Synthesis and Characterization of Group 4 Amidinate Amide Complexes $M[CyNC(Me)NCy]_2(NR_2)_2$ (R = Me, M = Ti, Zr, Hf; R = Et, M = Zr)

Jia-Feng Sun,[†] Shu-Jian Chen,[‡] Yuxi Duan,[‡] Yi-Zhi Li,[†] Xue-Tai Chen,^{*,†} and Zi-Ling Xue^{*,‡}

State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China, and Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

Received February 28, 2009

Amidinate amide complexes M[CyNC(Me)NCy]₂(NR₂)₂ (M = Ti, R = Me (1); M = Zr, R = Me (2), R = Et, (3); M = Hf, R = Me (4); Cy = cyclohexyl) have been prepared, and their crystal structures show distorted-octahedral coordination spheres. Variable-temperature NMR studies give $\Delta H^{\ddagger} = 2.8(0.2)$ kcal mol⁻¹, $\Delta S^{\ddagger} = -36(1)$ eu and $\Delta H^{\ddagger} = 0.5(0.3)$ kcal mol⁻¹, $\Delta S^{\ddagger} = -44(1)$ eu for interconversions in 2 and 3, respectively.

Amidinates are ligands containing two nitrogen donor atoms that, like their isoelectronic analogues carboxylates, bind to a wide range of metals and nonmetals in a bidentate fashion.¹ The fundamental chemistry of amidinate complexes and unique properties of the metal complexes containing versatile amidinate ligands have led to active studies of these complexes and their applications.^{1–5}Metal amidinate systems with lower electron counts at the metals have shown, for example, enhanced electrophilic behavior that leads to reactivities not observed in more commonly studied cyclopentadienyl (Cp) analogs.⁶ Applications of amidinate complexes include catalysis in several reactions such as olefin polymerization,² hydrosilylation of alkenes,³ and hydroamination,⁴ as well as the use of the complexes as precursors in chemical vapor deposition (CVD)/ atomic layer deposition (ALD) of metal-containing microelectronic materials. $^{5,7-10}$ Thin films of group 4 metal oxides with large dielectric constants are of particular interest as insulating

(2) (a) Zhang, Y.; Reeder, E. K.; Keaton, R. J.; Sita, L. R. Organometallics **2004**, 23, 3512. (b) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. J. Am. Chem. Soc. **2004**, 126, 9182. (c) Zhang, L.; Nishiura, M.; Yuki, M.; Luo, Y.; Hou, Z. Angew. Chem., Int. Ed. **2008**, 47, 2642. (d) Luo, Y.; Yao, Y.; Shen, Q.; Sun, J.; Weng, L. J. Organomet. Chem. **2002**, 662, 144.

(3) Ge, S.; Meetsma, A.; Hessen, B. Organometallics 2008, 27, 3131.
(4) Bambirra, S.; Tsurugi, H.; van Leusen, D.; Hessen, B. Dalton Trans. 2006, 1157.



materials in microelectronic devices.⁷ MO_2 (M = Ti, Zr, Hf) species have been prepared from their amide precursors $M(NMe_2)_{n}$ ^{8,9} tetraamidinates (Chart 1),^{5b} and guanidinate precursors.¹⁰

There are few known group 4 mixed amidinate amide complexes.^{1h,l,m} Triamide Ti and Zr complexes containing a

(6) (a) Dawson, D. Y.; Arnold, J. *Organometallics* **1997**, *16*, 1111. (b) Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279.

(7) (a) Wilk, G. D.; Wallace, R. M. Appl. Phys. Lett. 1999, 74, 2854.
(b) Lee, B. H.; Kang, L.; Nieh, R.; Qi, W.-J.; Lee, J. C. Appl. Phys. Lett. 2000, 76, 1926. (c) Kang, L.; Jeon, Y.; Onishi, K.; Lee, B. H.; Qi, W.-J.; Nieh, R.; Gopalan, S.; Lee, J. C. Symposium on VLSI Technology. Digest of Technical Papers; 2000; p 44. (d) Yang, F.; Kotecki, D. E.; Bernhardt, G.; Call, M. Mater. Res. Soc. Symp. Proc. 2002, 745, Paper No. N5.16. (e) Wilk, G. D.; Wallace, R. M.; Anthony, J. M. J. Appl. Phys. 2001, 89, 5243.

(8) (a) Ohshita, Y.; Ogura, A.; Hoshino, A.; Hiiro, S.; Suzuki, T.; Machida, H. *Thin Solid Films* 2002, 406, 215. (b) Hausmann, D. M.; Kim, E.; Becker, J.; Gordon, R. G. *Chem. Mater.* 2002, 14, 4350. (c) Bastianini, A.; Battiston, G. A.; Gerbasi, R.; Porchia, M.; Daolio, S. J. *Phys. IV France* 1995, 5, C5-525. (d) Deshpande, A.; Inman, R.; Jursich, G.; Takoudis, C. G. J. *Vac. Sci. Technol. A* 2004, 22, 2035. (e) Machida, H.; Hoshino, A.; Suzuki, T.; Ogura, A.; Ohshita, Y. J. Cryst. Growth 2002, 237–239, 586. (f) Takahashi, K.; Nakayama, M.; Yokoyama, S.; Kimura, T.; Tokumitsu, E.; Funakubo, H. *Appl. Surf. Sci.* 2003, 216, 296. (g) Lee, M.; Lu, Z.-H.; Ng, W.-T.; Landheer, D.; Wu, X.; Moisa, S. *Appl. Phys. Lett.* 2003, 83, 2638.

 $[\]ast$ To whom correspondence should be addressed. E-mail: xue@utk.edu (Z.-L.X.).

Nanjing University.

[‡] University of Tennessee.

^{(1) (}a) Barker, J.; Kilner, M. Coord. Chem. Rev. 1994, 133, 219. (b) Edelmann, F. T. Coord. Chem. Rev. 1994, 137, 403. (c) Berno, P.; Hao, S.; Minhas, R.; Gambarotta, S. J. Am. Chem. Soc. 1994, 116, 7417. (d) Littke, A.; Sleiman, N.; Bensimon, C.; Richeson, D. S.; Yap, G. P. A.; Brown, S. J. Organometallics 1998, 17, 446. (e) Otten, E.; Dijkstra, P.; Visser, C.; Meetsma, A.; Hessen, B. Organometallics 2005, 24, 4374. (f) Hirotsu, M.; Fontaine, P. P.; Zavalij, P. Y.; Sita, L. R. J. Am. Chem. Soc. 2007, 129, 12690. (g) Boyd, C. L.; Clot, E.; Guiducci, A. E.; Mountford, P. Organometallics 2005, 24, 2347. (h) Hagadorn, J. R.; McNevin, M. J.; Wiedenfeld, G.; Shoemaker, R. Organometallics 2003, 22, 4818. (i) Chen, W.-Z.; Fanwick, P. E.; Ren, T. Organometallics 2007, 26, 4115. (j) Brown, D. J.; Chisholm, M. H.; Gallucci, J. C. Dalton Trans. 2008, 1615. (k) Hao, S.; Gambarotta, S.; Bensimon, C.; Edema, J. J. H. Inorg. Chim. Acta 1993, 213, 65. (1) McNevin, M. J.; Hagadorn, J. R. Inorg. Chem. 2004, 43, 8547. (m) Ward, B. D.; Risler, H.; Weitershaus, K.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. Inorg. Chem. 2006, 45, 7777.

^{(5) (}a) Lim, B. S.; Rahtu, A.; Park, J.-S.; Gordon, R. G. Inorg. Chem. 2003, 42, 7951. (b) Gordon, R. G.; Lehn, J.-S.; Li, H. PCT Int. Appl. WO 2008002546, 2008. (c) Sadique, A. R.; Heeg, M. J.; Winter, C. H. Inorg. Chem. 2001, 40, 6349. (d) Wu, J.; Li, J.; Zhou, C.; Lei, X.; Gaffney, T.; Norman, J. A. T.; Li, Z.; Gordon, R.; Cheng, H. Organometallics 2007, 26, 2803. (e) Wilder, C. B.; Reitfort, L. L.; Abboud, K. A.; McElwee-White, L. Inorg. Chem. 2006, 45, 263. (f) Hunks, W.; Chen, P. S.; Chen, T.; Stender, M.; Stauf, G. T.; Maylott, L.; Xu, C.; Roeder, J. F. Mater. Res. Soc. Symp. Proc. 2008, 1071, Paper No. 1071-F09-11. (g) Päiväsaari, J.; Dezelah, C. L.; Back, D.; El-Kaderi, H. M.; Heeg, M. J.; Putkonen, M.; Niinistö, L.; Winter, C. H. J. Mater. Chem. 2005, 15, 4224.



binucleating bis(amidinate) ligand^{1h,1} and several bis(amidinate)bis(amide)titanium(IV) complexes supported by chiral amidinates (2-aminopyrrolines)^{1m} have been prepared. To our knowledge, group 4 bis(amidinate) bis(amide) complexes containing simple amidinate ligands [RN(Me)NR]⁻ (Chart 1) have not been reported. We have prepared and characterized such complexes with bulky [CyN(Me)NCy]⁻ ligands. Our work is reported here.

Results and Discussion

Synthesis and NMR Spectra of 1–4. The reaction of $TiCl_2(NMe_2)_2$ (6) with 2 equiv of [CyNC(Me)NCy]Li (5) (Scheme 1) proceeds smoothly at 23 °C to yield dark red 1. Repeated attempts to prepare 1 through the reaction of $Ti[CyNC(Me)NCy]_2Cl_2$ with 2 equiv of LiNMe₂ did not yield the product. The reaction of MCl₄ with 2 equiv of 5 at 23 °C gives M[CyNC(Me)NCy]_2Cl_2 (M = Zr, 7; M = Hf, 8). Subsequent treatment of 7 with 2 equiv of LiNR₂ (R = Me, Et) yields pale yellow crystalline 2 or 3. Similar treatment of the Hf complex 8 with 2 equiv of LiNMe₂ gives 4. 2 and 3 are also prepared in one pot by the reactions of ZrCl₄ with 5 and LiNR₂ (R = Me, Et) in a 1:2:2 ratio at 23 °C.

¹H NMR spectra of **1** and **3** at 23 °C show two broad resonances at 3.28, 3.13 ppm and 3.15, 3.05 ppm, respectively, for the Cy α -H atoms, suggesting the Cy groups are inequivalent. However, **2** and **4** show one broad resonance at 3.10 and 3.22 ppm, respectively. The equivalence of the Cy α -H resonances indicates that **2** and **4** are fluxional at 23 °C, since the two rings are inequivalent in the solid state, as their X-ray crystal structures below reveal. The only difference between **1** and **2** is the central metal atom: one is Ti and the other is Zr. Because the atomic radius of Ti is smaller than that of Zr, the environment around the Ti atom in **1** is more crowded, restricting its fluxionality. ¹³C NMR spectra of **2** show one signal (57.0 ppm) for the cyclohexyl α -C atom, while those of **3** show two signals (57.2 and 56.9 ppm) for its α -C atoms, indicating that the Cy groups in **2** are equivalent and the Cy groups in **3**

Table 1. Rate Constants of the Interconversions in 2 and 3^{11,14}

complex 2			complex 3		
Т	$\Delta v (\text{Hz})^a$	$k (s^{-1})$	Т	$\Delta v (\text{Hz})^a$	$k (s^{-1})$
253	0	293	313	0	520
243	36.1	245	303	39.5	490
233	54.5	164	293	56.0	457
223	58.7	133	286	63.8	437
213	63.0	85.7	276	72.1	410
205	65.9 (Δv_0)		266	78.8	385
			201	117.2 (Δv_0)	

^{*a*} The Cy α -H resonances in **2** and $-CH_2-$ resonances in **3**, respectively, were used in the kinetic studies.

are inequivalent. These observations suggested that the bulky NEt₂ groups slow down the fluxionality. In addition, several broad Cy peaks are found in 1-4 and the signals of the CH₃ group attached to the central C atom appear at ca. 1.7 ppm.

To further clarify the fluxional behavior, a variable-temperature ¹H NMR experiment was carried out for **2**.¹¹ As the temperature was lowered, the signal of Cy α -H starts to broaden; at 253 K, the peak starts to decoalesce. At 205 K, two separate signals appear at 3.20 and 3.03 ppm. The coalescence temperature was 253 K and the $\Delta G^{+}_{253 \text{ K}}$ value was calculated to be 11.9(0.5) kcal mol⁻¹,¹² which is very close to that found in a six-coordinate Ti(IV) complex containing bis(2-pyridyl)amine ligands.¹³ No splitting of the signals of the NMe₂ group is observed as a function of temperature until at least 205 K. The rate constants of this interconversion of **2** at various temperatures were calculated from eq 1

$$k = \pi \sqrt{2(\Delta \nu_0^2 - \Delta \nu^2)} \tag{1}$$

(where $\Delta \nu$ and $\Delta \nu_0$ are frequency differences (Hz) between exchange-broadened sites at temperature *T* and between the two sites at the slow exchange limit, respectively¹⁴), and they are given in Table 1.¹⁴ An Eyring plot¹¹ gives the activation parameters of the exchange: $\Delta H^{\ddagger} = 2.8(0.2)$ kcal mol⁻¹ and $\Delta S^{\ddagger} = -36(1)$ eu. This fluxional process and small ΔH^{\ddagger} and negative ΔS^{\ddagger} values can be explained by the Bailar twist mechanism.¹⁵ At room temperature, two enantiomers intercon-

^{(9) (}a) Woods, J. B.; Beach, D. B.; Nygren, C. L.; Xue, Z.-L. *Chem. Vap Deposition* **2005**, *11*, 289. (b) Wang, R.; Zhang, X.-H.; Chen, S.-J.; Yu, X.; Wang, C.-S.; Beach, D. B.; Wu, Y.-D.; Xue, Z.-L. J. Am. Chem. Soc. **2005**, *127*, 5204. (c) Chen, S.-J.; Zhang, X.-H.; Yu, X.; Qiu, H.; Yap, G. P. A.; Guzei, I. A.; Lin, Z.; Wu, Y.-D.; Xue, Z.-L. J. Am. Chem. Soc. **2007**, *129*, 14408.

^{(10) (}a) Devi, A.; Bhakta, R.; Milanov, A.; Hellwig, M.; Barreca, D.; Tondello, E.; Thomas, R.; Ehrhart, P.; Winter, M.; Fischer, R. *Dalton Trans.* **2007**, 1671. (b) Milanov, A.; Bhakta, R.; Baunemann, A.; Becker, H.-W.; Thomas, R.; Ehrhart, P.; Winter, M.; Devi, A. *Inorg. Chem.* **2006**, *45*, 11008.
(c) Thenappan, A.; Lao, J.; Nair, H. K.; Devi, A.; Bhakta, R.; Milanov, A.
PCT Int. Appl. WO 2007005088, 2007. (d) Thomas, R.; Bhakta, R.; Milanov, A.; Devi, A.; Ehrhart, P. *Chem. Vap. Deposition* **2007**, *13*, 98.

⁽¹¹⁾ See the Supporting Information for details.

⁽¹²⁾ Abrahams, R. J.; Fisher, J.; Loftus, P. Introduction to NMR Spectroscopy; Wiley: New York, 1988.

⁽¹³⁾ Fandos, R.; Hernández, C.; Otero, A.; Rodríguez, A.; Ruiz, M. J. *J. Organomet. Chem.* **2005**, *690*, 4828.

^{(14) (}a) Macomber, R. S. A Complete Introduction to Modern NMR Spectroscopy; Wiley: New York, 1998; pp 158–160. The rate constants here are the chemical rate constants, and they differ from the observed magnetization transfer rate constants by a factor of 2. See e.g.: (b) Green, M. L. H.; Wong, L.-L.; Sella, A. Organometallics **1992**, *11*, 2660.



vert rapidly on the NMR time scale via a trigonal-prismatic intermediate (Scheme 2), where all the Cy groups are equivalent, but they were distinguishable at lower temperatures. Such a behavior has been suggested for six-coordinate Zr(IV) complexes with N-aryl-substituted β -diketiminato ligands.^{15g,h,16} The ¹³C NMR spectra of **2** are also consistent with this dynamic feature. For example, the α -C resonance appears at 57.0 ppm, whereas at 205 K two sharp singlets at 56.9 and 56.3 ppm are observed.

The VT ¹H NMR spectrum of **3** at 23 °C displays two sets of multiplets for the two chemically inequivalent methylene signals (3.80 and 3.68 ppm) of -NEt₂ groups and two signals (3.15 and 3.05 ppm) for the ring α -H of Cy groups.¹¹ No splitting was found for the methyl protons of NEt₂ groups, which appear as a unique triplet centered at 1.11 ppm. In this case, the larger steric demand of the -NEt₂ groups further hinders the equilibration of the two enantiomers. Coalescence of the cyclohexyl α -H resonances was observed at 333 K. The rate constants of the interconversion in 3 were calculated from eq 1 and are given in Table 1.¹⁴ An Eyring plot¹¹ gives the activation parameters of the exchange: $\Delta H^{\ddagger} = 0.5(0.3)$ kcal mol⁻¹ and $\Delta S^{\dagger} = -44(1)$ eu. At the coalescence temperature of 313 K, $\Delta G^{\dagger}_{313 \text{ K}} = 14.3(0.6) \text{ kcal mol}^{-1}$. As in the interconversion in **2**, small ΔH^{\ddagger} and negative ΔS^{\ddagger} values are consistent with the Bailar twist mechanism.^{1e,15f,g} The coalescence temperature is higher than that in **2**. The activation entropy ΔS^{\ddagger} here is more negative than the -36(1) eu in 2. These could be attributed to the greater steric demand of the $-NEt_2$ groups in **3** as compared to that of the $-NMe_2$ groups in **2**.^{16,17} This phenomenon is similar to those found in β -diketiminato-based Zr complexes.¹⁶

X-ray Crystal Structures of 1–3. Selected bond distances and angles for 1–3 are given in Table 2. The Ti center in 1 is in a distorted-octahedral environment, surrounded by the four N atoms of the two amidinate anions and two *cis*-NMe₂ ligands (Figure 1). The bonding parameters within the two amidinate ligands are not dramatically different. The two N and bridging C atoms for each of the individual amidinate ligands lie in a plane, which includes the Ti atom, resulting in a solid-state molecular geometry with approximately C_2 symmetry. The nitrogen termini of the amidinate ligands can be divided roughly into two types: *cis*-NCy groups (N2, N4) with a N2–Ti1–N4 angle of 81.99(11)° and *trans*-NCy groups (N1, N5) with a N1–Ti1–N5 angle of 146.23(10)°. The two *cis*-Ti–N bonds

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 1-3

1-3						
1	l					
2.275(3)	N1-C7	1.343(4)				
2.092(3)	Ti1-N6	1.967(3)				
1.952(3)	N2-C7	1.311(4)				
2.258(3)	N4-C19	1.316(4)				
2.088(3)	N5-C19	1.334(4)				
60.81(10)	N4-Ti1-N5	60.73(10)				
146.23(10)	N1-C7-N2	113.2(3)				
81.99(11)	N4-C19-N5	112.3(3)				
94.61(12)						
2		3				
2.331(2)		2.3469(14)				
2.2446(18)		2.2520(14)				
2.2330(17)		2.2269(14)				
2.349(2)		2.3687(14)				
2.0933(19)		2.0761(14)				
2.0790(19)		2.0587(15)				
1.322(3)		1.324(2)				
1.342(2)		1.334(2)				
1.353(2)		1.353(2)				
1.318(2)		1.315(2)				
1–Zr1–N2 58.18(6)		57.87(5)				
N1-Zr1-N4 82.95(6)		80.06(5)				
142.12(6)		148.55(5)				
N3-Zr1-N4 58.30(6)		57.97(5)				
94.12(7)		102.18(6)				
113	.32(16)	113.73(14)				
113	.55(16)	113.41(15)				
	1 2.275(3) 2.092(3) 1.952(3) 2.258(3) 2.088(3) 60.81(10) 146.23(10) 81.99(11) 94.61(12) 2.33 2.24 2.23 2.34 2.09 2.07 1.32 1.34 1.35 1.31 58.1 82.9 142. 58.3 94.1 113. 113.	$\begin{array}{c c} 1 \\ \hline 1 \\ \hline 2.275(3) & N1-C7 \\ \hline 2.092(3) & Ti1-N6 \\ \hline 1.952(3) & N2-C7 \\ \hline 2.258(3) & N4-C19 \\ \hline 2.088(3) & N5-C19 \\ \hline 60.81(10) & N4-Ti1-N5 \\ \hline 146.23(10) & N1-C7-N2 \\ \hline 81.99(11) & N4-C19-N5 \\ \hline 94.61(12) \\ \hline $				

(2.275(3), 2.258(3) Å) are longer than the *trans*-Ti-N bonds (2.092(3), 2.088(3) Å), as a result of the strong π -donating effect of the dialkylamide groups. The N-C bond lengths around the central C7 and C19 atoms average 1.33 Å, indicating partial double-bonding character and a π -conjugated NCN chelate.

The structures of **2** and **3** are shown in Figure 2. As in **1**, the Zr center is in a distorted-octahedral environment. Similarly, the termini of the amidinate ligand can be divided roughly into two types, and the two *cis*-Zr–N bonds (2.331(2), 2.349(2) Å in **2**, 2.3469(14), 2.3687(14) Å in **3**) are longer than the *trans*-Zr–N bonds (2.2446(18), 2.2330(17) Å in **2**, 2.2520(14), 2.2269(14) Å in **3**). All Zr–N bond lengths are similar to the amidinate complexes Zr[CyNC(Me)NCy]₂Cl₂ and Zr[CyNC-(Me)NCy]₂Me₂.^{1d} The bond distances around NCN chelate average 1.33 Å, indicating partial double-bonding character. In **3**, the two *cis*-NEt₂ groups exhibit a N5–Zr1–N6 angle of 102.18(6)°, which is larger than that of the two *cis*-NMe₂ groups (94.12(7)°) in **2**.



Figure 1. ORTEP diagram of 1 showing 30% probability thermal ellipsoids.

^{(15) (}a) Bailar, J. C. J. Inorg. Nucl. Chem. 1958, 8, 165. (b) Wentworth,
R. A. D. Coord. Chem. Rev. 1972, 9, 171. (c) Fleischer, E. B.; Gebala,
A. E.; Swift, D. R.; Tasker, P. A. Inorg. Chem. 1972, 11, 2775. (d) Churchill,
M. R.; Reis, A. H. Inorg. Chem. 1972, 11, 1811. (e) Vanquickenborne,
L. G.; Pierloot, K. Inorg. Chem. 1981, 20, 3673. (f) Darensborg, D. J.;
Kump, R. L. Inorg. Chem. 1984, 23, 2993. (g) Rahim, M.; Taylor, N. J.;
Xin, S.; Collins, S. Organometallics 1998, 17, 1315. (h) Kakaliou, L.;
Scanlon, W. J.; Qian, B.; Baek, S. W.; Smith, M. R.; Motry, D. H. Inorg.
Chem. 1999, 38, 5964.

⁽¹⁶⁾ Franceschini, P. L.; Morstein, M.; Berke, H.; Schmalle, H. W. *Inorg. Chem.* **2003**, *42*, 7273.

⁽¹⁷⁾ Bei, X.; Swenson, D. C.; Jordan, R. F. Organometallics 1997, 16, 3282.



Figure 2. Molecular structures of 2 (left) and 3 (right).

The current work shows that amidinates are useful supporting ligands, yielding six-coordinated group 4 complexes 1–4. Preparation of the Ti amidinate amide from TiCl₄ requires the formation of TiCl₂(NMe₂)₂ (**6**), followed by the replacement of the two remaining Cl⁻ by amidinate ligands. In comparison, the Zr and Hf analogues were prepared from MCl₄ by first reacting with lithium amidinate to form M[CyNC(Me)NCy]₂Cl₂ (M = Zr, **7**; M = Hf, **8**). The formation of the M–NR₂ bonds occurs in the second step. Dynamic NMR studies of Zr[CyNC(Me)NCy]₂(NR₂)₂ (R = Me, **2**; R = Et, **3**) suggest that they undergo a Bailar twist interconversion in solution.

Experimental Section

All manipulations were carried out in either a nitrogen-filled glovebox or under nitrogen using standard Schlenk-line techniques. Solvents were dried using conventional methods and freshly distilled before use. MeLi (1.5-1.6 M in Et₂O), ⁿBuLi (2.5 M in hexane), LiNMe2, and 1,3-dicyclohexylcarbodiimide were purchased from Aldrich and used without further purification. Li[CyN(Me)NCy] (5) was prepared by a modified literature procedure.^{1k} MeLi (1 equiv) was added to a hexanes or Et₂O solution of 1,3-dicyclohexylcarbodiimide at room temperature. The resulting white precipitate was collected on a frit under N2 and either washed with hexane or directly used in the next step. LiNEt₂ was obtained by addition of ⁿBuLi to a hexanes solution of diethylamine and then evaporation of the solvent. $TiCl_2(NMe_2)_2$ (6) was prepared by a literature procedure.¹⁸ ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-400 FT spectrometer. Elemental analyses were conducted by Complete Analysis Laboratories, Inc., Parsippany, NJ.

The uncertainties in ΔH^{\ddagger} and ΔS^{\ddagger} were computed from the error propagation formulas derived by Girolami and co-workers from the Eyring equation.^{11,19}

Synthesis of 1. Compound 5 was prepared in situ by the addition of MeLi (6.5 mL, 1.5 M in Et₂O, 9.750 mmol) to CyN=C=NCy (1.994 g in 30 mL of hexanes, 9.664 mmol) at ambient temperature. After it was stirred overnight, the cloudy solution was added to a



solution of TiCl₂(NMe₂)₂ (**6**; 1.000 g, 4.832 mmol) in hexanes (50 mL). The red solution was stirred for 20 h, filtered, concentrated, and cooled to -30 °C to give dark red crystals of **1** (0.304 g, 0.525 mmol, 11% yield based on TiCl₂(NMe₂)₂). ¹H NMR (benzene-*d*₆, 399.79 MHz, 23 °C): δ 3.46 (s, 12H, 2NMe₂), 3.28 (br, 2H, C₆H₁₁), 3.13 (br, 2H, C₆H₁₁), 1.88–1.29 (m, 40H, C₆H₁₁), 1.68 (s, 6H, NC(*Me*)N). ¹³C NMR (benzene-*d*₆, 100.53 MHz, 23 °C) δ 171.5 (NC(Me)N), 59.1–26.5 (m, C₆H₁₁), 50.4 (NMe₂), 11.4 (NC(Me)N). Anal. Calcd for C₃₂H₆₂N₆Ti: C, 66.41; H, 10.80. Found: C, 66.49; H, 11.01.

Synthesis of 2. To CyN=C=NCy (2.100 g, 10.18 mmol) in Et₂O (40 mL) at -30 °C was added ca. 1 equiv of MeLi (6.4 mL, 1.6 M in Et₂O, 10.2 mmol). After the solution was stirred at 23 °C for 18 h, it was added to a THF solution of ZrCl₄ (1.189 g, 5.102 mmol). The mixture was stirred at 23 °C for 20 h, followed by filtration. Volatiles were removed in vacuo to give a yellow-green fluffy solid of ZrCl₂[CyNC(Me)NCy]₂ (7; 2.898 g, 4.780 mmol). This solid was added to a solution of LiNMe₂ (0.488 g, 9.56 mmol) in Et₂O (30 mL) at 0 °C. After it was stirred at 23 °C for 24 h, the solution was filtered and concentrated to give a solution containing white solids. A few drops of THF were added to help dissolve the white solids. The solution was cooled to -32 °C to give diamondlike crystals of 2 (1.070 g, 1.720 mmol, 36% yield based on 7). 1 H NMR (toluene-*d*₈, 399.7 MHz, 23 °C): δ 3.22 (s, 12H, N*Me*₂), 3.10 (br, 4H, C₆H₁₁), 1.80-1.26 (m, 40H, C₆H₁₁), 1.70 (s, 6H, NC-(Me)N). ¹³C NMR (toluene-d₈, 100.5 MHz, 23 °C): δ 174.6 (NC(Me)N), 57.0, 35.8, 26.6, 26.5 (C₆H₁₁), 46.2 (NMe₂), 11.0 (NC(Me)N). Anal. Calcd for C₃₂H₆₂N₆Zr: C, 61.78; H, 10.05. Found: C, 61.68; H, 10.13. For the preparation of 2 in toluene, see the Supporting Information.

Synthesis of 3. To CyN=C=NCy (2.100 g, 10.18 mmol) in Et₂O (40 mL) at 23 °C was added 1 equiv of MeLi (6.4 mL, 1.6 M in Et₂O, 10 mmol). The mixture was stirred for 80 min and was added to a THF solution of ZrCl₄ (1.189 g, 5.102 mmol). The mixture was filtered, and volatiles in the filtrate were removed to give a yellow-green fluffy solid of 7 (2.893 g, 4.780 mmol). The solid was dissolved in Et₂O (30 mL), and 2 equiv of LiNEt₂ (0.756 g, 9.56 mmol) in Et₂O (20 mL) was added. After it was stirred for 24 h, the solution was filtered, and volatiles were removed to give a solid. The solid was dissolved in hexanes and kept at -30 °C to give crystalline solids of 3 (0.499 g, 0.731 mmol, 15% yield based on 7). ¹H NMR (toluene-*d*₈, 399.7 MHz, 23 °C): δ 3.80 (br, C*H*₂CH₃, 4H), 3.68 (br, C*H*₂CH₃, 4H), 3.15 (br, C₆*H*₁₁, 2H), 1.85–1.17 (m, C₆*H*₁₁, 40H), 1.69 (s, 6H, NC-

⁽¹⁸⁾ Benzing, E.; Kornicker, W. Chem. Ber. 1961, 94, 2263.

⁽¹⁹⁾ Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. Organometallics 1994, 13, 1646.

^{(20) (}a) Sheldrick, G. M. Program for Empirical Absorption Correction; University of Göttingen, Göttingen, Germany, 2000. (b) Sheldrick, G. M. Program for Crystal Structure Solution and Refinement; University of Göttingen, Göttingen, Germany, 2000.

(*Me*)N), 1.11 (t, CH₂CH₃, 12H). ¹³C NMR (toluene- d_8 , 100.5 MHz, 23 °C): δ 173.0 (NC(Me)N), 57.2, 56.9 (C_6H_{11}), 41.4 (CH₂CH₃), 36.6, 36.3, 35.6, 34.0 (C_6H_{11}), 26.7, 26.6 (C_6H_{11}), 26.4, 26.2 (C_6H_{11}), 13.4 (CH₂CH₃), 11.6 (NC(*Me*)N). Anal. Calcd for C₃₆H₇₀N₆Zr: C, 63.76; H, 10.40. Found: C, 63.78; H, 10.47.

Synthesis of 4. To CyN=C=NCy (6.365 g, 30.85 mmol) in Et₂O (30 mL) at -30 °C was added 1 equiv of MeLi (19.3 mL, 1.6 M in Et₂O, 31 mmol). The mixture was stirred for 80 min and then added to a THF solution (30 mL) of HfCl₄ (4.940 g, 15.40 mmol) at -60 °C. The mixture was stirred at 23 °C for 2 days. LiNMe₂ (1.574 g, 30.85 mmol) in Et₂O (30 mL) was added to the mixture at 0 °C, and the mixture was stirred at 23 °C for another 20 h. Filtration, concentration, and recrystallization gave crystals of **4** (8.093 g, 11.41 mmol, 74% yield based on HfCl₄). ¹H NMR (benzene-*d*₆, 399.8 MHz, 23 °C): δ 3.33 (s, 12H, 2NMe₂), 3.22 (br, 4H, C₆*H*₁₁), 1.81–1.27 (m, 40H, C₆*H*₁₁), 1.66 (s, 6H, NC-(*Me*)N). ¹³C NMR (benzene-*d*₆, 100.5 MHz, 23 °C): δ 174.2 (NC(Me)N), 67.8, 56.8, 26.5, 26.3 (*C*₆H₁₁), 46.1 (NMe₂), 11.3 (NC(*Me*)N). Anal. Calcd for C₃₂H₆₂N₆Hf: C, 54.18; H, 8.81. Found: C, 53.94; H, 8.89.

X-ray Crystallography. Data were collected on a SMART APEX CCD diffractometer (1 and 2) and a Bruker CCD-1000 diffractometer (3), both with graphite-monochromated Mo K α radiation ($\lambda = 0.710$ 73 Å), and corrected for absorption using the

SADABS program.^{20a} The structures of **1** and **3** were solved by direct methods. The structure of **2** was solved by the heavy-atom method. The structures were refined on F^2 against all reflections by full-matrix least-squares methods with the SHELXTL (version 6.10) program.^{20b} The hydrogen atoms in the three compounds were positioned geometrically and refined in the riding-model approximation. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Acknowledgment. This work was supported by the National Basic Research Program of China (Nos. 2006CB806104 and 2007CB925102), the Natural Science Grant of China (No. 20721002), the National Science Foundation (No. CHE-0516928), and the Changjiang Lecture Professor program (Z.-L.X.).

Supporting Information Available: Text, figures, tables, and CIF files giving details of the preparation of 2 and 3 in toluene, crystal data and all bond lengths and angles in 1-3, and Eyring plots of the interconversion in 2 and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

OM900162B