

Letter

Synthesis of titanium(IV) complexes that contain the Bis(silylamide) ligand of the type $[1,8-C_{10}H_6(NR)_2]^{2-}$, and alkene polymerization catalyzed by $[1,8-C_{10}H_6(NR)_2]TiCl_2$ -cocatalyst system

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Received 4 September 1997; accepted 25 November 1997

Abstract

$[1,8-C_{10}H_6(NR)_2]TiCl_2$ (**3**; R = SiMe₃, SiⁱBuMe₂, SiⁱPr₃) complexes have been prepared from dilithio salts $[1,8-C_{10}H_6(NR)_2]Li_2$ (**2**) and TiCl₄ in diethyl ether in moderate yields (60–63%). These complexes showed significant catalytic activities for ethylene polymerization and for ethylene/1-hexene copolymerization in the presence of methylaluminoxane (MAO), methyl isobutyl aluminoxane (MMAO), AlⁱBu₃- or AlEt₃-Ph₃CB(C₆F₅)₄ as a cocatalyst. The catalytic activities performed in heptane (cocatalyst MMAO) were higher than those carried out in toluene (cocatalyst MAO): 709 kg-PE/mol-Ti · h could be attained for ethylene polymerization by using $[1,8-C_{10}H_6(NSi^iBuMe_2)_2]TiCl_2$ -MMAO catalyst system. © 1998 Elsevier Science B.V.

Keywords: Metal complexes; Alkene polymerization; Bis(silylamide) ligand

Group 4 metal complexes that contain bidentate bis(amide) ligand are promising systems for application in olefin polymerization catalysis because of their relationship to the well-studied metallocene analogues,² hybrid ‘half-metallocene’ complexes such as (C₅R₄SiR₂NR)MX₂,³

bis(amide) complexes of the type $(\bar{R}_2N)_2MX_2$ ⁴ or chelate bis(amide) complexes^{5,6} and others.⁷ Several reports concerning catalytic alkene polymerization using Ti and Zr complexes that contain various amide ligands are known. However, low cat-

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² For example, see Refs. [1,2].

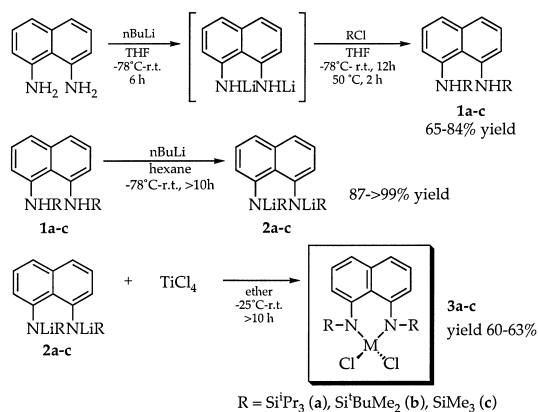
³ For example, see Refs. [3–12].

⁴ For example (recent reports) in (R₂N)₂MX₂ chemistry, see Refs. [13–17].

⁵ Examples for chelate group 4B bis(amide) complexes, see Refs. [18–31].

⁶ Examples for chelate tridentate bis(amide) complexes, see Refs. [32–34].

⁷ For example, see Refs. [35–38].



Scheme 1.

alytic activities were observed in most catalyst systems.⁸ One of our ongoing projects (particularly in the last 2 years) is the preparation of various 14e and 12e titanium and zirconium complexes containing chelate bis(amide) ligands, not only because of the relative ease in preparing these complexes but also because of their potential use as olefin polymerization catalysts.^{2,3,4,5,6,7} In this paper, we present the syntheses of [1,8-C₁₀H₆(NR)₂]TiCl₂ (**3**: R = SiMe₃, SiⁱBuMe₂, SiⁱPr₃), and the catalytic alkene polymerization in the presence of cocatalysts.

1,8-C₁₀H₆(NHR)₂ (**1a-c**) can be synthesized by the sequence of steps shown in Scheme 1.^{9, 10} THF was chosen as an effective solvent

⁸ Examples for catalytic ethylene polymerization using group 4 metal complexes containing bis(amide) ligands in the presence of cocatalyst were as follows: (a) [(Me₃SiN(CH₂CH₂NSiMe₃)₂)ZrCH₂Ph]⁺ [PhCH₂B(C₆F₅)₃]⁻ complex (330 kg-PE/mol-Zr·h, Mn 52200, Mw/Mn = 4.4, 25°C, 7.1 bar, 10 min) [32]. (b) [Ti(Me₃SiNCH₂CH₂NSiMe₃)Cl₂]-MAO catalyst (3.5 kg-PE/mol-Ti·bar·h, Al/Ti = 100, 50°C) [29]. (c) [(Me₃Si₂N)Zr(CH₂SiMe₂NSiMe₃)₂]⁺ [B(C₆F₅)₃]⁻ complex (34.0 kg-PE/mol-Zr·bar·h, Mn 414000, Mw/Mn = 8.4, 25°C, 7.1 bar) [16]. (d) [Zr(CH₂Ph)₂[(C₆H₃)₃-2,2'-(NCH₂C₆H₄Bu-4)-2,6,6'-Me₂)]-MAO catalyst (13 kg-PE/mol-Zr·bar·h, 10 bar, Al/Zr = 3130) [18]. (e) {[(ⁱBu-d₆)N-*o*-C₆H₄)₂O]ZrMe}[MeB(C₆F₅)₃] complex (104 kg-PE/mol-Zr·h, 1–2 atm, 22°C, 2 min), and {[(ⁱBu-d₆)N-*o*-C₆H₄)₂O]ZrMe(PhNMe₂)₂}[B(C₆F₅)₃] complex (810 kg-PE/mol-Zr·h, 1–2 atm, 22°C, 2 min) [31].

⁹ Related synthesis, see Ref. [19].

¹⁰ (a) Synthesis of 1,8-C₁₀H₆(NHSiⁱPr₃)₂ (**1a**): A solution of 1,8-naphthalenediamine(1,8-C₁₀H₆(NH₂)₂, 5.00 g, 31.6 mmol) in tetrahydrofuran (100 ml) was cooled to -78°C, and *n*BuLi (39.7 ml, 1.6 M solution in hexane, 63.5 mmol) was then added in several portions over 30 min. The stirred reaction mixture was warmed slowly to room temperature, and was stirred for 6 h. The reaction mixture was then cooled to -78°C, and ⁱPr₃SiCl (12.49 g, 64.8 mmol) was added slowly in several portions by using a hypodermic syringe over 30 min. The mixture was warmed slowly to room temperature, and was stirred for 12 h. The solution was then warmed to 50°C and stirred for an additional 2 h to complete the reaction. After the above procedures, the reaction mixture was taken to dryness under vacuum, and the resultant solid was extracted with hexane (200 ml). The hexane extract was concentrated to ca. 60 ml, and was dissolved completely by heating. The chilled (-25°C) hexane solution gave white-purple microcrystals of the titled compound (12.56 g) which were washed quickly with chilled hexane and dried in vacuo. Yield 84%. Further crops might increase the yields. ¹H NMR (C₆D₆): δ 1.16 (d, *J* = 7 Hz, 36H, SiCH(C₆H₅)₂), 1.32–1.43 (m, 6H, SiCHMe₂), 5.08 (s, 2H, NH), 6.88 (dd, *J* = 1 and 7 Hz, 2H, C₁₀H₆), 7.23 (t, *J* = 8 Hz, 2H, C₁₀H₆), 7.33 (dd, *J* = 1 and 8 Hz, C₁₀H₆). ¹³C NMR (C₆D₆): δ 13.4, 18.8, 113.9, 120.5, 125.9, 138.2, 145.1. (b) Synthesis of 1,8-C₁₀H₆(NLiSiⁱPr₃)₂ (**2a**): To a cold (-78°C) solution of 1,8-C₁₀H₆(NHSiⁱPr₃)₂ (**1a**, 9.95 g, 21.13 mmol) in hexane (100 ml) was added *n*BuLi (27.1 ml, 1.6 M solution in hexane, 43.32 mmol) slowly in several portions over 30 min. The reaction mixture was warmed slowly to room temperature, and was stirred overnight (> 10 h). The reaction mixture was concentrated to 50 ml, and was then cooled to -25°C. White-pale yellow solids were collected from the chilled solution, which were washed quickly with cold hexane, and dried in vacuo. Yield 10.2 g (> 99%). ¹H NMR (THF-d₈): δ 1.17 (d, *J* = 7 Hz, 36H, SiCH(C₆H₅)₂), 1.3–1.4 (m, 6H, SiCHMe₂), 6.51 (dd, *J* = 1 and 8 Hz, 2H, C₁₀H₆), 6.66 (dd, *J* = 1 and 8 Hz, C₁₀H₆), 6.81 (t, *J* = 8 Hz, 2H, C₁₀H₆). (c) Synthesis of [1,8-C₁₀H₆(NSiⁱPr₃)₂]TiCl₂ (**3a**): TiCl₄ (2.0 g, 10.54 mmol) was added drop wisely to a chilled diethyl ether (-25°C, 60 ml) solution over 30 min. To the cold ether solution (-25°C) containing yellow suspension of TiCl₄(ether)_{*n*}, 1,8-C₁₀H₆(NLiSiⁱPr₃)₂ (**2a**, 5.09 g, 10.54 mmol) was added in several portions over 30 min. The stirred reaction mixture was warmed slowly to room temperature, and was stirred overnight (> 10 h). The reaction mixture was then dried in vacuo, and the resultant solid was extracted with toluene (ca. 80 ml). The toluene extract was concentrated to ca. 50 ml, and was placed in the freezer (-25°C) for several days. Deep brown microcrystals were collected which were washed quickly with cold toluene, and dried in vacuo. First crop 3.42 g. The concentrated (to ca. 20 ml) mother liquor placed in the freezer (-25°C) gave another crop (460 mg). Total yield 3.88 g (63%). ¹H NMR (C₆D₆): δ 1.08 (d, *J* = 8 Hz, 36H, SiCH(C₆H₅)₂), 1.66 (m, 6H, SiCHMe₂), 6.93 (dd, *J* = 1 and 8 Hz, 2H, C₁₀H₆), 7.13 (t, *J* = 8 Hz, 2H, C₁₀H₆), 7.29 (dd, *J* = 1 and 8 Hz, C₁₀H₆). ¹³C NMR (C₆D₆): δ 14.8, 19.1, 118.5, 125.2, 126.3, 135.9, 147.2. Anal. Calcd. for C₂₈H₄₈N₂Cl₂Si₂Ti: C, 57.23; H, 8.23; N, 4.77. Found (1): C, 57.02; H, 8.50; N, 4.70. Found (2): C, 57.54; H, 8.68; N, 4.76.

to complete the reaction of chlorosilane with bislithium amide, which were prepared by the treatment of 1,8-naphthalenediamine with *n*-butyllithium. The desired products (**1a–c**) can be isolated by recrystallization in hexane at -25°C .¹¹ The corresponding dilithio salts $[1,8\text{-C}_{10}\text{H}_6(\text{NR})_2]\text{Li}_2$ (**2a–c**) can also be prepared through the reaction of **1a–c** with *n*BuLi in high yields, and isolated as a white-pale yellow solid from the chilled hexane solution due to their extremely low solubility.¹² The reaction of **2a–c** with TiCl_4 in diethyl ether (-25°C) gave the titled bis(silylamide) complexes, $[1,8\text{-C}_{10}\text{H}_6(\text{NR})_2]\text{TiCl}_2$ (**3a–c**), in relatively high yields as deep brown-purple microcrystals after the purification procedures.¹³

It was found that the ^1H and ^{13}C NMR spectra of these complexes were very similar to those of **1a–c** and **2a–c**, and were thus analo-

gous to the titled complexes, strongly supporting the formation of $[1,8\text{-C}_{10}\text{H}_6(\text{NR})_2]\text{TiCl}_2$ as a sole isolated product.¹⁴ In addition, **3b** and **3c** could be determined by mass spectroscopy as M^- fragment,¹⁵ and the results for elemental analysis of **3a** and **3b** were also satisfactory. Other characterization studies and the reaction chemistry derived from **3a–c** are in progress.

It is important to note that these complexes showed significant catalytic activities for polymerization of ethylene in the presence of methylaluminoxane (MAO), methyl isobutyl aluminoxane (MMAO), AlEt_3 - or Al^iBu_3 - $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ (Table 1).¹⁶ Noteworthy, the catalytic activities performed in heptane (cocatalyst: MMAO) were higher than those performed in toluene (cocatalyst: MAO). The reason of these results is not clear at this moment, probably due to the cocatalyst or due to the coordination of toluene to the catalytically-active species as was previously speculated [28]. It turned out that $[1,8\text{-C}_{10}\text{H}_6(\text{NSi}^i\text{BuMe}_2)_2]\text{TiCl}_2$ (**3b**) showed the highest catalytic activity among these complexes: the catalytic activity of 709 kg-PE/mol-Ti · h ($2.53 \times$

¹⁰ (continued) (d) $1,8\text{-C}_{10}\text{H}_6(\text{NHSi}^i\text{BuMe}_2)_2$ (**1b**): Yield 65%. ^1H NMR (C_6D_6): δ 0.23 (s, 12H, $\text{Si}(\text{CH}_3)_2\text{Bu}$), 0.99 (s, 18H, $\text{SiMe}_2\text{C}(\text{CH}_3)_3$), 5.27 (s, 2H, NH), 6.88 (dd, $J = 1$ and 8 Hz, 2H, C_{10}H_6), 7.22 (t, $J = 8$ Hz, 2H, C_{10}H_6), 7.35 (dd, $J = 1$ and 8 Hz, 2H, C_{10}H_6). ^{13}C NMR (C_6D_6): δ -3.0, 19.5, 38.0, 116.4, 122.1, 122.2, 125.7, 138.0, 144.8. (e) $1,8\text{-C}_{10}\text{H}_6(\text{NHSiMe}_3)_2$ (**1c**): Yield 80%. ^1H NMR (C_6D_6): δ 0.19 (s, 18H, SiMe_3), 5.39 (s, 2H, NH), 6.72 (dd, $J = 1$ and 7 Hz, 2H, C_{10}H_6), 7.20 (t, $J = 8$ Hz, 2H, C_{10}H_6), 7.34 (dd, $J = 1$ and 8 Hz, 2H, C_{10}H_6). (f) $1,8\text{-C}_{10}\text{H}_6(\text{NLSi}^i\text{BuMe}_2)_2$ (**2b**): Yield 96%. ^1H NMR (THF- d_8): δ 0.20 (s, 12H, $\text{Si}^i\text{Bu}(\text{CH}_3)_2$), 1.04 (s, 18H, $\text{Si}^i\text{Bu}(\text{CH}_3)_2$), 6.45 (dd, $J = 1$ and 8 Hz, 2H, C_{10}H_6), 6.63 (d, $J = 7$ Hz, 2H, C_{10}H_6), 6.81 (t, $J = 8$ Hz, 2H, C_{10}H_6). (g) $1,8\text{-C}_{10}\text{H}_6(\text{NLSiMe}_3)_2$ (**2c**): Yield 87%. ^1H NMR (THF- d_8): δ 0.17 (s, 18H, SiMe_3), 6.34 (dd, $J = 1$ and 7 Hz, 2H, C_{10}H_6), 6.47 (dd, $J = 1$ and 8 Hz, 2H, C_{10}H_6), 6.69 (t, $J = 8$ Hz, 2H, C_{10}H_6). (h) $[1,8\text{-C}_{10}\text{H}_6(\text{NSi}^i\text{BuMe}_2)_2]\text{TiCl}_2$ (**3b**): Yield 61% (1st crop). ^1H NMR (C_6D_6): δ 0.37 (s, 12H, $\text{Si}^i\text{Bu}(\text{CH}_3)_2$), 0.97 (s, 18H, $\text{Si}^i\text{Bu}(\text{CH}_3)_2$), 6.80 (dd, $J = 1$ and 8 Hz, 2H, C_{10}H_6), 7.13 (t, $J = 8$ Hz, 2H, C_{10}H_6), 7.26 (dd, $J = 1$ and 8 Hz, 2H, C_{10}H_6). ^{13}C NMR (C_6D_6): δ -0.5, 21, 29, 117.6, 125.6, 125.9, 136.4, 147.7. MS, calcd. for $\text{C}_{22}\text{H}_{36}\text{Cl}_2\text{N}_2\text{Si}_2\text{Ti}$, 503.5. Found (M^-), 502.0. Anal. Calcd.: C, 52.48; H, 7.21; N, 5.57. Found: C, 52.40; H, 7.54; N, 5.41. (i) $[1,8\text{-C}_{10}\text{H}_6(\text{NSiMe}_3)_2]\text{TiCl}_2$ (**3c**): Yield 60%. ^1H NMR (C_6D_6): δ 0.60 (s, 18H, SiMe_3), 6.66 (dd, $J = 1$ and 8 Hz, 2H, C_{10}H_6), 7.15 (t, $J = 8$ Hz, C_{10}H_6), 7.37 (dd, $J = 1$ and 8 Hz, 2H, C_{10}H_6). ^{13}C NMR (C_6D_6): δ 1.9, 110.9, 125.4, 126.8, 137.7, 148.5. MS calcd. for $\text{C}_{16}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Si}_2\text{Ti}$, 419.3. Found (M^-), 417.8.

¹¹ See (a), (d) and (e) of ¹⁰.

¹² See (b), (f) and (g) of ¹⁰.

¹³ See (c), (h) and (i) of ¹⁰.

¹⁴ Other peaks corresponding to the impurities were not observed. Characterization by X-ray crystallography is in progress.

¹⁵ All the mass spectra (negative) were recorded by using a JEOL JMS-700 double focusing mass spectrometer equipped with a frit-CI interface. The sample solutions in dehydrated toluene were introduced into the ion source of the mass spectrometer at the rate of 2–5 $\mu\text{l}/\text{min}$.

¹⁶ The catalytic polymerizations of ethylene were performed by using a 1 liter scale autoclave. Typical reaction procedure (Table 1, run 10) is as follows: Heptane (300 ml) was added into the autoclave filled with nitrogen, and the reaction apparatus was then introduced ethylene to 4 kgf/cm². The premixed toluene solution of $[1,8\text{-C}_{10}\text{H}_6(\text{NSi}^i\text{BuMe}_2)_2]\text{TiCl}_2$ **3b** (17.5 μmol) with MMAO (5.8 wt.% Al) in hexene, 17.5 mmol) was introduced into the autoclave under pressurized conditions. The reaction mixture was stirred for 1 h at 4 kgf/cm² (60°C), and the polymerization was terminated with the addition of ethanol (15 ml). The solution was then poured into ethanol (200 ml), and the resultant white precipitate was adequately washed with ethanol and then dried in vacuo for several hours. Molecular weight and the molecular weight distributions of the resultant polymers were measured at 145°C by means of gel-permeation chromatography (Waters 150 CV) using *o*-dichlorobenzene as solvent and the calibration with standard polystyrene samples.

Table 1

Ethylene polymerization with $[1,8\text{-C}_{10}\text{H}_6(\text{NR})_2]\text{TiCl}_2$ in the presence of various cocatalysts

Run	Cat. (μmol)	Cocatalyst		Solvent	Polymer yield (g)	Activity ^a	Mw $\times 10^4$	Mw/Mn
		Al (Al/Ti ^b)	Borate ^c					
1	3c (4.8)	MAO (1000)	–	toluene	0.35	72.9	97.4	6.4
2	3c (14.3)	MAO (1000)	–	toluene ^d	0.92	64.3		
3	3c (9.1)	MMAO (1000)	–	heptane	1.50	165	36.5	19.3
4	3c (14.5)	AlEt ₃ (500)	Ph ₃ CB(C ₆ F ₅)	toluene	0.90	62.1		
5	3c (9.5)	Al(<i>i</i> -Bu) ₃ (450)	Ph ₃ CB(C ₆ F ₅)	toluene	0.95	100		
6	3a (10.4)	MAO (1000)	–	toluene	0.40	38.5	55.8	10.5
7	3a (17.0)	MMAO (1000)	–	heptane	0.71	41.8	28.3	5.6
8	3a (30.0)	Al(<i>i</i> -Bu) ₃ (500)	Ph ₃ CB(C ₆ F ₅)	toluene	0.17	5.7		
9	3b (21.8)	MAO (1000)	–	toluene	1.62	74.3	39.8	4.8
10	3b (17.5)	MMAO (1000)	–	heptane	12.4	709	21.4	5.4
11	3b (4.4)	MMAO (1000)	–	heptane ^d	1.10	250	116	4.3
12	3b (9.9)	Al(<i>i</i> -Bu) ₃ (500)	Ph ₃ CB(C ₆ F ₅)	toluene	0.75	75.8		

Reaction conditions: toluene or heptane 300 ml, 1 liter-scale autoclave, ethylene 4 kg/cm², 60°C, 1 h. MAO: 9.5 wt.% (Al) in toluene, MMAO: 5.8 wt.% (Al) in hexane.

^aActivity: kg-PE/(mol-Ti · h).

^bMolar ratio of Al/Ti.

^cMolar ratio of Ph₃CB(C₆F₅)₄/Ti = 1.0.

^dTemperature 40°C.

10⁴ turnovers/h) could be achieved with **3b** in the presence of MMAO (run 10, C₂ 4 kg/cm², 60°C). The polymerization in the presence of 1-hexene (10 ml) under the same conditions of run 10 gave ethylene/1-hexene copolymer (600 kg-PE/mol-Ti · h, SCB (Side Chain Branching) 32.4/1000 carbons, Tm 121.4°C, Mn = 7.35 \times 10⁴, Mw/Mn = 4.8).

It was revealed that the molecular weight distributions (Mw/Mn) of the resultant polymers were relatively broad (Mw/Mn = 4.3–19.3, Table 1). These results were very similar to those reported by the previous catalysts such as [Me₃SiN(CH₂CH₂NSiMe₃)₂ZrCH₂Ph]⁺[PhCH₂B(C₆F₅)₃]⁻ (Mn 52200, Mw/Mn = 4.4) [32], [(Me₃Si)₂NZr(CH₂SiMe₂NSiMe₃)⁺B(C₆F₅)₄]⁻ complex (Mn 414000, Mw/Mn = 8.4) [16], or other catalyst using N–O type group 4 metal complexes containing quinolinolato or pyridine-alkoxide ligands [35–37]. The reason of the broad Mw/Mn values in the present catalytic reactions might be due to the fact that titanium–nitrogen bonds were broken during the reaction, or due to the formation of several catalytically-active species. We believe at this moment that this would be due to the

scission of titanium–nitrogen bond, not only because it depends upon the kind of N-substituent, but also because the relatively narrow Mw/Mn value was observed at the initial stage of the polymerization using the similar bis(alkylamide) complex-MMAO catalyst system.¹⁷

We are currently studying the effects of various cocatalyst under the various reaction conditions including the synthesis of other N-substituted bis(amide) complexes: these results will be introduced in the near future.

Acknowledgements

K.N. would like to express his heartfelt thanks to Mr. S. Kiuchi for experimental assistance, and Mr. A. Kondo (Sumitomo Chemical) for mass spectroscopy.

¹⁷ K. Nomura et al., unpublished results for the ethylene polymerization using [^{*i*}BuNCH₂CH₂CH₂N^{*i*}Bu]TiCl₂–MMAO catalyst system (in heptane).

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