Scandium terminal imido complex induced C–H bond selenation and formation of an Sc–Se bond[†]

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The reaction between scandium terminal imido complexes and elemental selenium showed an unprecedented C–H bond selenation and the formation of an Sc–Se bond.

Alkyl, amide and phosphide complexes of rare-earth metals have been extensively studied during the last three decades. These complexes exhibit diverse structural properties and rich reactivities.¹⁻³ However, chemistry of their counterparts, the terminal alkylidene, imido and phosphinidene complexes, which contain typical rare-earth metal main-group element double bonds, remain unexplored. The absence of rare-earth metal terminal alkylidene, imido and phosphinidene complexes is mainly due to the relative mismatch in LUMO/HOMO orbital energies between the d⁰ rare-earth metal ions and the alkylidene (imido or phosphinidene) groups.⁴ These complexes once formed easily assemble into more stable μ or μ_n (n = 3, 4) bridged bimetallic or multi-metallic species. Thus, up to 2009, only a few examples of bridged alkylidene,⁵ imido⁶ and phosphinidene⁷ complexes, phosphorus-stabilized "pincer" type alkylidene complexes,8 or imidazolin-2-iminato complexes⁹ of rare-earth metals have been reported. Meanwhile, the increased Lewis acidity of rare-earth metal ions compared to that of group 4, 5 and 6 metal ions and highly active Ln = E (Ln = rare-earth metal; E = C, N, P) double bond should lead to fascinating reactivities. The βdiketiminato rare-earth metal complexes have attracted a growing attention in the last decade.¹⁰ Recently, we had developed a type of β-diketiminato-based tridentate ligands^{10d} and synthesized the first terminal imido complex of a rare-earth metal, [MeC(NAr)CHC(Me)(NCH₂CH₂NMe₂) (DMAP)Sc=NAr] (DMAP = 4-dimethylaminopyridine, Ar = $2,6-{}^{i}\Pr_{2}C_{6}H_{3}$ (1), by employing one of these ligands.¹¹ Herein, we report the reactivities of scandium terminal imido complexes towards elemental selenium, which induce an C-H bond selenation and the formation of an Sc-Se bond.

¹H NMR spectral monitoring of the reaction of **1** with one equivalent of elemental selenium in C_6D_6 showed that **1** was nearly completely converted into a new complex **2** at ambient

temperature during 3.5 h. The reaction was then scaled up with toluene as a solvent and the complex 2 was isolated as brownish yellow crystals (Scheme 1). Complex 2 was characterized by ¹H, ¹³C and ⁷⁷Se NMR, elemental analysis and X-ray crystallography, indicating that 2 is a scandium anilide selenolate, in which one sp² carbon at the orthoposition of the DMAP ligand was selenolated. The Sc(III) center adopts a pseudo-octahedral geometry with three nitrogen atoms of the tridentate nitrogen ligand and a selenium atom of the 2-selenolated DMAP forming the equatorial plane, and a nitrogen atom of the anilide ligand and a nitrogen atom of the 2-selenolated DMAP occupying the apical positions (Fig. 1). The anilide ligand coordinates to the metal ion with the Sc-N^{anilide} distance being 2.074(4) Å, which is close to that in a scandium anilide alkyl complex (2.047(3) Å)and is significantly longer than the Sc-N^{imido} distance (1.881(5) Å) in the scandium terminal imido complex 1.11 The 2-selenolated DMAP serves as a monoanionic bidentate ligand with the Se atom at *cis*-position to the anilide ligand and the N atom in trans-position to the anilide ligand. The Sc-Se distance is 2.7654(11) Å. To the best of our knowledge, complex 2 is the first X-ray characterized scandium selenolate.¹² The Sc-N^{DMAP} distance is 2.270(4) Å, which is very close to that in 1 [2.271(5) Å].

The formation of 2 is intriguing. As the terminal imido complex 1 is thermostable even at 70 °C for 24 h, it is unlikely that 2 is formed via a DMAP Hortho abstraction to generate an anilide pyridyl complex and followed by an insertion of selenium into the Sc-C bond of the anilide pyridyl complex. We propose that the formation of **2** might proceed via a [2 + 1]cycloaddition intermediate, where one selenium atom adds onto the Sc=N bond of the terminal imido complex 1 to form a species containing a Sc-N-Se three-membered ring (Scheme 2). This intermediate is highly unstable due to the instability of the [N-Se]²⁻ functional group¹³ and the strain in the Sc-N-Se three-membered ring and subsequent rearrangements involving N-Se bond cleavage, the transfer of Hortho of DMAP to the N atom and Cortho of DMAP to the Se atom lead to the final product 2. It is also noteworthy that the experiment showed DMAP alone does not react with



Scheme 1 Synthesis of the complex 2.

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Fig. 1 Molecular structure of **2** with thermal ellipsoids at 30% probability level. Isopropyl groups at the Ar substituents, solvent molecule, minor component of the disordered C6, C7, C31 and C32 atoms, and hydrogen atoms (except of the anilide hydrogen atom) are omitted for clarity. Selected bond distances (Å) and angles (°): Sc–N6 2.074(4), Sc–Se 2.7654(11), Sc–N4 2.270(4), Sc–N1 2.213(4), Sc–N2 2.178(4), Sc–N3 2.427(4); Sc–N6–C40 156.1(4).



Scheme 2 Proposed [2 + 1] cycloaddition intermediate.

elemental selenium either at ambient temperature or even at 50 $^\circ\mathrm{C}.$

It is important to elucidate the reaction pattern of the scandium terminal imido complex with elemental selenium in the absence of DMAP ligand. To this end, a tetradentate nitrogen ligand precursor (LH) was designed and synthesized (Scheme 3). The alkane elimination reaction between LH and $Sc(CH_2SiMe_3)_3(thf)_2$ in hexane afforded a scandium dialkyl complex 3 in 73% yield. The protonolysis of 3 with 2,6-diisopropylaniline in toluene gave a scandium anilide alkyl complex 4 in 44% yield. Single crystals of 3 and 4 were obtained and characterized by X-ray diffraction studies and the molecular structures of 3 and 4 are given in ESI[†]



Scheme 3 Synthesis of complexes 3, 4 and 5.



Fig. 2 Molecular structure of 5 with thermal ellipsoids at 30% probability level. Isopropyl groups at the Ar substitutents and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sc–N5 1.8591(18), Sc–N1 2.2398(19), Sc–N2 2.2087(19), Sc–N3 2.3731(19), Sc–N4 2.369(2); Sc–N5–C36 167.90(17).

(Fig. S1 and S2). The structural data reveal that the ligand L serves as a monoanionic tridentate ligand and the -NMe₂ group of the ligand does not coordinate to the scandium ion in neither 3 nor 4. In the synthesis of our previously reported scandium terminal imido complex 1 from its anilide alkyl precursor, the presence of external Lewis base (DMAP) is essential. Unlike in the case of the formation of 1, heating the scandium anilide alkyl complex 4 alone in hexane at 50 °C for three days gives a new scandium terminal imido complex 5 in 48% yield. The solidstate structure of 5 was established by X-ray crystallography (Fig. 2). The metal center in 5 is in a distorted square pyramid coordination environment. Of interest, four nitrogen atoms of L form the basal plane and a nitrogen atom of the imido ligand occupies the apical position. L serves as a monoanionic ligand, and the distances from the metal center to four nitrogen atoms of L are 2.2398(19), 2.2087(19), 2.3731(19) and 2.369(2) Å, respectively. The Sc-N^{imido} distance [1.8591(18) Å] is much shorter than the Sc-N^{anilide} distance [2.054(3) Å] in the corresponding scandium anilide alkyl complex 4. The Sc-N^{imido}-C angle [167.90(17)°] is significantly larger than the Sc-N^{anilide}-C angle in 4 [147.8(2)°]. The complex 5 is thermostable at room temperature for several days and very slowly decomposes at 50 °C to generate a new complex {MeC[ArN]CHC[Me][NCH₂CH₂N(Me)]Sc(NHAr)}₂ along with the release of N,N-dimethyl vinylamine via C-N bond cleavage.14

Reaction of **5** with one equivalent of elemental selenium in C_6D_6 was monitored by ¹H NMR, which indicated that **5** was nearly completely converted into a new complex **6** at ambient temperature after 12 h. The reaction was scaled up (toluene as a solvent) and complex **6** was isolated as a yellow solid (Scheme 4). Complex **6** was characterized by ¹H, ¹³C and



Scheme 4 Synthesis of the complex 6.



Fig. 3 Molecular structure of **6** with thermal ellipsoids at 30% probability level. Isopropyl groups at the Ar substitutents, solvent molecule and hydrogen atoms (except of the anilide hydrogen atom) are omitted for clarity. Selected bond distances (Å) and angles (°): Sc–N5 2.051(6), Sc–Se 2.7360(15), Sc–N1 2.260(5), Sc–N2 2.208(5), Sc–N3 2.399(5), Sc–N4 2.396(5); Sc–N5–C36 154.6(5).

⁷⁷Se NMR, elemental analysis and X-ray crystallography, indicating that **6** is a scandium anilide selenolate, in which one sp³ carbon in the $-NMe_2$ group of the ligand L was selenolated. The coordination environment of the metal center is best described as a pseudo-octahedron with three nitrogen atoms and a selenium atom of the selenolated ligand L forming the equatorial plane and a nitrogen atom of the selenolated ligand L and a nitrogen atom of the anilide ligand occupying the apical positions (Fig. 3). The selenolated ligand L serves as a dianionic pentadentate ligand, and forms one four-membered ring, two five-membered rings, and one six-membered ring, all involving the metal center. The Sc–Se distance [2.7360(15) Å] in **6** is slightly shorter than that in **2** [2.7654(11)].

The reactivities of the scandium terminal imido complexes towards elemental selenium have been studied. The reaction of **1** with elemental selenium caused one of sp^2 carbons at the *ortho*-position of the DMAP ligand to be selenolated, while in the case of **5** selenolation occurred at one of the –NMe₂ group sp^3 carbon atoms in **L**. These unprecedented C–H bond selenations are thought to proceed *via* an intermediate containing an Sc/N/Se three-membered ring, which is formed by a [2 + 1] cycloaddition of a Se atom to the Sc=N double bond. Catalytic C–H bond selenation, such as selenation of nitrogen heterocycles, catalyzed by scandium terminal imido complexes is under investigation.

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