

Synthesis of Titanium and Zirconium Complexes That Contain the Tridentate Diamido Ligand, $[(t\text{-Bu-}d_6)\text{N-}o\text{-C}_6\text{H}_4)_2\text{O}]^{2-}$ ($[\text{NON}]^{2-}$) and the Living Polymerization of 1-Hexene by Activated $[\text{NON}]\text{ZrMe}_2$

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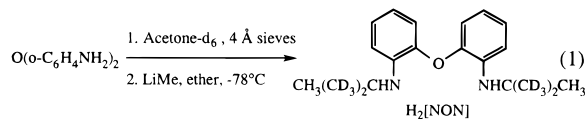
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Enormous advances have been made in the last decade in the design and synthesis of “well-defined” or “single-site” catalysts for the polymerization of terminal olefins.¹ The vast majority of such catalysts are metallocene derivatives, although some are known that contain one cyclopentadienyl ring and (for example) a pendant amido ligand.^{2–8} Recently, however, complexes that contain only a chelating dialkoxide^{9,10} or a chelating diamido ligand^{11–19} have received attention as potential Ziegler–Natta catalysts. An important recent result is the finding that propylene-bridged aryl-substituted diamido titanium complexes promote the living polymerization of neat α olefins.²⁰ As a part of our program to investigate the utility of triamidoamine ligands²¹ and new diamido¹⁵ ligands in early metal chemistry, we were attracted to the $[(t\text{-BuN-}o\text{-C}_6\text{H}_4)_2\text{O}]^{2-}$ ligand for preparing new noncyclopentadienyl group 4 olefin polymerization catalysts for a variety of reasons, among them the likely robust nature of the (*tert*-butyl)(phenyl)amide–metal linkage^{22–24} and the diphenyl ether linkage. We report here our preliminary results for Ti and Zr.

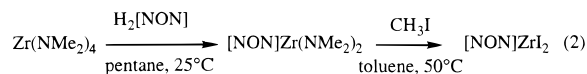
The species $[(t\text{-Bu-}d_6)\text{NH-}o\text{-C}_6\text{H}_4)_2\text{O}]$ ($\text{H}_2[\text{NON}]$, eq 1) can be prepared from $[(\text{NH}_2\text{-}o\text{-C}_6\text{H}_4)_2\text{O}]^{25}$ in a manner analogous

to that used to prepare $\text{NH}(t\text{-Bu})(\text{C}_6\text{H}_5)^{26}$ and $\text{NH}(t\text{-Bu-}d_6)(\text{aryl})$ derivatives.²² The yield of $\text{H}_2[\text{NON}]$, a yellow oil, is typically



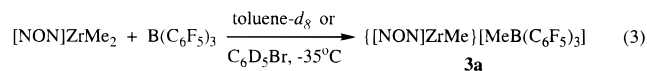
55% on a scale of 10–15g. Addition of 2 equiv of butyllithium to $\text{H}_2[\text{NON}]$ in ether at -35°C followed by addition of $\text{TiCl}_2(\text{NMe}_2)_2^{27}$ yields $\text{Ti}[\text{NON}](\text{NMe}_2)_2$ in $\sim 55\%$ yield, which can be converted to $\text{Ti}[\text{NON}]\text{Cl}_2$ with 2 equiv of Me_3SiCl .^{28–30} Alkylation of $\text{Ti}[\text{NON}]\text{Cl}_2$ with 2 equiv of MeMgCl affords $[\text{NON}]\text{TiMe}_2$ (**1**) in $\sim 75\%$ yield. An X-ray study of **1** (Figure 1) shows that it has a trigonal bipyramidal structure in which the Ti–O distance (2.402(4) Å) is much shorter than that between Ti and the (essentially uncoordinated) donor nitrogen in $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{N}(\text{SiMe}_3)]\text{TiMe}_2$ (2.732(2) Å),¹² although it is still longer than one might expect for a “normal” Ti–O_{donor} bond length ($\sim 2.15\text{--}2.20$ Å). The *tert*-butyl groups are “tipped” ($\text{O}_{\text{ax}}\text{--Ti--N}_{\text{eq}}\text{--C} = 136\text{--}137^\circ$), in part as a consequence of the enforced conformation of the $[\text{NON}]^{2-}$ ligand. Proton and carbon NMR spectra of **1** suggest that it has C_{2v} symmetry on the NMR time scale. We propose that the methyl groups equilibrate via an intermediate that contains a planar form of the $[\text{NON}]^{2-}$ ligand in which the methyl groups occupy two equatorial positions in a distorted trigonal bipyramid.

$[\text{NON}]\text{ZrI}_2$ can be prepared as shown in eq 2.²² Alkylation of $[\text{NON}]\text{ZrI}_2$ with MeMgI in diethyl ether gives $[\text{NON}]\text{ZrMe}_2$ (**2**) in 70% yield. NMR spectra of **2**, even at -70°C , suggest that it has C_{2v} symmetry on the NMR time scale. We assume



at this stage that the structure of **2** in the solid state is analogous to that found for **1** and that C_{2v} symmetry is achieved via a distorted trigonal bipyramidal molecule containing a planar $[\text{NON}]^{2-}$ ligand.

Addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to **2** in bromobenzene-*d*₅ or toluene-*d*₈ at -35°C yielded a bright yellow solution. NMR spectra suggest that a product is formed quantitatively in which the methyl groups are inequivalent. Addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to $[\text{NON}]\text{ZrMe}_2$ in pentane at -35°C yielded a bright yellow solution from which some yellow oil precipitated immediately. The pentane supernatant was filtered and cooled to -35°C to afford **3a** as yellow crystals (containing 0.5 equiv of pentane by NMR) in 47% yield. Compound **3a** is stable in the solid state at -35°C , but decomposes in toluene, pentane, or bromobenzene over a period of hours at 22°C .



An X-ray study of **3a** (Figure 2) showed it to be the “zwitterion” analogous to structurally-characterized compounds obtained by adding $\text{B}(\text{C}_6\text{F}_5)_3$ to group 4 methyl metallocenes^{31–34} in which the borane has partially abstracted the “apical” methyl

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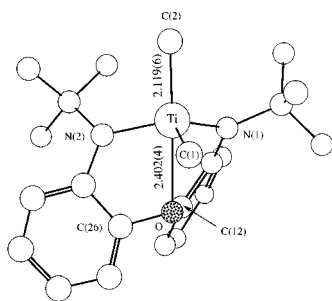


Figure 1. The structure of $\text{Ti}[\text{NON}]\text{Me}_2$ (bond lengths (Å) and angles (deg)): $\text{Ti}-\text{C}(1) = 2.097(6)$, $\text{Ti}-\text{N}(1) = 1.944(4)$, $\text{Ti}-\text{N}(2) = 1.936(4)$, $\text{Ti}-\text{O} = 2.402(4)$, $\text{C}(12)-\text{O}-\text{C}(26) = 115.5(4)$, $\text{Ni}(1)-\text{Ti}-\text{N}(2) = 113.5(2)$, $\text{N}(1)-\text{Ti}-\text{C}(1) = 115.1(2)$, $\text{N}(2)-\text{Ti}-\text{C}(1) = 114.6(2)$.

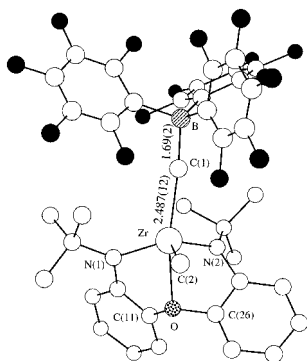


Figure 2. The structure of $\{[\text{NON}]\text{ZrMe}\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ (bond lengths (Å) and angles (deg)): $\text{Zr}-\text{C}(2) = 2.200(13)$, $\text{Zr}-\text{N}(1) = 2.049(10)$, $\text{Zr}-\text{N}(2) = 2.065(10)$, $\text{Zr}-\text{O} = 2.256(8)$, $\text{C}(11)-\text{O}-\text{C}(26) = 116.4(9)$, $\text{N}(1)-\text{Zr}-\text{N}(2) = 113.8(4)$, $\text{N}(1)-\text{Zr}-\text{C}(2) = 113.8(5)$, $\text{N}(2)-\text{Zr}-\text{C}(2) = 115.4(5)$, $\text{Zr}-\text{C}(1)-\text{B} = 174.8(10)$.

group ($\text{B}-\text{Me}_{\text{bridge}} = 1.69(2)$ Å; $\text{Zr}-\text{Me}_{\text{bridge}} = 2.487(12)$ Å). In related zirconocene complexes, $\text{Zr}-\text{Me}_{\text{bridge}}$ distances generally have been longer, typically 2.549–2.667 Å.^{31,33} The $\text{Zr}-\text{O}$ bond is what one might expect for a single $\text{Zr}-\text{O}_{\text{donor}}$ bond length. Therefore, the oxygen appears capable of stabilizing the incipient electrophilic Zr cation to a significant degree. To our knowledge **3a** is the only crystallographically-characterized methyl complex of the “boron-activated” type that does not contain a cyclopentadienyl ligand on the metal, although the structure of a complex that contains an $[\eta^6-\text{C}_6\text{H}_5\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3]^-$ ligand has been reported³⁵ and a variety of complexes in which a methyl group has been partially removed by $\text{B}(\text{C}_6\text{F}_5)_3$ have been characterized in solution by NMR methods.^{17,18}

Addition of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ ³⁶ to **2** in bromobenzene-*d*₅ generates “[$\{[\text{NON}]\text{ZrMe}(\text{PhNMe}_2)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ ” (**3b**). In **3b** a methyl resonance for PhNMe_2 can be observed at 2.74 ppm in the proton NMR spectrum at 22 °C (vs 2.62 ppm for free dimethylaniline), a fact that suggests that dimethylaniline is coordinating to the Zr center. (Coordination of dimethylaniline to cationic Zr centers has been observed in other systems.¹⁷) NMR spectra of **3b** in $\text{C}_6\text{D}_5\text{Br}$ suggest that it begins to decompose after ~1 h at 22 °C and in minutes above 50 °C.

Both **3a** and **3b** were found to be active catalysts for ethylene polymerization. In a typical experiment, **3a** (20 μmol, 50 mL of toluene, 1–2 atm of ethylene, 22 °C, 2 min) afforded 69 mg (~ 10^5 g mol_{cat}⁻¹ h⁻¹) of polyethylene, and **3b** (same conditions,

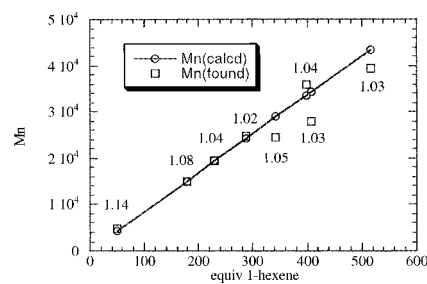


Figure 3. Poly(1-hexene) prepared using **3b** and PDI for each.

50 mL of chlorobenzene) afforded 540 mg (~ 8×10^5 g mol_{cat}⁻¹ h⁻¹) of polyethylene. Compound **3b** is also an active catalyst for the polymerization of 1-hexene. The activity in almost neat hexene is ~ 2×10^5 g mol_{cat}⁻¹ h⁻¹ (2 g of hexene and 2.5 μmol of catalyst in 0.25 mL of chlorobenzene yields 580 mg of poly(1-hexene) in 1 h; $M_n = 4.5 \times 10^4$ g/mol; $M_w/M_n = 1.2$). Since the exotherm raises the reaction temperature significantly when the reaction is begun at room temperature, and since intermediate cationic alkyl complexes that contain β protons may be even less stable than the cationic methyl complex, polymerizations of 1-hexene with **3b** were carried out at 0 °C in chlorobenzene batchwise.³⁷ The polydispersities and increase in molecular weight (by light scattering) vs monomer employed suggest that the polymerization is living under these conditions (Figure 3). At this stage we do not know if the deviation in molecular weights of polymers prepared from >300 equiv of 1-hexene is systematic or if it can be ascribed simply to catalyst weighing error. On the basis of the data we have so far, there does not appear to be any systematic deviation from theory that would result from catalyst decomposition during the course of the polymerization of up to at least 300 equiv of 1-hexene at 0 °C. The poly(1-hexene) obtained in these reactions is atactic according to carbon NMR studies.¹⁶ $[\text{NON}]\text{ZrMe}_2$ was found to be inactive under these conditions.

The results reported here, along with those reported recently for a Ti catalyst containing a chelating diamido ligand,²⁰ suggest that group 4 addition polymerization catalysts that contain diamido ligands can be designed that are much more stable with respect to loss of olefin via β elimination and consequent chain transfer than metallocene-based catalysts, but are still highly active. The relatively low cost and large variety of readily synthesized diamines are attractive further incentives for the development of diamido ligand catalysts.

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Supporting Information Available: Experimental procedures, a table listing data for synthesis and characterization of poly(1-hexene), and crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for $[\text{NON}]\text{TiMe}_2$ and $\{[\text{NON}]\text{ZrMe}\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ (21 pages). See any current masthead page for ordering and Internet access instructions. This information is also available in CIF format.

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