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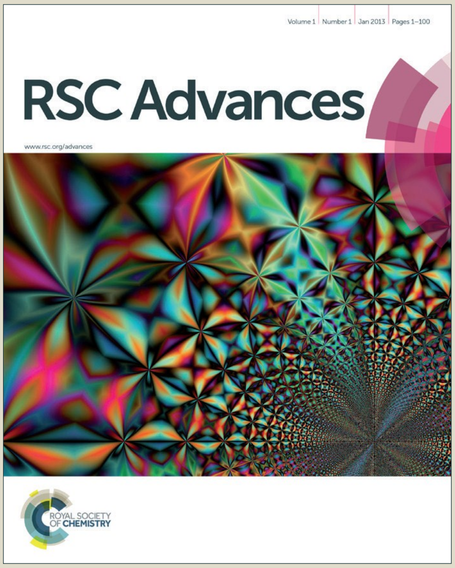

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Organoamido zirconium(IV) and titanium(IV) complexes and their catalysis towards ethylene polymerization

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The reaction of PhN(Li)SiMe$_3$ with 2 equiv of dimethylcyanmide, further addition of 2 equiv of CpTiCl$_3$ led via Me$_3$SiCl elimination to dinuclear titanium(IV) compound **1**. The reaction of DippN(Li)SiMe$_3$ with 1 equiv of dimethylcyanmide, further addition of 1 equiv of CpTiCl$_3$ afforded a centrosymmetric dimeric titanium(IV) compound **2** and monomuclear **3** with the elimination of Me$_3$SiCl. The zirconium(IV) compound **4** was obtained by the addition reaction of PhN(Li)SiMe$_3$ with 2 equiv of dimethylcyanmide and metathesis reaction with ZrCl$_4$. X-ray diffraction studies of **1–4** establish the dinuclear titanium(IV) structure in **1**, half-titanocene of **2** and **3**, and a propeller-like complex fragment of **4**. Complexes **2** and **4** show moderate or high activities in the polymerization of ethylene upon activation with methylaluminoxane (MAO).

Introduction

Amido-based ligands have played an important role in developing alternative ligands to cyclopentadienyl ligands in organometallic chemistry [1-3] and their zirconium(IV) and titanium(IV) complexes have shown catalytic activity in α-olefin polymerization [4]. Among which the tunable three atom, 4-electronic guanidinato and amidinato systems [5] and the five atom, 6-electronic systems such as β-diketiminato [6] and 1,3,5-triazapentadienato anions [7,8] were developed. The β-diketiminato ligands and non-symmetric guanidinato and amidinato ligands were synthesized via the addition reactions of carbon minus and nitrogen minus to α-hydrogen-free carbonitriles, respectively, and their zirconium(IV) or hafnium(IV) complexes were found to be olefin polymerization catalysts [9]. Guanidinate-supported titanium imido complexes could be used as a catalyst for alkyne hydroamination [10], and the zirconium–amido guanidinate as a potential precursor for the CVD of ZrO$_2$ thin films [11]. The 2,4- *N*, *N*′-disubstituted 1,3,5-triazapentadienato ligands were developed in our group via the insertion reactions of various nitriles to M-N bonds with the migrations of SiMe$_3$ group from N→N′ and concomitant N–C bond formation [12], and used to stabilize main and transition metals [13]. Because of their strong bond to the metals by the donor nitrogen atoms, tunable electronic and steric properties, and various bonding modes to metals, 1,3,5-triazapentadienato ligands might have considerable potential as spectator ligands especially in the area of catalysis. In addition, there is no precedent of 1,3,5-triazapentadienyl ligands in group 4 metals. Therefore the reaction of lithium trimethylsilylaniline with two equivalents of α-hydrogen-free dimethylcyanamide, and further with two equivalents of CpTiCl$_3$, led to dinuclear titanium 1,3,5-triazapentadienate complex **1**. The reaction of DippN(Li)SiMe$_3$ with 1 equiv of dimethylcyanmide, further addition of 1 equiv of CpTiCl$_3$ afforded a centrosymmetric dimeric titanium(IV) compound **2** and monomuclear **3** with the elimination of Me$_3$SiCl. Propeller-like zirconium 1,3,5-triazapentadienate complex **4** was obtained via the reaction of lithium trimethylsilylaniline with two equivalents of dimethylcyanamide**,** and one third equivalents of ZrCl$_4$. To our knowledge, this is a rare example of titanocene guanidinate system and the first example of

1,3,5-triazapentadienyl ancillary ligand used in group 4 metals. In this paper we report the synthesis and X-ray solid state structures of new titanocene and zirconium complexes **1–4** containing either guanidinato or 1,3,5-triazapentadienyl ligands, and also the use of **2** and **4** as catalyst precursors for the polymerization of ethylene.

Experimental Section

Materials and Procedures. All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were purchased from commercial sources. Deuterated $CDCl_3$ was dried over activated molecular sieves (4 Å) and vacuum transferred before use. Diethyl ether and THF were dried and distilled from sodium/benzophenone and stored over a sodium mirror under argon. Dichloromethane was distilled from activated molecular sieves (4 Å) or CaH_2. 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 ^1H spectra and ^{13}C spectra. Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were carried out using a Vario EL-III analyzer (Germany).

$[\{PhNC(NMe_2)NC(NMe_2)N\}\{TiCpCl_2\}_2]$ (1). $(CH_3)_2NCN$ (0.36 mL, 4.52 mmol) was added to a solution of $PhN(Li)SiMe_3$ (0.39 g, 2.26 mmol) in THF (30 mL) at –78 °C. The resulting mixture was warmed to *ca*.25 °C and stirred overnight. $CpTiCl_3$ (0.99g, 4.52 mmol) was added at –78 °C. The resulting mixture was warmed to *ca*.25 °C and stirred for 24 h. The volatiles were removed in *vacuo*, and the residue was extracted with 15 mL of dichloromethane and filtered. The filtrate was concentrated *in vacuo* to *ca.* 10 mL and left at room temperature for 3 d to give red crystals of **1**(0.53 g, 34.5 %). ^1H NMR ($CDCl_3$): δ 2.52-3.20 (m, 12H, $N(C\mathit{H}_3)_2$), 6.57, 6.58, 6.69, 6.70 (2d, 10 H, Cp), 6.89-7.51 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 41.1, 41.8, 43.4 ($N(\mathit{C}H_3)$)), 119.3, 124.9 (Cp), 128.1-150.9 (Ph), 161.3, 162.2 (N-*C*-N). Anal. Calcd for $C_{22}H_{27}Cl_4N_5Ti_2(CH_2Cl_2)$: C, 40.39; H, 4.27; N, 10.24. Found: C, 40.51; H, 4.26; N, 10.18.

$[\{DippNC(NMe_2)N\}TiCpCl]_2$ (2) and **$[\{DippN(H)C(NMe_2)\}TiCpCl_2]$ (3).** $(CH_3)_2NCN$ (0.25 mL, 3.04 mmol) was added to a solution of $DippN(Li)SiMe_3$ (0.78 g, 3.04 mmol) in THF (30 mL) at –78 °C. The resulting mixture was warmed to *ca*.25 °C and stirred overnight. $CpTiCl_3$ (0.67g, 3.04 mmol) was added at –78 °C. The resulting mixture was warmed to *ca*.25 °C and stirred for 48 h. The volatiles were removed in *vacuo*, and the residue was extracted with 20 mL of dichloromethane and filtered. The filtrate was concentrated *in vacuo* to *ca.* 15 mL and left at room temperature for 6 d to give a first crop of deep red block crystals of **2**(0.104 g, 13 %); filtered and the filtrate was stored at –25 °C for 10 days to give a second crop of minor red needles **3**, which were separated manually, only adequate for structural determination. **2**: ^1H NMR ($CDCl_3$): δ 1.18-1.44 (m, 24 H, $CH(C\mathit{H}_3)_2$), 3.15-3.26 (m, 12 H, $N(C\mathit{H}_3)_2$), 3.33-3.42 (m, 4 H, $C\mathit{H}(CH_3)_2$), 5.82, 5.98, 5.99, 6.23, 6.41, 6.64, 6.67 (s, 10 H, $C_5\mathit{H}_5$), 7.28-7.65 (m, 6 H, Ph). ^{13}C NMR ($CDCl_3$): δ 22.2, 24.7 ($CH(\mathit{C}H_3)_2$), 28.3 ($\mathit{C}H(CH_3)_2$), 39.4, 40.0, 41.1 ($N(\mathit{C}H_3)_2$), 115.6, 116.1, 116.8, 116.9, 119.2(C_5H_5), 123.7, 125.6, 129.2, 130.3, 132.1 (Ph), 147.2, 148.0 (C_{ipso}), 149.2 (N*C*N).

$[\{PhNC(NMe_2)NC(NMe_2)N(SiMe_3)\}_3ZrCl]$ (4). $(CH_3)_2NCN$ (0.34 mL, 4.12 mmol) was added to a solution of $PhN(Li)SiMe_3$ (0.35 g, 2.06 mmol) in Et_2O (30 mL) at –78 °C. The resulting mixture was warmed to *ca*.25 °C and stirred overnight. $ZrCl_4$ (0.160 g, 0.69 mmol) was added at –78 °C. The resulting mixture was warmed to *ca*.25 °C and stirred for 24 h, then filtered. The filtrate was concentrated *in vacuo* to *ca.* 10 mL and stored at –25 °C for several days, yielding colorless crystals of **4**(0.33g, 40 %). Mp: 73-75 °C. ^1H NMR ($CDCl_3$): δ -0.08-0.22 (m, 27

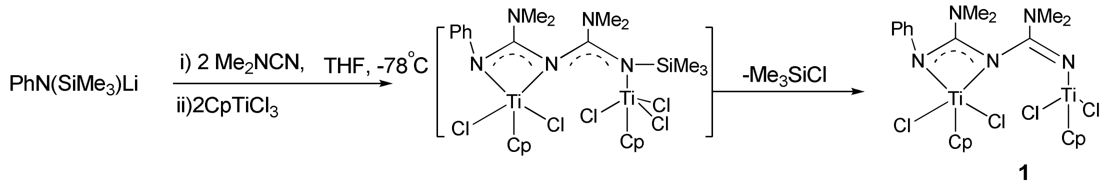
H, SiMe$_3$), 2.31-3.04 (m, 36 H, N(CH_3)$_2$), 1.12-1.16, 3.40-3.42 (Et$_2$O), 6.61-7.19 (m, 15H, Ph). ^{13}C NMR (CDCl$_3$): δ -3.62, -1.53, 0.65(3s, SiMe$_3$), 38.05, 39.91(2s, (N(CH$_3$)), 15.5, 66.1(Et$_2$O), 122.2, 123.1, 123.9, 125.9, 128.7, 148.6(Ph), 160.8, 164.1 (N-C-N). Found: C, 53.43; H, 8.11; N, 17.72. $C_{53}H_{98}ClN_{15}O_2Si_3Zr$ requires C, 53.57; H, 8.31; N, 17.68 %.

General procedure for ethylene polymerization. Ethylene polymerization was carried out in a 500 mL autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. Briefly, toluene, the desired amount of cocatalyst, and a toluene solution of the catalytic precursor (the total volume was 100 mL) were added to the reactor in this order under an ethylene atmosphere. When the desired reaction temperature was reached, ethylene at 10 atm pressure was introduced to start the reaction, and the ethylene pressure was maintained by constant feeding of ethylene. After 30 min, the reaction was stopped. The solution was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was filtered, washed with ethanol, and dried in vacuum at 60 °C to constant weight.

X-ray Crystallography. Data collection of **1**–**4** was performed with Mo-Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer using the omega scan mode yielding a total of *N* reflections. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. Corrections were applied for Lorentz and polarization effects as well as absorption using multi-scans (SADABS) [14]. The structure was solved by direct method (SHELXS-97) [15]. The remaining non-hydrogen atoms were obtained from the successive difference Fourier map. All non-H atoms were refined with anisotropic displacement parameters, while the H atoms were constrained to parent sites, using a riding mode (SHELXTL) [16]. Crystal data and details of data collection and refinements for **1**–**4** are summarized in Table 1. CCDC (reference numbers 1424470–1424472) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Results and Discussion

The reaction of PhN(Li)SiMe$_3$ with two equivalents of Me$_2$NCN and further with two equivalents of CpTiCl$_3$ in the presence of THF afforded compound **1** in a Me$_3$SiCl elimination reaction according to eq 1. ^{1}H and ^{13}C NMR spectra are in accordance with the formula and elemental analysis is consistent.



(1)

Suitable crystals for X-ray diffraction studies of **1** were obtained from the saturated dichloromethane solution at room temperature. The molecular structure of **1** is illustrated in Figure 1 including principal bond lengths and angles. X-Ray analysis shows that **1** is dinuclear, the twisted W-shaped 1, 3, 5-triazapentadienyl ligand coordinates to the two metal centers by η^2-coordination mode and terminal bonding mode, respectively. The Ti1 atom is located in a pyramidal environment(center of Cp ring as one vertex) from one η^5-cyclopentadienyl group, two nitrogen atoms from the ligand and two chlorine atoms, thus forming a distorted square pyramidal geometry at the Ti1 center with the Cp group occupying the apical position. The 1, 3, 5-triazapentadienyl ligand coordinates with Ti2 atom in the terminal bonding mode, and a flattened three-legged piano stool (N4–Ti2–Cl3 103.82(15) °; N4–Ti2–Cl4 101.11(14) °; Cl3–Ti2–Cl4 101.48(7) °) around Ti2 was formed. The piano stool structures were also found in other titanocene and yttrium guanidinate compounds [17] and in the amido and imido lathanide compounds with constrained bis(oxazoline)cyclopentadienyl ligand [18]. The distance of Ti2–N4 is 1.782(4) Å, comparable to that of titanium imido complex Cp[$Ph_2(CH_2N)_2C$=N]$TiCl_2$ [1.792(2) A˚] [19] and other Ti compound Cp(Ph_3P=N)$TiCl_2$ [Ti–N: 1.78 Å] with strong π-donating ligand [20]. The reaction of PhN(Li)$SiMe_3$ with two equivalents of Me_2NCN and further with one equivalent of Cp*$TiCl_3$ in the presence of THF afforded an unusual *ansa*-bridged cyclopentadienyl titanium complex [{η^5–$C_5Me_4CH_2$-C(NMe_2)=N}$TiCl_2$] [21], where the cyclopentadienyl ring and the mean plane of the Ti−N= C−C−C fragment form a dihedral angle of 88.08 (11) °.

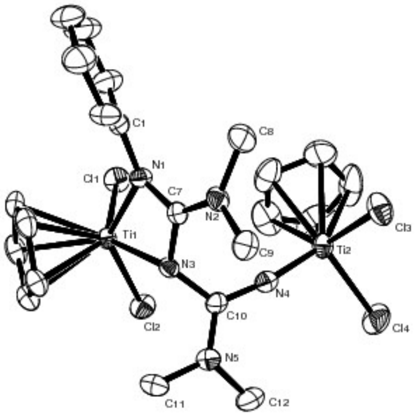
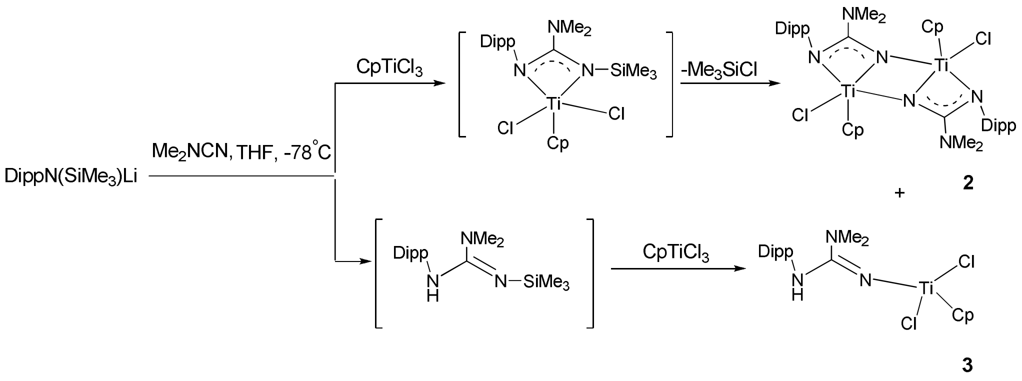


Figure 1. Perspective ORTEP drawing of the molecular structure of **1.** All non-hydrogen atoms are represented by thermal ellipsoids drawn to encompass 50% probability. Selected bond lengths (Å) and angles (deg): Ti(1)−N(1) 2.081(4), Ti(1)−N(3) 2.143(4), Ti(1)−Cl(1) 2.306(2), Ti(1)−Cl(2) 2.321(2), N(1)−C(7) 1.338(6), N(2)−C(7) 1.334(6), N(3)−C(7) 1.360(6), N(3)−C(10) 1.401(6), N(4)−C(10) 1.323(6), N(5)−C(10) 1.322(6), Ti(2)−N(4) 1.782(4), Ti(2)−Cl(3) 2.310(2), Ti(2)−Cl(4) 2.3169(2); N(1)−Ti(1)−N(3) 62.57(15), N(4)−Ti(2)−Cl(3) 103.82(15), N(4)−Ti(2)−Cl(4) 101.11(14), Cl(1)−Ti(1)−Cl(2) 89.59(7).

The titanocene guanidinates **2** and **3** were obtained from the same experiment, starting with equivalent portions of DippN(Li)$SiMe_3$, $(CH_3)_2NCN$ and Cp$TiCl_3$; and their separation was achieved by fractional crystallisation from dichloromethane. The formation of **2** underwent an attack of the *N*-centred nucleophile on Me_2NCN, a salt metathesis and elimination of Me_3SiCl during which an intermediate was thought to be formed and finally resulted in a thermodynamically product **2**. The formation of **3** involved an unexpected hydrolysis of lithium guanidinate and elimination of Me_3SiCl as well. The similar elimination reaction was found in other titanium(IV) complexes [22, 23].

The poor quality of crystals of **2** did not allow accurate information to be obtained on bond distances and angles but the data were adequate to establish its structure as shown in Scheme 1. **2** was characterised by multinuclear NMR spectra, while **3** was identified solely by its X-ray structure.



Scheme 1 Synthesis of compounds **2** and **3**.

As shown in Figure 2, complex **3** is a monomer, in which the titanium atom coordinated by one η^5-cyclopentadienyl group, one guanidinato ligand and two chlorine atoms and forms a three-legged piano stool. The guanidinato ligand contacted with the centre metal in the η^1-bonding mode. The distance of Ti−N(3) is 1.771(6) Å, significantly shorter than those of bis(imido)complex $(C_5H_5)_2Ti(-N=CPh_2)_2$[Ti−N(1): 1.944(3) Å, Ti−N(2): 1.956(2) Å] [24], imido titanium compounds $(C_5H_5)_2Ti(Cl)N=C(NMe_2)_2$ [Ti−N(1): 1.848(3) Å] and $(C_5H_5)Ti(Cl)(\mu\text{-}\eta^1\text{: }\eta^2\text{-}N=C(NMe_2)_2)_2$ [Ti−N(1): 1.809(3) Å, Ti−N(4): 1.817(3) Å][17] and slightly shorter than that in 8-quinolyl-linked guanidinate titanium salt [{8-(2-CH_3-C_9H_5N)N(H)C(NMe_2)N}Ti(MeC_5H_4)-Cl_2] [Ti1−N(3): 1.797(5) Å] [25], suggesting stronger Ti−N(gua) bond of compound **3**. The bond angle of Ti−N(3)−C(13) [172.2(5) °] in **3** is larger than the value in $(C_5H_5)_2Ti(Cl)N=C(NMe_2)_2$ [Ti−N(1)−C(11) [170.2(3) °]] [17], much larger than those in $(C_5H_5)_2Ti(-N=CPh_2)_2$ [Ti−N(1)−C(11) [160.8(2) °]; Ti−N(2)−C(24) [161.0(2) °]] [24] and in [{8-(2-CH_3-C_9H_5N)N(H)C(NMe_2)N}Ti(MeC_5H_4)-Cl_2] [Ti(1)−N(3)−C(10) [157.5(5) °] [26], also indicative of titanium imido feature of **3**.

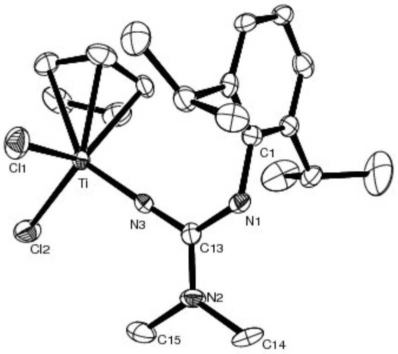
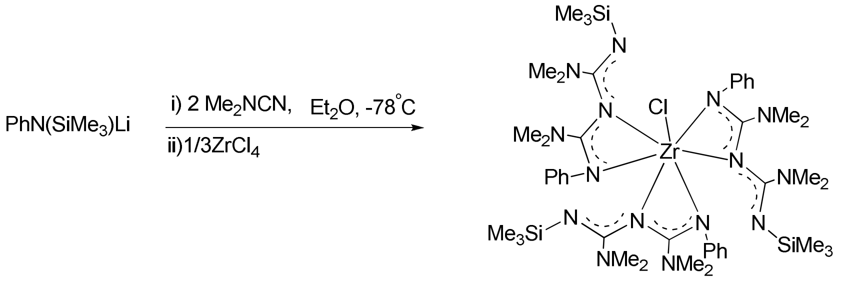


Figure 2. Perspective ORTEP drawing of the molecular structure of **3.** All non-hydrogen atoms are represented by thermal ellipsoids drawn to encompass 50% probability. Selected bond lengths (Å) and angles (deg): Ti−N(3) 1.771(6), Ti−Cl(1) 2.293(3), Ti−Cl(2) 2.335(3), N(1)−C(13) 1.350(8), N(2)−C(13) 1.348(9), N(3)−C(13) 1.329(9); N(3)−Ti−Cl(1) 102.2(2), N(3)−Ti−Cl(2) 102.9(2), Cl(1)−Ti−Cl(2) 102.3(1), Ti−N(3)−C(13) 172.2(5).



4

Scheme 2 Synthesis of compound **4**.

Compound **4** was conveniently prepared in 40% yield according to Scheme 2. Thus, treatment of PhN(SiMe$_3$)Li with two equivalents of (CH$_3$)$_2$NCN in diethyl ether at –78 °C and further with one third equivalents of ZrCl$_4$ resulted in the colorless crystalline [{PhNC(NMe$_2$)NC(NMe$_2$)N(SiMe$_3$)}$_3$ZrCl] (**4**). Complex **4** was air-sensitive and changed into white powder in 15 mins when it exposed to air.

The molecular structure of **4** is illustrated in Figure 3 including principal bond lengths and angles. The three chelated *C*$_1$-symmetric 1, 3, 5-triazapentadienyl ligands are disposed around the zirconium atom in a propeller-like fashion via η^2-coordination mode. The zirconium is the center of a chloride-capped distorted octahedron with three pairs of nitrogen atoms from three 1, 3, 5-triazapentadienyl ligands. Three C(NMe$_2$)(NSiMe$_3$) groups are located close to the chlorine atom and the three phenyl groups are arranged on the *trans*-position to the chlorine. The bond distance of Zr−Cl [2.437(1) Å] in **4** is slightly shorter than those of tris(benzamidinato)zirconium chloride complexes [(Siam)$_3$ZrCl][Siam = N, N' Bis(trimethylsilyl)benzamidinat]][Zr–Cl 2.464(2) Å] [26] and chiral zirconium benzamidinate complex [{C$_6$H$_5$C(N-TMS)(N-myrtanyl)}$_3$ZrCl][Zr–Cl 2.475(3) Å][27], and tris(guanidinato)zirconium chloride compound [{PhNC(NMe$_2$)NSiMe$_3$}ZrCl[Zr–Cl 2.515(2) Å] [9a].

The key bond lengths and angles of the ZrNCN moiety of **4** and its analogues zirconium guanidinate [PhNC(NMe$_2$)N(SiMe$_3$)] **I** [9a] and zirconium benzamidinate analogue [PhNC(C$_6$H$_4$Me-4)N(SiMe$_3$)] **II** [28] are shown in Scheme 3. In **4**, the slightly longer Zr–N(C(NMe$_2$)SiMe$_3$) bond length than that of Zr–N(Ph) indicated its less steric impact in **4** than in its analogues **I** and **II**. This is also supported by the narrower dihedral angles between the planes NCN and NZrN in **4** (0.8, 0.8 and 1.1°) than in **I** (5.4, 6.1 and 6.5°) and **II** (8.2, 8.8 and 8.3°).

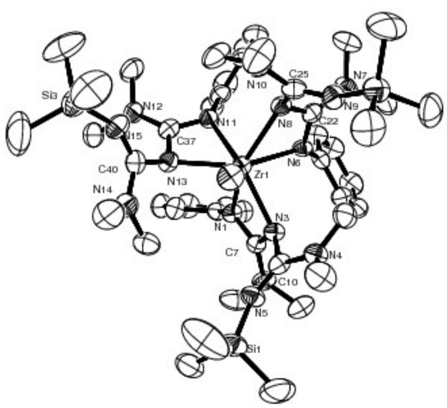
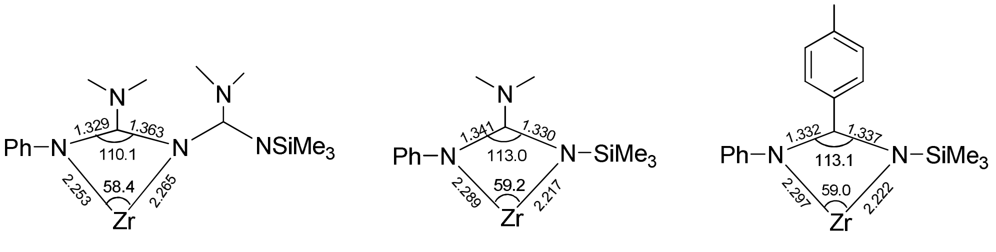


Figure 3. Perspective ORTEP drawing of the molecular structure of **4.** All non-hydrogen atoms are represented by thermal ellipsoids drawn to encompass 50% probability. Selected bond lengths (Å) and angles (deg): Zr(1)−Cl1(1)

2.437(1), Zr(1)−N(1) 2.249(3), Zr(1)−N(3) 2.268(3), Zr(1)−N(6) 2.250(3), Zr(1)−N(8) 2.268(3), Zr(1)−N(11) 2.260(3), Zr(1)−N(13) 2.259(3), N(5)−C(10) 1.267(4), N(9)−C(25) 1.271(5), N(15)−C(40) 1.281(5); N(1)−Zr(1)−N(3) 58.45(10), N(6)−Zr(1)−N(8) 58.38(10), N(11)−Zr(1)−N(13) 58.54(10), N(3)−C(10)−N(5) 122.1(3), N(8)−C(25)−N(9) 121.4(4), N(13)−C(40)−N(15) 121.9(4), N(1)−C(7)−N(3) 110.0(3), N(6)−C(22)−N(8) 110.2(3), N(11)−C(37)−N(13) 110.1(3).



4 **I** **II**

Scheme 3 Key mean intrametallacyclic bond lengths (Å) and angles (deg) of **4** and its analogues

Beside the synthesis of organoamido group 4 complexes, our interest is focused on their applications. Therefore, complexes **2** and **4** were tested as procatalysts for ethylene polymerization with methylaluminoxane (MAO) as the activator under varied conditions. Table 2 summarized ethylene polymerization results.

Table 2. Ethylene polymerization with **2** and **4** as precatalysts under various conditions[a]

Entry	Cat.	P/atm	T/°C	Al/M	Yield(mg)	Activity[b]	T_m /°C[d]	M_w[e] ($\times10^{-4}$)	M_w/M_n[e]
1	**4**	1	30	500	Trace	-	-	-	-
2	**4**	10	30	500	5.80	2.32×10^3	-	-	-
3	**4**	10	50	500	7.60	3.04×10^3	-	-	-
4	**4**	10	70	500	8.90	3.56×10^3	-	-	-
5	**4**	10	70	1500	18.1	7.24×10^3	-	-	-
6	**4**	10	70	2500	25.4	1.02×10^4	-	-	-
7	**2**	10	30	500	394	1.57×10^5	133.1	67.4	1.86
8	**2**	10	30	1500	659	2.63×10^5	133.1	82.6	2.01
9	**2**	10	30	2000	1623	6.49×10^5	131.6	87.8	1.94
10	**2**	10	30	2500	1134	4.54×10^5	130.5	71.6	1.95
11	**2**	10	50	2000	3792	1.52×10^6	132.8	23.5	3.76
12	**2**	10	70	2000	2646	1.06×10^6	133.4	42.8	3.17
13[c]	**2**	10	50	2000	1584	1.27×10^6	131.2	55.6	2.04

[a] Polymerization conditions: 5μmol catalyst, Cocat: MAO, 100 ml toluene, 0.5 hour. [b] g mol^{-1} h^{-1}. [c] 0.25 hour. [d] Determined by DSC. [e] Determined by GPC.

When activated with MAO under 1 atm of ethylene, complex **4** showed absent polymerization activity compared to that under 10 atm of ethylene (Entry 1 and 2), therefore, 10 atm pressure of ethylene was employed in the remaining experiments, in which other reaction parameters were changed. At a ratio of Al/Zr 500, with the temperature from 30 to 70 °C, the activity of **4** increased from 2.32×10^3 to 3.56×10^3 g PE mol^{-1} h^{-1} (Entry 2–4). At 70 °C, with the higher Al/Zr molar ratio of 2500 (Entry 6), complex **4** showed relatively higher activity (1.02×10^4 g PE mol^{-1} h^{-1}). Comparing with other **L**$_3$ZrCl type analogues, the catalytic activity of **4** is slightly higher than those of tris(benzamidinato)zirconium chloride complexes such as [N(SiMe$_3$)C(C$_6$H$_4$Me-4)NPh]$_3$ZrCl] (8.6×10^3 g PE mol^{-1} h^{-1} bar^{-1}) [28], [{PhC(NCy)(NSiMe$_3$)}$_3$ZrCl] (5.44×10^3 g PE mol^{-1} h^{-1}) [29]. The catalytic activity of **4** is comparable to that of sufficiently similar complex

$[PhNC(NMe_2)NSiMe_3]_3ZrCl$ (1.05 ×10^4 g PE mol^{-1} h^{-1}) [9a] that we reported, although the angle between the propeller flaps in complex **4** [mean value 92.3 °] is larger by 1.9 ° than that in $[PhNC(NMe_2)NSiMe_3]_3ZrCl$ [mean value 90.4 °], suggesting that the change of ligands in **4** didn't affect the catalytic activity of the compound significantly. The moderate activities were also found in other amide-based polymerization catalysts such as $[PhC(NR)_2]_2ZrCl_2$ (R= ^{i}Pr, Cy), and $[PhC(N^iPr)_2]_2ZrCl_2$ [30].

For **2**/MAO system, the optimal Al/Ti ratio was 2000 (Entry 9) and the highest activity of 1.52×10^6 g PE/mol Ti h (Entry 11) was observed at 50 °C. The titanocene guanidinate **2** showed relatively higher activity for the polymerization of ethylene than that of complex **4**. This is probably due to the introducing of the cyclopentadienyl group into the structure of **2**, the formation and stabilization of the catalytically active species can be achieved by more electron donation through the cyclopentadienyl fragment especially for the electron-deficient zirconium complex [31]. With the increase of the Al/Ti molar ratio from 500 to 2500 (Entries 7-10), the molecular weight of the polymers initially increased and then decreased. Meanwhile, the T_m of the resultant polyethylene decreased from 133.1 to 130.5 °C. Increasing the reaction temperature from 30 to 70 °C (Entries 9, 11 and 12), the activity initially increased and then decreased and the T_m of the resultant polymer increased from 131.6 to 133.4 °C. In addition, NMR data showed the formation of linear polyethylenes [32].

Conclusions

Several organoamido group 4 complexes have been synthesized. In titanocene guanidinate complexes **1** and **3**, the guanidinato ligand coordinated the metal center in an unusual terminal bonding mode. Both in titanocene guanidinate **2** and 1, 3, 5-triazapentadienyl zirconium complex **4**, the ligand coordinated to the metal via η^2-coordination mode, a bridge and side-on chelating coordination mode was found in **2** and a propeller-like fashion was found in **4**. Complexes **1** and **3** showed efficient ligand π-donation to the metal. Compounds **1** and **4** are the first examples of group 4 complexes bearing the 1, 3, 5-triazapentadienyl ligands. Complex **4** showed moderate and **2** showed high activity in ethylene polymerization. At present we are designing other chloroguanidinate zirconocene and hafnocene complexes and $\mathbf{L}_2MCl_2$ type group 4 complexes containing 1, 3, 5-triazapentadienyl ligands such that their catalytic activities will be higher in olefin polymerization.

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Table 1. Crystal data and refinements for compounds **1**, **3** and **4**

Compound	**1**	**3**	**4**
Formula	$C_{23}H_{29}Cl_6N_5Ti_2$	$C_{20}H_{29}Cl_2N_3Ti$	$C_{53}H_{98}ClN_{15}O_2Si_3Zr$
M	684.01	430.26	1188.40
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No.2)
a / Å	11.095(5)	8.966(9)	12.6863(19)
b / Å	19.886(9)	14.723(17)	14.732(2)
c / Å	13.656(6)	16.566(17)	18.976(3)
α / º	90.00	96.910(17)	87.593(4)
β/ º	98.13(3)	100.41(7)	76.510(3)
γ / º	90.00	90.190(19)	82.086(4)
U / $Å^3$	2983(2)	2151(4)	3415.7(9)
Z	4	4	2
Absorption coeff. (mm^{-1})	1.095	0.655	0.299
Unique reflections, R_{int}	5255, 0.0385	3773, 0.0660	12078, 0.0425
Reflections with $I > 2\square(I)$	4611	3252	7669
Final R indices [$I > 2\square(I)$] R_1, wR_2	0.0736, 0.0858	0.1122, 0.1294	0.0534, 0.1000
R indices (all data) R_1, wR_2	0.1495, 0.1553	0.2322, 0.2397	0.0997, 0.1201

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Organoamido zirconium(IV) and titanium(IV) complexes and their catalysis towards ethylene polymerization

Meisu Zhou*, Qiaokun Yang, Hongbo Tong, Lei Yan, Xiaoyang Wang

Novel organoamido zirconium(IV) and titanium(IV) complexes, their structural features and catalytic activity in the polymerization of ethylene are reported.