Lewis Acid Triggered Reactivity of a Lewis Base Stabilized Scandium-Terminal Imido Complex: C−H Bond Activation, Cycloaddition, and Dehydrofluorination

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Ⓢ *Supporting Information*

ABSTRACT: A stable scandium-terminal imido complex is activated by borane to form an unsaturated terminal imido complex by removing the coordinated Lewis base, 4-(dimethylamino)pyridine, from the metal center. The ensuing terminal imido intermediate can exist as a THF adduct and/or undergo cycloaddition reaction with an internal alkyne, C−H activation of a terminal alkene, and dehydrofluorination of fluoro-substituted benzenes or alkanes at room temperature. DFT investigations further highlight the ease of C−H activation for terminal alkene and fluoroarene. They also shed light on the mechanistic aspects of these two reactions.

Scheme 1. Generation and Reactivity of a Coordinatively Unsaturated Scandium-Terminal Imido Intermediate (I)

Terminal imido complexes of early transition metals have attracted intense interest and been extensively studied in the past two decades.[1] The research on such complexes has revealed rich reactivity and applications in group-transfer and catalytic reactions. One exception is those complexes with rare-earth-metal ions.[2] Due to the highly polarized nature of the rare-earth-metal−nitrogen double bond, the rare-earth-metal terminal imido species once formed can easily assemble into more stable μ- or μ_n ($n = 3, 4$)-bridged bimetallic or multimetallic species,[3] or undergo C−H bond activation to give the amides.[4] Recently, we synthesized and structurally characterized the first rare-earth-metal terminal imido complexes, a DMAP (4-(dimethylamino)pyridine)-containing scandium-terminal imido complex supported by a tridentate ligand and a scandium-terminal imido complex supported by a tetradentate ligand.[5] After our works, several DMAP-containing scandium-terminal imido complexes were prepared by other groups via DMAP-promoted alkane elimination of scandium anilido methyl complexes.[6] During the reactivity study of scandium-terminal imido complexes,[7] we found that coordination of Lewis base DMAP (or a pendant arm of the supporting ligand) to scandium ion stabilizes the complexes but also reduces their reactivity due to the congested environment and coordinative saturation of the scandium center. Therefore, the complexes do not exhibit the high reactivity one would expect from the highly polar Sc=N bond. For example, the complexes are unable to activate two important substrates, alkene and internal alkyne.[8] Herein we report that the coordinated DMAP can be removed by a borane,
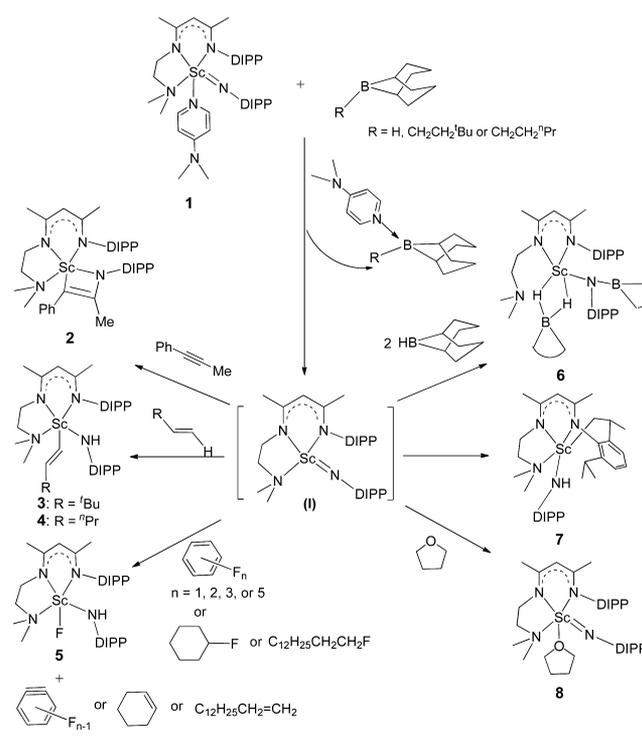
to provide a coordinatively unsaturated scandium-terminal imido intermediate (**I**), which shows an interesting reactivity toward various substrates. DFT mechanistic studies on the C−H bond activation of an α-olefin and the dehydrofluorination of pentafluorobenzene by the imido intermediate **I** are also presented to give further insight into this reactivity.

The scandium-terminal imido complex [LSc= NDIPP(DMAP)] (**1**; L = [MeC(N(DIPP))CHC(Me)(NCH₂- CH₂NMe)]⁻, DIPP = 2,6-ⁱPr₂C₆H₃),[5a] 9-BBN (9-borabicyclo- nonane), and 1-phenylpropyne were mixed in C₆D₆ at room temperature. Monitoring the reaction by ¹H NMR spectroscopy revealed the formation of a DMAP→BBN adduct and a new

complex (**2**).[9] A subsequent scaled-up reaction in toluene provided **2** in 68% yield. Complex **2** was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography, confirming that **2** is a scandium azascandacyclobutene complex, as shown in Scheme 1. To the best of our knowledge, complex **2** is the first azametallacyclobutene derivative of a rare-earth metal. Complex **2** apparently originates from a [2+2] cycloaddition between the Sc≡N double bond and the C≡C triple bond. The reaction is highly regioselective, and only the anti-Markovnikov addition product was observed. The molecular structure of **2** is shown in Figure 1. The C53−N4 bond (1.441(5) Å) is
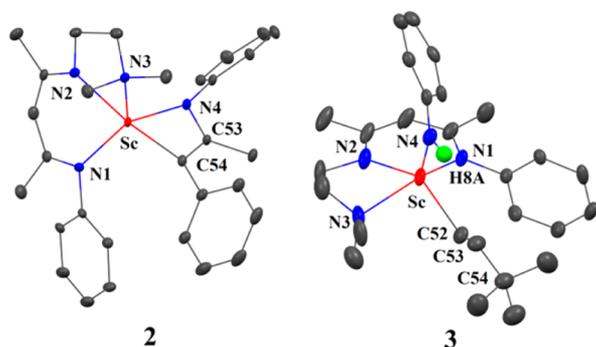

Figure 1. Molecular structures of **2** and **3** with thermal ellipsoids at 30% probability level. DIPP isopropyl groups and hydrogen atoms (except the anilido hydrogen atom) and solvent molecules in the lattice have been removed for clarity.

consistent with a single bond, whereas the C53−C54 bond (1.368(5) Å) reveals double-bond character. The C53−N4−Sc and C54−C53−N4 angles are 87.0(2)° and 118.7(3)°, respectively, the atoms C54, C53, N4, and Sc being coplanar.

Reaction of complex **1**/9-BBN with 3,3-dimethyl-1-butene at room temperature gave a scandium anilido alkenyl complex **3** in 83% yield. During the reaction, 9-BBN undergoes hydroboration with 3,3-dimethyl-1-butene to give BBN−CH$_2$CH$_2$^{t}Bu first, and the generated BBN−CH$_2$CH$_2$^{t}Bu reacts with complex **1** to provide DMAP→BBN−CH$_2$CH$_2$^{t}Bu adduct and the scandium-terminal imido intermediate **I**. Complex **3** was structurally characterized by single-crystal X-ray diffraction (XRD). There are two crystallographically independent molecules in the unit cell of **3**, and one of them is shown in Figure 1. Formation of complex **3** indicates that one terminal sp^2 C−H bond of 3,3-dimethyl-1-butene is cleaved by the scandium-terminal imido intermediate **I** during the reaction. Reaction of complex **1**/9-BBN with a less bulky terminal alkene, 1-pentene, was then studied, which showed the same reaction pattern and gave a scandium anilido alkenyl complex (**4**) in 58% yield. Complex **4** was also structurally characterized by single-crystal XRD, and its molecular structure is given in the Supporting Information (Figure S1). Although complexes **3** and **4** may have *cis* and *trans* isomers, only the *trans* isomers were observed due to steric congestion around the metal center (confirmed by the calculations). In complexes **3** and **4**, the C52−C53 bond lengths (1.317(6) (or 1.325(6)) and 1.312(6) Å, respectively) reveal substantial double-bond character. The alkenyl ligands coordinate to the scandium ion in *E*-configuration, with the Sc−C52 bond lengths being 2.221(4) (or 2.225(5)) and 2.223(4) Å, respectively. The Sc−N4 bonds in **3** and **4**, 2.046(3) (or 2.035(3)) and 2.050(3) Å, are significantly longer than the Sc═N^{imido} double bond in the scandium-terminal imido complex **1** (1.881(5) Å). This is, however, close to the Sc−N^{anilido} bond

distance in the scandium anilido methyl complex [L(CH$_3$)Sc−N(H)DIPP] (2.047(3) Å).[5a] This demonstrates that the imido ligand of **1** is transformed into an anilido in **2** and **3**. The reaction of complex **1** with 1.1 equiv of BBN−CH$_2$CH$_2$^{t}Bu, 20 equiv of 3,3-dimethyl-1-butene, and 20 equiv of deuterated 3,3-dimethyl-1-butene [(CH$_3$)$_3$CC(H)═CD$_2$] gave a substantial KIE value of 6.2, in line with a C−H bond activation. The kinetic study of the formation of **3** by the reaction of complex **1** with 2 equiv of BBN−CH$_2$CH$_2$^{t}Bu, and 50 equiv of 3,3-dimethyl-1-butene in the presence of 10 equiv of DMAP→BBN−CH$_2$CH$_2$^{t}Bu adduct, gave a pseudo-second order law, d[**3**]/dt = K_{obs}[**1**][borane]. An Eyring analysis provided activation parameters of $\Delta H^{\ddagger}$ = 11.4(5) kcal/mol, $\Delta S^{\ddagger}$ = −32(2) cal/mol, and $\Delta G^{\ddagger}$ = 20.9 kcal/mol for 298.15 K. The large negative entropy of activation observed implies a highly ordered transition state.

Based on the above experimental observations, we proceeded with the computational mechanistic investigation of the formation of complex **3**. DFT (B3PW91) calculations were conducted (see the SI for computational details). Three possible pathways for the protonation of the imido ligand using 3,3-dimethyl-1-butene were considered, namely a direct vinyl activation, 1,2-insertion followed by 1,3-hydride shift, and 2,1-insertion with subsequent 1,2-hydride shift. The latter is unlikely due to the energy-demanding 1,2-hydride shift step (Figure S34). Starting from the intermediate **I**, an intermolecular C−H activation can take place passing through **TS$_{II-3}$** to afford the final anilido complex **3** in one step (Figure 2).
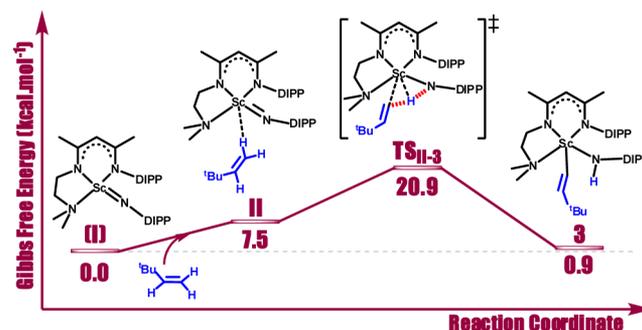

Figure 2. Plausible reaction profile for the intermolecular C−H activation.

This process is exoergic by 6.6 kcal/mol with respect to the adduct **II**. The possibility of the C−H activation to proceed from the third available hydrogen of the olefin was considered as well. However, due to the steric hindrance induced by the bulky environment of the tridentate ligand, this appears not to be possible. Instead of direct C−H activation, a reaction sequence consisting of a 1,2-insertion of the olefin and a 1,3-hydride shift was considered. Even though the activation barrier of the first step is very close in energy ($\Delta G^{\ddagger}$ = 26.8 kcal/mol) to the C−H activation barrier, the high activation barrier for the ensuing 1,3-hydride shift, 50.2 kcal/mol, makes it kinetically unreachable. The same energetic situation is revealed for the other possible isomeric pathway leading to the same product, as depicted in Figure S33.

Interestingly, reaction of complex **1**/9-BBN with 1,4-difluorobenzene at room temperature provided a scandium anilido fluoride (**5**). The molecular structure of the latter is shown in Figure S1. ^{1}H and ^{19}F NMR monitoring showed that reactions with fluorobenzene, 1,3,5-trifluorobenzene, and pentafluorobenzene at room temperature also produce complex **5**. The

reaction rate depends on the substrates as follows: fluorobenzene < 1,4-difluorobenzene ≈ 1,3,5-trifluorobenzene < pentafluorobenzene, which is inconsistent with the acidity of the substrate.[10] On the other hand, complex **1** only reacts with 1,3,5-trifluorobenzene and pentafluorobenzene at room temperature, with the reaction with 1,3,5-trifluorobenzene being very slow. NMR monitoring of the reactions revealed that a scandium anilido aryl complex **A** is first formed and converts eventually into the complex **5** (Scheme 2).

Scheme 2. Pathway for Dehydrofluorination of Fluoro-Substituted Benzenes by the Scandium-Terminal Imido Intermediate I
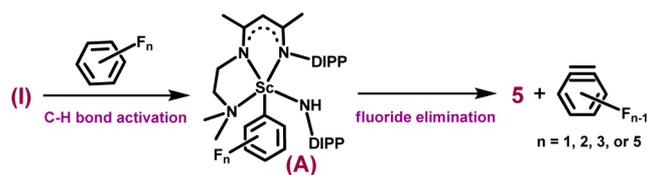
The reaction is thus defined as a sequence of an easy C−H activation followed by the break of the very strong C−F bond. The reaction with fluorobenzene is highly regioselective; only the *ortho* C−H bond activation product was observed. Such regioselectivity was already found by Mindiola and co-workers for the C−H bond activation of fluorobenzene with a transient titanium alkylidyne species.[11] Formation of complex **5** from the scandium anilido aryl complexes **A** may imply occurrence of β-fluoride elimination with subsequent benzyne formation, as previously demonstrated by Maron et al. in cerium chemistry.[12] The trapping of the putative *o*-benzynes was achieved by performing the reaction of complex **1** (or complex **1**/9-BBN) with pentafluorobenzene and durene. This gives rise to the formation of the 5,6,7,8-tetrafluoro-1,4-dihydro-2,3,9,10-tetramethyl-1,4-ethenonaphthalene, which is the product of the [2+4] cycloaddition of *o*-tetrafluorobenzyne with durene.[11] Furthermore, ^{1}H and ^{19}F NMR monitoring showed that reactions of complex **1**/BBN−$CH_2CH_2{}^tBu$ with fluoro-substituted alkanes, such as fluorocyclohexane and 1-fluorotetradecane, at room temperature gave complex **5** and olefins (cyclohexene and 1-tetradecene). To avoid the hydroboration reaction of the generated olefins with 9-BBN, the BBN−$CH_2CH_2{}^tBu$ was used instead.

A plausible reaction profile for the dehydrofluorination of C_6F_5H was computed and is given in Figure 3. It involves first a C−H activation step, which requires a relatively low energy barrier (10.5 kcal/mol). The ensuing intermediate **IV** is stabilized energetically by 9.6 kcal/mol with respect to the reactants, in agreement with the experimental observations of the formation of an anilido aryl complex (**A**). The subsequent C−F activation, yielding complex **5** and the ethenonaphthalene derivative, corresponds to the most energetically demanding step in the whole reaction coordinate, being 27.7 kcal/mol. The latter activation barrier is consistent with the experimental conditions of a slow reaction, and also in line with previous studies.[12] Overall, the reaction is exoergic by 40.9 kcal/mol, with the driving force being the energy stabilization offered by the reaction of the tetrafluorobenzene with durene. It should be noted that, in order to pass from **TS$_V$** to **TS$_{VI}$**, the side arm of the flexible amine ligand has to de-coordinate, in order to release a site for the C−F activation to proceed. The latter costs only few kcal/mol when the product of the **TS$_{V−VI}$** is stabilized by the formation of the adduct **VI**, in which the benzyne is formed a bond with the nitrogen.

The scandium-terminal imido intermediate **I** can react with 9-BBN in the absence of any substrate to provide a scandium anilido borohydride **6**. Reaction of complex **1** with 1 equiv of 9-BBN gives a DMAP→9-BBN adduct, a scandium anilido borohydride **6**, and some unreacted complex **1**. ^{1}H NMR monitoring showed that complex **1** is almost completely converted into complex **6** when 3 equiv of 9-BBN is used. A scaled-up reaction in toluene gave complex **6** in 83% yield. Therefore, addition of the B−H bond of 9-BBN to the Sc≡N double bond of **I** takes place, followed by the coordination of another 9-BBN molecule to provide the scandium anilido borohydride. The molecular structure of **6** was determined by single-crystal XRD (Figure 4). In complex **6**, the borohydrido ligand coordinates to the scandium center through two hydrogen atoms, with two different Sc−H bond distances (1.89 and 2.02 Å) and two different B−H bonds (1.20 and 1.15 Å). Due to steric congestion, the amino side arm of the tridentate nitrogen ligand (**L**) is no longer coordinated to the scandium center. The scandium-terminal imido intermediate **I** may perform an intramolecular C−H bond activation, as shown in Scheme 1. Reaction of complex **1** with 1 equiv of BBN−$CH_2CH_2{}^tBu$ at room temperature gave a scandium anilido complex (**7**) as the main product. The reaction is accelerated at 50 °C, and complex
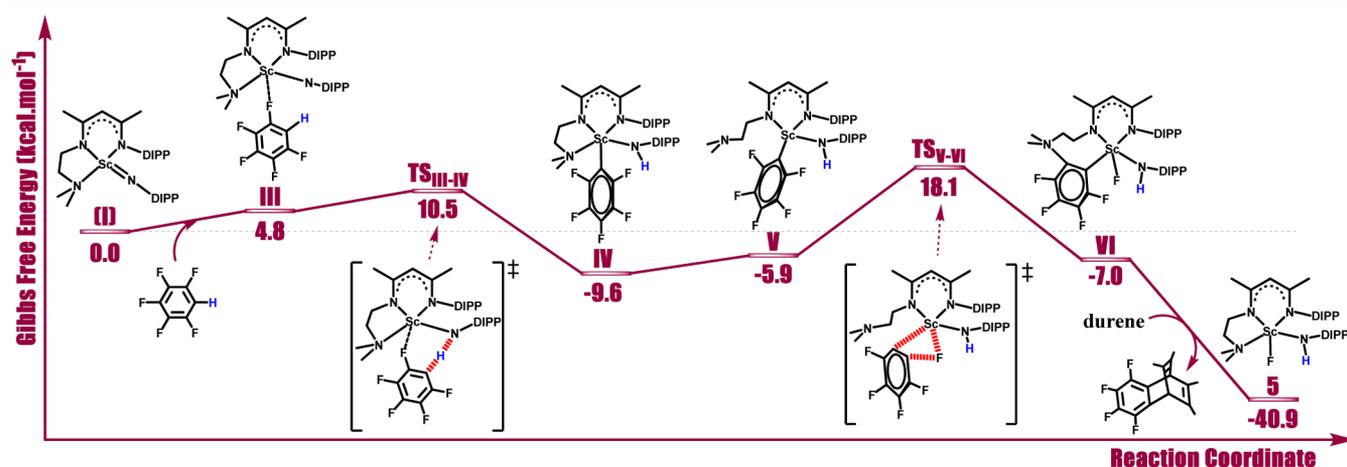

Figure 3. Plausible reaction profile for the C−H and C−F activation of pentafluorobenzene.

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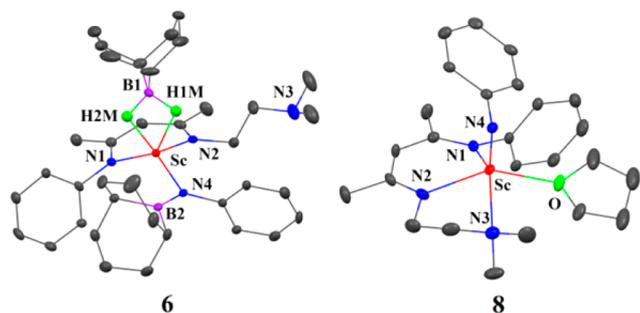dx.doi.org/10.1021/ja5061559 | *J. Am. Chem. Soc.* 2014, 136, 10894−10897

Figure 4. Molecular structures of **6** and **8** with thermal ellipsoids at the 30% probability level. DIPP isopropyl groups, hydrogen atoms (except the hydrogen atom on the borane), and solvent molecules in the lattice have been removed for clarity.

1 mostly disappeared in 16 h. A scaled-up reaction at 50 °C gave complex **7** in 52% yield. The molecular structure of **7** is shown in Figure S2. The scandium-terminal imido intermediate **I** can be trapped as a THF adduct (**8**) (Figure 4). The reaction of complex **1** with 1 equiv of 9-BBN in THF generates complex **8** almost quantitatively. The isolated yield is 45%, due to some loss in the washing procedure of the crude product by a toluene/hexane mixture in order to remove the byproduct DMAP→9-BBN adduct. XRD analysis shows that the Sc≡N(imido) bond distance and Sc−N^{imido}−C bond angle in **7** are 1.852(4) Å and 168.6(3)°, respectively. These values are close to those found in complex **1** (1.881(5) Å and 169.6(5)°, respectively).[5a]

In summary, a coordinatively unsaturated scandium-terminal imido complex is generated by removing the coordinated Lewis base, 4-(dimethylamino)pyridine, using a Lewis acid, such as a borane. The reactivity of this base-free scandium-terminal imido complex appears to be very high and especially for the activation of C−H bond of terminal alkene. Also, it can afford a cycloaddition reaction with an internal alkyne and trigger dehydrofluorination of fluoro-substituted benzenes or alkanes at room temperature. DFT mechanistic investigation of the reactivity with the 3,3-dimethyl-1-butene indicates that the reaction is a direct vinyl activation rather than a two-step reaction involving first an insertion. Similarly, computational studies of the dehydrofluorination reaction of C_6F_5H with complex **1** demonstrate that it involves first an easy C−H activation step followed by the most energy demanding *ortho* C−F abstraction.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details and a zip file containing CIFs for **1−8** and DMAP→BBN adduct. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(8) DMAP-containing scandium-terminal imido complex can react with phenylacetylene, which has the relatively acidic proton, to give a deprotonated product of scandium anilido phenylacetylido complex. The same observation was reported by Piers and co-workers in ref 6b.

(9) Some featured signals for DMAP→BBN adduct in the ^{1}H NMR spectrum (300 MHz, C_6D_6, 25 °C): δ 8.01 (d, $^3J_{HH}$ = 7.2 Hz, 2H; ortho *H* of DMAP), 5.55 (d, $^3J_{HH}$ = 7.2 Hz, 2H; *meta H* of DMAP), 1.94 (s, 6H; CN*Me$_2$*). DMAP→BBN adduct was also structurally characterized by single-crystal XRD, and its molecular structure is shown in Figure S3.

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