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Heterobimetallic Samarium(III) and Titanium(IV) Complexes with Bifunctional Catalytic Properties

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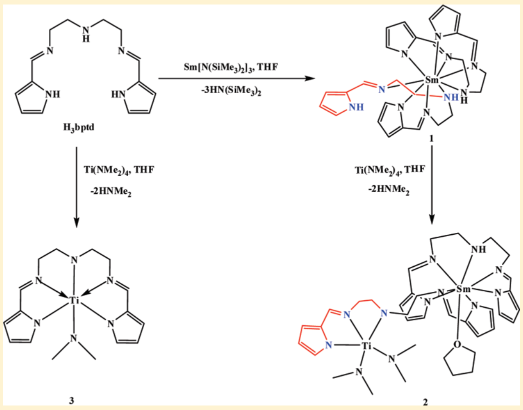
Supporting Information

ABSTRACT: Reaction of the bis-ligand-chelated samarium complex [Sm(Hbptd)(H_2bptd)] (**1**; H_3bptd =1,9-bis(2-pyrrolyl)-2,5,8-triazanona-1,8-diene), in which a pyrrolyl ring is dangling and metal-free, with $Ti(NMe_2)_4$ yielded the heterometallic complex [Sm(Hbptd)(THF)(bptd)Ti$(NMe_2)_2$] (**2**). Treatment of the H_3bptd ligand with 1 equiv of $Ti(NMe_2)_4$ gave the titanium amido complex [Ti(bptd)(NMe_2)] (**3**). Complexes **2** and **3** were able to catalyze the hydroamination of phenylacetylene with 2,4-dichloroaniline and 4-methoxyaniline, and high regioselectivities were observed for the two amines. Both **1** and **2** were active catalysts for the ring-opening polymerization of ε-caprolactone. **2** showed higher activity for the polymerization reactions, due to a decrease in the coordination number of the samarium atom (from 9 in **1** to 8 in **2**) by sharing its ligand with the titanium center.



The studies of heterobimetallic complexes have recently received great attention, because the heterometallic systems offer prospects for advantageous synergistic effects where the reactivity of the whole can be greater than the sum of the parts.[1] Recent advances have revealed the potential applications of these complexes in catalysis, optical devices, magnetism, and semiconductors.[2] Although a variety of heterometallic complexes composed of transition metal—transition metal[3,2a] and transition metal—main group metal[4] have been documented, those constructed with rare earth metal—transition metal are more uncommon due to synthetic difficulties,[5] and the complexes comprised of rare earth metal—early transition metal are even more sparse.[6] To date, there are only limited examples of alkoxide-,[7] carboxylate-,[8] and diolate-supported[9] lanthanide—early transition metal complexes.

We have been interested in heterobimetallic titanium(IV) and samarium(III) complexes supported by pyrrole-based ligands. It has been found that most of the pyrrole based ligand chelated samarium complexes exhibited high activity for the polymerization of MMA and ε-caprolactone.[10] Titanium imido or amido compounds incorporating a pyrrole-based ligand have proved to be some of the most useful catalysts thus far for the hydroamination of alkynes.[11] The combination of samarium(III), titanium(IV), and a pyrrole-based ligand in one compound offers the possibility of affording a bifunctional catalytic system, which is very active for both polymerization and hydroamination reactions.

With the idea of approaching the bifunctional heterobimetallic system in mind, we chose H_3bptd (H_3bptd = 1,9-bis(2-pyrrolyl)-2,5,8-triazanona-1,8-diene;[12] Scheme 1) as our target ligand in this study. We envisioned that use of the pentadentate ligand would provide a dangling and metal-free pyrrolyl ring, provided that 2 equiv of H_3bptd would chelate to 1 equiv of the samarium atom in order to meet the high coordination number (usually 9) of the samarium atom. This dangling and metal-free pyrrolyl ring would further coordinate with a titanium atom to yield a heterobimetallic samarium(III) and titanium(IV) complex. Along this line, we carried out a reaction involving $Sm(N(SiMe_3)_2)_3$, $Ti(NMe_2)_4$, and H_3bptd. The three complexes [Sm(Hbptd)(H_2bptd)] (**1**), [Sm(Hbptd)(THF)(bptd)Ti$(NMe_2)_2$] (**2**), and [Ti(bptd)(NMe_2)] (**3**) were synthesized. Herein, we report the syntheses and characterizations of **1**−**3**, the catalytic activities of **1** and **2** toward the ring-opening polymerization of ε-caprolactone, and the hydroamination of phenylacetylene catalyzed by **2** and **3**.

Readily accessible samarium(III), heterobimetallic samarium(III)/titanium(IV), and titanium(IV) complexes (see Scheme 1) with interesting structural features have been realized. The

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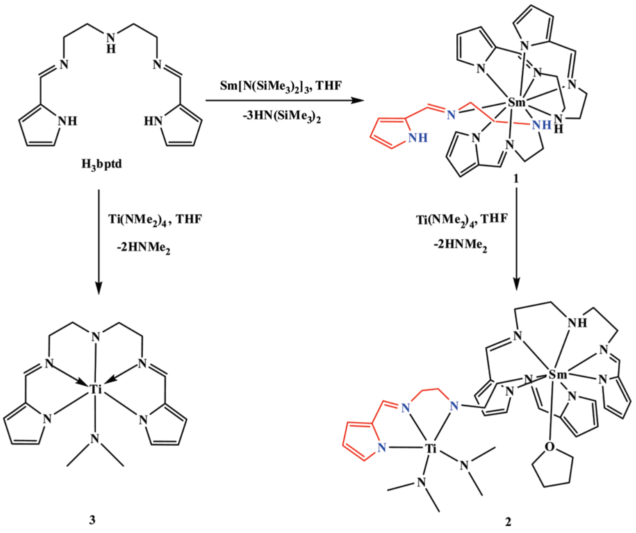
reaction of Sm(N(SiMe$_3$)$_2$)$_3$ with 2 equiv of H$_3$bptd in THF at room temperature yielded Sm(H$_2$bptd)(Hbptd) (**1**) after 16 h, with loss of 3 equiv of HN(SiMe$_3$)$_2$. Yellow **1** was synthesized in 76% of the theoretical yield.

Single-crystal X-ray diffraction studies reveal that complex **1** crystallizes in the monoclinic crystal system of the $P2_1/c$ space group.[13] The ORTEP representation of the crystal structure of **1** (Figure 1a) displays several interesting features. The overall structure is a bis-ligand-chelated mononuclear samarium complex. The two chelating ligands exhibit different coordination behaviors; i.e., 1 equiv of ligand is doubly deprotonated (the amine hydrogen atoms of the two pyrroles are deprotonated) and the doubly deprotonated ligand pentacoordinates (N1−N5) to the metal center, while the other 1 equiv of ligand is singly deprotonated and the deprotonated ligand tetracoordinates (N6, N8, N9, and N10) to the samarium atom. The coordination geometry of **1** is well described as either a distorted tricapped trigonal prism with the N2, N4, and N9 atoms as caps or as a distorted square monocapped antiprism, with the N2 atom as a cap (Figure S1, Supporting Information).

The Sm−N bond distances displayed by the doubly deprotonated ligand and the singly deprotonated ligand are remarkably different. In the doubly deprotonated ligand, the donor amine exhibits the longest bond length (Sm−N4 = 2.714(12) Å); a slight difference between Sm−N(pyrrolyl) and Sm−N(imine) is observed. The average Sm−N(pyrrolyl) bond distance is found to be 0.028 Å shorter than the average distance of the Sm−N(imine) bonds. In the singly deprotonated ligand, the trend of the Sm−N bond length is totally altered: one of the Sm−N(imine) bonds shows the longest bond distance, reaching 2.829(12) Å; the Sm−N(donor amine) is slightly shorter, being 2.671(12) Å.

Scheme 1. Syntheses of Complexes 1−3



The N8 and N9 atoms of the H$_2$bptd$^-$ ligand are weakly bonded with the metal center, and the N7 atom is protonated and metal-free. It seemed plausible that the protonated pyrrole might coordinate with another metal atom to form a new heterometallic complex.

Accordingly, stirring a 1:1 mixture of **1** and Ti(NMe$_2$)$_4$ in THF overnight led to quantitative formation of the desired complex [Sm(Hbptd)(THF)(bptd)Ti(NMe$_2$)$_2$] (**2**) (Scheme 1), which was isolated in 66% yield as an orange solid. Single-crystal X-ray analysis reveals **2** crystallizes in the triclinic crystal system of the $P\overline{1}$ space group.[13] The crystal structure of **2** is formed by one octacoordinated samarium atom and a pentacoordinated titanium atom (Figure 1b). The samarium atom is bound to five nitrogen atoms (N1 to N5) from one Hbptd^{2-} ligand, one deprotonated pyrrolyl nitrogen atom (N6), and one imine nitrogen atom (N7) from another bridging bptd^{3-} ligand. The remaining coordination position of the samarium atom is occupied by one oxygen atom of the solvate THF molecule. The overall geometry of the samarium atom is close to a distorted bicapped trigonal prism, with the N3 and O1 atoms as caps (Figure S2, Supporting Information). The average bond length of Sm−N(pyrrolyl) (2.496 Å) is shorter than the Sm−N(amine) (2.696 Å) bond length and the average Sm−N(imine) (2.548 Å) bond distance.

The titanium atom is bound to three nitrogen atoms from the bridging bptd^{3-} ligand (N8, N9, and N10) and two amide nitrogen atoms. The overall geometry of the titanium atom is remarkably close to tbp. Angles between equatorial nitrogen atoms add up to 353.46(20)°. The axial position occupied by dimethylamide is nearer to perpendicular with respect to the equatorial plane, having angles of 100.45(7), 101.75(7), and 93.85(7)° relative to those equatorial nitrogens. As expected, the imine exhibits the longest Ti−N bond in the complex: 2.1666(17) Å. A slight difference between Ti−N(pyrrolyl) and Ti−N(dimethylamide) bond lengths is observed. The Ti−N(pyrrolyl) bond distance is found to be 0.213 Å longer

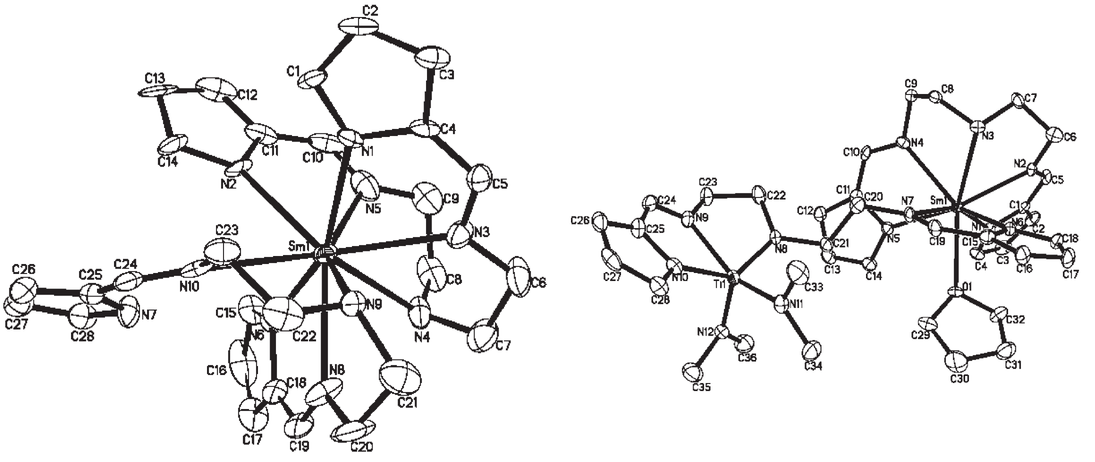


Figure 1. Molecular structures of (a) complex **1** and (b) complex **2**. H atoms have been omitted for clarity. Selected bond lengths and angles are given in the Supporting Information.

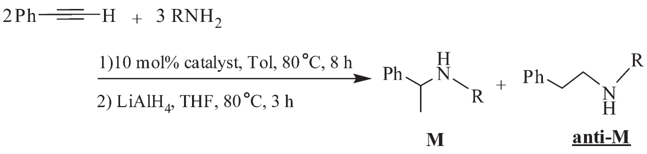
than the average Ti—N(amide) bond length. The axial Ti—N(NMe_2) bond is 1.8871(17) Å and is 0.014 Å shorter than the equatorial Ti—N(NMe_2) distance of 1.9015(17) Å.

Treatment of $Ti(NMe_2)_4$ with 1 equiv of the H_3bptd ligand in THF overnight gave [Ti(bptd)(NMe_2)] (**3**) in near-quantitative yield (Scheme 1). Complex **3** was characterized by ^1H NMR and elemental analysis (Supporting Information).

The successful isolation of the titanium amido complexes **2** and **3** prompted us to explore the catalytic activity of these two complexes in the hydroamination of alkynes, which has received intense attention.[14] The catalytic reactions were carried out at 80 °C in toluene for 8 h with a 2:3 molar ratio of phenylacetylene and amines (2,4-dichloroaniline and 4-methoxyaniline) in the presence of 10 mol % of catalyst (Table 1). Because the resulting imines are not stable to column chromatography, the hydroamination products were directly reduced to amines by $LiAlH_4$ in THF for 3 h. For comparison purposes, the results of hydroamination reactions catalyzed by $Ti(NMe_2)_4$ (**4**) are given in Table 1 as well.

The results shown in Table 1 indicated that **2**—**4** exhibited different catalytic activities and regioselectivities for the hydroamination of phenylacetylene by 2,4-dichloroaniline and 4-methoxyaniline. When complex **3** was employed as the catalyst, the two amines showed very good regioselectivity. The reaction of 2,4-dichloroaniline with phenylacetylene gave the anti-Markovnikov addition product and Markovnikov product with a ratio of 91:9. When 4-methoxyaniline was used for the reaction, the ratio of anti-Markovnikov to Markovnikov products changed to 99:1. The yields of 4-methoxyaniline (43%) and 2,4-dichloroaniline (35%) were moderate. The hydroamination results of the heterometallic complex **2** were quite similar to those of complex **3**. The anti-Markovnikov products were favored for both 4-methoxyaniline and 2,4-dichloroaniline hydroamination reactions; the yield of 4-methoxyaniline was improved (60%), and the yield of 2,4-dichloroaniline was nearly the same (31%).

Table 1. Hydroamination of Phenylacetylene with Amines Catalyzed by Complexes 2—4



cat.	amine	yield (%) (anti-M + M)	regioselectivity M:anti-M[a]
2	2,4-dichloroaniline	31	26:74
	4-methoxyaniline	60	1:99
3	2,4-dichloroaniline	35	9:91
	4-methoxyaniline	43	1:99
4	2,4-dichloroaniline	0	
	4-methoxyaniline	49	78:22

[a] Ratio of the Markovnikov and anti-Markovnikov products determined by GC-MS.

The results of the complex **4** catalyzed reactions were in contrast to utilizing **2** and **3** as catalysts. Hydroamination of phenylacetylene by 4-methoxyaniline gave predominantly Markovnikov product (M:anti-M = 78:22). No detectable catalytic activity was observed for the hydroamination reaction of 2,4-dichloroaniline under exactly similar reaction conditions.

A comparison of **2**—**4** as hydroamination catalysts leads to several conclusions. First, the active species in the complex **4** catalyzed reactions are not the same as those of **2** and **3**, for the regioselectivities and activities of these three complexes are different. Second, the titanium center of **2** retained its individual reactivity toward the hydroamination of phenylacetylene. Third, due to the fact that the coordination environment of the titanium atom in **2** is more open than that in **3**, 4-methoxyaniline hydroamination of phenylacetylene catalyzed by **2** gave higher yield.

The application of structurally well-defined organolanthanide complexes as initiators for the synthesis of poly(ε-caprolactone) (PCL) via the ring-opening polymerization of lactones has attracted particular interest.[15] These catalyst systems provide the possibility of understanding the catalyst structure/reactivity relationships.[16] To confirm the expected cooperativity of the two metal centers, the catalytic behavior of complexes **1** and **2** for the ring-opening polymerization of ε-caprolactone was examined.

The polymerization results are summarized in Table 2. It is found that both **1** and **2** can effectively initiate ε-caprolactone polymerization, and all of the obtained polymers have high molecular weights and relatively narrow molecular weight distributions (PDIs). The solvent has an obvious effect on the PDIs of the polymers. When the polymerization was conducted in ethereal solvent, such as DME and THF, relatively smaller PDIs of the polymers were found (1.26 and 1.33 for **1** in DME and THF; 1.46 and 1.58 for **2** in DME and THF), whereas the PDIs increased to 1.49 for **1** and 1.72 for **2** when the solvent was changed to toluene.

Complex **2** showed higher activity for the polymerization than compound **1**. Using **2** as the initiator, nearly quantitative yield was obtained in 2 h in DME at room temperature. In contrast, employing **1** as the initiator in the same solvent, no obvious catalytic polymerization reaction was observed at room temperature, and the system had to be heated to 60 °C to get a satisfactory yield (92%). The same trends were observed when the polymerization reactions were conducted in other solvents. The lower activity shown by complex **1** might be attributed to the fact that the nine nitrogen atoms of the two different ligands around the samarium atom make the

Table 2. Polymerization of ε-Caprolactone Initiated by 1 and 2

entry	initiator	solvent	[M]/[I]	T (h)	yield[a] (%)	temp (° C)	$10^{-4}M_n$ (calcd)[b]	$10^{-4}M_n$[c]	$10^{-4}M_n$[d]	PDI	efficiency (%)
1	**1**	DME	200	2	92	60	2.10	3.08	1.72	1.26	67.9
2	**2**	DME	200	2	97	20	2.21	3.79	2.12	1.46	61.9
3	**1**	THF	200	1	90	60	2.05	3.50	1.96	1.33	58.6
4	**2**	THF	200	1	93	20	2.12	4.07	2.28	1.58	55.3
5	**1**	Tol	200	0.4	92	60	2.10	5.77	3.23	1.49	36.3
6	**2**	Tol	200	0.3	96	40	2.19	7.49	4.19	1.72	31.0

[a] Yield: weight of polymer obtained/weight of monomer used. [b] M_n(calcd) = $M_{mono} \times [M]/[I] \times$ conv. [c] Measured by GPC relative to polystyrene standards. [d] Measured by GPC relative to polystyrene standards with Mark—Houwink corrections[17] for M_n(obsd) = $0.56M_n$ (GPC) for ε-caprolactone.

coordination sphere of the central metal much more crowded and the nonacoordinated samarium atom is relatively stable, which results in the difficulty in coordination and insertion of ε-caprolactone to the initiator. When the Ti(IV) atom was coordinated by the dangling pyrrolyl, amine, and imine nitrogen atoms of the ligand of **1**, the coordination environment of Sm(III) in **2** is less crowded, which allows facile attack by ε-caprolactone.

In summary, toward our goal of synthesis of a heterobimetallic complex and exploration of the cooperativity between the metal centers of the heterometallic complex, we have prepared the bis-ligand-chelated samarium complex **1**, the heterobimetallic samarium(III)/titanium(IV) complex **2**, and the titanium amido complex **3** by selecting H_3bptd as the ligand. The hydroamination of phenylacetylene catalyzed by **2** and **3** and the ring-opening polymerization reaction of ε-caprolactone initiated by **1** and **2** were carried out. The results of the catalytic reactions indicated that the titanium center and the samarium center retained their individual reactivities, and the heterobimetallic complex **2** showed higher activity in both hydroamination and polymerization reactions. This study could provide a rational method for the design of a heterobimetallic system with desirable properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Text, tables, figures, and CIF files giving experimental procedures and characterization and crystallographic details for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystallographic data are as follows. General information: all data sets were collected with Mo Kα radiation (graphite monochromator, $\lambda = 0.710\,73$ Å). **1**: $C_{28}H_{35}N_{10}Sm$, monoclinic, space group $P2_1/c$, $T = 293$ (2) K, $a = 9.390(1)$ Å, $b = 23.924(2)$ Å, $c = 13.7190(14)$ Å, $\beta = 113.470(2)°$, $V = 2827.0(5)$ Å^3, $Z = 4$, $F_{000} = 1340$; θ range 2.3−26.7°, 12 555 measured and 4713 independent reflections, final R index R1 = 0.0980. **2**: $C_{39.2}H_{53}N_{12}O_{1.8}SmTi$, triclinic, space group $P\overline{1}$, $a = 10.580(2)$ Å, $b = 13.715(3)$ Å, $c = 15.855(3)$ Å, $\alpha = 102.19(3)°$, $\beta = 101.24(3)°$, $\gamma = 95.28(3)°$, $V = 2184.2(8)$ Å^3, $Z = 2$, $F_{000} = 941$, θ range 1.79−20.6°, 11 119 measured and 4402 independent reflections, final R index 0.0515.

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