Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
www.zaac.wiley-vch.de
ARTICLE

DOI: 10.1002/zaac.201500072

Bis(2-cycloazylindolyl)titanium Complexes: Synthesis, Characterization, and the Catalytic Behaviors towards Hydroamination and Ring-opening Polymerization of ε-Caprolactone

Jing-Jing Zhao,[a] Hao Pei,[a] Yan-Mei Chen,[a,b] Ning Lu,[a] Jin-Na Liu,[a] Jin-Fa Hu,[a] Wei Liu,[a] Wu Li,[b] and Yahong Li*[a]

Keywords: Hydroamination; Titanium; Ring-opening polymerization; ε-Caprolactone

Abstract. The ligands 2-pyrazol-1-yl-1H-indole (HL1) and 2-[1,2,4]-triazol-1-yl-1H-indole (HL2) individually reacted with $Ti(NMe_2)_4$ in tetrahydrofuran to form the corresponding complexes $Ti(L1)_2(NMe_2)_2$ (**1**) and $Ti(L2)_2(NMe_2)_2$ (**2**), respectively. The titanium complexes were fully characterized by NMR measurement and elemental analysis as well as the single-crystal X-ray diffraction of **1** and **2**. Both **1** and **2** exhibit high activities towards intermolecular hydroamination of terminal alkynes with high selectivity, and they also efficiently promote the ring-opening polymerization of ε-caprolactone.

Introduction

The catalytic addition of N–H bond across a carbon–carbon multiple bond, known as hydroamination, is synthetically the most important approach for the substituted amines and imines.[1] Since the hydroamination reaction could provide the targeted products with 100% atom economic efficiency, both inter- and intramolecular hydroamination have attracted ever-increasing attention over the past two decades.[1] A plethora of metal-based catalytic systems have been reported to induce the hydroamination of alkynes and alkenes. Group 4 based organometallic complexes have played a prominent role in the field of catalytic hydroamination, due to their low cost, low toxicity, and high reactivity.[2] A mechanistic study for the titanium-catalyzed hydroamination of alkynes indicated that the ligand chelating to the central metal atom plays an outstanding role in controlling the regioselectivity of the hydroamination products.[3] Thus, the effects of a variety of ligands, e.g., Cp-based molecules,[4] amidate compounds,[5] pyrrolyl ligands,[6] guanidinate,[7] imidazole-containing compounds,[8] etc., on the regioselectivity of the hydroamination products have been scrutinized. All these results proved that the polydentate ligands with several nitrogen donors and deprotonable hydrogen atoms are good candidates for synthesizing titanium complexes with good catalytic activities and selectivities.

In this work, we employ 2-cycloazylindolyl ligands HL1 (HL1 = 2-pyrazol-1-yl-1H-indole) and HL2 (HL2 = 2-[1,2,4]triazol-1-yl-1H-indole) to synthesize titanium complexes. The organometallic chemistry of the titanium complexes based on these ligands remains unexplored. We anticipated that the donor (N, N) atoms of the ligands are well suited to bind high valent titanium, giving the titanium complexes with high reactivity.

The reactions of $Ti(NMe_2)_4$ with HL1 and HL2, respectively, generated $Ti(L1)_2(NMe_2)_2$ (**1**) and $Ti(L2)_2(NMe_2)_2$ (**2**). Herein, we report the synthesis and characterization of these complexes. The catalytic activities of **1** and **2** towards intermolecular hydroamination of alkynes and polymerization of ε-caprolactone were also investigated.

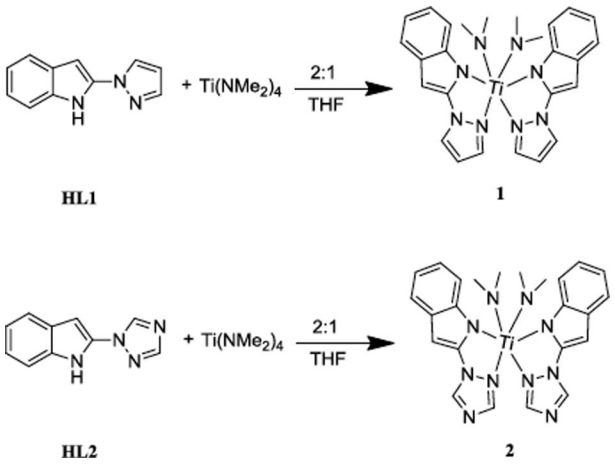
Results and Discussion

Syntheses of the Ligands and Titanium Complexes

HL1 and HL2 were prepared according to the literature procedures.[9] The addition of the HL1 ligand in THF to a cold $Ti(NMe_2)_4$ solution (–35 °C) followed by warming to room temperature afforded the product $Ti(L1)_2(NMe)_2$ (**1**) (Scheme 1). After recrystallization from Tol/hexane, dark red crystals were obtained. Complex **1** was characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. Comparison of the ^1H NMR spectrum of **1** with the corresponding ligand revealed that an additional resonance appeared in the high-field region (δ = 3.46 ppm), which was attributed to the methyl groups of NMe_2, while the N–H signal (single peak around 9.26 ppm) of the free ligand disappeared.

Complex **2** was prepared by a procedure similar to that of **1**. Complex **2** was also characterized by NMR spectroscopy

* Prof. Dr. Y. Li
Fax: +86-512-65880089
E-Mail: liyahong@suda.edu.cn
[a] Key Laboratory of Organic Synthesis of Jiangsu Province
College of Chemistry, Chemical Engineering and Materials Science
Soochow University
Suzhou, 215123, P. R. China
[b] Key Laboratory of Salt Lake Resources and Chemistry
Qinghai Institute of Salt Lakes
Chinese Academy of Sciences
Xining, 810008, P. R. China
Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201500072** or from the author.



Scheme 1. The synthesis of complexes **1** and **2**.

(^{1}H and ^{13}C) and elemental analysis. The ^{1}H NMR spectrum of **2** shows a large and broad singlet for the dimethylamido protons at δ = 3.50 being assigned to the protons of the methyl group.

The molecular structures of **1** and **2** in the solid states were confirmed by single-crystal X-ray analyses. Figure 1 and Figure 2 show the structures of **1** and **2**, respectively. The crystallographic data and experimental details for structural analyses are summarized in Table 1. The selected bond lengths and bond angles are given in Table 2.

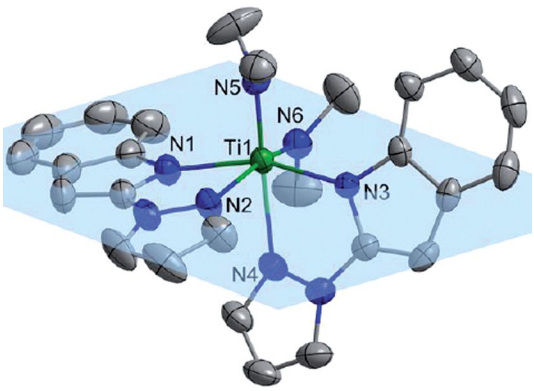


Figure 1. Molecular structure of **1** (N1, N2, N3, N6 are coplanar). Hydrogen atoms are omitted for clarity.

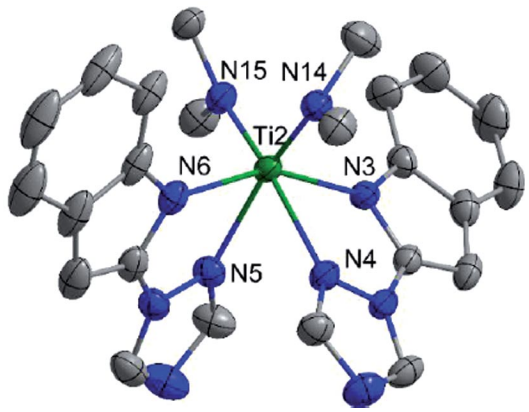


Figure 2. Molecular structure of **2** (only one of two molecules is shown). Hydrogen atoms are omitted for clarity.

Table 1. Crystallographic data and structure refinement for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{26}H_{28}N_8Ti$	$C_{24}H_{26}N_{10}Ti$
Formula weight	500.43	502.42
Temperature /K	296(2)	296(2)
Wavelength /Å	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$C2/c$
a /Å	10.0801(7)	27.195(3)
b /Å	10.3390(7)	9.5168(11)
c /Å	23.9680(17)	28.594(3)
α /°	90	90
β /°	90	94.807(2)
γ /°	90	90
V /Å^3	2497.9(3)	7374.4(14)
Z	4	12
ρ /mg·m^{-3}	1.331	1.358
μ /mm^{-1}	0.374	0.382
F(000)	1048	3144
Crystal size /mm^3	0.60 × 0.40 × 0.20	0.60 × 0.40 × 0.20
Theta range for data collection	2.15° to 26.99°	1.99° to 27.45°
Limiting indices	$-12 \le h \le 12$, $-13 \le k \le 13$, $-30 \le l \le 20$	$-31 \le h \le 35$, $-11 \le k \le 12$ $-35 \le l \le 37$
Reflections collected / unique	16160 / 5441	24168 / 8448
Data / restraints / parameters	5426 / 1 / 320	8425 / 648 / 480
GOF	1.032	1.050
R_1, wR_2 [$I > 2\sigma(I)$]	R_1 = 0.0341, wR_2 = 0.0798	R_1 = 0.0444, wR_2 = 0.1118
R_1, wR_2 (all data)	R_1 = 0.0437, wR_2 = 0.0851	R_1 = 0.0637, wR_2 = 0.1236
Largest diff. peak and hole /e·Å^{-3}	0.199 and –0.268	0.439 and –0.435

Table 2. Selected bond lengths /Å and angles /° for **1** and **2**.

1			
Ti(1)–N(5)	1.8843(19)	Ti(1)–N(3)	2.1157(17)
Ti(1)–N(6)	1.8888(17)	Ti(1)–N(4)	2.2633(17)
Ti(1)–N(1)	2.1148(18)	Ti(1)–N(2)	2.2661(16)
N(5)–Ti(1)–N(6)	104.83(8)	N(5)–Ti(1)–N(1)	99.21(7)
N(6)–Ti(1)–N(1)	97.07(7)	N(5)–Ti(1)–N(3)	94.25(7)
N(6)–Ti(1)–N(3)	96.66(7)	N(1)–Ti(1)–N(3)	157.61(7)
N(5)–Ti(1)–N(4)	158.92(7)	N(6)–Ti(1)–N(4)	93.42(7)
N(1)–Ti(1)–N(4)	88.71(7)	N(3)–Ti(1)–N(4)	72.88(6)
N(5)–Ti(1)–N(2)	89.98(7)	N(6)–Ti(1)–N(2)	163.87(8)
N(1)–Ti(1)–N(2)	73.84(7)	N(3)–Ti(1)–N(2)	88.43(6)
N(4)–Ti(1)–N(2)	73.40(7)		
2			
Ti(2)–N(3)	2.1064(18)	Ti(2)–N(15)	1.8883(18)
Ti(2)–N(4)	2.3016(18)	Ti(2)–N(14)	1.8916(19)
Ti(2)–N(5)	2.2654(19)	Ti(2)–N(6)	2.1178(18)
N(15)–Ti(2)–N(14)	104.16(8)	N(15)–Ti(2)–N(3)	97.83(7)
N(14)–Ti(2)–N(3)	98.30(8)	N(15)–Ti(2)–N(6)	100.51(7)
N(14)–Ti(2)–N(6)	95.27(8)	N(3)–Ti(2)–N(6)	153.73(7)
N(15)–Ti(2)–N(5)	93.28(8)	N(14)–Ti(2)–N(5)	160.61(7)
N(3)–Ti(2)–N(5)	87.46(7)	N(6)–Ti(2)–N(5)	72.91(7)
N(15)–Ti(2)–N(4)	164.64(8)	N(14)–Ti(2)–N(4)	89.62(7)
N(3)–Ti(2)–N(4)	73.08(7)	N(6)–Ti(2)–N(4)	84.67(7)
N(5)–Ti(2)–N(4)	74.29(7)		

Symmetry transformations used to generate equivalent atoms: #1 –x, y, –z+1/2.

Single crystal X-ray diffraction studies revealed that **1** crystallizes in the orthorhombic crystal system with $P2_12_12_1$ space group. The central metal atom shows a distorted octahedral arrangement. The $L1^-$ ligand adopts a bidentate binding motif. N1, N2, N3, and N6 atoms occupy equatorial positions about the titanium atom. The angles between the equatorial nitrogen atoms add up to 359.98°. Angles of N1–N6–N3, N1–N2–N3, N6–N1–N2, and N2–N3–N6 are 87.538(65)°, 93.322(72)°, 93.483(70)°, 85.638(63)°, respectively (Figure 1). N4 and N5 atoms occupy axial positions, and the N4–Ti–N5 angle is distorted away from the idealized position of 180° to 158.92(7)°. The two Ti–N(NMe_2) bond lengths are nearly identical [1.8843(19) and 1.8888(17) Å], and remarkably shorter than the average Ti–N(indolyl) (2.1153 Å) and Ti–N(pyrazolyl) (2.2647 Å) bond lengths.

For complex **2**, there are two independent molecules in the cell (Figure S2, Supporting Information). Only one of two is shown (Figure 2.). The central titanium atom adopts a distorted octahedral arrangement. The titanium atom is surrounded by four nitrogen atoms from two chelating ligands, and two nitrogen atoms from two dimethyamidos with one triazole nitrogen atom (N5) and one dimethylamido (N14) nitrogen atom occupying the axial positions and the other four nitrogen atoms (N3, N4, N6, N15) occupying equatorial positions. Angles between equatorial nitrogen atoms (N6–N15–N3: 84.838(67)°; N15–N3–N4: 94.507(73)°; N3–N4–N6: 94.150(78)°; N4–N6–N15: 86.435(66)°.) add up to 359.93°. The bond lengths between the titanium atom and donor nitrogen atoms [Ti(2)–N(5) = 2.2654(19) Å, Ti(2)–N(4) = 2.3016(18) Å] are apparently longer than Ti–N (indole) distances [Ti(2)–N(3) = 2.1064(18) Å, Ti(2)–N(6) = 2.1178(18) Å].

Hydroamination of Alkynes Catalyzed by 1 and 2

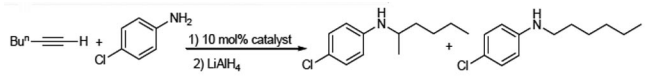
The successful determination of the crystal structures of the complexes prompted us to explore the catalytic activities of **1** and **2**. Subsequently, the intermolecular hydroamination of alkynes catalysed by **1** and **2**, respectively, were investigated.

Firstly, the reaction conditions were optimized. The reaction was performed between 1-hexyne and 4-chloroaniline in toluene by using **1** or **2** as the catalyst. The reactions were carried out at different temperature with a ratio of 2:3 of alkyne and amine. The hydroamination products were directly reduced to the secondary amines by $LiAlH_4$ in toluene. The final products were isolated by flash chromatography.

As shown in Table 3, when **1** was used as catalyst, 10 mol % catalyst loading at 100 °C in toluene gave a good yield within 12 h. However, complex **2** was found to be less active: 10 mol % at 100 °C in toluene gave lower yield within 12 h, and a moderate yield could be achieved by prolonging the reaction time to 24 h.

Under the optimized reaction conditions, we investigated the reactions of 4-chloroaniline with several alkynes. As seen in Table 4, the reaction of 4-chloroaniline with phenylacetylene gave the corresponding anti-Markovnikov imine in low yield (entry 1, Table 4). Both the yield and selectivity of the reaction of 1-octyne with 4-chloroaniline were inferior to that of 1-hexyne with 4-chloroaniline. So 1-hexyne was a good substrate

Table 3. Reaction of 4-chloroaniline with 1-hexyne catalyzed by **1** and **2** under different conditions.[a)]

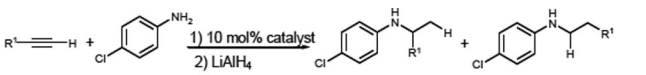


Entry	Catalyst	Temperature /°C	Time /h	Yield[b)] /%	Selectivity (M:anti-M)[c)]
1	1	80	12	59	86:14
2	2			35	87:13
3	1	80	24	70	75:25
4	2			42	92:8
5	1	100	12	90	89:11
6	2			45	96:4
7	1	100	24	86	86:14
8	2			72	99:1
9	1	120	12	80	74:26
10	2			61	97:3
11	1	120	24	44	94:6
12	2			60	94:6

a) Reaction conditions: 1-hexyne (1 mmol), 4-chloroaniline (1.5 mmol), catalyst (10 mol-%), toluene (4 mL). b) Isolated yield after reduced by $LiAlH_4$ and purified by column chromatography. c) Ratio of the Markovnikov and anti-Markovnikov products determined by GC-MS.

for the hydroamination catalysed by both **1** and **2**. Complex **1** gave better yields than **2**. However, **2** can catalyse the hydroamination with formation of almost exclusively Markovnikov imines.

Table 4. Intermolecular hydroamination of various alkynes with 4-chloroaniline catalyzed by **1** and **2**.[a)]



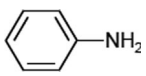
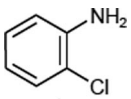
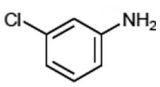
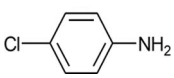
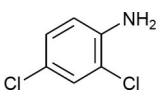
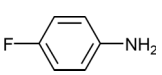
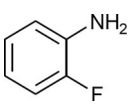
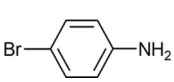
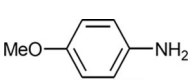
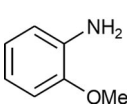
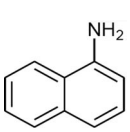
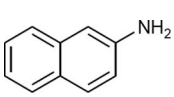
Entry	Catalyst	R^1	Isolated yield[b)] /%	Selectivity (M:anti-M)[c)]
1	1	Ph	26	20:80
2		*n*Bu	90	86:14
3		*n*Hex	86	62:38
4	2	Ph	18	83:17
5		*n*Bu	72	97:3
6		*n*Hex	55	81:19

a) Reaction conditions: 1-hexyne (1 mmol), 4-chloroaniline (1.5 mmol), catalyst (10 mol-%), toluene (4 mL), 12 h, 100 °C for **1**; 24 h, 100 °C for **2**. b) Isolated yield after reduced by $LiAlH_4$ and purified by column chromatograph. c) Ratio of the Markovnikov and anti-Markovnikov products determined by GC-MS.

With the optimized reaction conditions in hand, we further investigated the scope of the reaction by screening a large selection of amines. The results are listed in Table 5 and Table 6. In all cases, the Markovnikov products were favored.

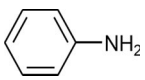
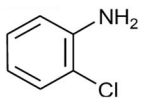
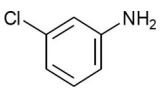
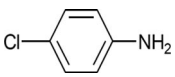
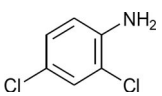
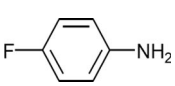
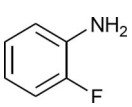
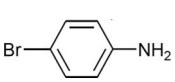
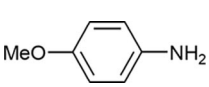
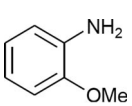
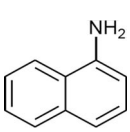
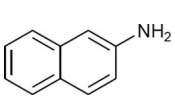
As can be seen from Table 5 and Table 6, the halo-substitutions on phenyl ring provided the corresponding imines in moderate yields. The position of the substituent seemed to influence the results greatly, as the *ortho*-substituted anilines

Table 5. Intermolecular hydroamination of 1-hexyne with various anilines catalyzed by **1**.[a)]

Entry	Amine	Isolated yield[b)] /%	Selectivity (M:anti-M)[c)]
1		92	98:2
2		31	86:14
3		88	99:1
4		90	86:14
5		48	95:5
6		80	96:4
7		72	93:7
8		70	94:6
9		93	92:8
10		12	65:35
11		97	92:8
12		60	96:4

a) Reaction conditions: 1-hexyne (1 mmol), anilines (1.5 mmol), catalyst (10 mol-%), toluene (4 mL), 12 h, 100 °C for **1**. b) Isolated yield after reduced by $LiAlH_4$ and purified by column chromatography. c) Ratio of the Markovnikov and anti-Markovnikov products determined by GC-MS.

Table 6. Intermolecular hydroamination of 1-hexyne with various anilines catalyzed by **2**.[a)]

Entry	Amine	Isolated yield[b)] /%	Selectivity (M:anti-M)[c)]
1		81	99:1
2		70	99:1
3		57	100:0
4		72	97:3
5		31	100:0
6		78	97:3
7		32	99:1
8		71	92:8
9		92	86:14
10		46	70:30
11		95	100:0
12		80	100:0

a) Reaction conditions: 1-hexyne (1 mmol), anilines (1.5 mmol), catalyst (10 mol-%), toluene (4 mL), 24 h, 100 °C for **2**. b) Isolated yield after reduced by $LiAlH_4$ and purified by column chromatography. c) Ratio of the Markovnikov and anti-Markovnikov products determined by GC-MS.

Table 7. Polymerization of ε-caprolactone initiated by **1** and **2** (conditions: [ε-CL]: [initiator] = 200:1).

Entry	Initiators	Solvent	Time /h	*T* /°C	M_n[b)] (calc)(10^4)	M_n[c)] (10^4)	M_n[d)] (10^4)	PDI	Efficiency /%	Yield[a)] /%
1	1	THF	3	60	2.07	3.79	2.12	1.37	55	91
2	1	THF	1	80	1.89	2.77	1.55	1.46	68	83
3	1	Tol	3	60	2.01	2.44	1.37	1.28	82	88
4	1	Tol	1	80	1.98	2.00	1.12	1.24	99	87
5	1	DME	3	60	1.23	2.35	1.32	1.27	52	54
6	1	DME	2	80	1.50	2.34	1.31	1.38	64	66
7	2	THF	3	60	1.05	2.95	1.65	1.35	36	46
8	2	THF	2	80	1.19	2.92	1.64	1.39	41	52
9	2	Tol	3	60	1.44	3.29	1.84	1.35	44	63
10	2	Tol	1.5	80	1.73	2.88	1.61	1.48	60	76
11	2	DME	3	60	1.09	3.07	1.72	1.33	36	48
12	2	DME	1.5	80	2.07	2.70	1.51	1.37	77	91

a) Yield: weight of polymer obtained/weight of monomer used. [M/I] = 200. Efficiency: the calculated average molecular weight [M_n[b](calc)]/ the experimentally measured value (M_n[c]). b) M_n(calc) = M mono × [M]/[I] × conv. c) Measured by GPC relative to polystyrene standards. d) Measured by GPC relative to polystyrene standards with Mark-Houwink corrections[13] for M_n (obsd) = 0.56 M_n (GPC) for ε-caprolactone.

gave the corresponding amines with relatively lower yields (entries 2, 7, and 10 in Table 5 and Table 6). Lower yield of imine for the hydroamination of 1-hexyne with 2,4-dichloroaniline is attributable to the bulky hindrance of aniline. Notably, exclusive regioselectivity for the Markovnikov products were achieved in the presence of **2** when 2,4-dichloroaniline and 3-chloroaniline were reacted with 1-hexyne (entries 3 and 5 in Table 6).

When 4-methoxyaniline was used as aniline source (entry 9 in Table 5 and Table 6), good yield was obtained. However, as 2-methoxyaniline was used as substrate, both **1** and **2** are not effective catalysts under the conditions employed, and low yields and poor regioselectivity are obtained (entry 10 in Table 5 and Table 6). It is possible that the *ortho*-methoxy group of 2-methoxyaniline coordinates to the central titanium atom, leading to the low yield.

When naphthalene-1-amine was employed as the amine source, complexes **1** and **2** showed higher activity with higher yields (entry 11 in Table 5 and Table 6). Complex **2** was found to be more selective with respect to the Markovnikov products.

Ring-Opening Polymerization of ε-Caprolactone Initiated by 1 and 2

Ring-opening polymerization (ROP) of ε-caprolactone initiated by transition metal catalysts is a very effective method for producing PCL, which is an important biodegradable and biocompatible polymer. Such polymer is an important building block for the production of segmented copolymers and polymer networks.[10] Among the various catalytic processes, titanium and zirconium compounds were proved to be effective initiators for the polymerization of lactones. However, only very few group 4 metal complexes was reported to initiate the polymerization of lactones,[11] and the examples for employing titanium amides[12] as the initiators for the polymerization of ε-caprolactone are very rare. Therefore, we studied the ring-opening polymerization of ε-caprolactone initiated by **1** and **2**.

To our delight, it is found that both **1** and **2** can initiate the polymerization of ε-caprolactone effectively. The preliminary results are summarized in Table 7. Both **1** and **2** were active for the ROP of ε-CL, forming poly(ε-CL) with a relatively narrow PDI and high molar mass ($M_n > 20000$).

As can be seen from Table 7, complex **1** exhibits good activity toward the ROP of ε-CL. Two polymerization experiments carried out at 60 and 80 °C in toluene demonstrated that the conversion increased significantly with the increase of reaction temperature (entries 3 and 4). At 60 °C, full conversion was obtained in 180 min, and the initiation efficiency was 82 %. When the same experiment was performed at 80 °C, the polymerization finished in 60 min with a higher efficiency (99 %). Moreover, the solvent also affected the polymerization results. Toluene was found to be the better solvent. It is because the coordination of ethereal solvents DME and THF molecules to the central metal atom may hinder the attack of ε-caprolactone to the same metal atom.

Complex **2** showed lower activity compared with **1**. When the polymerization was carried out in DME at 80 °C, full conversions could be achieved within 1.5 h with an efficiency of 77 %. Poor yields were afforded at 60 °C. Increasing of the polymerization temperature led to higher efficiency and broader molecular weight distribution. The reactions performed in THF gave lower efficiencies (entries 7 and 8).

The catalytic activities of **1** and **2** are much higher than those of sulfonamide-supported titanium complexes.[12a]

Conclusions

Two new complexes were synthesized and characterized. The catalytic activities toward intermolecular hydroamination reactions of alkynes were studied. Both **1** and **2** can catalyze the hydroamination reactions with selective Markovnikov products. Ring-opening polymerization of ε-caprolactone in different solvents and at different temperatures initiated by **1** and **2** were also carried out. The results show that both of them can initiate the polymerization to give polyesters with high molecular weights and low poly-disperisities.

Experimental Section

General Considerations: All manipulations of air-sensitive compounds were carried out with a Mikrouna glovebox in a purified nitro-

gen atmosphere. $Ti(NMe_2)_4$ was purchased from Acros and used without further purification. Amines were distilled from CaH_2. Tetrahydrofuran, toluene, and hexane were heated to reflux over sodium benzophenoneketyl for at least 4 d. $CDCl_3$ was distilled from P_2O_5 in a nitrogen atmosphere. Elemental analyses (C, H, N) were performed with a Carlo-Erba EA 1110 CHNO-S microanalyser. ^1H and ^{13}C spectra were recorded with an Innova-400 spectrometers at ambient temperature using TMS as an internal standard, and chemical shifts were reported in ppm. GC/MS spectra were recorded with a GCMS-QP2010.

X-ray Crystallography: Crystals grown from concentrated solutions at room temperature were quickly selected and mounted on a glass fiber in wax. The data collections were carried out on a Mercury CCD detector equipped with graphite-monochromated Mo-K_α radiation by using the ϕ/ω scan technique at room temperature. The structures were solved by direct methods with SHELXS-97.[14] The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97.

Synthesis of $Ti(L1)_2(NMe_2)_2$ (1): To a solution of $Ti(NMe_2)_4$ (0.224 g, 1 mmol) in THF (2 mL) was added a solution of HL1 (0.3364 g, 2 mmol) in THF (4 mL) at –35 °C. After being stirred at room temperature overnight, the solution was evaporated to dryness to give a red solid. Crystals of **1** were obtained from Tol/hexane. Yield: 0.380 g (76%). **^1H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 7.74–7.71 (m, 2 H, indole and ph), 7.64 (d, 1 H, ph), 7.21 (t, 1 H, ph), 7.13 (t, 1 H, ph), 6.69 (s, 1 H, py), 6.34 (s, 1 H, py), 6.08 (s, 1 H, py), 3.46 (s, 6 H, NMe_2). **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C): δ = 142.59, 141.93, 137.50, 130.90, 125.03, 120.26, 119.53, 119.19, 116.55, 107.80, 83.32, 77.48, 77.16, 76.84, 47.95(N-CH_3). $C_{26}H_{28}N_8Ti$ (500.43): calcd. C 62.40, H 5.64, N 22.39%; found, C 62.23, H 5.67, N 21.92%.

Synthesis of $Ti(L2)_2(NMe_2)_2$ (2): To a solution of $Ti(NMe_2)_4$ (0.224 g, 1 mmol) in THF (2 mL) was added a solution of HL2 (0.3684 g, 2 mmol) in THF (4 mL) at –35 °C. After being stirred at room temperature overnight, followed by the identical procedure reported for **1**, complex **2** was afforded as a dark red solid. Crystals of **2** were obtained from Tol/hexane. Yield: 0.248 g (49%). **^1H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 8.42 (s, 1 H, indole), 7.71–7.67 (m, 2 H, ph), 7.30–7.24 (m, 2 H, ph), 7.19–7.16 (m, 1 H, py), 6.53 (s, 1 H, py), 3.50 (s, 6 H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C): δ = 149.74, 142.24, 138.78, 138.45, 130.80, 121.80, 120.66, 120.24, 116.88, 86.19, 77.80, 77.48, 77.16, 48.38 (N–CH_3). $C_{24}H_{26}N_{10}Ti$ (502.42): calcd. C 57.38, H 5.22, N 27.88%. found: C 57.11, H 5.63 N 27.47%.

General Procedure for the Hydroamination Reaction: In a nitrogen filled dry box, 1-hexyne (0.08214 g, 1 mmol), aniline (1.5 mmol), and **1** (0.0500 g, 10 mol%) were added to a 35 mL pressure tube. A stirring bar was added to the pressure tube. The tube was taken out from the glovebox, heated with stirring at 100 °C for 12 h, and cooled down to 0 °C. The reaction solution was carefully added a suspension of $LiAlH_4$ (0.057 g, 1.5 mmol) and the mixture was heated at 60 °C for 3 h. After cooling the solution to 0 °C, the excess $LiAlH_4$ was hydrolyzed with $Na_2SO_4{\cdot}10H_2O$. The reaction solution was dried with excess $MgSO_4$. The organic layer was extracted with ethyl acetate (3×20 mL). Column chromatography of the residue on silica gel gave a pure product.

General Procedure for the Polymerization of ε-Caprolactone: A solution of the initiator (complex **1** or **2**) in toluene (THF or DME) and ε-caprolactone (1.14 g, 10 mmol, [M] / [I] = 200) was added to a 35 mL pressure tube. A stirring bar was added to the pressure tube. The tube was taken out from the glovebox. The reaction mixture was heated at the chosen temperature and terminated by addition of a mixture of conc. HCl / EtOH (1:5; v/v) (2 mL). The resulting polymers were precipitated from methanol (150 mL), filtered, and dried in a vacuum. The solids were dissolved in THF (10 mL), column chromatography on Al_2O_3 to give a white solid.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-990887 (**1**) and CCDC-990888 (**2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra of complexes **1** and **2** and the hydroamination products.

Acknowledgements

The authors appreciate the financial support of Natural Science Foundation of China (21272167 and 21201127), A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions and KLSLRC (KLSLRC-KF-13-HX-1).

References

[1] For selected reviews for hydroamination, see: a) J. F. Hartwig, *Nature* **2008**, *455*, 314–322; b) J. L. Klinkenberg, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2011**, *50*, 86–95; c) T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo, M. Tada, *Chem. Rev.* **2008**, *108*, 3795–3892; d) A. L. Odom, *Dalton Trans.* **2005**, 225–233; e) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675–704; f) L. D. Julian, J. F. Hartwig, *J. Am. Chem. Soc.* **2010**, *132*, 13813–13822; g) J. Hannedouche, E. Schulz, *Chem. Eur. J.* **2013**, *19*, 4972–4985.

[2] a) G. Zi, *J. Organomet. Chem.* **2011**, *696*, 68–75; b) Q. Wang, H. Song, G. Zi, *J. Organomet. Chem.* **2010**, *695*, 1583–1591; c) G. Zi, F. Zhang, L. Xiang, Y. Chen, W. Fang, H. Song, *Dalton Trans.* **2010**, *39*, 4048–4061; d) L. Xiang, H. Song, G. Zi, *Eur. J. Inorg. Chem.* **2008**, *7*, 1135–1140; e) F. Pohlki, S. Doye, *Chem. Soc. Rev.* **2003**, *32*, 104–114; f) J. C.-H. Yim, L. L. Schafer, *Eur. J. Org. Chem.* **2014**, *31*, 6825–6840; g) F. Basuli, H. Aneetha, J. C. Huffman, D. J. Mindiola, *J. Am. Chem. Soc.* **2005**, *127*, 17992–17993; h) M. C. Wood, D. C. Leitch, C. S. Yeung, J. A. Kozak, L. L. Schafer, *Angew. Chem. Int. Ed.* **2007**, *46*, 354–358; i) D. A. Watson, M. Chiu, R. G. Bergman, *Organometallics* **2006**, *25*, 4731–4733; j) L. T. Kaspar, B. Fingerhut, L. Ackermann, *Angew. Chem. Int. Ed.* **2005**, *44*, 5972–5974.

[3] J. S. Johnson, R. G. Bergman, *J. Am. Chem. Soc.* **2001**, *123*, 2923–2924.

[4] a) F. Pohlki, I. Bytschkov, H. Siebeneicher, A. Heutling, W. A. Konig, S. Doye, *Eur. J. Org. Chem.* **2004**, *9*, 1967–1972; b) K. Marcsekova, B. Wegener, S. Doye, *Eur. J. Org. Chem.* **2005**, 4843–4851; c) A. Heutling, F. Pohlki, S. Doye, *Chem. Eur. J.* **2004**, *10*, 3059–3071; d) T. Janssen, R. Severin, M. Diekmann, M. Friedemann, D. Haase, W. Saak, S. Doye, R. Beckhaus, *Organometallics* **2010**, *29*, 1806–1817; e) K. Weitershaus, B. D. Ward, R. Kubiak, C. Muller, H. Wadepohl, S. Doye, L. H. Gade, *Dalton Trans.* **2009**, 4586–4602; f) R. Severin, S. Doye, *Chem. Soc. Rev.* **2007**, *36*, 1407–1420; g) L. Ackermann, R. G. Bergman, R. N. Loy, *J. Am. Chem. Soc.* **2003**, *125*, 11956–11963; h) L. Ackermann, R. G. Bergman, *Org. Lett.* **2002**, *4*, 1475–1478; i) L. L. An-

derson, J. Arnold, R. G. Bergman, *J. Am. Chem. Soc.* **2005**, *127*, 14542–14543; j) V. Khedkar, A. Tillack, M. Beller, *Org. Lett.* **2003**, *5*, 4767–4770; k) A. Tillack, I. G. Castro, C. G. Hartung, M. Beller, *Angew. Chem. Int. Ed.* **2002**, *41*, 2541–2543; l) A. Tillack, H. Jiao, I. G. Castro, C. G. Hartung, M. Beller, *Chem. Eur. J.* **2004**, *10*, 2409–2420.

[5] a) C. Li, R. K. Thomson, B. Gillon, B. O. Patrick, L. L. Schafer, *Chem. Commun.* **2003**, 2462–2463; b) Z. Zhang, L. L. Schafer, *Org. Lett.* **2003**, *5*, 4733–4736; c) J. A. Bexrud, J. D. Beard, D. C. Leitch, L. L. Schafer, *Org. Lett.* **2005**, *7*, 1959–1962; d) J. A. Bexrud, L. L. Schafer, *Dalton Trans.* **2010**, *39*, 361–363; e) R. O. Ayinla, L. L. Schafer, *Dalton Trans.* **2011**, *40*, 7769–7776; f) P. R. Payne, R. K. Thomson, D. M. Medeiros, G. Wan, L. L. Schafer, *Dalton Trans.* **2013**, *42*, 15670–15677; g) E. Chong, L. L. Schafer, *Org. Lett.* **2013**, *15*, 6002–6005; h) D. C. Leitch, R. H. Platel, L. L. Schafer, *J. Am. Chem. Soc.* **2011**, *133*, 15453–15463; i) C. E. Hayes, R. H. Platel, L. L. Schafer, D. B. Leznoff, *Organometallics* **2012**, *31*, 6732–6740; j) J. C.-H. Yim, J. A. Bexrud, R. O. Ayinla, D. C. Leitch, L. L. Schafer, *J. Org. Chem.* **2014**, *79*, 2015–2028.

[6] a) Y. Li, Y. Shi, A. L. Odom, *J. Am. Chem. Soc.* **2004**, *126*, 1794–1803; b) B. Ramanathan, A. J. Keith, D. Armstrong, A. L. Odom, *Org. Lett.* **2004**, *6*, 2957–2960; c) C. Cao, Y. Shi, A. L. Odom, *Org. Lett.* **2002**, *4*, 2853–2856; d) C. Cao, J. T. Ciszewski, A. L. Odom, *Organometallics* **2001**, *20*, 5011–5013; e) C. Cao, Y. Li, Y. Shi, A. L. Odom, *Chem. Commun.* **2004**, 2002–2003; f) Y. Shi, C. Hall, J. T. Ciszewski, C. Cao, A. L. Odom, *Chem. Commun.* **2003**, 586–587; g) D. L. Swartz II, R. J. Staples, A. L. Odom, *Dalton Trans.* **2011**, *40*, 7762–7768; h) C. Cao, Y. Shi, A. L. Odom, *J. Am. Chem. Soc.* **2003**, *125*, 2880–2881; i) F. Zhou, M. Lin, L. Li, X. Zhang, Z. Chen, Y. Li, Y. Zhao, W. Li, *Organometallics* **2011**, *30*, 1283–1286; j) X. Han, Y. Li, H. Wei, Y. Zhang, *Chin. J. Chem.* **2007**, *25*, 1334–1339.

[7] T.-G. Ong, G. P. A. Yap, D. S. Richeson, *Organometallics* **2002**, *21*, 2839–2841.

[8] Y. Zhao, M. Lin, Z. Chen, H. Pei, Y. Li, W. Li, *RSC Adv.* **2012**, *2*, 144–150.

[9] W. Wu, J. Huang, *Org. Lett.* **2012**, *14*, 5832–5835.

[10] a) W. J. Zhang, S. F. Liu, W. H. Yang, X. Hao, R. Glaser, W. H. Sun, *Organometallics* **2012**, *31*, 8178–8188; b) P. Dubois, P. Degee, R. Jerome, P. Teyssie, *Macromolecules* **1993**, *26*, 2730–2735.

[11] a) C. Li, C. Yu, B. T. Ko, *Organometallics* **2013**, *32*, 172–180; b) Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey, M. Bochmann, *Dalton Trans.* **2006**, 340–350; c) L. Postigo, J. Sanchez-Nieves, P. Royo, M. E. G. Mosquera, *Dalton Trans.* **2009**, 3756–3765; d) H. Wang, H. Chan, J. Okuda, Z. Xie, *Organometallics* **2005**, *24*, 3118–3124.

[12] a) A. D. Schwarz, A. L. Thompson, P. Mountford, *Inorg. Chem.* **2009**, *48*, 10442–10454; b) A. D. Schwarz, K. R. Herbert, C. Paniagua, P. Mountford, *Organometallics* **2010**, *29*, 4171–4188; c) A. D. Schwarz, Z. Chu, P. Mountford, *Organometallics* **2010**, *29*, 1246–1260; d) R. L. Webster, N. Noroozi, S. G. Hatzikiriakos, J. A. Thomson, L. L. Schafer, *Chem. Commun.* **2013**, *49*, 57–59.

[13] A. Kowalski, A. Duda, S. Penczek, *Macromolecules* **1998**, *31*, 2114–2122.

[14] a) G. M. Sheldrick, *SHELXS 97*, Program for the Solution of Crystal Structures, University of Göttingen, Germany, **1997**; b) G. M. Sheldrick, *SHELXL 97*, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.

Received: February 8, 2015
Published Online: May 6, 2015

