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Reactivity of a Scandium Terminal Imido Complex Towards Unsaturated Substrates**

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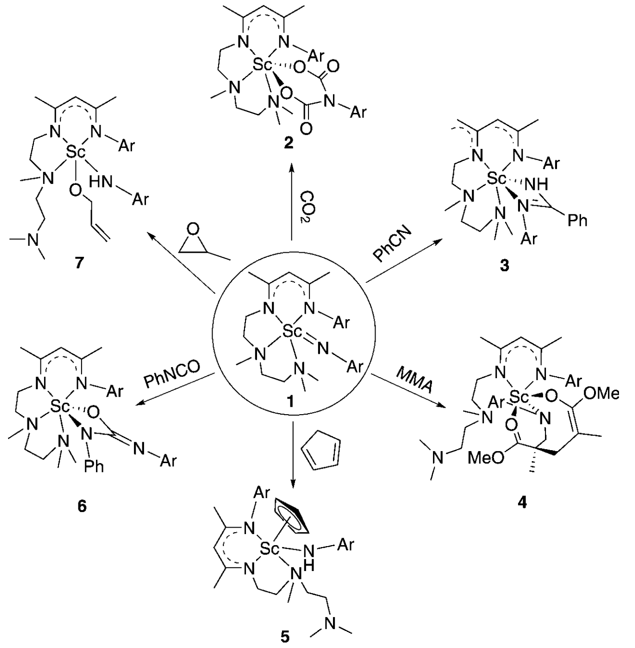
Over the last two decades, terminal imido complexes of early transition metals, which contain the M=N double bond, have attracted intensive interest and have been extensively studied.[1] The research on such complexes has revealed rich reactivities and applications in the group transfer and catalytic reactions. In contrast, the chemistry of rare-earth-metal terminal imido complexes remains unexplored. Owing to a relative mismatch in LUMO/HOMO orbital energies between the d^0 rare-earth-metal ions and the imido groups, the Ln=N (Ln = rare-earth metal) bonds are highly polar and reactive.[2] 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,[3,4] or undergo reactions with solvents by C–H bond activation.[5] Meanwhile, the chemistry of the rare-earth-metal terminal imido complexes is of great interest, as the highly polar and reactive Ln=N bonds should lead to rich reactivity. Recently, we have synthesized and characterized the first rare-earth-metal terminal imido complex, a scandium terminal imido complex.[6] Herein, we uncover reactions of the scandium terminal imido complex with a series of unsaturated substrates that show interesting reactivity and lead to novel products.



Scheme 1. Reactions of **1** with unsaturated substrates. MMA = methyl methacrylate, Ar = 2,6-(iPr)$_2$C$_6$H$_3$.

When a C$_6$D$_6$ solution of the scandium terminal imido complex, [MeC(NAr)CHC(Me)(NCH$_2$CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$)Sc=NAr] (Ar = 2,6-(iPr)$_2$C$_6$H$_3$) (**1**),[7,8] was exposed to CO$_2$ (1.0 atm) at room temperature, the solution changed from red to pale yellow in 30 minutes. Monitoring of the reaction by ^{1}H NMR spectroscopy revealed that **1** was almost completely converted into a new complex **2**. A subsequent scaled-up reaction provided **2** as colorless crystals in 53% isolated yield. **2** was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography, confirming that **2** is a scandium dicarboxylate (Scheme 1). Rare-earth-metal carboxylates are common, but to our knowledge, this type of rare-earth-metal dicarboxylate complexes has not been reported before. The formation of **2** implies two CO$_2$ molecules were activated and inserted into the Sc=N double bond of **1** during the reaction. In **2** (Figure 1), the dicarboxyl ligand coordinates to the scandium center through two carboxylic oxygen atoms with the Sc–O bond lengths of 2.002(3) and 2.026(3) Å, respectively, while the other two carboxylic oxygen atoms are not coordinated to the scandium center.

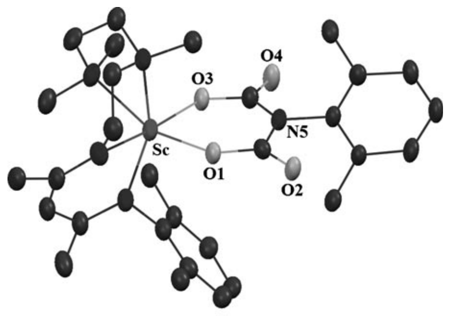


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Figure 1. Molecular structure of **2** with ellipsoids set at 20% probability. Methyl groups of the isopropyl groups on the aryl rings, hydrogen atoms, and solvent molecules in the lattice have been omitted for clarity.

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The reaction of **1** with one equivalent of benzonitrile at room temperature gave an unexpected scandium amidinate **3** with a dianionic tetradentate nitrogen ligand; complex **3** was isolated with a yield of 60 % (Scheme 1). This complex was structurally characterized by the single crystal X-ray diffraction (Figure 2). The C1–C2 (1.51 Å) and C3–C4 (1.49 Å) bonds are consistent with single bonds, whereas the C2–C3 (1.33 Å) and C4–C5 (1.34 Å) bonds reveal substantial double-bond character. The Sc–N1 (2.12 Å) and Sc–N2 (2.10 Å) bonds are significantly shorter than the Sc–N3 (2.44 Å) and Sc–N4 (2.42 Å) bonds. These structural data clearly indicate the tetradentate nitrogen ligand in **3** is dianionic, as shown in Scheme 1. This reaction is different from that of benzonitrile with rare-earth-metal-bridged imido complexes, which gave the bridged dianionic amidinate species.[3h] Scheme 2 depicts a proposed mechanism for the formation of **3**. Specifically, **1** undergoes [2+2] cycloaddition with benzonitrile to give an intermediate containing the dianionic amidinate ligand. As the bulky tetradentate nitrogen ligand prohibits the intermediate from aggregation into more stable bridged species, the dianionic amidinate ligand of the intermediate abstracts a hydrogen from the tetradentate nitrogen ligand to form the final product **3**.

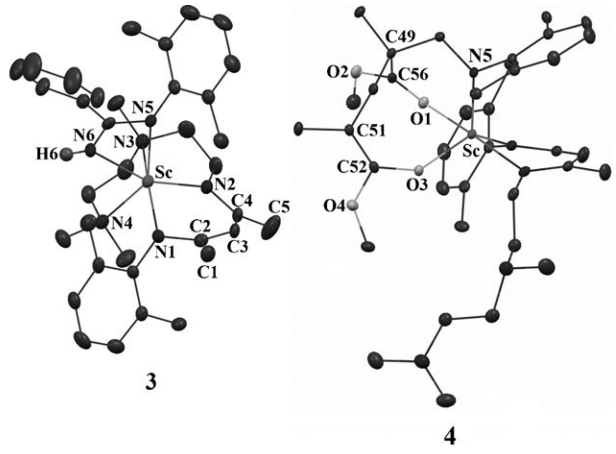
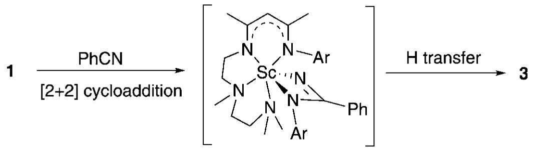
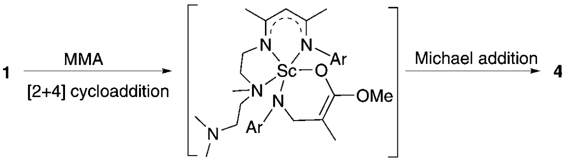


Figure 2. Molecular structures of **3** and **4** with ellipsoids set at 30% probability. Methyl groups of the isopropyl groups on the aryl rings and hydrogen atoms (except the amidinate hydrogen atom) have been omitted for clarity.



Scheme 2. Suggested reaction pathway for the formation of **3**.

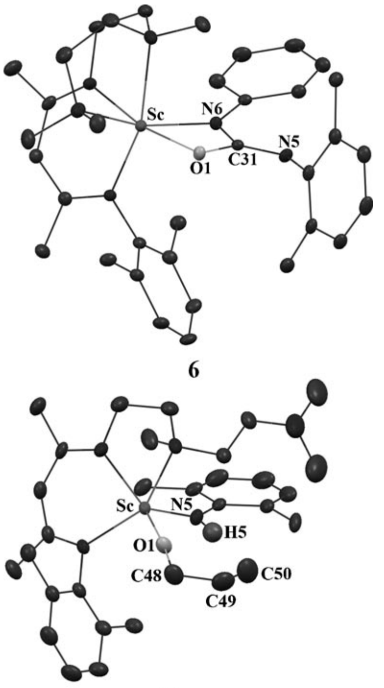
The reaction of **1** with one equivalent of methyl methacrylate (MMA) gave two products **A** and **4** along with unreacted **1**, whereas the reaction with 3.8 equivalents of MMA afforded **4** along with unreacted MMA. Complex **A** generated from the reaction of **1** with one equivalent of MMA could be rapidly converted into **4** by adding MMA. Attempts to isolate the pure products from the mixture of the reaction of **1** with one equivalent of MMA were unsuccessful. However, the reaction of **1** with 3.8 equivalents of MMA gave the pure **4** in 92 % yield of isolated product. Complex **4** is a novel scandium enolate containing two eight-membered rings (Scheme 1). Apparently, **4** is formed through two steps (Scheme 3): 1) [2+4] cycloaddition of **1** with a MMA molecule to generate a six-membered enolate intermediate; and 2) Michael addition of this enolate with another MMA molecule to give the final product **4**. The second step mimics the propagation step in early-translation-metal catalyzed MMA polymerization. The reaction of a zirconium terminal imido complex with MMA was recently reported.[9] The reaction gives a [2+4] cycloaddition product, which is robust and does not undergo Michael addition with additional MMA. In **4**, the enolate and ester fragments were characterized by the X-ray diffraction structural data (Figure 2). The bond lengths of C52–O3 (1.331(2) Å) and C51–C52 (1.344(3) Å) indicate that the C51-C52-O3 fragment has an enolate structure, while those of C56–O1 (1.229(2) Å) and C49–C56 (1.507(3) Å) reveal that the C49-C56-O1 fragment has an ester structure. Furthermore, the Sc–O3 (enolate) bond is significantly shorter than the Sc–O1 (ester) bond (1.9907(15) Å versus 2.1616(14) Å).



Scheme 3. Suggested reaction pathway for the formation of **4**.

The reaction of **1** with cyclopentadiene gave a hydrogen transfer product, a scandium cyclopentadienyl amide **5**, instead of a [2+4] or [2+2] cycloaddition product. The ^{1}H NMR spectrum of the complex shows a sharp singlet at $\delta = 6.32$ ppm with an integration value of five, which is typical for the η^5-coordinated cyclopentadienyl ligand. The signal for the amide proton appears at $\delta = 4.84$ ppm as a singlet. In contrast to those observed in complexes **1** and **2**, the two hydrogen atoms on the same CH_2 unit of the $CH_2CH_2NMe_2$ fragment in the tetradentate nitrogen ligand are equal, and two CH_2 units show two triplets at $\delta = 2.42$ and 2.55 ppm. The methyl groups of the $CH_2CH_2NMe_2$ fragment show one peak at $\delta = 2.15$ ppm. These observations indicate that the terminal amine group of the tetradentate nitrogen ligand in **5** is not coordinated to the scandium center to give the coordination sites for the cyclopentadienyl ligand.

Complex **1** also reacted with phenyl isocyanate to give a scandium N,O-bound ureate **6** in 71 % yield (Scheme 1). The X-ray diffraction analysis of the complex reveals that the nitrogen atom bound to the phenyl substituent coordinates to the scandium center (Figure 3). Therefore, an isomerization occurs after [2+2] cycloaddition of **1** with phenyl isocyanate to minimize steric interactions between the bulky 2,6-



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7

Figure 3. Molecular structures of **6** and **7** with ellipsoids set at 30% probability. Methyl groups of the isopropyl groups on the aryl rings, hydrogen atoms (except the anilide hydrogen atom), and solvent molecules in the lattice have been omitted for clarity.

diisopropylphenyl substituent and the tetradentate nitrogen ligand. The solution 2D NOESY NMR spectra of **6** are consistent with the X-ray structure.

The reactivity of **1** towards propylene oxide was also studied. The reaction provided a scandium allylic alkoxide amide **7** in 86% yield. The ^{1}H NMR spectrum of **7** shows two sets of signals in a 1:1 ratio. For example, the amido group displays two singlets at $\delta = 5.52$ and 5.55 ppm, and the methyl group of the $CH_2N(CH_3)CH_2$ fragment has two singlets at $\delta =$ 2.30 and 2.32 ppm. Therefore, **7** exists as two isomers. The solution 2D NOESY NMR spectra of the complex reveal that one isomer has the amido group located *cis* to the methyl group of the $CH_2N(CH_3)CH_2$ fragment and the other isomer has the amido group located *trans* to the methyl group of the $CH_2N(CH_3)CH_2$ fragment. Single crystals of this complex were also obtained and the structure was determined by X-ray diffraction (Figure 3).[10] It is the isomer that has the amido group located *trans* to the methyl group of the $CH_2N(CH_3)CH_2$ fragment. The bond lengths of C48−C49 (1.477(8) Å) and C48−O1 (1.390(6) Å) are consistent with single bonds, whereas the C49−C50 bond (1.272(9) Å) reveals double-bond character, indicating an allylic alkoxide structure. The formation of **7** apparently involves ring-opening and hydrogen transfer steps, but the detailed mechanism is presently unclear. The reaction possibly proceeds through a zwitterionic intermediate similar to that suggested for the reaction of zirconium terminal imido complexes with epoxides.[11]

In summary, scandium terminal imido complex **1** undergoes [2+2] or [2+4] cycloaddition with CO_2, PhCN, MMA, and PhNCO, thus clearly demonstrating the nitrogen nucleophilicity and the scandium Lewis acidity of the Sc=N double bond. The hydrogen transfer between **1** and cyclopentadiene reveals that the terminal imido group is also a good proton acceptor. The cycloaddition of **1** with unsaturated substrates is followed by other interesting reactions, including Michael addition, hydrogen transfer, and isomerization, giving rise to some structurally intriguing products. The catalytic application of the scandium terminal imido complex in organic synthesis is under investigation.

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