anionic amido moiety.<sup>18</sup> Some complexes of these anionic chelate ligands have shown promising activity in alkene polymerization.<sup>18b–f,19</sup> We hypothesized that the imine group of an imino-NHC might undergo a similar transformation, potentially providing a route to strongly donating, anionic heterochelate ligands.



**Scheme 1** Carbon abstraction from an imino N-heterocyclic carbene upon reaction with tetrabenzylhafnium.

Treatment of known imino-imidazolium salt **1** (Scheme 1)<sup>13f</sup> with potassium or lithium hexamethyldisilazide (KHMDs or LiHMDs) in  $C_6D_6$  at 25° afforded species that lacked a downfield peak for the acidic proton at C2 and exhibited somewhat broadened <sup>1</sup>H NMR peaks for other hydrogen atoms (see Figure S1, ESI), suggestive of fluxional alkali metal coordination to the free iminocarbene (**2**).<sup>20</sup> Attempts to isolate **2** afforded material that contained significant impurities and underwent faster degradation in solution; thus, **2** was generated

in situ for metalation reactions. Addition of tetrabenzylhafnium to a  $C_6H_6$  solution of **2** prepared with  $KHMDS^{21}$  resulted in slow appearance, over 24 h, of a deep red color. Red crystals were obtained by concentrating a filtered pentane solution of the residue obtained after removal of benzene. Although NMR tube experiments indicated nearly quantitative conversion to a new product, the isolated yield of the material was modest due to its high hydrocarbon solubility. The  $^1H$  NMR spectrum of the isolated compound (**3**) showed two sets of diastereotopic benzyl  $CH_2$  peaks in a 3:1 ratio, along with the expected number of peaks for the iminocarbene ligand. However, no carbene resonance was observed in the expected range for a Group 4 metal-NHC complex in the  $^{13}C$  NMR spectrum (175 – 225 ppm),<sup>22</sup> and a signal consistent with an intact imine was apparent at 164.1 ppm.

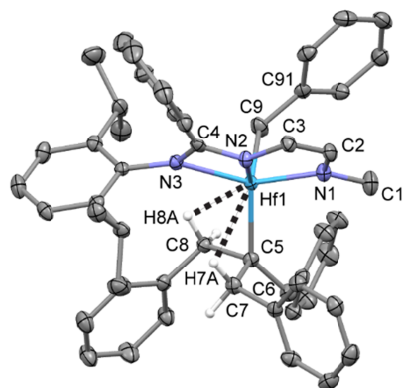


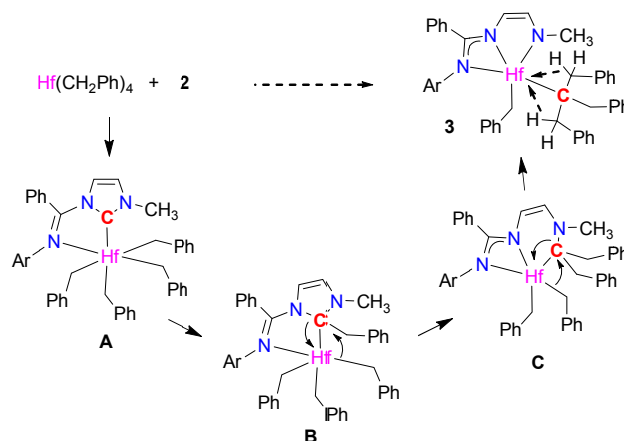
Figure 1 Molecular structure of **3** with 50% probability ellipsoids.

X-ray crystallographic analysis revealed that the iminocarbene had undergone complete excision of the carbene carbon to yield a tridentate, formally dianionic new chelate ligand coordinated to hafnium via three nitrogen atoms in **3** (Figure 1). The C-N distances in the 4-membered chelate ring are indicative of delocalized  $\pi$ -bonding [N2-C4 1.320(3) Å, N3-C4 1.359(3) Å], characterizing **3** as an eneamido-amidinate complex. To the best of our knowledge, this type of chelate ligand has not been previously reported, although a few related amino-amidinate<sup>23</sup> and amido-amidinate<sup>24</sup> ligands with saturated 5-membered chelate rings are known. Similarly to these ligands, the eneamido-amidinate of **3** is a fairly constrained tridentate chelate, with small N-Hf-N bite angles [N1-Hf-N2 70.8(1)°, N2-Hf-N3 58.8(1)°] and a slight butterfly distortion of the two chelate rings to accommodate  $\kappa^3$  binding. The former carbene carbon (C5) remains attached to Hf in a separate, and unprecedented, tribenzylmethyl ligand. An  $\eta^1$ -bound benzyl ligand with an unusually large M-CH<sub>2</sub>-Ph angle<sup>25</sup> [Hf-C9-C91 121.1(2)°] completes the Hf coordination sphere, which is best described as a distorted trigonal bipyramid with a highly bent N1-Hf1-N3 axis [129.0(1)°].

The tribenzylmethyl ligand of **3** is severely tilted, with one benzyl group canted away [Hf-C5-C6 136.9(2)°] and the other two held closely to accommodate apparent “preagostic”  $\beta$ -C-H $\cdots$ Hf interactions<sup>26</sup> [Hf $\cdots$ H7A 2.43 Å, Hf-C5-C7 94.7(1)°; Hf $\cdots$ H8A 2.33 Å, Hf-C5-C8 89.5(1)°] on the exposed side of the bent N1-Hf-N3 axis. These interactions are evidently too weak to persist in solution; the three benzyl groups appear as one AX pattern in the  $^1H$  NMR spectrum at 25 °C in toluene- $d_8$  ( $\delta$  3.4, 3.0;  $J=14.4$  Hz). Between –60 and –85 °C, this signal

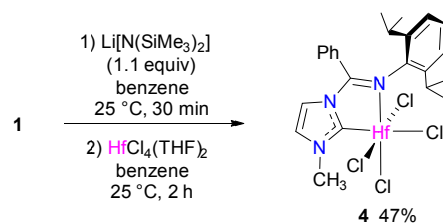
undergoes severe broadening indicative of slow exchange, but separation into distinct  $CH_2$  peaks is not observed (Figure S2, ESI). Although it is not clear whether the C-H $\cdots$ Hf interactions play a stabilizing role,<sup>27</sup> complex **3** is relatively stable toward  $\beta$ -hydrogen elimination despite the presence of six  $\beta$ -C-H bonds. No degradation of **3** was observed in toluene- $d_8$  over a week at room temperature. However, heating at 90 °C for 12 h resulted in disappearance of **3** and formation of the  $\beta$ -H elimination product 2-benzyl-1,3-diphenylpropene as indicated by characteristic  $^1H$  NMR resonances at  $\delta$  3.3, 3.5, and 6.5.<sup>28</sup>

A plausible mechanism for the formation of **3** can be proposed on the basis of previously reported carbon-centered reactions of metal-bound NHC ligands. Upon binding of the iminocarbene to Hf (**A**, Scheme 2), migration of one benzyl group likely affords a Hf-bound N-heterocyclic alkyl complex (**B**), following similar precedent for Pd and Zr.<sup>7a,8</sup> A second benzyl migration then triggers Hf insertion into a C-N bond to form a metallacycle (**C**), mirroring similar NHC ring-expansion reactions reported for a Ni-Ph complex<sup>10</sup> and a few main group hydrides.<sup>11</sup> Finally, a third benzyl ligand migrates concomitant with a second C-N bond cleavage, completing the extraction of the carbene carbon from the NHC backbone. To the best of our knowledge, there is no documented precedent for multiple alkyl/benzyl migration to an NHC or for metal-induced carbon abstraction from an NHC.<sup>29</sup> The closest report involves a minor side product of iridium-NHC metalation that contained a CO ligand apparently derived from the imidazolium C2.<sup>30</sup> However, in that case removal of carbon likely occurred following hydrolysis of the imidazolium salt precursor<sup>31</sup> rather than by metal-mediated reactions of the carbene.



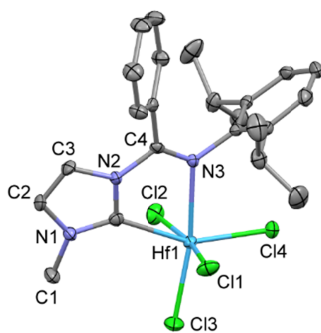
Scheme 2 Proposed mechanism for the formation of **3**.

Scheme 3 Synthesis of tetrachlorohafnium iminocarbene complex **4**.



No intermediate species en route to **3** could be obtained at shorter reaction times. However, an analogous metalation

reaction<sup>21</sup> with HfCl<sub>4</sub>(THF)<sub>2</sub> (Scheme 3) cleanly afforded the tetrachlorohafnium iminocarbene complex **4** (Figure 2), demonstrating that the NHC chelate is unmodified in the absence of strongly nucleophilic co-ligands.



**Figure 2** Molecular structure of **4** with 50% probability ellipsoids.

Reported conditions for olefin polymerization using iminocarbene-Group 4 metal complexes similar to **4** as precatalysts<sup>15c,15d,17</sup> utilize alkylaluminum cocatalysts that likely replace chloride ligands with metal alkyls. Thus, alkyl migration reactions that modify the NHC unit, such as those leading to **3**, might plausibly occur during catalyst activation. Neither **3** nor **4** showed ethylene polymerization activity under activation with methylaluminoxane. However, use of Al*i*Bu<sub>3</sub> in combination with a sulfated alumina activator/support<sup>32</sup> resulted in comparable activities for both precatalysts in ethylene polymerization and ethylene/1-hexene copolymerization (Table 1), with **3** displaying an almost two-fold increase in activity per mole of Hf relative to **4**.<sup>33</sup> These results are consistent with similar active species—possibly containing eneamido-amidinate ligands or related NHC modifications—being formed in polymerization reactions with both **3** and **4**. Although the observed activities are relatively modest, variants of **3** could be promising candidates for more useful catalysts, given high polymerization activities reported for several catalysts with tridentate hard-donor chelate ligands.<sup>34,35</sup>

**Table 1** Alkene polymerization experiments with precatalysts **3** and **4**.<sup>a</sup>

entry	catalyst	monomer(s)	yield, g	activity <sup>b</sup>	productivity <sup>c</sup>
1	<b>3</b>	C <sub>2</sub> H <sub>4</sub>	1.65	47.2	733
2	<b>4</b>	C <sub>2</sub> H <sub>4</sub>	1.29	27.6	428
3	<b>3</b>	C <sub>2</sub> H <sub>4</sub> /1-hexene <sup>[d]</sup>	1.02	29.2	453
4	<b>4</b>	C <sub>2</sub> H <sub>4</sub> /1-hexene <sup>[d]</sup>	0.73	15.6	242

<sup>a</sup>Reaction conditions: Al*i*Bu<sub>3</sub> (0.50 mmol), support (100 mg), catalyst (2 mg), isobutane (2 L), C<sub>2</sub>H<sub>4</sub> (31 bar), 80 °C, 30 min. <sup>b</sup>(g polymer)/(mmol Hf)<sup>-1</sup>bar<sup>-1</sup>h<sup>-1</sup>. <sup>c</sup>(g polymer)/(mmol Hf)<sup>-1</sup>. <sup>d</sup>2 × 10<sup>5</sup> mol hexene per mol Hf.

In summary, transfer of an imino-N-heterocyclic carbene ligand to tetrabenzylhafnium triggers three successive benzyl migrations, furnishing a dianionic chelate ligand from which the carbene carbon has been fully removed. This builds on previous reports of carbon-based reactivity at NHCs bound to strongly activating metals<sup>7-10</sup> but demonstrates a more extreme outcome than previously observed. Rather than serving as a site for benzyl migration,<sup>18</sup> the imine moiety may instead function as an electronically activating group which, in cooperation with Hf, renders the carbene carbon highly electrophilic. Given the

increasing use of NHC ligands with activating early metals<sup>36</sup> and the growing number of NHCs with electronegative substituents,<sup>14</sup> this chemistry may have implications for a number of known catalyst systems. The relevance of related NHC transformations to catalyst degradation<sup>37</sup> and/or activation processes is a topic of ongoing studies.

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## Notes and references

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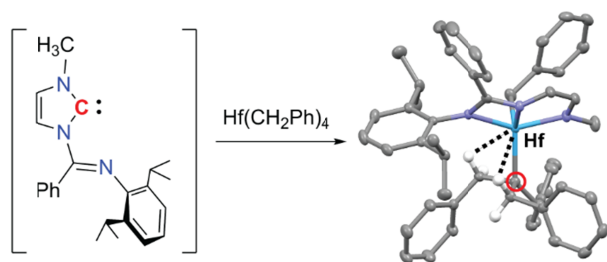
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† This paper is dedicated Prof. Peter T. Wolczanski on the occasion of his 60th birthday.

‡ Electronic Supplementary Information (ESI) available: Synthetic procedures and analytical data. CCDC 1033344 (**3**) and 1033345 (**4**). For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c000000x/

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37. NHC ring expansion was recently identified as a likely deactivation pathway in Zn catalysis: S. K. Bose, K. Fucke, L. Liu, P. G. Steel and T. B. Marder, *Angew. Chem. Int. Ed.*, 2014, **53**, 1799.

**Graphical Abstract****Table of Contents Summary**

Binding of an imino *N*-heterocyclic carbene to tetrabenzylhafnium triggers complete removal of the carbene carbon via three successive benzyl migrations.