Polymerization of α-Olefins by Chelating Diamide Complexes of Titanium

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Although soluble group 4 olefin polymerization catalyst precursors such as Cp_2MX_2,[1] $CpMX_3$,[2] and linked Cp−amide[3] derivatives have been studied extensively, new non-Cp ligand environments remain relatively unexplored.[4] Previously we have investigated the chemistry of chelating diamide ancillaries[5] that incorporate the voluminous 2,6-diisopropylphenyl moiety at nitrogen. The chelating diamide complexes, $[ArN(CH_2)_3NAr]ZrR_2$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; R = Me, CH_2Ph),[5b] were targeted as possible catalyst precursors for the polymerization of olefins via putative cationic derivatives (e.g., $[ArN(CH_2)_3NAr]ZrR^+$). Although these complexes display little or no activity for the polymerization of olefins under the conditions employed in this study,[6] they nevertheless exhibit a rich chemistry including C−H activation.[5b] We have since turned our attention to titanium and report here the synthesis of d^0 chelating diamide complexes which, when activated with a Lewis acid cocatalyst, are active catalysts for the polymerization of 1-hexene.

The silylated diamines **2a,b** (obtained from the diamines $[RHN(CH_2)_3NHR]$: **1a**, R = Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$;[5b] **1b**, R = Ar′ = 2,6-Me$_2$C$_6$H$_3$)[7] react with $TiCl_4$ in refluxing xylenes to afford 2 equiv of $ClSiMe_3$ and the orange dichloride complexes **3a,b** (Scheme 1).[8] Characteristic second-order patterns are observed for the methylene protons (NCH_2 and NCH_2CH_2) of the coordinated ligands in the proton NMR spectra[8] of complexes **3a,b**. In addition, the isopropyl methyl groups of complex **3a** are diastereotopic, which we interpret as a consequence of restricted rotation about the $N-C_{ipso}$ bond. In particular, the aryl groups lie perpendicular to the N_2Ti plane, necessarily protecting the metal above and below this plane. A similar observation has been made in late metal complexes bearing bis(imine) ligands with analogous aryl substituents.[9] The molecular structure of complex **3a** and selected bond distances and angles are shown in Figure 1.[10]

Compounds **3a,b** react with 2 equiv of methyl Grignard to afford the crystalline, thermally stable, dimethyl derivatives **4a,b** (Scheme 1).[11] The crystalline dibenzyl derivatives **5a,b**[7] are obtained under similar conditions. The proton and carbon NMR spectra[11] of **4b** display Ti−CH_3 and Ti−CH_3 resonances at 0.70 and 51.1 ppm, respectively. Similar shifts are observed for **4a**. These resonances are comparable to other known bis(amide)-$TiMe_2$ species.[12] The molecular structure of complex **4b** and selected bond distances and angles are shown in Figure 1.[13]

The titanium diamide complexes described above are active catalyst precursors for the aspecific[4e] polymerization of 1-hexene. A summary of the polymerization results is shown in Table 1.[7] The catalyst systems generate high molecular weight polymers with narrow

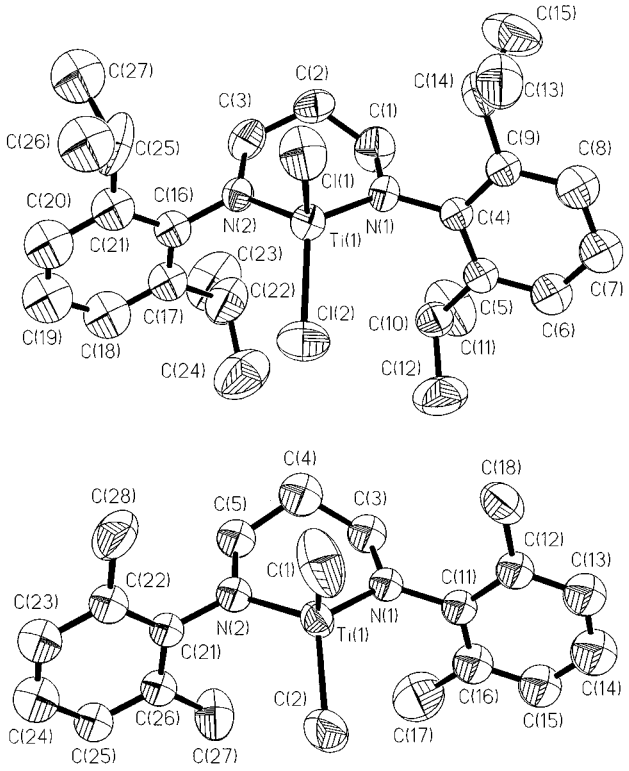
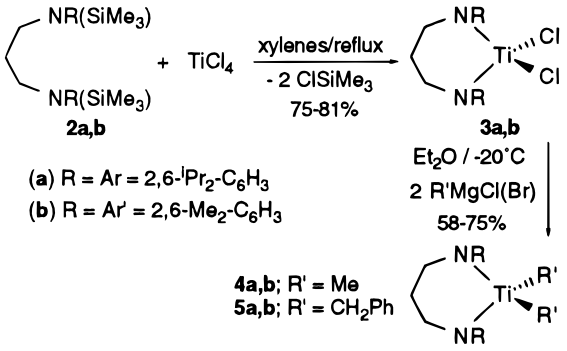


Figure 1. (Top) ORTEP drawing of **3a**. Selected bond distances (Å) and angles (deg): Ti1−N1 = 1.856(5), Ti1−N2 = 1.839(5), Ti1−Cl1 = 2.257(2), Ti1−C2 = 2.240(2), N1−Ti1−N2 = 99.2(2). (Bottom) ORTEP drawing of **4b**. Selected bond distances (Å) and angles (deg): Ti1−N1 = 1.858(6), Ti1−N2 = 1.867(6), Ti1−C1 = 2.100(9), Ti1−C2 = 2.077(9), N1−Ti1−N2 = 102.6(3).

Scheme 1



molecular weight distributions. We have been unable to observe olefinic resonances in the $^{13}C\{^1H\}$ NMR spectra[7] of the polymers or oligomers (*vide infra*) prepared with these catalyst systems. We can only speculate that chain transfer to aluminum must be relatively fast compared to β-elimination. Deuterium and carbon-13 labeling experiments are in progress to determine the mode(s) of olefin addition (2,1- vs 1,2-insertion).

Activities as high as 350 000 g of poly(1-hexene)/mmol of catalyst·h were obtained for catalyst **4a**/MAO (entry 1). For comparison, the bis(amide) system $[(Me_3Si)_2N]_2ZrCl_2$/MAO polymerizes propylene with an activity of 62 g of polypropylene/mmol of catalyst·h under similar conditions.[4b] Lower initial activities are observed for **4a**/MAO at lower temperatures (i.e., 22 °C) until sufficient heat is released at the onset of polymerization. This apparent activation barrier may reflect the relative difficulty in generating a putative 10-

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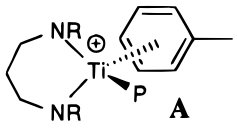
Table 1. Polymerization of 1-Hexene[a]

entry	catalyst system	yield (g)	time (min)	M_w[b]	M_n[b]	M_w/M_n	activity[c]
1	**4a**/MAO, 68 °C	2.96	0.5	81500	47000	1.73	350000
2	**4b**/MAO, 68 °C	2.42	0.5	54000	30400	1.78	290000
3	**4a**/MMAO, 68 °C	0.25	1.0	28200	17800	1.58	15000
4	**4b**/MMAO, 68 °C	0.73	1.0	23500	13400	1.75	44000
5	**4a**/$B(C_6F_5)_3$, 22 °C[d]	0.18	5.0	29600	16100	1.84	2000
6	**4b**/$B(C_6F_5)_3$, 22 °C[d]	0.22	5.0	26200	14500	1.81	2000
7	**4a**/MAO, 68 °C[e]	0.76	0.5	32700	18600	1.76	91000
8	**4b**/MAO, 68 °C[e]	0.56	0.5	29900	16500	1.81	67000
9	**3a**/MAO, 68 °C[e]	0.96	0.5	55600	31000	1.79	115000
10	**3b**/MAO, 68 °C[e]	0.73	0.5	33800	19200	1.76	88000

[a] 1 μmol of catalyst in 0.5 mL of pentane was mixed with 250 equiv of solid cocatalyst and added to 5.0 g of 1-hexene (250 equiv of cocatalyst as scavenger), unless otherwise stated. [b] By GPC vs polystyrene standards. [c] g of poly(1-hexene)/mmol of catalyst·h. [d] 1 equiv of $B(C_6F_5)_3$ (preactivated) and 500 equiv of MAO as scavenger in the reactor at 22 °C. [e] 1 μmol of catalyst in 0.5 mL of toluene.

electron cationic alkyl complex.[14] Interestingly, the activity of **4a**/MAO decreases by a factor of nearly 4 when the polymerizations are performed in the presence of small amounts of toluene (entry 7). A similar decrease in activity is observed for **4b**/MAO when toluene is present (entry 2 vs 8). More importantly, **4a**/MAO yields a very small amount of low molecular weight polymer when the polymerization is performed at 22 °C in the presence of toluene (activity = 800 g of poly(1-hexene)/mmol of catalyst·h, M_w = 2000, M_n = 1300). Assuming a cationic alkyl as the active species,[14] we interpret these results as possible competitive binding of toluene to titanium (**A**), which may decrease the



A

rate of insertion of 1-hexene. Given the low coordination number of these diamide complexes and the reports of authentic cationic η^6-toluene species,[15] the possibility of such an interaction should be borne in mind. We have prepared the cyclopentadienyl complex [ArN-$(CH_2)_3$NAr]Ti(η^5-C_5H_5)Cl,[6] suggesting that the metal can accommodate ligands of this size.

The catalysts bearing the 2,6-^{i}Pr$_2$C$_6$H$_3$ group at nitrogen (**3a**, **4a**) show higher activities than the 2,6-$Me_2C_6H_3$-substituted complexes (**3b**, **4b**) (MAO activation), possibly a reflection of the increased steric protection afforded by the former ligand. In contrast, the catalyst system **4a**/MMAO (MMAO = isobutyl-modified methylaluminoxane) is less active than **4b**/MMAO (entries 3 and 4). This may reflect structural differences between MMAO and MAO.[16] Under identical conditions of MAO activation, the dichloride precursors **3a,b** are about 30% more active than the dimethyl derivatives **4a,b** (entries 7−10). The dimethyl derivatives **4a,b** can also be activated with the Lewis acid $B(C_6F_5)_3$ (entries 5 and 6). We observe no activity when polymerizations are performed at 68 °C, possibly due to catalyst decomposition at this temperature; moderate activity is observed at 22 °C. We are examining the apparent anion effects that are operative in these systems.[17]

In summary, these chelating diamide complexes of titanium serve as active catalyst precursors for the polymerization of 1-hexene. A variety of cocatalysts can be used to activate the complexes; however, the presence of toluene appears to compete with monomer insertion. Successful polymerization of other olefins and further ligand variations will be reported shortly.

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Supporting Information Available: Details of compounds, polymer synthesis and characterization, and crystallographic details (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(7) Complete details are given in the supporting information.

(8) **3a**: ^{1}H NMR δ 7.09 (m, 6H, Ar), 3.75 (m, 4H, NCH_2), 3.53 (sept, 4H, CHMe$_2$), 2.48 (m, 2H, NCH$_2$CH_2), 1.44 (d, 12H, CHMe_2), 1.18 (d, 12H, CHMe_2). ^{13}C{^{1}H} NMR δ 144.5, 143.3,

129.2, 125.0, 64.4, 31.1, 28.9, 26.2, 24.4. Anal. Calcd for $C_{27}H_{40}Cl_2N_2Ti$: C, 63.41; H, 7.88; N, 5.48. Found: C, 63.05; H, 8.12; N, 5.27. **3b**: ^{1}H NMR δ 6.93 (m, 6H, Ar), 3.46 (m, 4H, NCH_2), 2.34 (s, 12H, Ar*Me*), 2.34 (m, 2H, NCH$_2$CH_2). ^{13}C{^{1}H} NMR δ 144.2, 133.3, 129.4, 128.5, 62.1, 32.4, 19.0. Anal. Calcd for $C_{19}H_{24}Cl_2N_2Ti$: C, 57.16; H, 6.06; N, 7.02. Found: C, 57.28; H, 6.19; N, 6.89.

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(10) Crystal data for **3a**: a = 9.771(1) Å, b = 14.189(1) Å, c = 21.081(2) Å, β = 96.27(1)°, V = 2905.2(5) Å^3, space group $P2_1/n$, Z = 4, mol wt = 511.41 for $C_{27}H_{40}Cl_2N_2Ti$, T = 25 °C, R = 0.0701, R_w = 0.1495, GOF = 1.081.

(11) **4a**: ^{1}H NMR δ 7.21 (m, 6H, Ar), 3.72 (sept, 4H, C*H*Me$_2$), 3.58 (m, 2H, NCH_2), 2.12 (m, 2H, NCH$_2$CH_2), 1.39 (d, 12H, CH*Me*$_2$), 1.28 (d, 12H, CH*Me*$_2$), 0.86 (s, 6H, Ti*Me*$_2$). ^{13}C{^{1}H} NMR δ 145.3, 144.7, 127.4, 124.6, 61.5, 52.0, 31.2, 28.5, 26.4, 24.9. Anal. Calcd for $C_{29}H_{46}N_2Ti$: C, 74.02; H, 9.85; N, 5.95. Found: C, 74.32; H, 9.91; N, 5.85. **4b**: ^{1}H NMR δ 7.11 (m, 4H, Ar), 7.02 (m, 2H, Ar), 3.40 (m, 2H, NCH_2), 2.39 (s, 12H, Ar*Me*), 2.04 (m, 2H, NCH$_2$CH_2), 0.70 (s, 6H, Ti*Me*$_2$). ^{13}C-{^{1}H} NMR δ 146.6, 134.4, 129.1, 126.6, 58.5, 51.1, 32.0, 18.7. Anal. Calcd for $C_{21}H_{30}N_2Ti$: C, 70.38; H, 8.44; N, 7.82. Found: C, 69.98; H, 8.73; N, 7.56.

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(13) Crystal data for **4b**: a = 8.0955(10) Å, b = 15.288(4) Å, c = 16.909(3) Å, V = 2092.8(7) Å^3, space group $P2_12_12_1$, Z = 4, mol wt = 358.38 for $C_{21}H_{30}N_2Ti$, T = 23 °C, R = 0.0759, R_w = 0.1498, GOF = 0.947.

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