

CH Bond Activation in Cations of the Type $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrR}\}^+$ and a Simple Solution that Yields a Catalyst for the Living Polymerization of 1-Hexene

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Summary: $\{[(\text{MesNCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ and intermediates in the polymerization reaction of 1-hexene that are formed from it decompose as a consequence of CH activation in an ortho methyl group in the mesityl substituent. The intermediates in the polymerization reaction decompose significantly more readily than does $\{[(\text{MesNCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$. On the other hand, analogous cationic complexes that contain the $\{[(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_2\text{NMe}]^2\}$ ligand are relatively stable and will consume 1-hexene in a strictly first-order and apparently living manner at 0 °C in chlorobenzene.

We are interested in exploring and developing diamido/donor ligands for early transition metal chemistry. A diamido/donor ligand is one variation within a large class of diamido ligands that have been employed for early metal chemistry.^{1–19} One of the important applications of diamido/donor ligands in our laboratory is the synthesis of Zr and Hf cations that are active for

the polymerization of ordinary olefins, in particular living polymerizations.^{20–21} Some of the most readily accessible ligands in this category are of the type $\{[\text{ArNCH}_2\text{CH}_2)_2\text{D}]^2\}$, where D = O,²² S,²² NH,^{23,24} or NR^{23,24} and Ar is a sterically protected aryl such as 2,6-*i*-Pr₂C₆H₃ or 2,4,6-Me₃C₆H₂ (Mes). However, all polymerization systems based on such ligands that we have examined so far appear to suffer from some termination step in polymerization of 1-hexene that does not involve formation of olefinic end groups. In this communication we show that deactivation consists of CH bond activation in a mesityl ortho methyl group in complexes of the type $\{[(\text{MesNCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrR}\}^+$ and that, in contrast, $\{[(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrR}\}^+$ is a highly active living catalyst for the polymerization of 1-hexene.

We have reported that $\{[(\text{MesNCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) will initiate the polymerization of 1-hexene in chlorobenzene, but the molecular weight is limited and the polydispersity is not what one would expect from a living polymerization.²⁴ Since no olefinic end groups are observed, β -hydride elimination within the growing polymer chain does not appear to be responsible, at least not to a significant and detectable degree.²⁵ We have found that **1** decomposes in bromobenzene in a first-order manner ($k_{20^\circ\text{C}} = 6.0 \times 10^{-5} \text{ s}^{-1}$ at $[\text{Zr}]_0 = 19.0$ and 38.0 mM; $k_{60^\circ\text{C}} = 2.1 \times 10^{-3} \text{ s}^{-1}$ at $[\text{Zr}]_0 = 38.0$ mM) to give methane and an insoluble species which immediately oils out of solution and ultimately crystallizes as a dark orange material in 85% yield. X-ray diffraction showed that this species is the dimeric dication shown in Figure 1. We propose that this compound forms by dimerization of some solvated version of the monomeric monocation (**2**) shown in eq 1. Apparently the configuration of the ligand in **2** leaves the Zr exposed to binding of the arene ring (whose methyl group has been attacked) in the “apical” position

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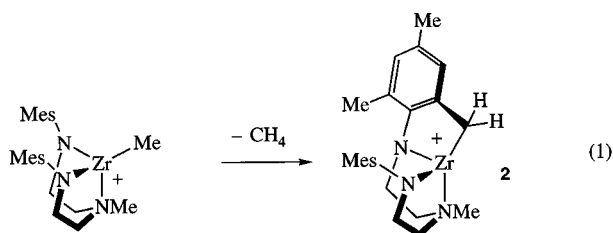
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(25) In contrast, zirconium complexes that contain $[(\text{RN}-o\text{-C}_6\text{H}_4)_2\text{O}]^{2-}$ ligands (R = isopropyl, cyclohexyl, or mesityl) appear to be catalysts only for the oligomerization of 1-hexene as a consequence of β hydride elimination.



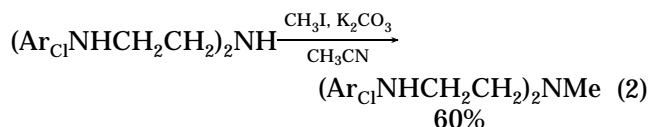
trans to the amine donor. This structure is related to that proposed (on the basis of NMR studies) for the product of CH activation in an amido TMS methyl group in $\{[(\text{TMSNCH}_2\text{CH}_2)_2\text{NTMS}]\text{ZrCH}_2\text{Ph}\}[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$, in which the anion forms a π arene complex through the benzyl's phenyl ring.¹⁰

Polymerization reactions of 1-hexene initiated by **1** are too rapid to be monitored readily by NMR methods. (Approximately 250 equiv of 1-hexene are polymerized within ~ 5 min by **1** (0.25 mM) at 0 °C in bromobenzene.) Addition of 20 equiv of 1-hexene to a solution of **1** in bromobenzene at -30 °C followed by warming to 20 °C gave crystals of the dimer of **2** in high yield, according to X-ray crystallography (unit cell match). Therefore the intermediates in the polymerization reaction also decompose by the same CH activation process.

1-Hexene is polymerized by $\{[(\text{MesNCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrMe}(\text{PhNMe}_2)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**·PhNMe₂), which is formed upon addition of $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ to $[(\text{MesNCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrMe}_2$ at 0 °C in bromobenzene, but at a rate that is slow enough to be followed readily by NMR methods. A plot of $\ln[1\text{-hexene}]$ versus time in this reaction shows considerable curvature. The rate of consumption can be modeled assuming that a concomitant first-order decomposition of intermediates in the polymerization reaction is responsible for the curvature. The rate constant for the first-order and irreversible decomposition of the intermediates in the polymerization reaction obtained in this manner is $k_{0^\circ\text{C}} = 5.0 \times 10^{-4} \text{ s}^{-1}$. We propose that the decomposition of poly-

merization intermediates when **1**·PhNMe₂ is the initiator is due to CH bond activation similar to that shown in eq 1. Interestingly, it is clear that these intermediates decompose considerably faster than does **1** ($k_{0^\circ\text{C}} = 5.0 \times 10^{-4} \text{ s}^{-1}$ compared to $k_{20^\circ\text{C}} = 6.0 \times 10^{-5} \text{ s}^{-1}$ for **1**). We suggest that the larger alkyl chain keeps the base (dimethylaniline, bromobenzene, or $[\text{B}(\text{C}_6\text{F}_5)_4]^-$) further away from the zirconium cationic center, thereby allowing a faster intramolecular CH bond activation by the lower coordinate metal center. The dimethylaniline adduct of **1** was found to decompose in a first-order manner at 60 °C ($k_{60^\circ\text{C}} = 1.3 \times 10^{-4} \text{ s}^{-1}$ at $[\text{Zr}]_0 = 21.0 \text{ mM}$) to give a dimethylaniline adduct of **2**, although identification of that adduct was based solely on NMR studies.²³

To eliminate CH activation, but provide approximately the same steric protection of the amido nitrogens, we considered replacing the mesityl group with a 2,6-Cl₂C₆H₃ group. The reaction between commercially available 2,6-dichlorobromobenzene and $(\text{H}_2\text{NCH}_2\text{CH}_2)_2\text{NH}$ under conditions employed for the synthesis of $(\text{MesNHCH}_2\text{CH}_2)_2\text{NH}$ proceeded smoothly in 5 days at 100 °C to give $(\text{Ar}_\text{Cl}\text{NHCH}_2\text{CH}_2)_2\text{NH}$ ($\text{Ar}_\text{Cl} = 2,6\text{-Cl}_2\text{C}_6\text{H}_3$) in 80% yield. The proton on the central nitrogen can be replaced by a methyl group in 60% yield under the conditions shown in eq 2. The $(\text{Ar}_\text{Cl}\text{NHCH}_2\text{CH}_2)_2\text{NMe}$



$\text{CH}_2)_2\text{NMe}$ ligand then can be added to $\text{Zr}(\text{NMe}_2)_4$ to produce $[(\text{Ar}_\text{Cl}\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{Zr}(\text{NMe}_2)_2$ in 90% yield, which upon treatment with Me_3SiCl gives $[(\text{Ar}_\text{Cl}\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrCl}_2$ in 90% yield. Alkylation of $[(\text{Ar}_\text{Cl}\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrCl}_2$ with MeMgBr in diethyl ether then affords $[(\text{Ar}_\text{Cl}\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrMe}_2$ (**3**) in 70% yield. (See Supporting Information for all experimental details.) All reactions are identical to those employed to prepare $(\text{MesNHCH}_2\text{CH}_2)_2\text{NMe}$ and analogous Zr complexes that contain the $[(\text{MesNHCH}_2\text{CH}_2)_2\text{NMe}]^{2-}$ ligand.²³ An X-ray structure²⁶ of $[(\text{Ar}_\text{Cl}\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{Zr}^*\text{Me}_2$ (**3***; *Me = $^{13}\text{CH}_3$) showed it to be isostructural with $[(\text{MesCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrMe}_2$.^{23,24} (See Supporting Information for crystallographic details.)

The reaction between $[(\text{Ar}_\text{Cl}\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{Zr}^*\text{Me}_2$ and $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ in bromobenzene at -20 °C yielded a bright yellow solution, proton and ^{13}C NMR spectra of which are consistent with formation of a cationic species that has mirror symmetry that we propose is $\{[(\text{Ar}_\text{Cl}\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{Zr}^*\text{Me}(\text{PhNMe}_2)]\text{B}(\text{C}_6\text{F}_5)_4\}$ (**4**). The methyl resonance is found at -0.03 ppm in the proton NMR spectrum ($J_{\text{CH}} = 117 \text{ Hz}$) and 37.80 ppm in the carbon NMR spectrum at -14 °C. Compound **4** is stable for hours at 0 °C. Addition of

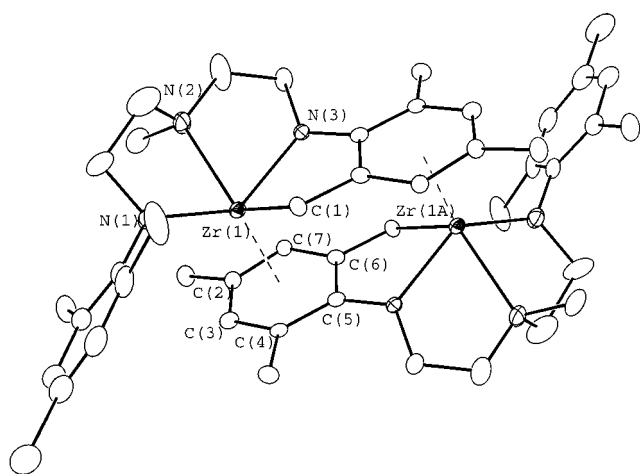


Figure 1. ORTEP diagram of the dimer of **2**. Selected bond distances (Å): Zr(1)–N(1) = 2.068(7); Zr(1)–N(3) = 2.190(6); Zr(1)–C(1) = 2.251(7); Zr(1)–N(2) = 2.355(7); Zr(1)–C(3) = 2.608(8); Zr(1)–C(2) = 2.617(7); Zr(1)–C(7) = 2.671(8); Zr(1)–C(4) = 2.722(7); Zr(1)–C(6) = 2.854(8). Selected bond angles (deg): N(1)–Zr(1)–N(3) = 132.8(3); N(1)–Zr(1)–C(1) = 98.6(3); N(3)–Zr(1)–C(1) = 73.9(2); N(1)–Zr(1)–N(2) = 74.2(3); N(3)–Zr(1)–N(2) = 70.8(2); C(1)–Zr(1)–N(2) = 120.4(3).

(26) Crystal data and structure refinement details for $[(\text{Ar}_\text{Cl}\text{N}_2\text{NMe})\text{Zr}(\text{Me})_2]\cdot\text{THF}$ (**3***): $a = 8.186(4) \text{ Å}$, $b = 12.142(7) \text{ Å}$, $c = 13.747(6) \text{ Å}$, $\alpha = \gamma = 90^\circ$, $\beta = 95.17(4)^\circ$, $V = 1360.9(12) \text{ Å}^3$, monoclinic $P2_1/m$, $T = 183(2) \text{ K}$, $\lambda = 0.71073 \text{ Å}$, $Z = 2$, $\rho_{\text{calc}} = 1.449 \text{ g/cm}^3$, $\mu = 0.816 \text{ mm}^{-1}$, $F(000) = 603$, 2θ range = $5.00\text{--}44.96^\circ$, limiting indices $-4 \leq h \leq 8$, $-10 \leq k \leq 8$, $-13 \leq l \leq 14$, no. of reflections collected/unique = 2380/1568, $R_{\text{int}} = 0.0162$, FMLS on F^2 refinement method, no. of data/restraints/parameters = 1568/0/170, GoF on $F^2 = 1.051$, final R indices $[I > 2\sigma(I)]$ are $R_1 = 0.0399$, $wR_2 = 0.1061$ and R indices (all data) are $R_1 = 0.0417$, $wR_2 = 0.1080$ with largest difference peak and hole = 0.508 and -0.519 e Å^{-3} .

Table 1. Poly(1-hexene) Prepared Using $\{[ArClN_2NMe]Zr^*Me(PhNMe_2)\}[B(C_6F_5)_4]^a$

equiv 1-hexene	$10^3 M_n$ (calcd)	$10^3 M_n$ (found)	M_n (found/calcd)	$10^3 M_w$	PDI
100	8.4	24.2	2.9	24.6	1.02
150	12.6	31.5	2.5	32.1	1.02
200	16.8	35.6	2.1	36.3	1.02
600	50.5	78.5	1.6	79.6	1.01
150 ^b	12.6	48.8	3.9	50.5	1.03
150 ^c	12.6	62.1	4.9	64.9	1.04

^a [4] = 3 mM in chlorobenzene, 0 °C, 1 h. ^b 4 equiv of PhNMe₂ added. ^c 8 equiv of PhNMe₂ added.

1-hexene (50 equiv) at 0 °C leads to its consumption in strictly a first-order manner with an observed first-order rate constant of $k_{0^\circ C} = 2.5 \times 10^{-3} s^{-1}$. According to NMR spectroscopy the initiator ($[Zr]_0 = 3.0$ mM) is completely consumed only when the amount of 1-hexene exceeds 200 equiv. The PDI values are uniformly low for all polymers in bulk polymerizations, and the measured molecular weights (by light scattering) are closest to those expected for a living polymerization (in which k_p is of the same order as k_t) for the highest number of equivalents of 1-hexene (see Table 1, M_n (found/calcd) = 1.6 for 600 equiv of 1-hexene).

Addition of free dimethylaniline (4–16 equiv) to $\{[(ArClNCH_2CH_2)_2NMe]Zr^*Me(PhNMe_2)\}[B(C_6F_5)_4]$ before 1-hexene is added leads to increasingly slower rates of consumption of 1-hexene (Figure 2), consistent with competitive inhibition of 1-hexene polymerization by dimethylaniline. A simple treatment of the data shown in Figure 2 reveals that K_{eq} for formation of the dimethylaniline adduct of the cationic complex formed during 1-hexene polymerization is $\sim 160 M^{-1}$, while the rate constant for the reaction between the “base-free” cationic propagating species and 1-hexene is $0.80 M^{-1} s^{-1}$ at 0 °C.²⁷ The more dimethylaniline that is added, the greater amount of $\{[(ArClNCH_2CH_2)_2NMe]Zr^*Me(PhNMe_2)\}[B(C_6F_5)_4]$ that remains after polymerization is complete and the greater the disparity between the observed M_n and that calculated for a perfect living polymerization in which initiation and propagation are roughly comparable in rate. For example M_n (found/calcd) values increase from 2.5 in a run in which no dimethylaniline has been added to 3.9 in a run in which 4 equiv of PhNMe₂ has been added, to 4.9 in a run in which 8 equiv of PhNMe₂ has been added (Table 1). We propose that dimethylaniline binds more strongly to the methyl initiator than to the metal in the complex that contains the growing polymer chain (for steric reasons) and that the dimethylaniline that is “liberated” upon initiation *represses* dissociation of dimethylaniline from the remaining initiator, thereby effectively preventing further initiation. For this reason, the polydispersities

(27) If $[cat] + [cat(B)] = [Zr]_T$ (where $cat = \{[(ArClNCH_2CH_2)_2NMe]ZrR\}[B(C_6F_5)_4]$, $cat(B) = \{[(ArClNCH_2CH_2)_2NMe]ZrR(PhNMe_2)\}[B(C_6F_5)_4]$, R is the growing polymer chain, and B is dimethylaniline), and the equilibrium between cat and B to give cat(B) is fast in both directions, then $[Zr]_T/k(obs) = 1/k + K[B]/k$ where k is the rate constant for the reaction between cat and 1-hexene and $K = [cat(B)]/[cat][B]$. A plot of $[Zr]_T/k(obs)$ vs $[B]$ gives $1/k$ and K/k .

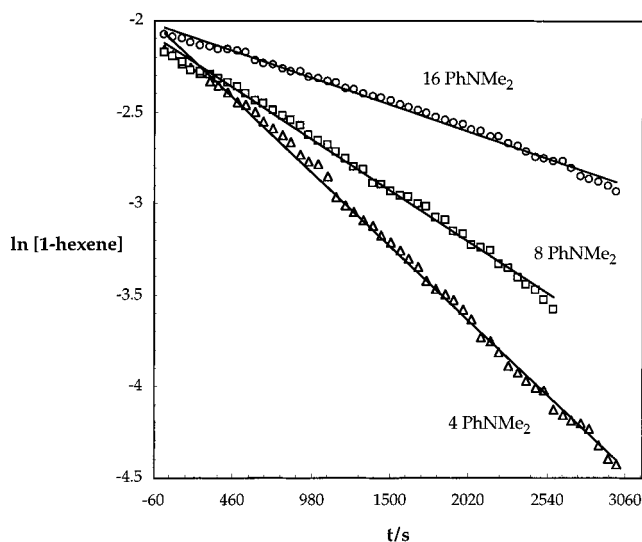


Figure 2. Competitive inhibition of 1-hexene polymerization (50 equiv) by PhNMe₂ using $\{[ArClN_2NMe]Zr^*Me(PhNMe_2)\}[B(C_6F_5)_4]$ (3 mM) in C₆D₅Br at 0 °C (followed by ¹H NMR). For 16 equiv of PhNMe₂ $k_{obsd} = 2.78(3) \times 10^{-4} s^{-1}$; for 8 equiv of PhNMe₂ $k_{obsd} = 5.37(6) \times 10^{-4} s^{-1}$; for 4 equiv of PhNMe₂ $k_{obsd} = 7.78(6) \times 10^{-4} s^{-1}$.

of the resulting polymers are uniformly low and the molecular weights approach those expected for a well-behaved living process only at high initial monomer concentrations.

The findings reported here suggest that CH activation in a mesityl ortho methyl group in an intermediate of the type $\{[(MesNCH_2CH_2)_2NMe]ZrR\}[B(C_6F_5)_4]$ is a termination step in a 1-hexene polymerization reaction and that comparable polymerizations by a catalyst that contains a 2,6-dichlorophenyl group are well-behaved. Use of 2,6-dichlorophenyl groups might be useful in other circumstances in which 2,6-disubstituted aryl groups bound to amido nitrogen ligands have been employed in the last several years, at least those in which CH activation might be taking place. At this stage we do not know the extent to which the 2,6-dichlorophenyl group in the cations discussed here might actually stabilize cations via “light” (or transiently dative) coordination of the chloride to the metal or the degree to which electronic differences between the 2,6-dichlorophenyl group and the mesityl group might contribute to the high activity of the 2,6-dichlorophenyl catalysts.

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Supporting Information Available: Experimental details and fully labeled ORTEP drawings, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for the dimer of **2** and **3*** are available free of charge via the Internet at <http://pubs.acs.org>.

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