Polyhedron 65 (2013) 161–169

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

An alkyl-ended *ansa*-bis(amidine) and solvent-influenced complexation modes of its group IV metal derivatives

Sheng-Di Bai [a,*], Rui-Qin Liu [a], Tao Wang [a], Fei Guan [a], Yan-Bo Wu [b], Jian-Bin Chao [a], Hong-Bo Tong [a], Dian-Sheng Liu [a,*]

[a] Institute of Applied Chemistry, Shanxi University, Taiyuan, Shanxi 030006, PR China

[b] Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of Ministry of Education, Shanxi University, Taiyuan, Shanxi 030006, PR China

ARTICLE INFO

Article history:
Received 21 May 2013
Accepted 4 August 2013
Available online 22 August 2013

Keywords:
Group IV metal
Silyl-linked
Ansa-bis(amidine)
Transformation
Polymerization

ABSTRACT

The ^{t}Bu-ended *ansa*-bis(amidine) $SiMe_2[NC(Ph)NH(^tBu)]_2$ (**1**) was prepared by treating $^tBuNH_2$ with one equivalent of both $LiBu^n$ and PhCN, and half equivalent of $SiMe_2Cl_2$ in a one-pot reaction. **1** combined with HCl to give an ion pair complex $[(^tBu)NHC(Ph)NH]SiMe_2[NC(Ph)NH(^tBu)]Cl$ (**2**) and one N–C–N moiety was converted to a cationic amidinium ion. The complexation behaviour of **1** with group IV metal chlorides was explored. Treating **1** with $TiCl_4(thf)_2$ in CH_2Cl_2 gave the titanium complex $[(^tBu)NHC(Ph)N]Ti(thf)_2Cl_3$ (**3**), in which the mono-amidinato ligand was supposedly derived from N–Si cleavage of **1** due to the high Lewis acidity of the titanium salt. The zirconium complex $[(^tBu)NHC(Ph)NH]SiMe_2[NC(Ph)N(^tBu)]ZrCl_4$ (**4**) and the hafnium complex **5** were obtained by treating **1** with MCl_4 (M = Zr and Hf) in THF and these complexes were crystallized from CH_2Cl_2. Reaction of **1** with $TiCl_4(thf)_2$ in toluene yielded $\{SiMe_2[NC(Ph)NH(^tBu)]_2Ti[NC(Ph)NH_2(^tBu)]Cl_3\}Cl$ (**6**), indicating the N–Si cleavage could be partially suppressed in a less polar environment. Recrystallization of **4** in toluene afforded $SiMe_2[NC(Ph)NH(^tBu)]_2ZrCl_4$ (**7**). Similarly, recrystallization of **5** in toluene gave **8**, which is isostructural to **7**. The reaction of **4** with $AlMe_3$ in THF yielded the zirconium complex $[(^tBu)NHC(Ph)N]Zr(thf)_2Cl_3$ (**9**), which is analogous to **3**. The solid state structures of complexes **2**, **3**, **4**, **6**, **7**, **8** and **9** were investigated by single crystal X-ray structural analysis. Complexes **3** and **9** were found to be moderately active towards ethylene polymerization in the presence of methylaluminoxane (MAO).

1. Introduction

Amidinates are four-electron, monoanionic and N-donor bidentate chelating ligands. They demonstrate a great diversity by the variation of substituents on the conjugated N–C–N backbone. Meanwhile, the steric and electronic properties are easily modified to meet the needs of different metal centers [1–3]. The coordination chemistry of amidinates towards various metals has been well studied over the past few decades [4,5]. Amidinate complexes have proven to be promising as potential catalysts for the oligomerization and polymerization of olefins, hydroamination, intramolecular hydroamination/cyclization and hydrosilylation [6–11]. The numerous features and widespread applications have made amidinate ligands an important ancillary ligand array comparable to the ubiquitous cyclopentadienyl (Cp) system.

As shown in Scheme 1, the monocyclopentadienyl (Cp) ligand could be bridged to give the more rigid *ansa*-Cp ligand system. This type of transformation has influenced stereospecific olefin polymerization deeply. Inspired by such a remarkable impetus on upgrading from Cp to *ansa*-Cp to organometallic chemistry, increasing interest has been aroused towards metal complexes with dianionic linked bis(amidinate) ligands incorporated as spectator ligands [9–21]. For example, a series of mononuclear and binuclear lanthanide compounds were capable of catalyzing the ring-opening polymerization of lactones and lactides efficiently [17]. The linked bis(amidinate) ligands had several kinds of linking modes, including flexible carbon chains [10,11,17], chiral 1,2-cyclohexanyl [9,15,16] and a kind of rigid aromatic ring linker [20]. We explored a class of silyl linked bis(amidinate) ligands, $[SiMe_2\{NC(Ph)N(R)\}_2]^{2-}$ [22]. They displayed a close contact between the two amidinate moieties and had the advantage of affording binuclear complexes or mononuclear complexes analogous to "ansa-metallocene". With respect to the bridged biscyclopentadienyl η^5:η^5 ligands, the silyl-linked bis(amidinate) ligands can be considered as η^3:η^3 alternative systems. Since the latter are more electron-deficient than the former, it is supposedly helpful to enhance the electrophilic behaviour of the metal center and then improve its activity for olefin polymerization. It should be noted that the type of the terminal group R in $[SiMe_2\{NC(Ph)N(R)\}_2]^{2-}$ would impact deeply the corresponding

* Corresponding authors. Tel./fax: +86 351 7011743.
E-mail addresses: sdbaisxu@163.com, sdbai@sxu.edu.cn (S.-D. Bai), dsliu@sxu.edu.cn (D.-S. Liu).

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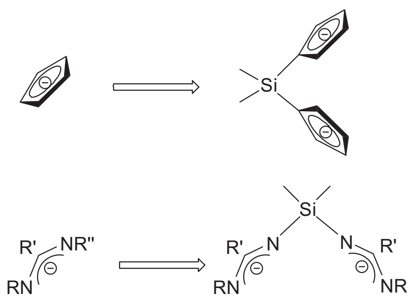
http://dx.doi.org/10.1016/j.poly.2013.08.042



Scheme 1. The schematic comparison of Cp and amidinate ligands.

complexes in the aspects of both structure and properties. Herein, we report a newly developed pathway for the ligand precursor ^{t}Bu-ended *ansa*-bis(amidine), and the synthesis and catalytic properties with regard to ethylene polymerization of its metal derivatives.

2. Experimental

2.1. General considerations

All manipulations and reactions were performed under a purified nitrogen atmosphere using standard Schlenk techniques on a dual manifold Schlenk line. Solvents were purchased from commercial sources. The deuterated solvent $CDCl_3$ was dried over activated molecular sieves (4 Å) and vacuum-transferred before use. Tetrahydrofuran, diethyl ether and toluene were distilled from sodium/benzophenone and stored over a potassium mirror under nitrogen. Dichloromethane was distilled from CaH_2 under nitrogen. $LiBu^n$ and the metal chlorides were used as purchased from Alfa Aesar. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded on a Bruker DRX-300 instrument, and solvent resonances were used as the internal references for both ^{1}H and ^{13}C NMR spectra. Elemental analyses were performed with a Vario EL-III analyzer.

2.2. Synthesis of the metal complexes

2.2.1. $SiMe_2[NC(Ph)NH(^tBu)]_2$ (**1**)

A solution of $LiBu^n$ (2.2 mol L^{-1}, 3.6 mL, 10 mmol) in hexane was added to a stirred solution of $^tBuNH_2$ (1.06 mL, 10 mmol) in THF (ca 30 mL) by syringe at 0 °C. The reaction mixture was warmed to room temperature and kept stirring for 3 h and then PhCN (1.00 mL, 10 mmol) was added by syringe at 0 °C. The reaction mixture was warmed to room temperature and kept stirring for 4 h and then $SiMe_2Cl_2$ (0.61 mL, 5 mmol) was added by syringe at 0 °C. After stirring at room temperature for 4 h, it was dried in vacuum to remove all volatiles. The residue was extracted with CH_2Cl_2 (30 mL) and recrystallized with hexane. It gave **1** as colorless crystals. Yield: 1.98 g (97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.47–7.22 (m, 10H; phenyls), 1.43, 1.37, 1.30 (t, 18H; 2C*Me*$_3$), −0.36, −0.40 (d, 6H; Si*Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 142.5–127.4 (phenyls), 52.6, 52.1 (*C*Me$_3$), 31.2, 29.8 (C*Me*$_3$), 3.2, 2.7 (Si*Me*$_2$). *Anal.* Calc. For $C_{24}H_{36}N_4Si$ (408.65): C, 70.54; H, 8.88; N, 13.71. Found: C, 70.81; H, 8.95; N, 13.58%.

2.2.2. $[(^tBu)NHC(Ph)NH]SiMe_2[NC(Ph)NH(^tBu)]Cl$ (**2**)

H_2O (0.027 mL, 1.50 mmol) was added to a stirred slurry of $AlCl_3$ (0.20 g, 1.50 mmol) in THF (ca 20 mL) by syringe at 0 °C. The mixture was warmed to room temperature and kept stirring for 4 h and filtered. Then **1** (0.61 g, 1.50 mmol) was added into the filtrate. The solution was stirred overnight and dried in vacuum to remove all volatiles. The residue was extracted with CH_2Cl_2 (25 mL) and filtrate was concentrated to give **2** as colorless crystals. Yield: 0.51 g (76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 10.80, 9.76 (d, 2H; $[NH–C–NH]^+$), 7.56–7.10 (m, 10H; phenyls), 4.96 (s, 1H; N*H*–C–N), 1.43, 1.36, 1.05 (t, 18H; 2C*Me*$_3$), 0.04, −0.30 (d, 6H; Si*Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 131.7–127.3 (phenyls), 31.4, 29.9, 29.2 (C*Me*$_3$), 1.6, 1.1 (Si*Me*$_2$). *Anal.* Calc. For $C_{24}H_{37}ClN_4Si$ (445.12): C, 64.76; H, 8.38; N, 12.59. Found: C, 64.21; H, 8.13; N, 12.71%.

2.2.3. $[(^tBu)NHC(Ph)N]Ti(thf)_2Cl_3$ (**3**)

$TiCl_4(thf)_2$ (0.59 g, 1.77 mmol) was added to a stirred solution of **1** (0.72 g, 1.77 mmol) in CH_2Cl_2 (ca 30 mL) at 0 °C. The reaction mixture was warmed to room temperature and kept stirring overnight. The resulting solution was filtered and the filtrate was concentrated to yield red crystals of **3**. Yield: 0.41 g (49%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.88 (d, J_{HH} = 7.2 Hz, 2H; 2,6-H of phenyl), 7.54–7.45 (m, 3H; 3,4,5-H of phenyl), 6.68 (s, 1H; N*H*–C–N), 3.93 (t, J_{HH} = 6.3 Hz, 8H; O*CH*$_2$ of thf), 1.86 (p, J_{HH} = 3.3 Hz, 8H; 3,4-2*CH*$_2$ of thf), 1.72 (s, 9H; C*Me*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 160.8 (N–*C*–N), 135.5–129.1 (phenyl), 70.9 (O*CH*$_2$ of thf), 26.3 (3,4-2*CH*$_2$ of thf), 57.1 (*C*Me$_3$), 30.1 (C*Me*$_3$). *Anal.* Calc. For $C_{19}H_{31}Cl_3N_2O_2Ti$ (473.71): C, 48.18; H, 6.60; N, 5.91. Found: C, 48.29; H, 6.63; N, 5.82%.

2.2.4. $[(^tBu)NHC(Ph)NH]SiMe_2[NC(Ph)N(^tBu)]ZrCl_4$ (**4**)

$ZrCl_4$ (0.29 g, 1.25 mmol) was added to a stirred solution of **1** (0.51 g, 1.25 mmol) in THF (ca 20 mL) at 0 °C. The reaction mixture was warmed to room temperature and kept stirring overnight. The resulting solution was dried in vacuum and the residue was extracted with CH_2Cl_2. The filtrate was concentrated to yield colorless crystals of **4**. Yield: 0.57 g (71%). *Anal.* Calc. For $C_{24}H_{36}Cl_4N_4SiZr$ (641.68): C, 44.92; H, 5.65; N, 8.73. Found: C, 44.68; H, 5.52; N, 8.52%.

2.2.5. $\{SiMe_2[N(H)C(Ph)N(^tBu)]_2\}HfCl_4$ (**5**)

$HfCl_4$ (0.64 g, 1.97 mmol) was added to a stirred solution of **1** (0.81 g, 1.97 mmol) in CH_2Cl_2 (ca 30 mL) at 0 °C. The reaction mixture was warmed to room temperature and kept stirring overnight. The resulting solution was filtered and the filtrate was concentrated to yield colorless crystals of **5**. Yield: 1.18 g (81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.68 (s, 2H; N*H*–C–N), 7.44–7.27 (m, 10H; phenyls), 1.16 (s, 18H; 2C*Me*$_3$), −0.46 (s, 6H; Si*Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 172.1 (N–*C*–N), 134.2–128.8 (phenyls), 56.8 (*C*Me$_3$), 31.7 (C*Me*$_3$), 2.7 (Si*Me*$_2$). *Anal.* Calc. For $C_{24}H_{36}Cl_4N_4SiHf$ (728.96): C, 39.54; H, 4.98; N, 7.69. Found: C, 39.78; H, 5.02; N, 7.79%.

2.2.6. $\{SiMe_2[NC(Ph)NH(^tBu)]_2Ti[NC(Ph)NH_2(^tBu)]Cl_3\}Cl\cdot(C_7H_8)$ (**6**)

To a stirred solution of **1** (0.39 g, 0.94 mmol) in toluene (ca 30 mL), $TiCl_4(thf)_2$ (0.31 g, 0.94 mmol) was added at 0 °C. The reaction mixture was warmed to room temperature and kept stirring overnight whereupon the color changed from yellow to red. The resulting solution was filtered and the filtrate was concentrated to yield orange crystals of **6**. Yield: 0.43 g (53%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.87, 8.18 (d, 4H; ^{t}BuN*H*), 7.48–6.88 (m, 20H; phenyls), 2.36 (s, 3H; *Me* of toluene), 1.82–0.97 (m, 27H; C*Me*$_3$), −0.49 (s, 6H; Si*Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 168.9 (N–*C*–N), 138.8–126.2 (phenyl), 54.6 (*C*Me$_3$), 32.3–30.8 (C*Me*$_3$), 22.3 (*Me* of toluene), 3.3 (Si*Me*$_2$). *Anal.* Calc. For $C_{35}H_{52}Cl_4N_6SiTi\cdot(C_7H_8)$ (866.75): C, 58.20; H, 6.98; N, 9.70. Found: C, 58.49; H, 7.09; N, 9.55%.

2.2.7. $SiMe_2[NC(Ph)NH(^tBu)]_2ZrCl_4\cdot(C_7H_8)$ (**7**)

Compound **7** could be obtained by recrystallization of **4** in toluene or by the following reaction. $ZrCl_4$ (0.41 g, 1.76 mmol) was