Heteroatom-Substituted Constrained-Geometry Complexes. Dramatic Substituent Effect on Catalyst Efficiency and Polymer Molecular Weight

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*Summary: The new constrained-geometry complexes (CGC) [(η^5-C_9H_5X)($SiMe_2$-t-Bu)TiR_2 (X = 2-OEt (**1a,b**), 2-NMe_2 (**2a,b**) , 3-OMe (**3a,b**), 3-NC_4H_4 (**4a,b**); R = Cl, Me) have been synthesized with alkoxy and amino substituents attached to a second and third indenyl position. Four of the new complexes (**1a−4a**) have been characterized by single-crystal X-ray analysis. An ethylene/1-octene copolymerization study revealed an enormous substituent effect, both on the catalysts' activity and the molecular weight of produced polymers. The 3-amino-substituted complex **4b** exhibits the highest catalytic activity and forms the highest molecular weight ethylene/octene copolymers that have ever been reported for this class of catalysts.*

It is advantageous to conduct commercial solution polymerization reactions at very high temperatures (>130 °C).[1] Two major catalyst limitations often preventing access to such high reactor temperatures are the catalyst efficiency and the molecular weight of produced polymers, as both of these factors decrease as a function of rising temperature. Catalysts capable of producing high-molecular-weight polymers at high temperature with very high catalytic activities would be therefore greatly desired. In the last two decades there has been a considerable amount of research aimed at understanding the factors that govern fundamental metallocene properties in olefin polymerization reactions, such as efficiency, comonomer incorporation, tacticity, and polymer molecular weight.[2] Early studies on the constrained-geometry catalyst (CGC) systems suggest[3] that catalyst efficiency could be enhanced by an increase in electron density at the metal center. It was shown, for example, that the tetramethyl-substituted CGC complex (η^5-C_5Me_4)($SiMe_2$-N-*t*-Bu)$TiCl_2$ was 3 times more active than (η^5-C_5H_4)($SiMe_2$-N-*t*-Bu)$TiCl_2$ in ethylene/octene polymerization when activated with MAO.[4,5] In looking for ways to further increase electron density at the metal center, we focused our attention on alkoxy and amino substituents, as they have been shown to be very effective electron-donating groups in electrophilic aromatic substitution reactions[6] as well as in substituted ferrocenes.[7] In this communication we wish to report[8] the synthesis and characterization of new alkoxy (**1**, **3**) and amino (**2**, **4**) substituted CGC complexes as well as the remarkable substituent effect on catalyst polymerization activity and polymer molecular weight.

Complexes **1−4** (Chart 1) have been synthesized by previously described methods[3b,8b,c,9] and characterized by 1D and 2D (COSY, NOESY, HSQC, and gHMBC) NMR spectroscopy, elemental analysis, HRMS, and single-crystal X-ray analysis (**1a−4a**).[9,10] The complexes exhibit C_1 symmetry both in solution and in the solid state (vide infra). In addition to four multiplets (H4−H7) and a singlet (H2) observed in the aromatic region of ^{1}H NMR spectra of **1b−4b**, there are two sets of singlets in the region 0−1 ppm corresponding to two diastereotopic silicon and titanium methyl groups. The chemical shifts of the two titanium methyl peaks differ substantially from one another—CH_3^b (assigned on the basis of NOESY measurements) is shifted upfield by

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[9] See Supporting Information for details.

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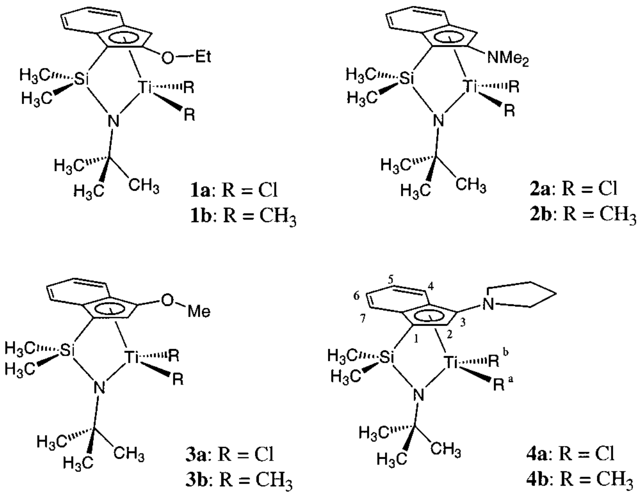
Chart 1. Heteroatom-Substituted CGC Complexes Studied



1a: R = Cl
1b: R = CH$_3$

2a: R = Cl
2b: R = CH$_3$

3a: R = Cl
3b: R = CH$_3$

4a: R = Cl
4b: R = CH$_3$

about 0.7−1 ppm relative to CH$_3^a$, presumably as a result of diamagnetic shielding of the indenyl fragment. Interestingly, in the ^{13}C{^{1}H} NMR spectrum of **1b**−**4b**, the chemical shift of the CH$_3^b$ group is always observed downfield relative to that of CH$_3^a$, as shown by C−H correlation spectroscopy (HSQC). There is only one peak for the dimethylamino group in complex **2b** and only two resonances for methylene groups next to nitrogen of the pyrrolidine group in **4b** in the ^{1}H NMR spectrum, indicating fast rotation of amino substituents about the C$_{\text{indenyl}}$−N bond at room temperature.

The comparison of reduction potentials of the titanium dichlorides **1a**−**4a** and C−H coupling constants of Ti−CH$_3$ groups[11] in complexes **1b**−**4b** with those of the unsubstituted indenyl complexes (η^5-C$_9$H$_6$)(SiMe$_2$-N-*t*-Bu)TiR$_2$ (**6a**, R = Cl; **6b**, R = CH$_3$) revealed that, with the exception of the 2-OEt group, the other heteroatom groups increase electron density at the titanium atom.[9] Additionally, substituents in the third indenyl position are more effective as electron donors than those in the second position.

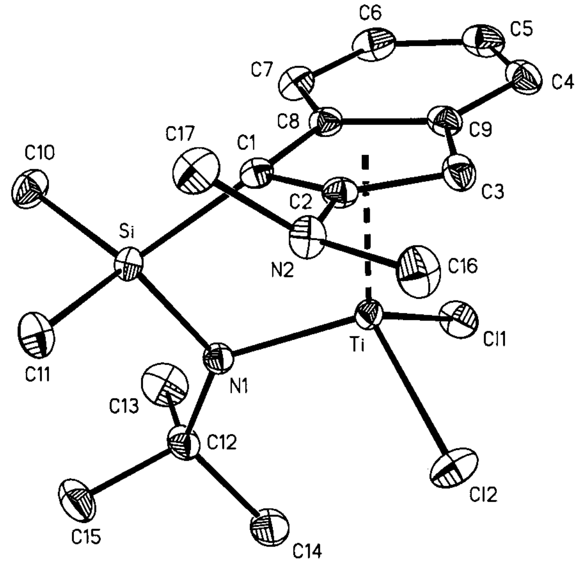


Figure 1. Thermal ellipsoid drawing of **2a** shown at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti−N1 = 1.914(1); Ti−C1 = 2.282(2); Ti−C3 = 2.423(2); Ti−Cn = 2.055; Si−N1 = 1.752(1); Si−C1 = 1.871(2); N2−C2 = 1.381(2); N2−C16 = 1.460(2); N2−C17 = 1.465(2); N1−Si−C1 = 91.45(7); Si−N1−Ti = 104.05(7); Cn−Ti−N1 = 108.3.

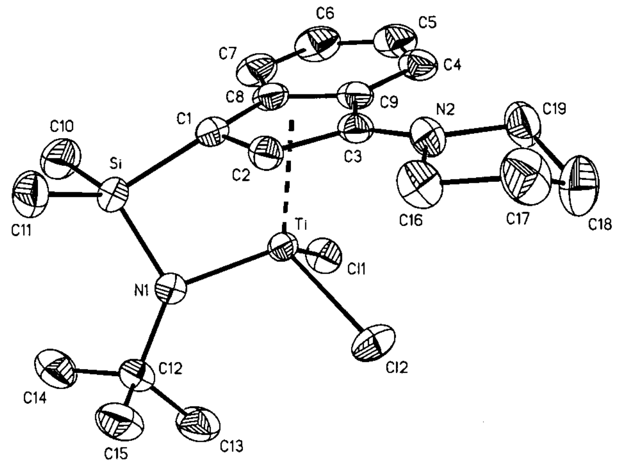


Figure 2. Thermal ellipsoid drawing of **4a** shown at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti−N1 = 1.898(2); Ti−C1 = 2.208(2); Ti−C3 = 2.611(2); Ti−Cn = 2.115; Si−N1 = 1.751(2); Si−C1 = 1.857(2); N2−C3 = 1.347(2); N2−C16 = 1.466(2); N1−Si−C1 = 92.28(7); Si−N1−Ti = 101.07(7); Cn−Ti−N1 = 111.0.

The molecular structures of complexes **1a**−**4a** were determined by single-crystal X-ray analysis.[9] Molecular structures of **2a** and **4a** are presented in Figures 1 and 2, respectively.[12] The short O1−C2 (1.334(2) Å, **1a**), N2−C2 (1.381(2) Å, **2a**), O1−C3 (1.346(2) Å, **3a**), and N2−C3 (1.347(2) Å, **4a**) bond lengths indicate delocalization of oxygen and nitrogen lone pairs into the indenyl system. The nitrogen atom in **2a** is slightly pyramidalized (sum of angles around N2 equal to 346.3°), presumably as a result of steric interaction between the silyl methyl group C11 and methyl groups of the dimethyl-

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(10) Analytical data for **4b**. ^{1}H NMR (C$_6$D$_6$): δ 0.08 (s, 3H, TiC*H*$_3^b$), 0.49 (s, 3H, SiC*H*$_3$, C11), 0.66 (s, 3H, SiC*H*$_3$, C10), 0.76 (s, 3H, TiC*H*$_3^a$), 1.51 (s, 9H, C(C*H*$_3$)$_3$), 1.52 (m, 4H, N(CH$_2$C*H*$_2$)$_2$), 3.24 (m, 2H, N(C*H*$_2$-CH$_2$)$_2$), 3.41 (m, 2H, N(C*H*$_2$CH$_2$)$_2$), 5.38 (s, 1H, H2), 6.89 (ddd, 1H, $^3J_{\text{H-H}}$ = 8.7 Hz, $^3J_{\text{H-H}}$ = 6.6 Hz, $^4J_{\text{H-H}}$ = 1.2 Hz, H6), 7.03 (ddd, 1H, $^3J_{\text{H-H}}$ = 8.7 Hz, $^3J_{\text{H-H}}$ = 6.6 Hz, $^4J_{\text{H-H}}$ = 1.2 Hz, H5), 7.51 (dt, 1H, $^3J_{\text{H-H}}$ = 8.7 Hz, $^4J_{\text{H-H}}$ = 0.9 Hz, H7), 7.73 (dt, 1H, $^3J_{\text{H-H}}$ = 8.7 Hz, $^3J_{\text{H-H}}$ = 0.9 Hz, H4). ^{13}C NMR (^{1}H-gated) (C$_6$D$_6$): δ 2.35 (q, $^1J_{\text{C-H}}$ = 118.9 Hz, Si*C*H$_3$, C11), 4.56 (q, $^1J_{\text{C-H}}$ = 118.8 Hz, Si*C*H$_3$, C10), 25.92 (t, $^1J_{\text{C-H}}$ = 131.8 Hz, N(CH$_2$*C*H$_2$)$_2$), 34.68 (qs, $^1J_{\text{C-H}}$ = 125.0 Hz, $^4J_{\text{C-H}}$ = 4.4 Hz, C(*C*H$_3$)$_3$), 48.87 (q, $^1J_{\text{C-H}}$ = 118.7 Hz, Ti*C*H$_3^b$), 50.47 (t, $^1J_{\text{C-H}}$ = 139.8 Hz, N(*C*H$_2$CH$_2$)$_2$), 54.13 (q, $^1J_{\text{C-H}}$ = 119.5 Hz, Ti*C*H$_3^a$), 57.81 (m, *C*(CH$_3$)$_3$), 83.87 (s), 104.09 (d, $^1J_{\text{C-H}}$ = 168.2 Hz, C2), 123.90 (dd, $^1J_{\text{C-H}}$ = 160.2 Hz, $^2J_{\text{C-H}}$ = 8.0 Hz, C5), 124.45 (s, C9), 125.04 (dd, $^1J_{\text{C-H}}$ = 159.5 Hz, $^2J_{\text{C-H}}$ = 8.4 Hz, C6), 125.64 (dd, $^1J_{\text{C-H}}$ = 160.6 Hz, $^2J_{\text{C-H}}$ = 7.2 Hz, C4), 128.16 (dd, $^1J_{\text{C-H}}$ = 160.2 Hz, $^2J_{\text{C-H}}$ = 7.2 Hz, C7), 133.66 (s, br, C8), 143.66 (s, C3). HRMS (EI, M$^+$): *m/z* calcd 390.197, found 390.193. Anal. Calcd for C$_{21}$H$_{34}$N$_2$SiTi: C, 64.60; H, 8.78; N, 7.17. Found: C, 64.30; H, 8.95; N, 6.72.

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(12) Crystallographic data for **2a**: C$_{17}$H$_{26}$Cl$_2$N$_2$SiTi, M_w = 405.29, triclinic, space group $P\bar{1}$, a = 8.3173(3) Å, b = 9.1847(3) Å, c = 13.2048(5) Å, α = 91.324(1)°, β = 91.541(1)°, γ = 103.384(1)°, V = 980.54(6) Å^3, Z = 2, D_{calcd} = 1.373 Mg/m^3, absorption coefficient 0.770 mm^{-1}, F(000) = 424, 7842 reflections collected, 4362 independent reflections, GOF = 1.061, R1 = 0.0293 ($I > 2\sigma(I)$), wR2 = 0.0782 (all data). Crystallographic data for **4a**: C$_{19}$H$_{28}$Cl$_2$N$_2$SiTi, M_w = 431.32, monoclinic, space group $P2_1/n$, a = 8.995(1) Å, b = 9.481(1) Å, c = 25.654(4) Å, β = 97.586(3)°, V = 2168.7(5) Å^3, Z = 4, D_{calcd} = 1.321 Mg/m^3, absorption coefficient 0.702 mm^{-1}, F(000) = 904, 15 220 reflections collected, 4955 independent reflections, GOF = 1.024, R1 = 0.0296 ($I > 2\sigma(I)$), wR2 = 0.0788 (all data).

Table 1. Ethylene and 1-Octene Copolymerizations Results Catalyzed by Complexes 1b−6b[a]

entry	cat. (amt, μmol)	activator (amt, μmol)	polym temp (°C)	activity (10^8 g/(mol h))[b]	density (g/cm^3)	M_w	M_w/M_n
1	**1b** (0.8)	$B(C_6F_5)_3$ (0.8)	140	2.94	0.897	92 700	2.78
2	**2b** (1.2)	$B(C_6F_5)_3$ (1.2)	140	0.75	0.928	98 800	3.50
3	**3b** (0.8)	$B(C_6F_5)_3$ (0.8)	140	1.35	0.894	148 000	2.13
4	**4b** (0.05)	$B(C_6F_5)_3$ (0.05)	140	**24.1**	0.906	**280 000**	2.05
5	**5b** (1)	$B(C_6F_5)_3$ (1)	140	3.50	0.897	78 000	2.58
6	**6b** (1.2)	$B(C_6F_5)_3$ (1.2)	140	0.86	0.894	105 000	2.24
7	**5b** (1)	$B(C_6F_5)_3$ (1)	160	1.80	0.902	47 100	2.18
8	**4b** (0.05)	$B(C_6F_5)_3$ (0.05)	160	**14.78**	0.908	**237 000**	2.92

[a] Conditions: carried out at 500 psi in a 2 L Parr reactor; run time 15 min. See the Supporting Information for detailed polymerization procedures. **5b** = (η^5-C_5Me_4)($SiMe_2$-N-*t*-Bu)$TiMe_2$; **6b** = (η^5-C_9H_6)($SiMe_2$-N-*t*-Bu)$TiMe_2$. [b] Average of two consecutive runs.

amino fragment. In **4a** the nitrogen atom is planar (sum of angles around N2 equal to 358.9°) and coplanar with the indenyl fragment. The main structural difference between 2-substituted (**1a**, **2a**) and 3-substituted (**3a**, **4a**) complexes lies in the coordination symmetry of the indenyl group to the titanium atom. In the case of **1a** and **2a** the five-membered ring of the indenyl ligand is relatively symmetrically bound to the titanium atom, as shown by similar values for Ti−C1 and Ti−C3 bond lengths (Δ(Ti−C3)−(Ti−C1) = 0.14−0.18 Å). In complexes **3a** and **4a**, however, the titanium slips in the direction of C1 (toward η^3 coordination), thus increasing the Ti−C3/Ti−C1 bond difference to 0.303 and 0.403 Å in **3a** and **4a**, respectively. The shortening of Ti−C1 and the elongation of Ti−C3 bond lengths in **3a** and **4a** gives rise to noticeable geometry changes in these complexes, as indicated by the increase of Cn−Ti−N2 and decrease of Si−N1−Ti angles. This change results in a small opening of the coordination sphere at the metal center in **3a**/**4a** relative to that in **1a**/**2a**. This phenomenon appears to be purely electronic in nature.

Ethylene/octene copolymerization reactions were carried out at 140 °C (**1b**−**6b**) and 160 °C (**4b**, **5b**) using $B(C_6F_5)_3$[13] as the activator (Table 1). The initial concern was that Lewis acid activators such as $B(C_6F_5)_3$ might react with the amino and alkoxy substituents of complexes **1b**−**4b**, thus inhibiting methide abstraction and polymerization.[14] This was found not to be the case, at least for **4b**, which cleanly and instantaneously reacts with $B(C_6F_5)_3$ via methide group abstraction[15] to give a mixture of two diastereomeric ion pairs.[16,17] The alkoxy-substituted complexes **1b** and **3b** exhibit catalytic activities noticeably higher than that of the unsubstituted analogue (η^5-C_9H_6)($SiMe_2$-N-*t*-Bu)$TiMe_2$ (**6b**). The most dramatic effect, however, is observed in the case of the 3-amino-substituted complex **4b**, which is over 25 times more active than the 2-amino-substituted analogue **2b**[18] and complex **6b** (entries 2, 4, and 6).[19] Complex **4b** was found to be the most active catalyst, well surpassing even the activity of (η^5-C_5Me_4)($SiMe_2$-N-*t*-Bu)$TiMe_2$ (**5b**) (entries 4 and 5). Most importantly, **4b** produces polymers with molecular weight 3−5 times higher than that of **5b** under identical polymerization conditions. Even at polymerization temperatures as high as 160 °C, **4b** (entries 7 and 8) is an extremely efficient catalyst, still producing very high molecular weight polymers. To our knowledge complex **4b** is the most efficient ethylene/octene catalyst and forms the highest molecular weight ethylene/octene copolymers reported to date for any CGC catalyst under polymerization conditions studied. The dramatic amino effect described here for CGC complexes is in stark contrast to that in bis(indenyl) zirconocene complexes. In these types of complexes both 2-amino[20] and 3-amino[21] substitutions lead to poor catalysts.

Investigations aimed at better understanding the heteroatom effect on the catalytic behavior of CGC complexes is underway and will be reported in due course.

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Supporting Information Available: Text giving experimental procedures, thermal ellipsoid drawings for **1a**−**4a**, and tables of atomic positions, anisotropic thermal parameters for non-hydrogen atoms, and comprehensive bond lengths and angles for **1a**−**4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Details of this chemistry will be described in future publications.

(17) Surprisingly, there is no reaction between the nitrogen of the pyrrolidine ring and $B(C_6F_5)_3$ even in the absence of an ionizable methyl group. Mixing **4a** with $B(C_6F_5)_3$ in C_6D_6 solution did not lead to any reaction, as shown by ^1H and ^{19}F NMR.

(18) The 2-pyrrolidino-substituted complex (direct analogue of **4b**) was also prepared and was found to exhibit polymerization characteristics very similar to those of **2b**.

(19) The polymerization activity of complexes **1b**−**3b** and **5b** at 0.05 μmol loading was also studied and was not enhanced compared to that of higher catalyst loading. The amount of **4b** was kept below 0.1 μmol to maintain a polymerization exotherm within 10 °C.

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