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# Hydroaminoalkylation of sterically hindered alkenes with *N*,*N*-dimethyl anilines using a scandium catalyst<sup>†</sup>

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Received 26th October 2018, Accepted 10th December 2018 DOI: 10.1039/c8ob02657b An atom- and step-economical  $C(sp^3)$ -H addition of *N*,*N*-dimethyl anilines to various sterically demanding 1,1- and 1,2-disubstituted alkenes has been achieved by using a simple  $\beta$ -diketiminato ligand supported scandium dialkyl complex in combination with a borate compound. The corresponding  $C(sp^3)$ - $C(sp^3)$  bond forming reaction occurs with excellent regioselectivities to give a variety of tertiary aromatic amines.

## Introduction

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The development of efficient and selective methods to synthesize amines plays a leading role in synthetic organic chemistry because of the great importance of nitrogen-containing compounds in the fine chemical, pharmaceutical, and agrochemical industries.<sup>1</sup> Among various synthesis approaches,<sup>2-4</sup> transition-metal catalyzed direct addition of an  $\alpha$ -C(sp<sup>3</sup>)-H bond of an amine across a C=C double bond of an alkene, namely hydroaminoalkylation, has attracted considerable interest because it offers a route to substituted alkylamines with 100% atom economy.<sup>5</sup> Catalysts based on early transition metal complexes including Ti,<sup>6</sup> Zr,<sup>7</sup> and Ta<sup>8</sup> have made substantial progress in this area over the last decade. However, the substrate scope is still limited in primary and secondary amines because the presence of an N-H bond in the starting material is essential to form catalytically active species.

With the assistance of suitable directing groups,<sup>9–11</sup>  $\alpha$ -C (sp<sup>3</sup>)–H alkylation of tertiary amines with terminal alkenes could also be achieved by using Ru or Ir catalysts to give linear addition products (Scheme 1a). The first example of scandium-catalyzed hydroaminoalkylation of aliphatic tertiary amines with terminal or activated alkenes was recently reported by Hou and co-workers (Scheme 1b).<sup>12</sup> We subsequently showed that a scandium complex based on a  $\beta$ -diketiminato ligand with a pendant phosphine group

enabled hydroaminoalkylation of aromatic tertiary amines with terminal alkenes affording branched products for the first time (Scheme 1c).<sup>13</sup> Mechanistic studies revealed that a switch of *ortho*-C(sp<sup>2</sup>)–H activation to  $\alpha$ -C(sp<sup>3</sup>)–H activation of *N*,*N*-dimethyl aniline occurred during the reaction, which led to this anti-intuitive result.

Although intermolecular hydroaminoalkylation of tertiary aniline was realized using a scandium catalyst, only mono-substituted terminal alkenes could be used as substrates, which greatly restricted its synthesis utility. We propose that the sterically demanding β-diketiminato ancillary ligand may hinder the coordination and/or insertion of crowded alkene substrates, thus resulting in a limited substrate scope. With this in mind, we decided to investigate whether the substrate scope could be expanded by modifying the ligand framework of the scandium catalyst. We herein report the first examples of hydroaminoalkylation of tertiary amines with sterically hindered alkenes, such as 1,1-disubstituted alkenes and internal alkenes, using a scandium catalyst supported by easily accessible and less sterically encumbered an β-diketiminato ligand with substrate-dependent regioselectivity (Scheme 1d).

## **Results and discussion**

Considering both the steric and electronic features of the ligand, which are crucial to stabilize rare-earth alkyl complexes,<sup>14</sup> we decided to synthesize a less sterically demanding  $\beta$ -diketiminato ligand precursor HL <sup>15</sup> and prepare the corresponding scandium dialkyl complex 1 through the well-established alkane elimination reaction (Scheme 2). Complex 1 was solvent-free, isolated in 78% yield, and fully characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray

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Scheme 1 Intermolecular hydroaminoalkylation of tertiary amines with alkenes.



diffraction. It is notable that complex 1 is thermally stable, with no decomposition observed over 12 h at 80  $^{\circ}C$  in  $C_6D_6$  solution.

We initially examined the newly prepared scandium dialkyl complex 1 together with one equivalent of [PhNMe<sub>2</sub>H] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] for the hydroaminoalkylation of *N*,*N*-dimethyl aniline (**2a**) with 1,1-disubstituted alkene  $\alpha$ -methylstyrene, which was not tolerated by our previous catalytic system.<sup>13</sup> Excitingly, the expected  $\alpha$ -C(sp<sup>3</sup>)–H alkylation reaction took place, exclusively affording the olefin functionalized product **4a** in 91% isolated yield within 48 h under the same conditions as those in our previous work (10 mol% catalyst loading, amine/alkene molar ratio = 1.5 : 1, 120 °C, toluene as the solvent, Table 1). Notably, the hydroaminoalkylation reaction was highly regioselective with the formation of a linear product which is consistent

with that of rare-earth metal-catalyzed C–H functionalization of styrenic substrates.<sup>12,16</sup> Neither neutral complex **1** nor [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] alone showed any activity under otherwise identical conditions.

Based on this result, we subsequently investigated hydroaminoalkylation reactions of *N*,*N*-dimethyl aniline (**2a**) with a variety of **1**,**1**-disubstituted alkenes catalyzed by the scandium complex **1**/[PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] system at 120 °C in toluene and the results are summarized in Table **1**. With 10 mol% catalyst loading, a range of *meta*- and *para*-substituted  $\alpha$ -methylstyrenes were functionalized to generate the corresponding linear amination products **4b**-**4g** in good to excellent isolated yields. When using **1**,**3**- or **1**,**4**-diisopropenylbenzene as the olefinic substrate, the dialkylation product **4h** or **4i** could be selectively obtained by increasing the amount of the



<sup>*a*</sup> Reaction conditions: 2a (0.81 mmol), 3 (0.54 mmol), toluene (2.0 mL), isolated yield. <sup>*b*</sup> 2a (1.62 mmol), 3 (0.54 mmol). <sup>*c*</sup> The reaction was performed at 150 °C.

starting aniline. Even with more crowded a-substituted styrenes, the reactions still occurred, providing access to the expected addition products 4j-4l although with a prolonged reaction time. Bulky 1,1-diphenylethylene, which is quite a challenging alkene substrate, was converted to the functionalization product 4m by increasing the reaction temperature from 120 °C to 150 °C. Furthermore, two gem-dialkyl substituted alkenes, methylenecyclopentane and methylenecyclohexane, were also tested as substrates. Remarkably, the reactions showed completely different regioselectivities from those of the styrenic substrates. The  $C(sp^3)-C(sp^3)$  bond forming reactions took place exclusively at a more substituted carbon to generate branched products 5a and 5b with newly formed β-quaternary carbon centers, albeit requiring an elevated temperature (150 °C) and a prolonged reaction time (96 h). Attempts to use halogen- or oxygen-containing alkenes, such as 4-bromo-a-methylstyrene or 4-methoxy- $\alpha$ -methylstyrene, in the hydroaminoalkylation reaction failed under the standard conditions, which is probably caused by the intrinsic affinity of the rare-earth metal ion for halogens and oxygen.

Encouraged by the excellent performance of the scandiumbased catalyst system in the hydroaminoalkylation of sterically demanding 1,1-disubstituted alkenes with N,N-dimethyl aniline, we next investigated a variety of linear and cyclic internal alkenes as coupling partners under analogous conditions (Table 2). Initially, treatment of cis-3-hexene with *N*,*N*-dimethyl aniline afforded the expected  $C(sp^3)$ -H alkylation product 6a in 65% isolated yield in 48 h without other regioisomers being observed (Table 2, entry 1). In contrast, the catalytic activity of the system was much lower when using trans-3-hexene as the alkene substrate, producing compound 6a in only 21% yield even with a prolonged reaction time of 72 h (Table 2, entry 2). Hydroaminoalkylation of unactivated cyclic alkenes was also successfully achieved giving the corresponding addition products 6b-6d in moderate yields (Table 2, entries 3–5). Norbornene was highly active in the reaction, exhibiting complete conversion within 12 h (Table 2, entry 6).

Reactions of a variety of tertiary anilines with  $\alpha$ -methylstyrene promoted by the scandium complex 1/ [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] system were subsequently performed



Table 2 Scandium-catalyzed hydroaminoalkylation of *N*,*N*-dimethyl aniline with internal alkenes<sup>a</sup>

<sup>*a*</sup> Reaction conditions: **2a** (0.81 mmol), **3** (0.54 mmol), toluene (2.0 mL), isolated yield.

under our typical conditions and the results are listed in Table 3. A number of *meta-* and *para-*substituted *N,N-*dimethyl anilines containing methyl, phenyl, and ring-fused groups were efficiently alkylated at the  $\alpha$ -*N*-methyl position with sterically hindered  $\alpha$ -methylstyrene, exclusively yielding linear alkylation products **7a–7f** in 75–87% isolated yields. Polar functional groups such as –NMe<sub>2</sub> were found to be tolerated in this case, giving the monoalkylation product **7g** without noticeably changing the catalytic activity. A substituent at the *ortho*-position of *N,N-*dimethyl aniline was not tolerated even with increased catalyst loading, highlighting the importance of the presence of an *ortho-*C(sp<sup>2</sup>)–H bond in this C(sp<sup>3</sup>)–H alkylation.<sup>13</sup>

It is generally believed that *ortho*-C(sp<sup>2</sup>)–H activation will most probably occur when the stoichiometric treatment of a cationic rare-earth alkyl species with aromatic heteroatom-containing compounds *e.g.* pyridines,<sup>17</sup> anisoles,<sup>18</sup> and tertiary anilines is performed,<sup>19</sup> resulting in highly regioselective *ortho* functionalization reactions. Although the same situation occurred initially for our previous system, it finally gave a

formal  $\alpha$ -C(sp<sup>3</sup>)–H alkylation product exclusively. We thus proposed a conversion of ortho-C(sp<sup>2</sup>)-H metalation to  $\alpha$ -C(sp<sup>3</sup>)-H metalation in the mechanistic framework, which was probably induced by a sterically encumbered ligand.<sup>13</sup> To examine whether a similar reaction course might be followed in this highly regioselective scandium-catalyzed hydroaminoalkylation, we first reacted N,N-dimethyl aniline with the less hindered terminal alkene 1-octene promoted by the  $1/[PhNMe_2H][B(C_6F_5)_4]$  system under our typical conditions (Scheme 3a). After workup, this reaction gave a mixture of the branched C(sp<sup>3</sup>)-H alkylation product 8 in 30% yield and the arene ortho- $C(sp^2)$ -H alkylation product 9 in 60% yield. Second, we performed a deuterium labeling experiment to obtain more information about this reaction. The reaction of N,N-(dimethyl- $d_6$ )-p-toluidine with  $\alpha$ -methylstyrene catalyzed by  $1/[PhNMe_2H][B(C_6F_5)_4]$  gave the hydroaminoalkylation product 7a-d6, which contained 18% deuterium incorporation at the ortho position of the arene (Scheme 3b). These results, together with the finding that ortho-substituted N,N-dimethyl anilines were not tolerated by this catalytic reaction, indicated

#### Table 3Scandium-catalyzed hydroaminoalkylation of tertiary anilines with $\alpha$ -methylstyrene<sup>a</sup>



<sup>a</sup> Reaction conditions: 2 (0.81 mmol), 3a (0.54 mmol), toluene (2.0 mL), isolated yield. <sup>b</sup> 1 (20 mol%), [PhNHMe<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (20 mol%).





that *ortho*-C(sp<sup>2</sup>)-H activation might be still involved in this  $\alpha$ -C(sp<sup>3</sup>)-H alkylation reaction.

Finally, a plausible pathway for the formation of the  $C(sp^3)$ – H alkylation product was proposed based on the above observations and a previous report, and is depicted in Scheme 4. The reaction of the Sc complex 1 with [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] gives cationic Sc monoalkyl species which then reacts with *N*,*N*-dimethyl aniline to afford *ortho*-C(sp<sup>2</sup>)–H activation intermediate **A**.<sup>20</sup> Complex **A** may undergo intramolecular proton migration upon the coordination of a sterically hindered alkene to the scandium center to give **B**<sup>21</sup> rather than direct Sc–C(sp<sup>2</sup>) insertion. Subsequent 2,1-insertion of the styrenic substrate into the Sc–C(sp<sup>3</sup>) bond leads to the formation of five-membered azametallacyclic complex C,<sup>22</sup> followed by the *ortho* C(sp<sup>2</sup>)–H activation of another molecule of the amine substrate with the release of the alkylation product. Alternatively, the reaction of **C** with the amine substrate could also take place in *N*-methyl C(sp<sup>3</sup>)–H activation to give **D** with the release of the final alkylation product, which may give rise to a lower deuterium incorporation at the *ortho* 



DIPP =  $2,6^{-i}Pr_2-C_6H_3$  Cations with  $[B(C_6F_5)_4]^-$  counteranions

Scheme 4 Plausible pathway for the Sc-catalyzed hydroaminoalkylation reaction.

position as expected in the above deuterium labeling experiment.

#### Conclusions

In summary, we developed an efficient and highly regioselective catalytic hydroaminoalkylation of various sterically hindered alkenes with tertiary *N*,*N*-dimethyl anilines by using an easily accessible  $\beta$ -diketiminato ligand supported scandium dialkyl complex in the presence of [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. The experimental results revealed that an *ortho*-C(sp<sup>2</sup>)–H activation of the aniline substrate was involved in this formal  $\alpha$ -C(sp<sup>3</sup>)–H alkylation reaction. Compared with that of a previous report,<sup>13</sup> the substrate scope was expanded to 1,1- and 1,2-disubstituted alkenes by simply modifying the ligand framework of the scandium precatalyst, which may provide new insights into the rare-earth catalyst design and development.<sup>23</sup> Future work will focus on mechanistic investigations and enantioselective hydroaminoalkylation by rare-earth catalysis.

## Experimental

For a general procedure, see the ESI.†

#### Preparation of complex 1<sup>24</sup>

A toluene solution (1.5 mL) of HL (334 mg, 1.0 mmol) was added to a solution of Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (448 mg, 1.0 mmol) in toluene (1.5 mL) at room temperature. The reaction mixture was stirred for 8 h, and then the volatiles were removed under vacuum. The resulting residue was washed with *n*-hexane  $(2 \text{ mL}^*3)$  to finally give 1 as a pale yellow solid (434 mg, 78%). Crystals suitable for X-ray single crystal structure analysis were grown at -30 °C from a mixture of toluene and hexane (v/v = 1:1). Elemental analysis: calcd for C<sub>31</sub>H<sub>51</sub>N<sub>2</sub>ScSi<sub>2</sub>: C, 67.34; H, 9.30; N, 5.07; found: C, 67.77; H, 9.02; N, 4.91. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 7.20 (m, 4H, o-Ph, m-Ph), 7.10 (m, 3H, m-Ph<sup>Dipp</sup>, p-Ph<sup>Dipp</sup>), 6.99 (m, 1H, p-Ph), 5.00 (s, 1H, N=CCH), 3.15 (m, 2H, CHMe2), 1.72 (s, 3H, NCMe), 1.56 (s, 3H, NCMe), 1.35 (d,  ${}^{3}J_{HH} = 6.9$  Hz, 6H, CHMe<sub>2</sub>), 1.15 (d,  ${}^{3}J_{HH} = 6.9$  Hz, 6H, CHMe<sub>2</sub>), 0.12 (overlapped, 4H,  $CH_2SiMe_3$ , 0.11 (s, 18H, SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 168.2 (N=C), 165.4 (N=C), 145.7 (i-Ph), 142.8 (o-Ph<sup>Dipp</sup>), 140.7 (i-Ph<sup>Dipp</sup>), 130.2 (m-Ph), 127.3 (p-Ph<sup>Dipp</sup>), 126.1 (p-Ph), 125.1 (o-Ph), 124.6  $(m-Ph^{Dipp})$ , 98.7 (N=CCH), 45.0 (ScCH<sub>2</sub>Si), 28.7 (CHMe<sub>2</sub>), 25.4 (CHMe<sub>2</sub>), 24.2 (CHMe<sub>2</sub>), 23.4 (NCMe), 23.1 (NCMe), 3.4 (CH<sub>2</sub>SiMe<sub>3</sub>).

#### General procedure for the hydroaminoalkylation

Complex 1 (30 mg, 0.054 mmol) in 0.5 mL of toluene was added to a solution of  $[PhNHMe_2][B(C_6F_5)_4]$  (43 mg, 0.054 mmol) in 0.5 mL of toluene. After stirring at room temperature for 1 h, amine 2 (0.81 mmol) and alkene 3 (0.54 mmol) were added and the reaction mixture was heated and maintained at 120 °C. After completion of the reaction (monitored by <sup>1</sup>H NMR), the mixture was cooled to room temperature and the volatiles were removed under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate: 100/1, silica gel, a small amount of Et<sub>3</sub>N if necessary) to afford the alkylation product.

#### Conflicts of interest

There are no conflicts to declare.

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