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COMMUNICATION

Mononuclear titanium compounds based on the silyl-linked bis(amidinate) ligand: synthesis, characterization and ethylene polymerization[†]

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The mononuclear silyl-linked bis(amidinate) titanium compound 2 was prepared by salt metathesis of 1 and $TiCl_4(thf)_2$. Alkylation of 2 with methyllithium gave analogue 3. Both 2 and 3 exhibited a configuration similar to *ansa*-metallocene and showed good activity towards ethylene polymerization after activation with MAO.

Since the landmark discovery of Ziegler-Natta catalysts in early 1950s, innumerous attentions have been paid to this exciting area in order to obtain excellent catalyst systems. Among the successive progresses, Kaminsky and Sinn found systems of metallocene (I) activated with methylaluminoxane (MAO) were efficient catalysts.^{1,2} Subsequently, the stereorigid ansa-metallocene (II) complexes reported by Brintzinger^{3,4} also showed impressively high efficiency. This opened a broad range of research work in stereospecific polymerization of α -olefins to polymers with stereoregular microstructures.⁵ These groundbreaking developments pushed Cp (cyclopentadienyl) to be ubiquitous for over half a century in organometallic chemistry.^{6,7} In that surge of research, both Erker's and Liu's groups developed a class of allyl-bridged group 4 metallocene complexes.^{8,9} As a great deal of effort was made to seek Cp alternatives such as N-centered donor ligands in recent decades, the half-sandwich species with a mixed-ligand environment were generated, including the commercialized constrained geometry compounds (CGC) (III¹⁰⁻¹² and IV¹³⁻¹⁶ in Fig. 1). In recent years, our research interest was focused on the small conjugated framework with N-centered donor ligands. Group 4 metal compounds supported with the monovalent bidentate aminosilylanilido ligand and the further derived η^3 -azaallyl ligand have been prepared and show good activities toward ethylene (co)polymerization.17

Amidinate ligands are easily modified by variation of substituents on the conjugated N-C-N backbone to meet the requirements of different metal centers. The corresponding



Fig. 1 Cyclopentadienyl and amidinate group 4 metal compounds.

coordination chemistry is well established.18,19 The amidinate complexes were promising catalysts for oligomerization and polymerization of olefins,20-29 hydroamination, intramolecular hydroamination/cyclization,30 and hydrosilylation.31 Moreover, some of them, such as the bis(amidinate) group 4 metal complexes V, showed high performance in activation and reduction of dinitrogen or other molecules.32-34 A class of silyl-linked bis(amidinate) ligands ${SiMe_2[NC(Ph)N(R)]_2}^{2-}$ were developed in our recent research.35,36 The special bianionic ligands had the advantage of affording both binuclear complexes and mononuclear complexes.³⁷⁻⁴¹ The group 4 metal compounds based on them were therefore synthesized and investigated. The mononuclear species adopting the configuration of VI were presumed to be more rigid in contrast to V, which was comparable to the upgrade from I to II. On the other hand, in terms of the bridged biscyclopentadienyl η^5 : η^5 ligands, the silyl-linked bis(amidinate) ligands can be considered as an η^3 : η^3 alternative system. Since the latter is more electron-deficient than the former, it is supposedly helpful to enhance the electrophilic behavior of the metal center and then improve its activity for olefin polymerization. Herein the syntheses and characterization of the silyl-linked bis(amidinato) titanium are reported as well as the catalytic properties for ethylene polymerization.

The ligand transfer reagents, with general formula $Li_2{SiMe_2[NC(Ph)N(R)]_2}$ (R = phenyl, 2,6-Me_2C_6H_3, 2,6-'Pr_2C_6H_3 and 'Bu), were prepared according to the reported methods.³⁵ Regarding those with aromatic terminal groups, the titanium derivatives like **VI** could not be obtained when reacting with titanium tetrachloride. If metal salts coordinated with Cp in advance were used instead, it may lead to a series of

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versatile products, some involving ligand transformation process. The related mechanism was presumed.³⁹ It was interesting that replacing the aromatic groups with 'Bu at the terminal positions could prevent the ligand rearrangement and give product in the expected fashion VI. As shown in Scheme 1, treatment of lithium compound 1 with titanium tetrachloride tetrahydrofuran solvate in molar ratio of 1 : 2 gave the titanium compound 2 as red crystals in good yield up to 80%. Subsequently, compound 2 was alkylated by two equivalents of methyl lithium in diethyl ether solution. Compound 3 was obtained as yellow crystals in moderate yield after extraction and crystallization with dichloromethane. Both 2 and 3 were characterized by NMR, elemental analysis as well as X-ray crystallography.[‡]





The crystal structure of **2** is illustrated in Fig. 2 with selected bond lengths and angles. The tetradentate ligand fixes the Ti ion in the central position. The molecule exhibits C_2 rotational symmetry along the Ti1–Si1 axis. Each amidinate unit bites the metal center with a N–Ti–N angle of $61.33(12)^\circ$. The distances between Ti and N are 2.247(3) Å and 1.981(3) Å, respectively. The weaker affinity of Ti with the terminal N atoms implies the constrained force of bending the N–C–N–Si–N–C–N seven-membered chain to adopt the half circle fashion. Compound **3** is isostructural to **2** except for the replacement of Ti–CH₃ bonds for Ti–Cl bonds. It makes the affinity between Ti and the *N*-donor ligand in **3** marginally smaller.



Fig. 2 Molecular structure of compound 2. Thermal ellipsoids are set at 30% probability and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ti1-N1 = 2.247(3), Ti1-N2 = 1.981(3), Ti1-C11 = 2.2735(12), N1-C5 = 1.303(5), N2-C5 = 1.353(5), N2-Si1 = 1.697(4); N1-Ti1-N2 = 61.33(12), N1-Ti1-N1A = 168.24(16), N2-Ti1-N2A = 70.3(2), C11-Ti1-C11A = 133.19(8), N1-C5-N2 = 109.4(3), N2-Si1-N2A = 84.5(2).



Fig. 3 Comparison of titanocene complexes and titanium amidinates.

Structural comparison was made to a series of titanium compounds including 2 (shown in Fig. 3) in order to demonstrate some remarkable differences resulting from the ligand-changing. In the titanocene reported by Clearfield et al., the angle between the two Cp (cyclopentadienyl) planes is 51.73°.42 The Ti center exhibits tetrahedral geometry composed of two pairs of Ti-Cp_{centroid} and Ti-Cl bonds. The Cp_{centroid}-Ti-Cp_{centroid} and Cl-Ti-Cl angles are 130.91 and 94.43°, respectively. In the ansa-titanocene, two Cps are pulled together by the silvl bridge and forced to adopt the same orientation toward the silvl bridge, resulting in the widened related angle of the Cp planes.⁴³ Correspondingly, the Cp_{centroid}-Ti-Cp_{centroid} angle is decreased and the Cl-Ti-Cl angle is enlarged. By comparing two titanocene complexes, closure of the Cp side in ansa-titanocene leads the Ti center to be more "open" in some degree. This phenomenon could be observed more obviously in the following two titanium amidinates. Bis(benzamidinate) titanium dichloride demonstrates the cis-Cl₂ configuration as do most group 4 metal L_2MX_2 complexes with two bidentate ligands, and the molecule obeys C2 symmetry along the midnormal line across Ti of triangular [TiCl₂].⁴⁴ Two independent amidinate backbone planes are perpendicular to each other and interestingly, they meet across the line of two outer nitrogen atoms. The Cl-Ti-Cl angle is 98.66°. The six-coordinate Ti center has a distorted octahedral configuration. Compound 2 also bears C_2 symmetry along the Ti-Si axis. Two amidinate units are linked by the silyl bridge and are closely coplanar. Deviations from four nitrogen atoms to both sides of the plane [Ti-C5-Si1-C5A] are very small, distances of the terminal and inner N atoms to the plane being 0.093 and 0.159 Å, respectively. The two terminal N and Ti are nearly linear, which is similar to that in above bis(benzamidinate) titanium dichloride. While the inner N atoms are pulled so close to the horizontal plane due to linkage, two Cl atoms show the increasing tendency of occupying the vertical positions. The Cl-Ti-Cl angle is released in large degree to be 133.19(8)°. It displays a rare transitional configuration between the cis-Cl₂ and trans- Cl_2 .¹² The silyl-linked bis(amidinate) η^3 : η^3 ligand imposes upon the metal center a closely planar coordinate environment, which is far less shielding than when there are two separate amidinate η^3 ligands. It makes compound 2 present an "open" Ti center similar to ansa-titanocene.

Catalytic properties of both **2** and **3** for ethylene polymerization in the presence of MAO were investigated. Their activities were found to be highly dependent on pressure. At normal pressure, they were inactive at 30 °C and only trace amount of polymer could be observed when heating the reaction system to 50 °C. Increasing both the ethylene pressure from 1 to 10 atm and the A1: Ti molar ratio led to the abrupt magnification of the polymerization activities. Catalytic efficiency of **2** climbed to 46 kg (PE) mol⁻¹ (Ti) h⁻¹ at 50 °C and the corresponding value of **3** was doubled. Further increase of A1: Ti molar ratio and reaction temperature would promote their activities in large degree, demonstrating high values of 1020 kg (PE) mol⁻¹ (Ti) h⁻¹ at 100 °C for **2** and 1614 kg (PE) mol⁻¹ (Ti) h⁻¹ at 80 °C for **3**, respectively. These activities are much higher than the Cp₂ZrCl₂ standard (627 kg (PE) mol⁻¹ h⁻¹). It was noteworthy that high concentration of MAO did not suppress or even deactivate their performance.⁴⁵

In summary, among the silyl-linked bis(amidinate) ligands, only the alkyl-ended one could support a titanium center ascribed to the matched electronic property. Both 2 and 3 show high activities for ethylene polymerization and the methylated species 3 displayed higher performance than chloride compound 2. They were presumed to be A1: Ti molar ratio, pressure and temperaturepromoted procatalysts. It indicates the derivatives of this family are promising catalysts.

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Notes and references

‡ Crystal data for **2**: C₂₄H₃₄Cl₂N₄SiTi, M = 525.44, orthorhombic, space group *Fdd*2, a = 22.585(5), b = 26.749(6), c = 9.093(2) Å, V = 5493(2) Å³, Z = 8, $D_c = 1.271$ g cm⁻³, μ (Mo-Kα) = 0.568 mm⁻¹ ($\lambda = 0.71073$ Å), T = 203(2) K, R_1 [2145 with $I > 2\sigma(I)$] = 0.0490, Rw = 0.1157, 5712 reflections ($R_{int} = 0.0317$), GOF = 1.065. CCDC 804643.

Crystal data for **3**: C₂₆H₄₀N₄SiTi, M = 484.61, orthorhombic, space group *Fdd2*, a = 22.957(15), b = 26.990(18), c = 9.165(6) Å, V = 5679(2) Å³, Z = 8, $D_c = 1.134$ g cm⁻³, μ (Mo-K α) = 0.362 mm⁻¹ ($\lambda = 0.71073$ Å), T = 298(2) K, R_1 [1815 with $I > 2\sigma(I)$] = 0.0692, Rw = 0.1818, 5702 reflections ($R_{int} = 0.0535$), GOF = 1.077. CCDC 804644.

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