Synthesis, Characterization, Selective Catalytic Activity, and Reactivity of Rare Earth Metal Amides with Different Metal–Nitrogen Bonds

Xiancui Zhu,[†] Jiaxi Fan,[†] Yunjun Wu,[†] Shaowu Wang,^{*,†,‡} Lijun Zhang,[†] Gaosheng Yang,[†] Yun Wei,[†] Chengwei Yin,[†] Hong Zhu,[†] Shihong Wu,[†] and Hongtao Zhang[†]

[†]Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, Institute of Organic Chemistry, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, People's Republic of China, and [‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

Received March 12, 2009

A series of neutral rare earth metal amides with different metal–nitrogen bonds were synthesized and characterized. The selective catalytic activity and reactivity of the complexes incorporating different metal–nitrogen (Ln–N, Ln = rare earth metal) bonds were studied. Treatment of $(Me_2Si)[(2,6-R^1_2-4-R^2-C_6H_2)NH]_2$ with $[(Me_3Si)_2N]_3Ln^{III}(\mu$ -Cl)Li(THF)_3 in toluene produced the neutral rare earth metal complexes { $(Me_2Si)[(2,6-R^1_2-4-R^2-C_6H_2)N]_2$ }LnN(SiMe_3)_2(THF) (R¹ = ^{*i*}Pr, R² = H, Ln = Yb (1), Y (2), Eu (3), Sm (4), Nd (5); R¹ = R² = H, Ln = Yb (6), Sm (7)) incorporating different Ln–N bonds in good yields. Reaction of 6 or 7 with grease (Me_2SiO)_3 in toluene produced the selective insertion products [C₆H₅N(Me_2Si)N(C₆H₅)(Me_2SiO)LnN(SiMe_3)_2]_2 (Ln = Yb (8), Sm (9)). The structures of complexes 1, 2, 4, 5, 8, and 9 were additionally determined by single-crystal X-ray analyses. Investigation of catalytic activity of the complexes indicated that the complexes displayed a high selectivity on cyclotrimerization or cyclodimerization toward isocyanates depending on the nature of the isocyanates. These catalysts have the advantages of a high reactivity and good selectivity toward isocyanates, easy preparation, low catalyst loading, and high conversion, as well as mild reaction conditions.

Introduction

It has been demonstrated that rare earth metal complexes exhibit versatile catalytic activity on polyolefin functionalization with heteroatoms.¹ Recent interest in the use of amido ligands for the preparation of early transition metal complexes stems from the recognition that the electronic properties and steric effects of the ligands can be modified by variation of the substituents of nitrogen atoms and that complexes incorporating the amido ligands exhibited catalytic activity in various transformations of polyolefins and the ring-opening polymerization of δ -caprolactone and other polar monomers.^{1,2} Reports on these transformations catalyzed by rare earth metal amides including hydroamination,³ monocoupling reactions of isocyanides with terminal alkynes,⁴ Cannizzaro-type disproportionation of aromatic aldehydes,⁵ guanylation of amines,⁶ amidination of alkyne,⁷

ORGANOMETALLICS

^{*}Corresponding author. E-mail: swwang@mail.ahnu.edu.cn.

Amin, S. B.; Marks, T. J. Angew. Chem., Int. Ed. 2008, 47, 2006.
 (2) (a) Villiers, C.; Thuery, P.; Ephritikhine, M. Eur. J. Inorg. Chem. 2004, 3, 4624. (b) Luo, Y. J.; Yao, Y. M.; Shen, Q.; Sun, J.; Weng, L. H. J. Organomet. Chem. 2002, 662, 144. (c) Qian, C. T.; Nie, W. L.; Sun, J. Organometallics 2000, 19, 4134. (d) Qian, C. T.; Zou, G.; Chen, Y. F.; Sun, J. Organometallics 2001, 20, 3106. (e) Hou, Z. M.; Koizumi, T.; Nishiura, M.; Wakatsuki, Y. Organometallics 2001, 20, 3323. (f) Lou, Y. J.; Yao, Y. M.; Li, W. J.; Chen, J. L.; Zhang, Z. Q.; Zhang, Y.; Shen, Q. J. Organomet. Chem. 2003, 679, 125. (g) Lou, Y. J.; Yao, Y. M.; Shen, Q.; Yu, K. B.; Weng, L. H. Eur. J. Inorg. Chem. 2003, 2, 318. (h) Chen, J. L.; Yao, Y. M.; Lou, Y. J.; Zhou, L. Y.; Zhang, Y.; Shen, Q. J. Organomet. Chem. 2004, 689, 1019. (i) Kirillov, E.; Toupet, L.; Lehmann, C. W.; Razavi, A.; Carpentier, J. F. Organometallics 2003, 22, 4467. (j) Zhou, L. Y.; Yao, Y. M.; Zhang, Y.; Xue, M. Q.; Chen, J. L.; Shen, Q. Eur. J. Inorg. Chem. 2004, 10, 2167. (k) Zhou, S.; Wang, S.; Sheng, E.; Zhang, L.; Yu, Z.; Xi, X.; Chen, G.; Luo, W.; Li, Y. Eur. J. Inorg. Chem. 2007, 11, 1519. (l) Li, S.; Miao, W.; Tang, T.; Dong, W.; Zhang, X.; Cui, D. Organometallics 2008, 27, 718–725. (m) Zimmermann, M.; Törnroos, K.; Waymouth, R.; Anwander, R. Organometallics 2008, 27, 4310–4317.

⁽³⁾ For general reviews on hydroamination reactions, see: (a) Müller, T. E.; Beller, M. Chem. Rev. **1998**, 98, 675. (b) Nobis, M.; Driessen-Hölscher, B. Angew. Chem., Int. Ed. **2001**, 40, 3983. (c) Brunet, J. J.; Neibecker, D. In Catalytic Heterofunctionalization from Hydroamination to Hydrozirconation; Togni, A., Grützmacher, H., Eds.; Wiley-VCH: Weinheim, Germany, 2001; pp 91–141. (d) Roesky, P. W.; Müller, T. E. Angew. Chem., Int. Ed. **2003**, 42, 2708. (e) Pohlki, F.; Doye, S. Chem. Soc. Rev. **2003**, 32, 104. (f) Beller, M.; Tillack, A.; Seayad, J. In Transition Metals for Organic Synthesis, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 2, pp 403–414.

^{(4) (}a) Komeyama, K.; Sasayama, D.; Kawabata, T.; Takehira, K.; Takali, K. *J. Org. Chem.* **2005**, *70*, 10679. (b) Komeyama, K.; Sasayama, D.; Kawabata, T.; Takehira, K.; Takaki, K. *Chem. Commun.* **2005**, 634.

^{(5) (}a) Zhang, L.; Wang, S.; Zhou, S.; Yang, G.; Sheng, E. J. Org. Chem. 2006, 71, 3149. (b) Seo, S. Y.; Marks, T. J. Org. Lett. 2008, 10, 317–319. (c) Wang, S.; Qian, H.; Yao, W.; Zhang, L.; Zhou, S.; Yang, G.; Zhu, X.; Fan, J.; Liu, Y.; Chen, G.; Song, H. Polyhedron 2008, 27, 2757–2764. (d) Li, J.; Xu, F.; Zhang, Y.; Shen, Q. J. Org. Chem. 2009, 74, 2575–2577.

^{(6) (}a) Li, Q.; Wang, S.; Zhou, S.; Yang, G.; Zhu, X.; Liu, Y. J. Org. Chem. **2007**, 72, 6763. (b) Zhang, W.-X.; Nishiura, M.; Hou, Z. Synlett **2006**, 8, 1213. (c) Zhang, W.-X.; Nishiura, M.; Hou, Z. Chem.—Eur. J. **2007**, 13, 4037.

^{(7) (}a) Zhou, S.; Wang, S.; Yang, G.; Li, Q.; Zhang, L.;
Yao, Z.; Zhou, Z.; Song, H. Organometallics 2007, 26, 3755.
(b) Zhang, W.-X.; Nishiura, M.; Hou, Z. J. Am. Chem. Soc. 2005, 127, 16788.

Article

addition reactions of amines to nitriles,⁸ cross-Aldol reactions,⁹ dimerization of terminal alkynes,¹⁰ hydrosilylation,¹¹ hydroboration,¹² Tishchenko aldehyde dimerization,¹³ and hydroalkoxylation¹⁴ have shown a wide application of the rare earth metal amides as catalysts or precatalysts in organic synthesis. Although stoichiometrically insertion of isocyanate to the rare earth metal Ln–C, Ln–N, Ln–O, and Ln–S bonds to produce the corresponding insertion products has been extensively studied,¹⁵ lanthanocene complexes Cp₂-LnNⁱPr₂(THF)^{16a} (Cp' = MeC₅H₄, Ln = Y, Er, Yb) or Cp₂LnCl/*n*-BuLi^{16b} as catalysts or catalytic systems for cyclo-trimerization of phenyl isocyanate are documented. Selective transformation of the isocyanates to their corresponding cyclodimerization or cyclotrimerization products with cyclopentadienyl-free rare earth metal amides as catalysts is far less explored.¹⁷

As we know, isocyanates can undergo cyclodimerization, cyclotrimerization, and polymerization in the presence of catalysts. Investigation of catalysts that can selectively catalyze the cyclodimerization, cyclotrimerization, or polymerization of isocyanates is one active topic of modern chemistry. Triaryl isocyanurates are known to improve the stability of polyurethane networks with respect to thermal resistance, flame retardation, chemical resistance, and film-forming characteristics.¹⁸ Different isocyanate

(10) (a) Komeyama, K.; Kawabata, T.; Takehira, K.; Takaki, K. J. Org. Chem. 2005, 70, 7260–7266. (b) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. J. Am. Chem. Soc. 2003, 125, 1184–1185.
(c) Nishiura, M.; Hou, Z. J. Mol. Catal. A 2004, 213, 101–106.

(11) (a) Horino, Y.; Livinghouse, T. Organometallics 2004, 23, 12–14.
 (b) Gountchev, T.; Tilley, T. D. Organometallics 1999, 18, 5661–5667.
 (12) Horino, Y.: Livinghouse, T.: Stan, M. Synlett 2004, 2639–2641.

(12) Horino, Y.; Livinghouse, T.; Stan, M. Synlett 2004, 2639–2641.
 (13) (a) Chen, Y. H.; Zhu, Z. Y.; Zhang, J.; Shen, J. Z.; Zhou, X. G. J. Organomet. Chem. 2005, 690, 3783–3789. (b) Burgstein, M. R.; Berberich, H.; Roesky, P. W. Chem.—Eur. J. 2001, 7, 3078–3085. (c) Berberich, H.; Roesky, P. W. Angew. Chem., Int. Ed. 1998, 37, 1569–1571.

(14) (a) Yu, X.; Seo, S.; Marks, T. J. J. Am. Chem. Soc. **2007**, 129, 7244–7245. (b) Seo, S.; Yu, X.; Marks, T. J. J. Am. Chem. Soc. **2009**, 131, 263–276.

(15) (a) Zhang, J.; Ruan, R. Y.; Shao, Z. H.; Cai, R. F.; Weng, L. H.; Zhou, X. Organometallics 2002, 21, 1420. (b) Zhang, J.; Cai, R. F.; Weng, L. H.; Zhou, X. J. Organomet. Chem. 2003, 672, 94. (c) Zhang, J.; Cai, R. F.; Weng, L. H.; Zhou, X. Organometallics 2003, 22, 5385. (d) Zhang, J.; Cai, R. F.; Weng, L. H.; Zhou, X. Organometallics 2004, 23, 3303. (e) Zhang, J.; Ma, L. P.; Cai, R. F.; Weng, L. H.; Zhou, X. Organometallics 2005, 24, 738. (f) Zhang, J.; Zhou, X.; Cai, R. F.; Weng, L. H. Inorg. Chem. 2005, 44, 716. (g) Zhang, C. M.; Liu, R. T.; Zhang, J.; Chen, Z. X.; Zhou, X. Inorg. Chem. 2006, 45, 5867. (h) Wang, H. P.; Li, H. W.; Xie, Z. W. Organomatallics 2003, 22, 4522. (i) Shen, Q.; Li, H.; Yao, C.; Yao, Y.; Zhang, L.; Yu, K. Organometallics 2001, 20, 3070– 3073. (j) Xu, X.; Qi, R.; Xu, B.; Yao, Y.; Nie, K.; Zhang, Y.; Shen, Q. Polyhedron 2009, 28, 574–578.

 (16) (a) Mao, L.; Shen, Q.; Xue, M.; Sun, J. Organomatallics 1997, 16,
 3711. (b) Zhou, X.; Zhang, L.; Zhu, M.; Cai, R.; Weng, L. Organometallics 2001, 20, 5700.

(17) Wu, Y.; Wang, S.; Zhu, X.; Yang, G.; Wei, Y.; Zhang, L.; Song,
 H. *Inorg. Chem.* 2008, 47, 5503–5511.

(18) (a) Tang, J.; Verkade, J. G. Angew. Chem., Int. Ed. Engl. 1993, 32, 896. (b) Tang, J.; Mohan, T.; Verkade, J. G. J. Org. Chem. 1994, 59, 4931. (c) Spirkova, M.; Kubin, M.; Spacek, P.; Krakovsky, I.; Dusek, K. J. Appl. Polym. Sci. 1994, 53, 1435. (d) Spirkova, M.; Kubin, M.; Spacek, P.; Krakovsky, I.; Dusek, K. J. Appl. Polym. Sci. 1994, 52, 895. (e) Nambu, Y.; Endo, T. J. Org. Chem. 1993, 58, 1932. (f) Mizura, J.; Yokozawa, T.; Endo, T. J. Polym. Sci., Polym. Chem. 1991, 29, 1545. (19) (a) Srinivas, B.; Chang, C.-C.; Chen, C.-H.; Chiang, M. Y.;

(19) (a) Srinivas, B.; Chang, C.-C.; Chen, C.-H.; Chiang, M. Y.; Chen, I.-T.; Wang, Y.; Lee, G.-H. J. Chem. Soc., Dalton Trans. **1997**, 957. (b) Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S. Inorg. Chem. **2000**, 39, 924–929. (c) Paul, F.; Moulin, S.; Piechaczyk, O.; Le Floch, P.; Osborn, J. J. Am. Chem. Soc. **2007**, 129, 7294–7304, and references therein.



Figure 1. Molecular structure of complex 1.

cyclotrimerization catalysts have been reported with a majority of the conventional catalysts being anions or neutral Lewis bases.¹⁸ Some metal-based catalysts have been described, and a Lewis acid pathway could be envisioned for these systems.¹⁹ Conventional catalysts for isocyanurate formation suffer from low activity, necessitating severe conditions, and poor selectivity, resulting in byproducts and difficulties in separating the catalysts from the products. However, lanthanide complexes have displayed advantages for this transformation.^{16,17} Selective transformation of isocyanates to substituted ureas after elimination of CO from the cyclodimerization products still needs further exploration.

We have observed that rare earth metal complexes supported by a diamido ligand with a CH₂Me₂Si link are excellent catalysts for the cyclotrimerization of aryl isocyanates to yield triaryl isocyanurates with a high selectivity.¹⁷ In an effort to elucidate the generality of this observation and the features that dictate the activity and selectivity in this reaction, we have extended the complexes employed in this reaction to include rare earth metal complexes incorporating dimethylsilylene-bridged diamido ligands. We report herein the synthesis, characterization, and catalytic activity of a series of rare earth metal amides, and the selective reactivity of different metal–nitrogen bonds will also be reported for the first time.

Results and Discussion

Synthesis and Characterization of Rare Earth Metal Complexes with Different Metal–Nitrogen Bonds. Treatment of $(Me_2Si)[(2,6-R_2^{1}-4-R^2-C_6H_2)NH]_2$ with $[(Me_3Si)_2N]_3L-n^{III}(\mu-CI)Li(THF)_3$ in toluene, after workup, produced the rare earth metal complexes { $(Me_2Si)[(2,6-R_2^{1}-4-R^2-C_6H_2)-N]_2$ }LnN(SiMe_3)_2(THF) ($R^1 = {}^iPr, R^2 = H, Ln = Yb(1), Y(2), Eu(3), Sm(4), Nd(5); R^1 = R^2 = H, Ln = Yb(6), Sm(7))$ in good yields. The structures of the complexes 1, 2, 4, and 5 were additionally determined by single-crystal X-ray diffraction study. These complexes are sensitive to moisture, but they are stable in an inert atmosphere for months. They are soluble in THF, DME, CH_2Cl_2, and toluene, but complexes 6 and 7 are only slightly soluble in *n*-hexane.

X-ray analyses revealed that complexes 1, 2, 4, and 5 are neutral compounds supported by a dimethylsilylene-bridged diamido ligand, an amido ligand $N(SiMe_3)_2$, and a coordinated THF molecule (the representative structure of the complexes is shown in Figure 1; figures for complexes 2, 4,

⁽⁸⁾ Wang, J.; Xu, F.; Cai, T.; Shen, Q. Org. Lett. 2008, 10, 445–448.
(9) Zhang, L.; Wang, S.; Sheng, E.; Zhou, S. Green Chem. 2005, 7, 683–686.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of Complexes 1, 2, 4, 5, 8, and 9

	1	2	4	5
Ln-N _{av}	2.181(14)	2.213(4)	2.268(3)	2.295(2)
Ln-O _{av}	2.286(16)	2.314(4)	2.397(3)	2.439(2)
N(2)-Ln(1)-N(1)	73.0(5)	72.55(13)	70.83(12)	69.44(7)
N(3)-Ln(1)-N(1)	131.8(5)	135.94(14)	138.59(12)	132.60(8)
N(3)-Ln(1)-N(2)	135.9(5)	134.58(14)	137.16(12)	137.01(9)
N(1)-Ln(1)-O(1)	108.2(3)	107.37(16)	103.39(12)	106.31(7)
N(2)-Ln(1)-O(1)	106.5(5)	106.11(15)	106.05(13)	107.52(7)
N(3)-Ln(1)-O(1)	98.7(5)	97.27(15)	96.33(13)	100.14(8)
N(5)-Ln(2)-N(4)	76.7(5)		70.18(11)	70.23(8)
N(6)-Ln(2)-N(4)	136.3(5)		137.15(13)	138.68(9)
N(6) - Ln(2) - N(5)	130.1(6)		133.39(11)	136.93 (9)
N(4)-Ln(2)-O(2)	104.6(6)		106.90(10)	103.69(10)
N(5)-Ln(2)-O(2)	110.7(6)		106.50(10)	106.56(10)
N(6)-Ln(2)-O(2)	96.6(5)		99.14(11)	96.50(10)
8		9		
Yb-N _{av}	2.175(3)	Sm-N _{av}	2.272(7)	
Yb-O _{av}	2.232(3)	Sm-O _{av}	2.326(5)	
Yb(1) - N(2)	2.659(3)	Sm(1)-N(2)	2.792(6)	
N(1) - Yb(1) - O(1)#1	107.01(11)	N(1)-Sm(1)-O(1)#1 110.2(2)		
N(1) - Yb(1) - N(3)	109.47(13)	N(1)-Sm(1)-N(3) 112.3(2)		
O(1)#1 - Yb(1) - N(3)	108.52(11)	O(1)#1-Sm(1)-N(3) 111.1(2)		
N(1) - Yb(1) - O(1)	102.87(11)	N(1)-Sm(1)-O(1) 101.3(2)		
O(1)#1 - Yb(1) - O(1)	75.01(10)	O(1)#1-Sm(1)-O(1) 74.21(19)		
N(3) - Yb(1) - O(1)	144.27(11)	N(3)-Sm(1)-O(1) 140.3(2)		
N(1) - Yb(1) - N(2)	67.27(12)	N(1) - Sm(1) - N(2) 63.8(2)		
O(1)#1 - Yb(1) - N(2)	134.34(10)	O(1)#1-Sm(1)-N(2)	131.63(18)	
N(3) - Yb(1) - N(2)	116.09(11)	N(3)-Sm(1)-N(2)	115.2(2)	
O(1) - Yb(1) - N(2)	63.42(9)	O(1) - Sm(1) - N(2)	61.57(18)	

and **5** are in the Supporting Information). The angles around the central metal are in the range of $73.0(5)^{\circ}$ to $135.9(5)^{\circ}$ in **1**, $72.55(13)^{\circ}$ to $135.94(14)^{\circ}$ in **2**, $70.83(12)^{\circ}$ to $138.59(12)^{\circ}$ in **4**, and $69.44(7)^{\circ}$ to $137.01(9)^{\circ}$ in **5** (Table 1), deviating from the ideal tetrahedron, so the coordination geometry around the central metal can be described as a distorted tetrahedral.

The usual lanthanide contraction on moving from Nd³⁺ to Yb³⁺ is reflected in the average Ln–N bond distances of 2.295(2) Å in 5, 2.268(3) Å in 4, 2.213(4) Å in 2, and 2.181(14) Å in 1 and the Ln–O bond distances found in the above complexes (Table 1). These average Ln-N bond distances in the above complexes are comparable with those found in $\{(CH_2SiMe_2)[(2,6-^{i}Pr_2C_6H_3)N]_2\}LnN(SiMe_3)_2(THF)(2.178)$ (4) Å for Yb, 2.194(12) Å for Y, 2.219(3) Å for Dy, 2.263(7) Å for Sm, 2.294(5) Å for Nd),¹⁷ but they are slightly shorter than the average Ln-N bond distances of 2.342(4) and 2.299 (2) Å for the corresponding yttrium and lutetium complexes in $[(NPN^{Ph})Ln(CH_2SiMe_3)_2(THF)]$ $(NPN^{Ph}:N(Ph)PPh_2 =$ $NC_6H_2Me_3-2,4,6)$,^{2m} even if the ionic radii differences between the two types of complexes were taken into account.²⁰ It is found that the distances of the central metal to the nitrogen atoms of the bridged ligand are generally shorter than those of metal to the nitrogen atom of the $N(SiMe_3)_2$ ligand (Table 1).

The average Yb–N bond distance of 2.181(14) Å found in **1** is comparable with the average Yb–N bond distance of 2.174(1) Å found in the cyclic binuclear Yb(III) complex $[{\mu-2-p-(Me_3SiN)_2C_6H_4}YbCl(THF)_2]_2$.²¹ The corresponding average Ln–N distances of 2.181(14) Å in **1**, 2.268(3) Å in **4**, and 2.295(2) Å in **5** are shorter than those found in corresponding dimethylsilylene-bridged diamido anionic or other neutral lanthanide amido complexes.^{22–25}

The N(2)–Ln(1)–N(1) angles (formed by the nitrogen atoms of the bridged diamido ligand and the center metal) (69.44(7)° to 73.0(5)°, Table 1) found in the above complexes are smaller than the corresponding N(2)–Ln(1)–N(1) angles 90.0(2)° to 92.1(5)° found in the complexes {(CH₂SiMe₂)-[(2,6-ⁱPr₂C₆H₃)N]₂}LnN(SiMe₃)₂(THF) (Ln = Yb, Y, Dy, Sm, Nd)¹⁷ and LYbCl₂(THF)₂ (80.2(1)°) (L = *N*,*N*-bis(2,6dimethylphenyl)-2,4-pentanediiminate),²⁵ but these angles are comparable with those found in dimethylsilylene-bridged diamido ligand complexes,^{23,24} suggesting different strain force in the ring.

As indicated in Figure 1 and Scheme 2, there are different metal-nitrogen bonds in the above complexes. One type of metal-nitrogen bond is from the metal to the nitrogen atom of the N(SiMe₃)₂, and the other type of metal-nitrogen bond is from the metal to the nitrogen atoms of the bridged ligands. To search for the selective reactivity of these different metal-nitrogen bonds, the reactions of complexes **6** and **7** with (Me₂SiO)₃ were studied for the stoichiometric reactions of the lanthanide amides with aromatic isocyanates giving the unclear results.

Treatment of $\{(Me_2Si)[(C_6H_5)N]_2\}LnN(SiMe_3)_2(THF)$ (Ln = Yb (6), Sm (7)) with grease (Me_2SiO)_3 respectively produced the selective insertion products $[C_6H_5N(Me_2Si)N-(C_6H_5)(Me_2SiO)LnN(SiMe_3)_2]_2$ (Ln = Yb (8), Sm (9)) (Scheme 2). Complexes 8 and 9 are sensitive to moisture and are soluble in THF and DME, but they are only slightly soluble in *n*-hexane. Their structures were determined by

⁽²⁰⁾ Shannon, R. D. Acta Crystallogr. 1976, A32, 751.

⁽²¹⁾ Zhao, B.; Li, H.; Shen, Q.; Zhang, Y.; Yao, Y. M.; Lu, C. R. Organometallics **2006**, *25*, 1825.

⁽²²⁾ Zhou, S.; Wang, S.; Yang, G.; Liu, X.; Sheng, E.; Zhang, K.; Cheng, L.; Huang, Z. *Polyhedron* **2003**, *22*, 1019.

⁽²³⁾ Zhou, L. Y.; Sheng, H. T.; Yao, Y. M.; Zhang, Y.; Shen, Q. J. Organomet. Chem. 2007, 692, 2990.

⁽²⁴⁾ Zhou, L. Y.; Yao, Y. M.; Li, C.; Zhang, Y.; Shen, Q. Organometallics **2006**, *25*, 2880.

⁽²⁵⁾ Xue, M. Q.; Yao, Y. M.; Shen, Q.; Zhang, Y. J. Organomet. Chem. 2005, 690, 4685.



Figure 2. Molecular structure of complex 8.







single-crystal X-ray diffraction study (Figure 2). X-ray analyses revealed that the Me₂SiO group selectively inserted to the Ln-N bond of the metal to the nitrogen atom of the bridged ligand, not the Ln-N bond of the metal to the N(SiMe₃)₂ group, indicating a high selective reactivity of the metal-nitrogen bonds (Scheme 2). These results suggested that the Ln-N bonds in the strained four-membered ring are more reactive than the other Ln-N(SiMe₃)₂) bond. The representative structure of the complexes is presented in Figure 2. From the figure, we can see that they are central symmetrical dimeric complexes with two central metals bridged by the oxygen atoms of the Me₂SiO group. Each of the central metals adopts a distorted square-pyramidal geometry, and the line formed by O and O#1 atoms are shared by the two distorted pyramids.

From Table 1, we can see that the Ln-N(2) distances of 2.659(3) Å found in 8 and 2.792(6) Å found in 9 are

Table 2. Optimal Conditions for the Cyclotrimerization of Phenyl Isocyanate

entry	cat. $(mol \%)^a$	solvent	temp (°C)	time (h)	yield $(\%)^b$
1	1	THF	room temp	12	97
2	1	toluene	room temp	12	27
3	1	Et_2O	room temp	12	44
4	1	<i>n</i> -hexane	room temp	12	40
5	2	CH_2Cl_2	room temp	12	24
6	1	THF	60	3	80
7	1	THF	40	6	93
8	1	THF	40	12	97
9	1	THF	60	6	80
10	0.5	THF	60	12	97
11	0.5	THF	40	12	97
12	0.25	THF	40	12	98
13	0.25	toluene	40	12	21
14	0.25	toluene	60	12	19
15	0.25	<i>n</i> -hexane	40	12	29
16	0.25	<i>n</i> -hexane	60	12	22

 a Catalyst: samarium complex 4, catalyst loading: mole percentage (mol %). b Isolated yield.

significantly longer than the corresponding Ln–N(1) and Ln–N(3) distances, suggesting that the bonds between the metal and N(2) are coordination bonds. The average Yb–N (the anionic nitrogen atoms) distance of 2.178(3) Å found in **8** is shorter than that of 2.272(7) Å found in **9**, which is in agreement with the lanthanide contraction. The average Yb–N distance of 2.178(3) Å found in **8** is comparable with that of 2.181(14) Å found in **1**, and the average Sm–N distance of 2.272(7) Å found in **9** is comparable with that of 2.268(3) Å found in **4** and those of lanthanide dinuclear complexes²⁶ if the ionic difference between different coordination numbers of the metals is taken into account.²⁰

Catalytic Cyclotrimerization of Aromatic Isocyanates. As we know that isocyanates could undergo cyclodimerization, cyclotrimerization, and polymerization reactions, the catalytic activities of the complexes 1-7 on selective cyclotrimerization or cyclodimerization of isocyanates were investigated (Scheme 3). The samarium complex 4 was used to search for catalytic activity. The results are listed in Table 2. From the table, we can see that the complex exhibited catalytic activity for the selective cyclotrimerization of phenyl isocyanate (based on HR-MS and ¹H NMR analytical results) in several solvents such as THF, toluene, Et₂O, n-hexane, and CH₂Cl₂ at room temperature (Table 2, entries 1 to 5); it exhibited the highest activity in THF. When the reaction temperature was raised to 40 °C, a 93% yield of the cyclotrimerization product can be obtained in the presence of 1 mol % catalyst in THF in 6 h (Table 2, entry 7), and the conversion of the phenyl isocyanate to cyclotrimer can be raised to 97% when the reaction time was prolonged to 12 h. An even higher (98%) yield can be obtained by carrying out the reaction in THF at 40 °C in the presence of 0.25 mol % catalyst loading for 12 h (Table 1, entry 12). However, the results of the reactions in other solvents under the same conditions were not improved (Table 2, entries 13 to 16), indicating solvents effects on the catalytic activity of the complexes.

The catalytic activities of other rare earth metal amides on the selective cyclotrimerization of phenyl isocyanate were

^{(26) (}a) Wang, Q.; Xiang, L.; Zi., G. J. Organomet. Chem. 2008, 693,
68–76. (b) Wang, Q.; Xiang, L.; Song, H.; Zi., G. J. Organomet. Chem.
2009, 694, 691–696. (c) Wang, Q.; Xiang, L.; Song, H.; Zi., G. Inorg. Chem. 2008, 47, 4319–4328.

Table 3. Catalytic Activity of Different Rare Earth Metal Amides on the Cyclotrimerization of Phenyl Isocyanate

entry	cat.	cat. loading (mol %)	temp (°C)	time (h)	solvent	yield (%) ^a
1	1	0.25	40	12	THF	98
2	2	0.25	40	12	THF	97
3	3	0.25	40	12	THF	96
4	4	0.25	40	12	THF	98
5	5	0.25	40	12	THF	92
6	6	1.0	60	24	THF	95
7	7	1.0	60	24	THF	98
8	8 ^b	0.25	40	12	THF	96

^a Isolated yield. ^b Catalyst: [(Me₃Si)₂N]₃Yb(µ-Cl)Li(THF)₃ as catalyst.

Table 4. Data for the Cyclodimerization or Cyclotrimerization of Different Isocyanates

entry	catalyst ^a	R-	temp (°C)/time	yield (%) b
1	1	benzyl	40/12 h	93
2	2	benzyl	40/12 h	97
3	4	benzyl	40/12 h	94
4	1	phenyl	40/12 h	98
5	2	phenyl	40/12 h	97
6	4	phenyl	40/12 h	98
7	1	4-isopropylphenyl	40/12 h	96
8	2	4-isopropylphenyl	40/12 h	97
9	4	4-isopropylphenyl	40/12 h	94
10	1	4-nitrophenyl	40/12 h	0
11	2	4-nitrophenyl	40/12 h	0
12	4	4-nitrophenyl	40/12 h	0
13	1	cyclohexyl	40/12 h	43
14	2	cyclohexyl	40/12 h	61
15	4	cyclohexyl	40/12 h	48
16	1	isopropyl	40/12 h	51
17	2	isopropyl	40/12 h	63
18	4	isopropyl	40/12 h	49
19	1	allyl	40/12 h	0

 $^a\mathrm{Catalyst}$ loading: 0.25 mol %. $^b\mathrm{Isolated}$ yield by running the reaction in THF.

also investigated. The results are given in Table 3. It can be seen that selective cyclotrimerization products could be isolated in near-quantitative yield in the presence of complexes 1-5 as catalysts with low catalyst loading (0.25 mol %) (Table 3, entries 1 to 5). High yields of the selective cyclotrimerization products could also be isolated in the presence of complexes 6 and 7 as catalysts with 1 mol % catalyst loading in THF at 60 °C (Table 3, entries 6 and 7). As shown in Table 3, complexes 1-5 exhibited a similar catalytic activity for the cyclotrimerization of phenyl isocyanate, and the amido complex $[(Me_3Si)_2N]_3Yb(\mu-Cl)Li-$ (THF)₃ also displayed a similar catalytic activity to complexes 1-5 (Table 3, entry 8), so some of these complexes were selected as catalysts to study their catalytic activity on other isocyanates. The results are presented in Table 4.

As shown in Table 4, all the complexes (1, 2, and 4) examined exhibited high catalytic activity for the cyclotrimerization of aromatic isocyanates such as phenyl isocyanate, benzyl isocyanate, 4-isopropylbenzyl isocyanate (Table 4, entries 1–9). However, 4-nitrophenylisocyanate cannot be catalyzed to its corresponding cyclotrimerization product by all the complexes examined under the same conditions (Table 4, entries 10–12). This result is similar to our previous report,¹⁷ which needs to be further investigated. It is notable that other byproducts such as cyclodimerization products or polymerization products were not observed in the reactions, indicating a high selectivity of the catalysts. Scheme 3. Catalytic Cyclodimerization or Cyclotrimerization of Isocyanates



Scheme 4. Proposed Catalytic Mechanism



When we tried to cyclotrimerize the aliphatic isocyanates such as the isopropyl isocyanate, cyclohexyl isocyanate, and allyl isocyanate to their corresponding cyclotrimerization products using the above complexes as catalysts under the same conditions, no cyclotrimerization products of the corresponding aliphatic isocyanates were isolated from the HR-MS and ¹H NMR results of the reaction products; instead, substituted ureas such as N,N'-diisopropylurea and N,N'-dicyclohexylurea were isolated from the corresponding reactions (Scheme 3, Table 4, entries 13 to 18). The formation of the substituted ureas is believed to proceed through elimination of CO from the corresponding isocyanate cyclodimerization products. These results are completely different from our previous work on the catalytic activity of lanthanide amides $\{(CH_2SiMe_2)[(2,6-Pr_2C_6H_3)N]_2\}LnN (SiMe_3)_2(THF)$ (Ln = Yb, Y, Dy, Sm, Nd), which can selectively catalyze the corresponding aliphatic isocyanate cyclotrimerization,¹⁷ suggesting ligand effects on the selectivity of the catalysts. It was found that the yttrium complex exhibited higher catalytic activity than the other complexes examined (complexes 1 and 4) (Table 4, entries 13 to 18). However, in the case of allyl isocyanate, no cyclotrimerization or substituted urea was isolated under the same conditions.

The catalytic reaction mechanism is proposed as follows (Scheme 4): Coordination of the isocyanate to the central metal under liberation of the coordinated THF molecule

Article

gave the intermediate I, insertion of the isocyanate into the metal-nitrogen bond of the metal to the bridged ligand leads to the formation of the six-memebered intermediate II to release the stain force of the four-membered ring,¹⁵ the intermediate II then reacted with another molecule of isocyanate to give the eight-membered intermediate III. The intermediate III either eliminated the cyclodimerization product followed by giving off a molecule of carbon monoxide (CO), producing the urea when the isocyanates are the aliphatic isocyanates and thus furnishing the catalytic cycle, or further reacted with isocyanate, producing the cyclotrimerization products and the intermediate I when the isocyanates are aromatic isocyanates and thus furnishing a catalytic cycle. The selectivity of these complexes on different isocyanates may be due to the electronic properties of different isocyanates causing a different reactivity of the intermediate III. However, other possibilities such as reaction of the $Ln-N(SiMe_3)_2$ bond in the intermediate II with isocyanate to give the catalytic products as proposed in our previous work¹⁷ cannot be ruled out.

Conclusion

In summary, a series of four-coordinated neutral lanthanide amides { $(Me_2Si)[(2,6-R_2^1-4-R^2-C_6H_2)N]_2$ }LnN(Si-Me₃)₂(THF) (R¹ = ^{*i*}Pr, R² = H, Ln = Yb (1), Y (2), Eu (3), Sm (4), Nd (5); R¹ = R² = H, Ln = Yb (6), Sm (7)) having different metal-nitrogen bonds have been synthesized and characterized. Results of reactions of the complexes with (Me₂SiO)₃ indicated that the Ln-N bonds in the complexes displayed different reactivity. Investigation of the catalytic activity of complexes { $(Me_2Si)[(2,6-R_2^1-4-R_2^2-C_6H_2)]$ N]₂{LnN(SiMe₃)₂(THF) indicated that these complexes exhibited a high selectivity on cyclotrimerization or cyclodimerization of isocyanates depending on the nature of the isocyanates. These complexes exhibited a high catalytic activity and a high selectivity on cyclotrimerization of aromatic isocyanates; all the complexes showed a similar catalytic activity. The complexes exhibited a good catalytic activity and a high selectivity on cyclodimerization of aliphatic isocyanates; the yttrium complex had a higher catalytic activity than other complexes examined. The complexes not only have a high selective reactivity toward isocyanates but also have the advantages of easy preparation, low catalyst loading, high conversion, mild reaction conditions, and compatibility with different substrates and solvents.

Experimental Section

Materials and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were performed under a dry argon and oxygen-free atmosphere using standard Schlenk techniques. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. [(Me₃Si)₂N]₃Ln^{III}(μ -Cl)Li(THF)₃ (Ln = Yb, Y, Eu, Sm, and Nd),²² (Me₂Si)[(2,6-ⁱPr₂C₆H₃)NH]₂,²⁷ and (Me₂Si)[(C₆H₅)-NH]₂²³ were prepared according to literature methods. Elemental analyses data were obtained on a Perkin-Elmer 2400 Series II elemental analyzer. ¹H NMR and ¹³C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer (300 MHz for ¹H; 75.0 MHz for ¹³C) in C₆D₆ for lanthanide complexes and in CDCl₃ for organic compounds. Chemical shifts (δ) were reported in ppm. *J* values are reported in Hz. IR spectra were recorded on a Shimadzu FTIR-8400s

spectrometer (KBr pellet). Mass spectra were performed on a Micromass GCT-MS spectrometer. Melting points were determined in capillaries and were uncorrected.

Preparation of $\{(Me_2Si)[(2,6-iPr_2C_6H_3)N]_2\}$ YbN(SiMe_3)₂-(THF) (1). To a toluene (10.0 mL) solution of (Me₂Si)- $[(2,6-Pr_2C_6H_3)NH]_2$ (1.20 g, 2.92 mmol) was added a toluene (40.0 mL) solution of $[(Me_3Si)_2N]_3$ Yb^{III}(μ -Cl)Li(THF)₃ (2.67 g, 2.92 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was then refluxed for 24 h, and the color of the solution gradually changed from yellow to red. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (2 \times 15.0 mL). The extractions were combined and concentrated to about 10.0 mL. The red crystals were obtained by cooling the concentrated solution at 0 °C for several days (1.92 g, 81% yield). IR (KBr pellet, cm⁻¹): v 3063 (m), 3028 (m), 2962 (m), 2866 (m), 1620 (s), 1512(s), 1458(m), 1361 (s), 1330 (w), 1254 (s), 1196 (s), 1111 (w), 1045 (w), 957 (s), 879 (s), 829 (s), 686 (m), 628 (m). Anal. Calcd for C36H66N3OSi3Yb: C, 53.10; H, 8.17; N, 5.16. Found: C, 53.43; H, 7.99; N, 4.98.

Preparation of {(Me₂Si)[(2,6^{-*i*}Pr₂C₆H₃)N]₂}YN(SiMe₃)₂-(THF) (2). This compound was prepared as white crystals in 74% (1.21 g) yield by treatment of (Me₂Si)[(2,6^{-*i*}Pr₂C₆H₃)NH]₂ (0.92 g, 2.24 mmol) with [(Me₃Si)₂N]₃Y^{III}(μ-Cl)Li(THF)₃ (1.86 g, 2.24 mmol) using procedures similar to those described above for the preparation of 1. ¹H NMR (C₆D₆, ppm): δ7.32–7.12 (m, 6H) (C₆H₃), 3.93 (m, 4H, OC₄H₈), 3.59 (m, 4H, CH(CH₃)₂), 1.43 (m, 4H, OC₄H₈), 1.24–1.19 (m, 24H, CH₃), 0.35–0.09 (s, 24H, Si(CH₃)₃). ¹³C NMR (C₆D₆, ppm): δ 147.9, 141.4, 122.9, 120.1, 28.0, 27.3, 24.4, 23.2, 3.2, 0.8. IR (KBr pellet, cm⁻¹): ν 3063 (m), 2928 (m), 2866 (m), 1527 (s), 1458 (m), 1438 (m), 1381(s), 1361 (s), 1330 (w), 1253 (s), 1195 (s), 1099 (w), 1041 (w), 906 (s), 879 (s), 806 (m), 786 (m), 748 (w), 675(m). Anal. Calcd for C₃₆H₆₆N₃OSi₃Y: C, 59.22; H, 9.11; N, 5.76. Found: C, 58.88; H, 9.09; N, 5.67.

Preparation of {(Me₂Si)](2,6⁻Pr₂C₆H₃)N]₂}EuN(SiMe₃)₂-(THF) (3). This compound was obtained as a red powder in 45% yield following the procedures described for complex 1 from the reaction of $(Me_2Si)[(2,6⁻Pr_2C_6H_3)NH]_2$ (0.38 g, 0.93 mmol) with $[(Me_3Si)_2N]_3Eu^{III}(\mu$ -Cl)Li(THF)₃ (0.82 g, 0.93 mmol). IR (KBr pellet, cm⁻¹): ν 3028 (m), 2962(m), 1635 (s), 1462 (s), 1438 (m), 1361 (s), 1327 (w), 1257 (s), 1195 (s), 1057 (w), 910 (s), 802 (m), 744 (m). Anal. Calcd for C₃₆H₆₆N₃OSi₃Eu: C, 54.51; H, 8.39; N, 5.30. Found: C, 54.25; H, 7.93; N, 5.18.

Preparation of {(Me₂Si)[(2,6-^{*i*}Pr₂C₆H₃)N]₂}SmN(SiMe₃)₂-(THF) (4). Following the procedures described for the preparation of complex 1, complex 4 was prepared as yellow crystals in 77% yield from the reaction of $(Me_2Si)[(2,6^{-$ *i* $}Pr_2C_6H_3)NH]_2$ (0.94 g, 2.28 mmol) with $[(Me_3Si)_2N]_3Sm^{III}(\mu$ -Cl)Li(THF)₃ (2.03 g, 2.28 mmol). IR (KBr pellet, cm⁻¹): ν 3063 (m), 2962 (m), 2928 (m), 2866 (m), 1624 (s), 1458 (m), 1438 (m), 1253 (s), 1195 (s), 1111 (w), 1045 (w), 933 (s), 906 (s), 879 (m), 786 (w), 748 (m), 678 (m). Anal. Calcd for C₃₆H₆₆N₃OSi₃Sm: C, 54.63; H, 8.40; N, 5.31. Found: C, 54.77; H, 8.03; N, 5.02.

Preparation of {(Me₂Si)](2,6-ⁱPr₂C₆H₃)N]₂}NdN(SiMe₃)₂-(THF) (5). This compound was prepared as blue crystals in 53% yield from the reaction of $(Me_2Si)[(2,6-ⁱPr_2C_6H_3)NH]_2$ (0.87 g, 2.12 mmol) with [(Me₃Si)₂N]₃Nd^{III}(μ -Cl)Li(THF)₃ (1.88 g, 2.12 mmol) in toluene using procedures similar to those described above for the preparation of **1**. IR (KBr pellet, cm⁻¹): ν 2962 (m), 2870 (m), 1620 (s), 1462 (m), 1438 (m), 1384 (s), 1365(m), 1261 (s), 1207 (s), 1091 (w), 860 (m), 744 (m), 659 (m). Anal. Calcd for C₃₆H₆₆N₃NdOSi₃: C, 55.05; H, 8.47; N, 5.35. Found: C, 54.96; H, 8.12; N, 5.02.

Preparation of {(Me₂Si)[(C₆H₅)N]₂}YbN(SiMe₃₎₂(THF) (6). This complex was prepared as red crystals in 73% yield from reaction of $(Me_2Si)[(C_6H_5)NH]_2$ (0.45 g, 1.87 mmol) with $[(Me_3Si)_2N]_3Yb^{III}(\mu$ -Cl)Li(THF)₃ (1.71 g, 1.87 mmol) in toluene using procedures similar to those described above for the preparation of 1. IR (KBr pellet, cm⁻¹): ν 2962 (m), 1600 (s), 1496(s), 1384 (s), 1288 (m), 1261 (s), 1091 (w), 1030 (m), 914 (w), 798 (s), 752 (m), 690 (w), 720 (m), 669 (m). Anal. Calcd for $C_{35}H_{58}N_3O_2Si_3Yb$ ($6+C_7H_8+THF$): C, 51.89; H, 7.22; N, 5.19. Found: C, 51.67; H, 7.06; N, 4.94.

Preparation of {(Me₂Si)[(C₆H₅)N]₂}SmN(SiMe₃)₂(THF) (7). This complex was prepared as yellow crystals in 67% yield from reaction of (Me₂Si)[(C₆H₅)NH]₂ (0.55 g, 2.27 mmol) with [(Me₃Si)₂N]₃Sm^{III}(μ -Cl)Li(THF)₃ (2.03 g, 2.27 mmol) in toluene using procedures similar to those described above for the preparation of **1**. IR (KBr pellet, cm⁻¹): ν 3086 (m), 3036 (m), 2962 (m), 2901 (m), 1600 (s), 1500 (s), 1388 (s), 1288 (m), 1257 (s), 1180 (w), 1153 (w), 1076 (m), 1030 (m), 995 (m), 887 (s), 614 (w). Anal. Calcd for C₂₇H₄₂N₃Si₃Sm (7+C₇H₈-THF): C, 50.41; H, 6.58; N, 6.53. Found: C, 50.06; H, 6.09; N, 6.55.

Preparation of $[C_6H_5N(Me_2Si)N(C_6H_5)(Me_2SiO)YbN(SiMe_3)_{2|2}$ (8). To a toluene solution of { $(Me_2Si)[(C_6H_5)N]_2$ }YbN(SiMe_3)_2-(THF) (6) (1.30 g, 2.00 mmol) was added grease (Me_2SiO)_3 (0.22 g, 1.00 mmol), and the reaction was refluxed for 12 h. The solution was concentrated to about 10 mL. Orange crystals were obtained by cooling the solution at $-5 \,^{\circ}C$ for several days (0.84 g, 55% yield). IR (KBr pellet, cm⁻¹): ν 3036 (m), 2958 (m), 1921 (w), 1832 (m), 1774 (m), 1600 (s), 1498 (s), 1384 (s), 1288 (m), 1257 (m), 1176 (s), 1153 (s), 1111 (w), 1076 (m), 1030 (s), 995 (m), 914 (w), 883 (w), 829 (w), 798 (m), 752 (m), 694 (w), 659 (w). Anal. Calcd for C₅₈H₉₆N₆O₂Si₈Yb₂ (8+2C₇H₈): C, 47.06; H, 6.54; N, 5.68. Found: C, 47.17; H, 5.98; N, 5.92.

Preparation of $[C_6H_5N(Me_2Si)N(C_6H_5)(Me_2SiO)SmN(Si-Me_3)_2]_2$ (9). This complex was prepared as yellow crystals by reaction of $\{(Me_2Si)[(C_6H_5)N]_2\}SmN(SiMe_3)_2(THF)$ (7) (1.12 g, 1.80 mmol) with $(Me_2SiO)_3$ (0.20 g, 0.90 mmol) following procedures similar to those used for the preparation of **8** (0.78 g, 60% yield). IR (KBr pellet, cm⁻¹): ν 3039 (m), 2958 (m), 1925

(w), 1847 (m), 1774 (m), 1600 (s), 1496 (s), 1388 (s), 1292 (m), 1257 (m), 1176 (s), 1153 (m), 1076 (m), 1030 (s), 995 (m), 914 (w), 887 (w), 829 (w), 798 (m), 752 (m), 694 (w), 659 (w). Anal. Calcd for $C_{65}H_{104}N_6O_2Si_8Sm_2$ (9 + $3C_7H_8$): C, 51.13; H, 6.86; N, 5.50. Found: C, 51.77; H, 7.25; N, 5.56.

General Procedure for the Cyclotrimerization or Cyclodimerization of Isocyanates Catalyzed by $\{(Me_2Si)|(2,6-R_2^1-4-R^2-C_6H_2)N]_2\}LnN(SiMe_3)_2(THF)$ (10 as an example). A 30 mL Schlenk tube under dried argon was charged with complex 1 (0.016 g, 0.02 mmol), and THF (5 mL) and phenyl isocyanate (0.95 g, 8.0 mmol) were added. The resulting mixture was stirred at room temperature for 12 h. After the solvent was removed under reduced pressure, the residue was washed with hexane (3 × 5 mL). The final product, 10, was isolated as colorless crystals by recrystallization from THF (98%): ¹H NMR (CDCl₃, ppm) δ 7.53–7.40 (m, 15H, aromatic CH); ¹³C NMR (CDCl₃, ppm) δ 148.4, 133.2, 129.1, 128.0.

X-ray crystallography section and crystallographic data can be found in the Supporting Information.

Acknowledgment. This work was co-supported by the National Natural Science Foundation of China (Grant Nos. 20672002, 20832001) and grants from Anhui Province (Nos. TD200707, 2007Z016).

Supporting Information Available: Text for characterization data of compounds 10–14, figures for compounds 2, 4, 5, 9, and 12–14, table giving bond lengths, crystallographic data, and CIF files giving crystal data for complexes 1, 2, 4, 5, 9, and 12–14. This material is available free of charge via the Internet at http://pubs.acs.org.