J. Am. Chem. Soc. **2000,** *122,* 7841−7842 7841

A Comparison of Cationic Zirconium Methyl and Isobutyl Initiators that Contain an Arylated Diamido-Pyridine Ligand for Polymerization of 1-Hexene. Elucidation of a Dramatic “Initiator Effect”

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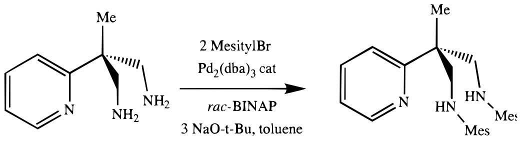
Received March 3, 2000

We are developing the chemistry of d^0 zirconium complexes that contain diamido/donor ligands,[1] e.g., $[(t\text{-Bu-N-}o\text{-C}_6H_4)_2O]^{2-}$,[2−4] $[(MesNCH_2CH_2)_2NR]^{2-}$,[5] and others,[6−10] in particular chemistry that concerns cationic monoalkyl complexes as initiators for olefin polymerization. In the case of the $[Ph_3C][B(C_6F_5)_4]$-activated $[(t\text{-BuN-}o\text{-C}_6H_4)_2O]ZrMe_2$ system, polymerization of 1-hexene takes place in a living fashion in chlorobenzene below 10 °C via 1,2-insertions into the Zr−Me bond, as shown by ^{13}C labeling[3] and kinetic[11] studies. Until now we have employed ligands that have a central donor and two atoms in the two arms that connect the amido atom to the central donor, and which, with two exceptions,[10,12] are relatively flexible. In this communication we report a variation of the relatively rigid diamido pyridine derivative reported by Gade,[13] and elucidate a striking difference between two observable cationic alkyl initiators in 1-hexene polymerization reactions and dramatically different stabilities of cationic alkyls toward β elimination.

The pyridyl diamine shown in eq 1 was prepared according to the method reported by Gade.[13] Arylation under conditions reported by Buchwald[14,15] gave the dimesityl derivative, $H_2[MesNpy]$, in good yield. Addition of $H_2[MesNpy]$ to $Zr(NMe_2)_4$ gave $[MesNpy]Zr(NMe_2)_2$, in which the dimethylamido ligands are inequivalent, according to ^1H and $^{13}C\{^1H\}$ NMR spectra. $[MesNpy]Zr(NMe_2)_2$ was converted into $[MesNpy]ZrCl_2$ in high yield employing Me_3SiCl (3 equiv, ether, 1 h at 22 °C). Subsequent alkylation of $[MesNpy]ZrCl_2$ with RMgBr (R = Me or *i*-Bu) yielded the dialkyl derivatives, $[MesNpy]ZrR_2$ (R = Me (**1a**) or *i*-Bu (**1b**)). The diisobutyl derivative is thermally stable for days at room temperature in the dark in the solid state, but appears to decompose slowly in fluorescent room light. Slow rotation of the mesityl rings on the NMR time scale about the $N-C_{ipso}$ bond is observed in all compounds at low temperatures, and in $[MesNpy]ZrCl_2$ even at 22 °C.



$H_2[MesNpy]$

(1)

An X-ray study of **1a** (Figure 1; see Supporting Information) showed it to have approximately a trigonal bipyramidal structure with planar equatorial amido nitrogens (N(1) and N(2)), one which closely resembles the structures found for $[Me_3SiNpy]TiBr_2$ and $[Me_3SiNpy]Ti(CH_2SiMe_3)Br$.[13] The plane of each mesityl ring is roughly perpendicular to the $Zr-N-C_{ipso}$ plane, while the N(1)−Zr−N(2) angle (102.24(12)°) is significantly smaller than the analogous angle found in (for example) $[(MesNCH_2CH_2)_2NMe]ZrMe_2$ (140.5(2)°).[5]

The reaction between $[MesNpy]ZrMe_2$ and $[Ph_3C][B(C_6F_5)_4]$ in bromobenzene-d_5 results in the formation of Ph_3CCH_3 and what appears to be an orange species that is stable for days at −30 °C (under dinitrogen, according to NMR spectra) that we formulated initially as “$\{[MesNpy]ZrMe\}[B(C_6F_5)_4]$”. However, we find that addition of only 0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$ gives a yellow species that has virtually identical proton and carbon NMR spectra as that formed by adding 1 equiv of $[Ph_3C][B(C_6F_5)_4]$. At 22 °C the Zr−Me resonance is found at 0.66 ppm in the proton NMR spectrum, while in the $Zr^{13}CH_3$ analogue a broad Zr−Me carbon resonance is found at ∼38 ppm. At −60 °C in a mixed solvent (1:1 $C_6D_5Br:C_6D_5CD_3$) two methyl resonances are observed in a ratio of ∼2:1 at 32.1 and 41.9 ppm; J_{CH} was found to be 113 Hz for the downfield resonance. All data are consistent with formation of a dimeric monocationic species having the formula $\{[MesNpy]_2Zr_2Me_3\}[B(C_6F_5)_4]$ (**2**) that is relatively unreactive toward additional $[Ph_3C][B(C_6F_5)_4]$ at room temperature at the concentrations employed. (The orange color that is present upon addition of 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ is ascribed to excess $[Ph_3C][B(C_6F_5)_4]$.) One possible formulation for **2** is analogous to the crystallographically characterized monocationic dimer formed from a zirconocene dimethyl species and 0.5 equiv of activator in which one of the three methyl groups bridges the two zirconium centers symmetrically.[16]

Addition of 80 equiv of 1-hexene to a 1:1 mixture of **2** and $[Ph_3C][B(C_6F_5)_4]$ (formed from **1a** and 1 equiv of $[Ph_3C][B(C_6F_5)_4]$, 0.01 M Zr, 22 °C, C_6D_5Br) leads to formation of poly(1-hexene) over a period of 3−4 h. A plot of ln[1-hexene] versus time (Figure 2) shows significant curvature, and a significant amount (at least 50%) of **2** remains (according to proton NMR) after all 80 equiv of 1-hexene has been consumed. The most linear portion of the plot (>100 min) yields a k_{obs} of 0.016 min^{-1} at 294 K ($[Zr]_o$ = 10 mM). Similar behavior is observed at higher temperatures (k_{obs} = 0.021 min^{-1} at 298 K, 0.034 min^{-1} at 303 K, and 0.074 min^{-1} at 313 K). An Eyring plot yielded $\Delta H^{\ddagger}$ = 14.3(5) kcal/mol and $\Delta S^{\ddagger}$ = −26(2) cal/(mol K). Addition of a second 80 equiv of 1-hexene to the 294 K sample after consumption of the first 80 equiv led to further polymer formation with a k_{obs} = 0.018 min^{-1} derived from a now somewhat more linear ln[1-hexene] versus time plot. However, a significant amount of the initiator is still present even after 160 equiv of 1-hexene have been consumed. GPC analysis of two different poly(1-hexene) samples formed from the methyl initiator showed them to have relatively high M_n values (approximately 10× theory based on *all* Zr present), but a surprisingly narrow molecular weight distribution (PDI = 1.02, 1.08).

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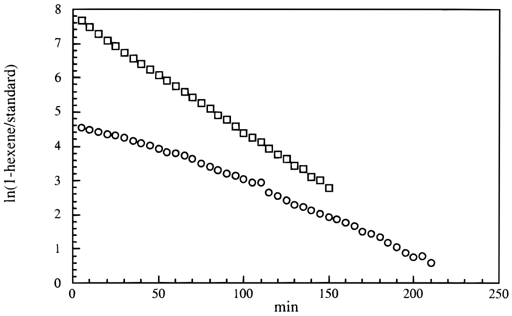

Figure 2. Circles: Plot of ln[1-hexene/standard] vs time after addition of 80 equiv of 1-hexene to the activator formed from [MesNpy]ZrMe$_2$ and 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.01 M in C$_6$D$_5$Br) at 25 °C. Squares: Plot of ln[1-hexene/standard] vs time after addition of 100 equiv of 1-hexene to the activator formed from [MesNpy]Zr(i-Bu)$_2$ and 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.00073 M in C$_6$D$_5$Br) at −10 °C.

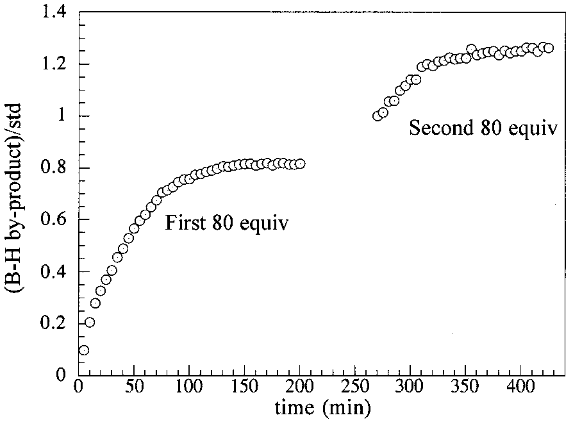

Figure 3. Plot of [2-heptenes]/[standard] vs time (min) for two consecutive additions of 80 equiv of 1-hexene to the activator formed from [MesNpy]ZrMe$_2$ and 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (25 °C, C$_6$D$_5$Br); standard = hexamethylbenzene.

In the polymerization reactions described immediately above weak resonances grow in at 5.36 ppm, rapidly at first, but then more slowly, and finally stop when all 1-hexene has been consumed. They grow in again upon addition of a second 80 equiv aliquot of 1-hexene and stop again upon consumption of the second 80 equivalents of 1-hexene (Figure 3); note that less of this product is formed during the second phase. By proton NMR comparison with authentic samples this product has been identified as a mixture of *trans*-2-heptene and *cis*-2-heptene (∼3:1). Vacuum transfer of the volatile components yields a sample with an identical olefinic pattern near 5.36 ppm. We propose that the 2-heptenes form by selective β elimination in a 3-heptyl complex, the 2,1 "misinsertion" product of the reaction between a cationic zirconium methyl species and 1-hexene, that the product of β elimination is inactive, and that the fraction of 3-heptyl complex that reacts with 1-hexene does so in a 1,2-fashion and produces an alkyl that is relatively stable to β elimination.

Addition of 1-hexene to **2** that is prepared by addition of 0.5 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to **1a** (0.01 M Zr, 22 °C, C$_6$D$_5$Br) also leads to formation of poly(1-hexene) and 2-heptenes, but the rate of polymerization is ∼25% of the rate when the initiator is prepared by addition of 1.0 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to **1a**. Addition of 0.4 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to **1a** leads to a mixture of **2** and ∼0.1 equiv of **1a** that is virtually unreactive toward 1-hexene (∼50 equiv yields a trace of poly(1-hexene) in 1 day). We propose that {[MesNpy]ZrMe}[B(C$_6$F$_5$)$_4$] is the active initiator in the presence or absence of excess [Ph$_3$C][B(C$_6$F$_5$)$_4$], and that it and **1a** are in an equilibrium with **2** that lies far to the side of **2**.

Activation of **1b** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Br at −30 °C produced Ph$_3$CH, isobutene, and a yellow species that we formulate as monomeric {[MesNpy]Zr(i-Bu)}[B(C$_6$F$_5$)$_4$] in at least 85% yield versus an internal diphenylmethane standard. At 0 °C the isobutene begins to disappear (we propose that it is polymerized), and the amount of {[MesNpy]Zr(i-Bu)}[B(C$_6$F$_5$)$_4$] decreases to ∼65% of theory. {[MesNpy]Zr(i-Bu)}[B(C$_6$F$_5$)$_4$] decomposes with time in a smooth first-order manner (k_{obs} = 0.0017 min^{-1}; $t_{1/2}$ = 40 min) at 0 °C to give isobutene (which is observed to increase in concentration and then ultimately decrease as it is polymerized) and a Zr species that we believe to be catalytically inactive. Addition of 100 equiv of 1-hexene at 263 K to {[MesNpy]Zr(i-Bu)}[B(C$_6$F$_5$)$_4$] led to quantitative formation of poly(1-hexene) over a period of 2 h, *complete consumption* of {[MesNpy]Zr(i-Bu)}[B(C$_6$F$_5$)$_4$], a plot of ln[1-hexene] vs time that was *linear throughout* the polymerization time period (Figure 2), and *no* formation of any significant olefinic byproducts, in particular none with olefinic resonances near 5.36 ppm. The observed rate constant was found to be 0.019 min^{-1} at [Zr]$_o$ = 7.3 mM, or k_{obs}/[Zr]$_o$ = k = 0.0436 M^{-1} s^{-1}. Polymerizations at 253 (k = 0.0268 M^{-1} s^{-1}), 273 (k = 0.0833 M^{-1} s^{-1}), and 283 K (k = 0.164 M^{-1} s^{-1}) were similarly well-behaved. An Eyring plot yielded $\Delta H^\ddagger = 8.1(7)$ kcal/mol and $\Delta S^\ddagger = -33(3)$ cal/(mol K). GPC analysis of the poly(1-hexene) formed from the isobutyl initiator at 0 °C was found to have an M_n value approximately 3× theory based on all Zr present and a PDI of 1.03. The initial rate of consumption of 100 equiv of 1-hexene ([Zr] = 7.3 mM) was found to be approximately 1000 times more rapid than the rate of decomposition of {[MesNpy]Zr(i-Bu)}[B(C$_6$F$_5$)$_4$] at 0 °C, which accounts for complete initiation to give the (much more stable) propagating cation.

We propose that the active species in each system (activated **1a** or **1b**) is a solvated form of {[MesNpy]Zr(R)}[B(C$_6$F$_5$)$_4$] (R = Me or i-Bu). However, for steric reasons{[MesNpy]ZrMe}-[B(C$_6$F$_5$)$_4$] reacts with 1-hexene to a significant extent by 2,1 insertion to give a 3-heptyl complex that is highly susceptible to β hydride elimination to yield 2-heptenes; only a fraction reacts via a 1,2 insertion to give a stable propagating species. In contrast, {[MesNpy]Zr(i-Bu)}[B(C$_6$F$_5$)$_4$] does not form a strong adduct with [MesNpy]Zr(i-Bu)$_2$. Therefore, virtually all the Zr is available to react with 1-hexene, and a steric environment is created in which only 1,2 insertion of 1-hexene can take place. In each case the propagating alkyl for steric reasons is the most likely to react in a 1,2 fashion and is the most stable to β elimination. The reason the PDI of the poly(1-hexene) in the potentially complex and dynamic methyl system is so low is not yet clear.

We believe the results presented here are a clear-cut example of an "initiator effect" in olefin polymerization by relatively well-characterized group 4 catalysts.[17,18] Further exploration of the phenomena uncovered here and their implications for a variety of alkyls, monomers, and catalysts that contain more bulky aryl groups on nitrogen is under way.

Acknowledgment. We thank the Department of Energy (DE-FG02-86ER13564) and Exxon Corporation for supporting this research and Dr. Arturo Casado for useful discussions.

Supporting Information Available: Figure 1, experimental procedures, fully labeled ORTEP drawing, crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for [MesNpy]ZrMe$_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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