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NMR detection of living intermediates prepared from activated $[NON]ZrMe_2$ ($[NON]^{2-} = [(t\text{-Bu-}d_6\text{-N-}o\text{-}C_6H_4)_2O]^{2-}$) and olefins

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Abstract

The ^{13}C-NMR spectrum of $\{[NON]Zr(^{13}CH_3)(S)\}^+$ (S = bromobenzene-d_5) after addition of one equivalent of 1-hexene reveals resonances at 30.8 ppm for the terminal $^{13}CH_3$ group in the first insertion product, at 24.0 ppm for the terminal $^{13}CH_3$ group in the second insertion product and near 20 ppm for the terminal $^{13}CH_3$ group in higher insertion products. The latter are consistent with 'insertion' of the 1-hexene into the Zr–CH_3 bond in a 1,2 manner. Addition of ten equivalents of 1-nonene to $\{[NON]Zr(CH_3)(S)\}^+$ followed by one equivalent of $^{13}CH_2{=}CHC_7H_{15}$ led to a ^{13}C-NMR spectrum consistent with formation of $\{[NON]Zr[^{13}CH_2CH(C_7H_{15})(Polymer)](S)\}^+$, which confirms that 1-nonene 'inserts' into the Zr–C bond primarily in a 1,2 fashion. A discussion as to why β elimination is relatively slow in $\{[NON]Zr(R)(S)\}^+$ systems that have been examined so far focuses on reversible addition of a terminal olefin only to the CNN face of the pseudo-tetrahedral cation, $\{[NON]Zr(R)\}^+$, to yield a trigonal bipyramidal transition state. After the equatorial alkyl group migrates to the substituted carbon of the incoming olefin, the new bulky alkyl in $\{[NON]Zr(CH_2CHPR')\}^+$ cannot 'back up' toward the two t-butyl groups in preparation for β elimination relative to the rate at which $\{[NON]Zr(CH_2CHPR')\}^+$ reacts with either base or more olefin.

Keywords: Living intermediates; NON; Olefins

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1. Introduction

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]. Although the vast majority of such catalysts contain at least one and usually two cyclopentadienyl rings, 'noncyclopentadienyl' compounds that contain a chelating dialkoxide [2,3] or a chelating diamido ligand [4–17] have shown moderate to excellent catalytic potential. Perhaps the most important of the recent findings is that propylene-bridged aryl-substituted diamido titanium complexes promote the living polymerization of neat α olefins [13]. We were attracted to the possibility that pseudo *four*-coordinate group 4 cationic species would be more stable intermediates in an addition polymerization reaction than pseudo *three*-coordinate species. This idea arose, in part, from findings relating to olefin metathesis reactions, including ring opening metathesis polymerization, by well-defined four-coordinate tungsten and molybdenum complexes of the type $M(CHR)(NR')(OR'')_2$ [18–20], where the olefin is proposed to approach one of the two CNO faces of the pseudotetrahedral catalyst to give a fluxional five-coordinate intermediate metallacyclobutane complex. The idea also derived from research concerning triamidoamine complexes [21], which in general are relatively unreactive as a consequence of the crowded nature of the trigonal 'triamido' coordination pocket. We settled on the synthesis of a 'diamido/donor' ligand of the type $[(t\text{-BuN-}o\text{-}C_6H_4)_2O]^{2-}$ ($[NON]^{2-}$) for a variety of rea-

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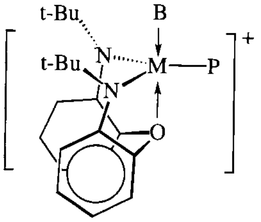
sons, among them the potentially robust nature of the (t-butyl)(phenyl)amide–metal [22–24] and the diphenyl ether linkages, and the absence of any protons β to the metal that might be removed in a type of β elimination reaction, a type of decomposition reaction that has been documented for certain triamidoamine complexes of tantalum [25,26].

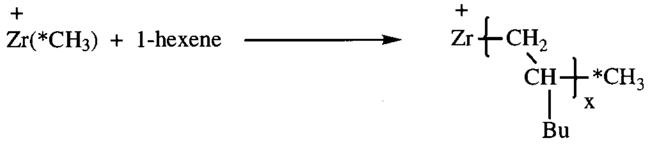
We recently reported the synthesis and structures of titanium and zirconium complexes that contain the $[NON]^{2-}$ ligand and evidence that the polymerization of 1-hexene by $[NON]ZrMe_2$ in chlorobenzene activated by $[PhNMe_2H][B(C_6F_5)_4]$ is in fact living at 0°C [27]. Atactic poly(1-hexene) samples were prepared from up to 500 equivalents of 1-hexene that had the expected molecular weights (determined by a combination of refractometer and light scattering detection) and polydispersities < 1.1. The X-ray structure of $\{[NON]ZrMe\}[MeB(C_6F_5)_3]$ suggested that the apical methyl group in trigonal bipyramidal $[NON]ZrMe_2$ is the one removed in the process of forming the catalytically active cationic species, and that a base (dimethylaniline or even chlorobenzene) is perhaps bound competitively in that apical position. The structure of the living species therefore is proposed to be the following, where P is the growing polymer chain and B is some perhaps very weakly bound base:



If the system is truly living then we should be able to observe the living species under the polymerization conditions. The results of these investigations are reported here.

2. Results

The ^{13}C-NMR spectrum of $[NON]Zr(^{13}CH_3)_2$ shows a resonance for the methyl carbon at 45.2 ppm in bromobenzene-d_5. Upon addition of one equivalent of $[Ph_3C][B(C_6F_5)_4]$, one of the now standard methods of generating metallocene cations [28], a ^{13}C-NMR spectrum at ~0°C reveals two resonances (Fig. 1), one for $Ph_3C^{13}CH_3$ and one for the methyl group at 53.6 ppm in what we propose is a 'cation' that for simplicity we shall call $\{[NON]Zr(^{13}CH_3)(S)\}^+$, where S = bromobenzene-d_5. The shift of the methyl resonance in $[NON]Zr(^{13}CH_3)_2$ ca. 8 ppm downfield upon formation of $\{[NON]Zr(^{13}CH_3)(S)\}^+$ is consistent with formation of a 'cationic' species. Upon addition of one equivalent of 1-hexene to the solution containing $\{[NON]Zr(^{13}CH_3)(S)\}^+$, part of it is consumed to form a propagating species, as shown in Fig. 2. The resonance at ~30.8 ppm is assigned to the terminal $^{13}CH_3$ group in the first insertion product and that at ~24.0 ppm to the terminal $^{13}CH_3$ group in the second insertion product, while resonances near 20 ppm are assigned to the terminal $^{13}CH_3$ group in higher insertion products. If we assume that the 1-hexene mixes rapidly with the initiator before any significant amount of initiation takes place, we can conclude that the rate of initiation is less than the rate of propagation, i.e. $k_p > k_i$. This is the result one might expect if the base (assumed to be bromobenzene-d_5) must dissociate from Zr before 1-hexene can react, since the base should be bound most strongly in the sterically least demanding coordination site, i.e. in the initiator, since if the rate of initiation and the rate of propagation are of approximately the same order of magnitude as the rate of mixing, then a similar result might be obtained. (Yet another possibility is that the more bulky, but more basic, alkyl in essentially a base-free species migrates more quickly to the incoming olefin than does a methyl group.) The other conclusion that is possible is that 'insertion' of 1-hexene into the $Zr–CH_3$ bond takes place in a 1,2 manner. The reason is that 2,1 addition would yield a species in which the ^{13}C labeled methyl group would be bound to a methylene carbon, i.e. $Zr[CH(Bu)CH_2]_x{}^{13}CH_3$, and in that case a chemical shift for the labeled methyl carbon would be expected to be in the range of 10–12 ppm [29]. The living species is stable for several hours at 0°C but begins to decompose within minutes above 25°C. The rate of decomposition has not yet been quantified.



$$\overset{+}{Zr}(*CH_3) + \text{1-hexene} \longrightarrow \overset{+}{Zr}\left[CH_2-\underset{Bu}{CH}\right]_x{*CH_3}$$

$[NON]Zr(^{13}CH_2CHMe_2)_2$ was prepared from $[NON]ZrCl_2$ and shown to yield a ^{13}C-NMR spectrum in bromobenzene-d_5 that contained a resonance at 81.5 ppm. Upon addition of one equivalent of $[Ph_3C][B(C_6F_5)_4]$ at ca. −30°C followed by one equivalent of 2,4-lutidine the colorless solution turns light yellow. A ^{13}C-NMR spectrum of this solution at ~0°C revealed a resonance ca. 13 ppm downfield of 81.5 ppm (at 94.4 ppm) for the methylene carbon atom in what we propose to be $\{[NON]Zr(^{13}CH_2CHMe_2)(2,4\text{-lutidine})\}^+$. This compound is *inactive* for the polymerization of 1-hexene under conditions that were

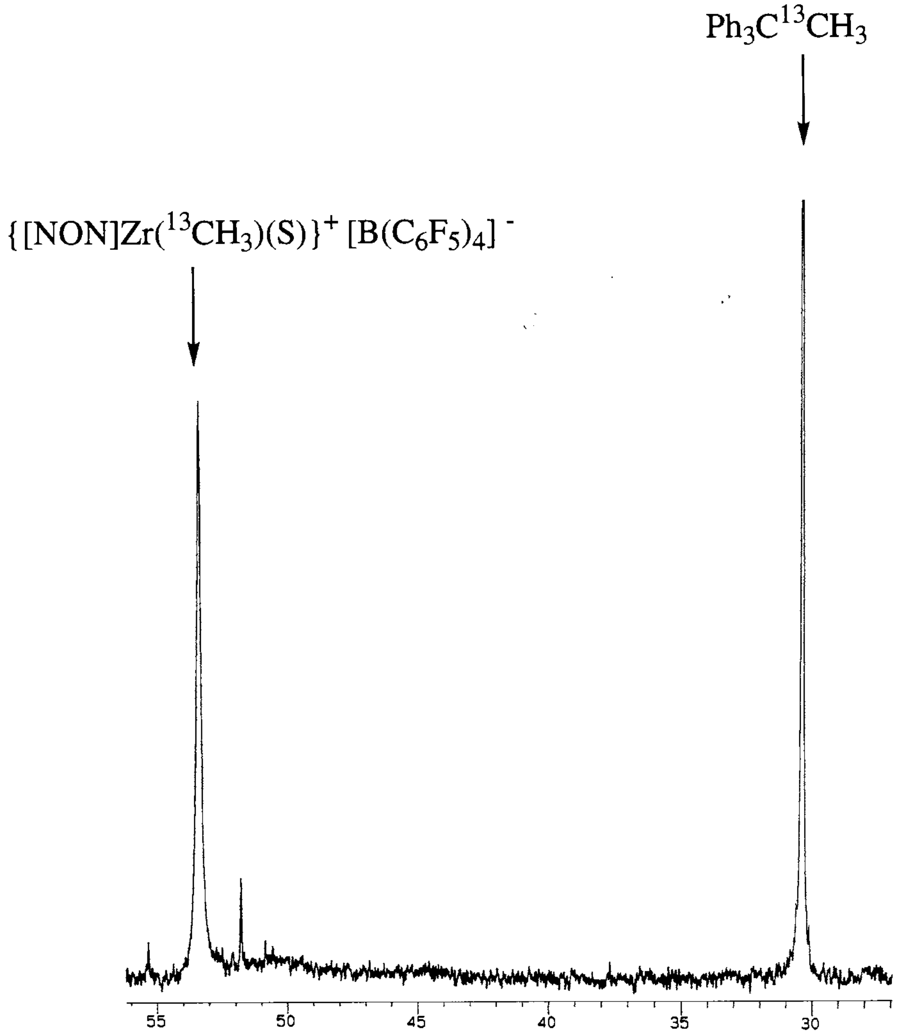


Fig. 1. ^{13}C-NMR spectrum (at ~0°C) in bromobenzene-d_5 of $[NON]Zr(^{13}CH_3)_2$ after addition of $[Ph_3C][B(C_6F_5)_4]$ at ca. −30°C.

employed to prepare poly(1-hexene) in chlorobenzene [27]. However, the 94.4 ppm chemical shift of the ^{13}C α carbon atom in $\{[NON]Zr(^{13}CH_2CHMe_2)(2,4\text{-lutidine})\}^+$ is an important result, as $\{[NON]Zr(^{13}CH_2CHMe_2)(2,4\text{-lutidine})\}^+$ serves as a model for the growing polymer chain (P) in a catalytically-active base adduct, $\{[NON]Zr(^{13}CH_2CHMeP)(S)\}^+$, i.e. one in which the base (S) is chlorobenzene or bromobenzene solvent.

Addition of ten equivalents of 1-nonene at 0°C to $\{[NON]Zr(CH_3)(S)\}^+$ prepared from $[Ph_3C][B(C_6F_5)_4]$ in bromobenzene-d_5 at ca. −30°C leads to essentially complete consumption of $\{[NON]Zr(CH_3)(S)\}^+$ and formation of propagating species. Subsequent addition of one equivalent of $^{13}CH_2{=}CHC_7H_{15}$ to the propagating species led to the ^{13}C-NMR spectrum shown in Fig. 3. The key feature of the spectrum in Fig. 3 is the broad resonance at 93 ppm (~140 Hz at half height) that we assign on the basis of the 94.4 ppm resonance for the methylene carbon atom in $\{[NON]Zr(^{13}CH_2CHMe_2)(2,4\text{-lutidine})\}^+$ as the resonance for the labeled carbon next to the metal in $\{[NON]Zr[^{13}CH_2CH(C_7H_{15})(\text{Polymer})](S)\}^+$. This result confirms that 1-nonene 'inserts' into the Zr–C bond primarily in a 1,2 fashion. We cannot conclude that absolutely no 2,1 insertion takes place on the basis of this experiment, but it seems unlikely that both 1,2 and 2,1 insertions would be taking place to a significant extent simultaneously. $[NON]Zr[^{13}CH_2{=}CH(C_7H_{15})(\text{Polymer})](S)\}^+$ is stable for several hours at 0°C but decomposes within minutes when heated to 40°C; the 93 ppm resonance disappears and a sharp resonance appears at 110.7 ppm (a trace of which can be seen in the spectrum shown in Fig. 3) that we ascribe to the terminal methylene carbon in $^{13}CH_2 = C(C_7H_{15})(\text{Polymer})$. This direct observation of β elimination proves that β elimination is very slow in the living polymer made from 1-nonene at 0°C and relatively fast at 40°C. Accurate studies of the rate of decomposition at various temperatures remain to be done.

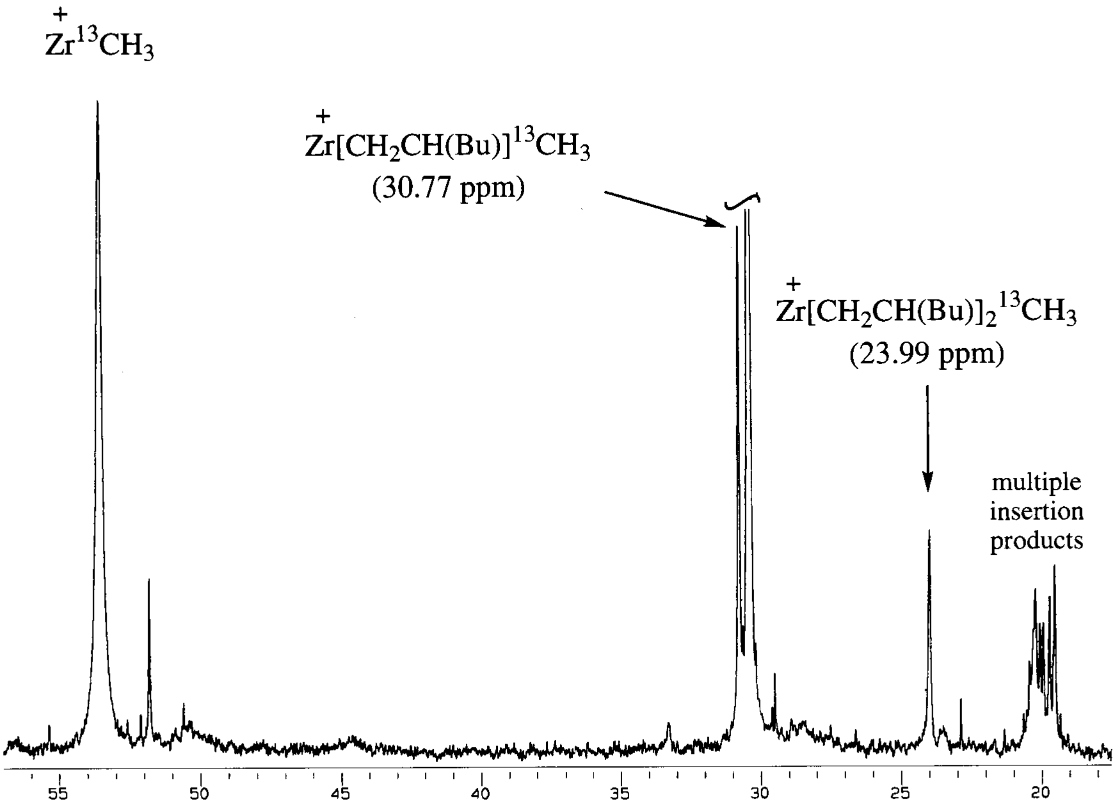


Fig. 2. ^{13}C-NMR spectrum (at ~0°C) of a sample identical to that in Fig. 1 after addition of 1-hexene at ca. -30°C.

An important question is why β elimination is relatively slow in $\{[\mathrm{NON}]\mathrm{Zr(R)(S)}\}^+$ systems that we have examined so far. In Scheme 1 we show a 'first generation' attempt to rationalize this unusual finding. We propose that the 'base' is bound in the apical position and that it is lost in a reversible and competitive manner to give a pseudo-tetrahedral cationic complex (or tight ion pair [1,30,31]). When this base is chlorobenzene or bromobenzene, we believe that it is bound relatively weakly, and either the rate of loss from the metal is high, the equilibrium that yields the pseudo-tetrahedral cationic species or tight ion pair is large, or both. A terminal olefin, $\mathrm{CH_2{=}CHR'}$, can add to the CNN face of the pseudo-tetrahedral cation to yield a trigonal bipyramidal intermediate, or more likely, a transition state in which the R′ group is oriented away from the bulky t-butyl substituents on the equatorial amido ligands. Such an orientation would be consistent with 1,2 insertion. When the equatorial alkyl group migrates to the substituted carbon a new pseudo-tetrahedral species is formed, to which either base or another olefin can bind. The process of β elimination should correspond to approximately the reverse of alkyl migration, i.e. the bulky alkyl in the $\mathrm{ZrCH_2CHPR'}$ intermediate must 'back up' toward the two t-butyl groups and the β carbon must turn so that the polymer chain (P) and the R′ group are pointing away from the metal, and the β proton therefore is presented to the metal's incipient equatorial site in order that the olefin product of β elimination can pass out of the 'axial' site. It is this process that we believe to be slow for steric reasons, compared to the rate of either binding base or another equivalent of olefin to the metal center.

Unlike systems which have an approximate or true C_2 axis or mirror plane relating the 'empty' and 'alkyl' sites, i.e. virtually all metallocenes [1], the $\{[\mathrm{NON}]\mathrm{Zr(alkyl)}\}^+$ species has mirror symmetry in which the 'empty' and 'alkyl' sites lie in the mirror plane and are inequivalent to a significant degree. Although we proposed that the methyl ligands in $[\mathrm{NON}]\mathrm{MMe}_2$ ($\mathrm{M = Ti}$ or Zr) are equivalent on the NMR time scale as a consequence of forming the C_{2v} symmetric TBP species containing equatorial methyl groups [27], we believe that the $[\mathrm{NON}]^{2-}$ ligand backbone in $\{[\mathrm{NON}]\mathrm{Zr(B)(alkyl)}\}^+$ does not 'flip' rapidly on the NMR time scale, or perhaps even on the chemical time scale, i.e. the base prefers to be in an axial position in a TBP complex formed when it attacks the CNN face of the pseudo-tetrahedral cation. Whether the diamido/donor ligand 'flips' through a species that has a pseudo planar N–O–N backbone as a consequence of equatorial alkyl migration to the axial olefin is not yet known. In any case an olefin rarely attacks one of the two CNO faces of the four-coordinate cation to give a transition state that contains an equatorially

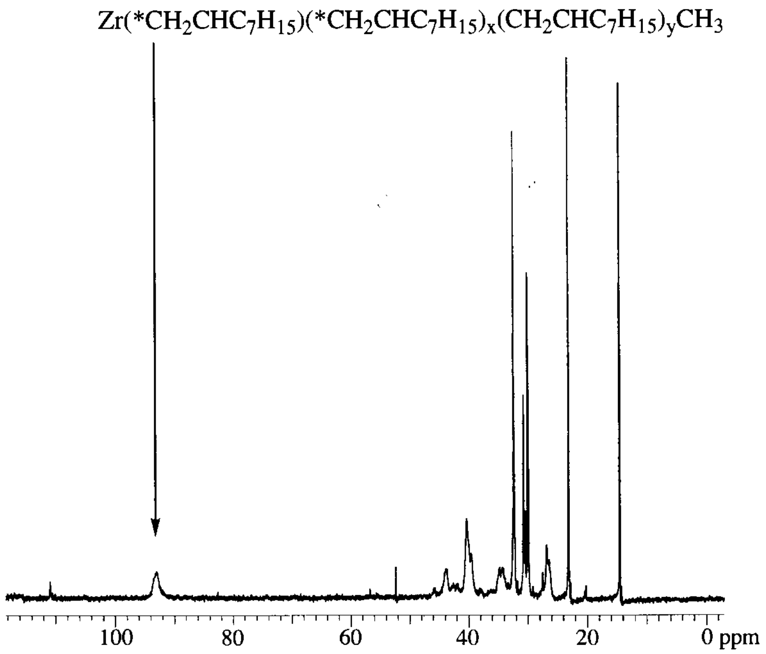
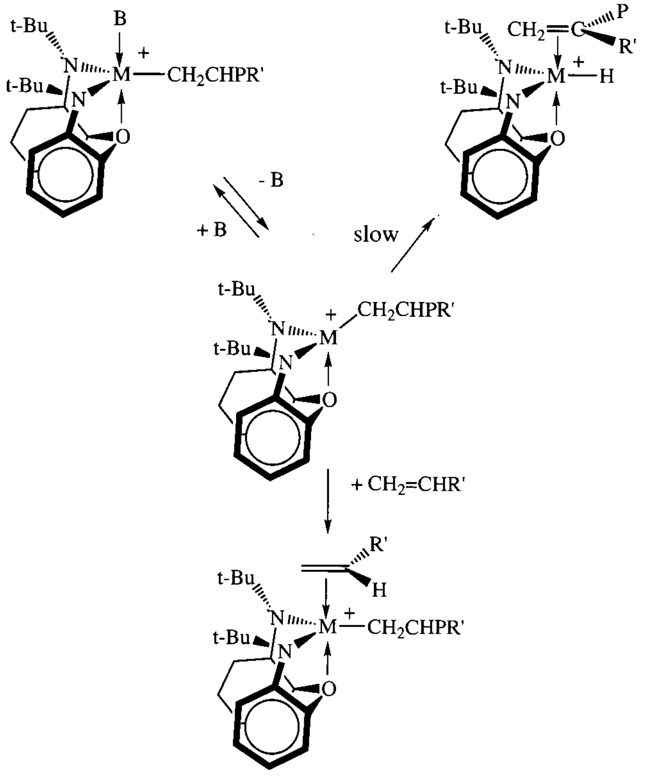


Fig. 3. ^{13}C-NMR spectrum (at ~0°C) in bromobenzene-d_5 of [NON]Zr$(CH_3)_2$ after the addition of $[Ph_3C][B(C_6F_5)_4]$, ten equivalents of 1-nonene and one equivalent of $^{13}CH_2{=}CHC_7H_{15}$, all at ca. −30°C.

bound olefin, since that would require that O and N in the ligand occupy equatorial positions ca. 120° to one another, which would seem to require an unacceptable contortion of the ligand backbone. Olefin attack on the NNO face is least likely from a steric point of view, since the $[NON]^{2-}$ would have to occupy all three equatorial positions in the TBP transition state, and would be nonproductive anyway, as the incoming olefin would be *trans* to the alkyl on the metal. Therefore olefin attack on the CNN face of the four-coordinate cationic species is by far the most facile route to a suitable low energy transition state that precedes alkyl migration to the olefin.



Scheme 1.

3. Conclusions

We have found that the living polymerization of 1-hexene by activated [NON]ZrMe$_2$ can be ascribed to formation of an intermediate cationic species or tight ion pair, {[NON]Zr(alkyl)}{$B(C_6F_5)_4$}, that is relatively stable toward β elimination, but still highly reactive toward additional 1-hexene. The lack of β hydrogens in the ligand itself, the stability of the C–N and C–O bonds in the ligand, and the sterically bulky nature of the t-butyl groups bound to the equatorial amido nitrogens all conspire to produce a relatively stable four-coordinate cation that readily forms only one five-coordinate TBP base adduct, or (with an olefin) one transition state. Although other explanations of the activity of catalysts of this general type are certain to develop with time, we believe that what has been glimpsed so far here and what has been observed by others who have been investigating chelating diamido group 4 metal catalysts [4–12], hold promise for further exciting developments in noncyclopentadienyl group 4 olefin polymerization catalyst chemistry. Diamido/donor ligands of the type described here are rare in the literature [5,6,10,32]. Robust examples of the type discussed here might also prove useful for a variety of other chemistry that involves aggressively reactive early transition metals in relatively high oxidation states [33].

4. Experimental section

General experimental procedures can be found elsewhere [8]. Labeled 1-nonene ($^{13}CH_2=CH(C_7H_{13})$) was prepared from $[(^{13}CH_3)P(C_6H_5)_3]^+I^-$, butyllithium, and octanal in diethyl ether in a standard manner. Labeled isobutyl chloride ($Cl^{13}CH_2CHMe_2$) was prepared by a method analogous to that published for unlabeled material [34]. [NON]Zr$(NMe_2)_2$ was prepared as described in the literature [27]. [NON]Zr$(^{13}CH_3)_2$ was prepared in a manner analogous to that described in the literature for [NON]Zr$(CH_3)_2$ [27].

4.1. Synthesis of [NON]ZrCl$_2$

Me_3SiCl (1.50 g, 13.7 mmol) was added to a suspension of [NON]Zr$(NMe_2)_2$ (2.30 g, 4.58 mmol) in diethyl ether (50 ml). After stirring the mixture at room temperature for 20 h all volatile components were removed from the mixture in vacuo and the yellow solid was washed with pentane (10 ml) and dried; yield 2.06 g (93%). An analytically pure sample was obtained by recrystallization from ether. For alkylation reactions the crude material was used without further purification: ^{1}H-NMR (C_6D_6) δ 6.79 (m, 6), 6.54 (m, 2), 1.29 (s, 6, C*Me*$(CD_3)_2$); ^{13}C-NMR (C_6D_6) δ 147.1, 141.0, 127.4, 122.8, 122.4, 118.9, 58.7, 30.6, 30.1 (m). Anal. Calc. for $C_{20}H_{14}Cl_2D_{12}N_2OZr$: C, 49.77; H, 5.43; N, 5.80. Found: C, 49.84; H, 5.21; N, 5.68.

4.2. Synthesis of [NON]Zr(*i*-Bu)$_2$

A solution of *i*-BuMgCl in diethyl ether (2.0 M, 950 µl) was added to a suspension of [NON]ZrCl$_2$ (462 mg, 954 µmol) in diethyl ether (12 ml) at ca. −30°C. The reaction mixture was allowed to warm to room temperature and was stirred for 5 min. All volatile solvents were then removed in vacuo and the off-white residue was extracted with pentane (10 ml). After 5 min two drops of 1,4-dioxane were added to the pentane extract. The extract was filtered and the pentane was reduced in volume in vacuo to about 1 ml. Diethyl ether (1 ml) was added. This solution was stored at −35°C overnight and produced 244 mg (49%) of an analytically pure pale yellow, waxy solid: ^{1}H-NMR (C_6D_5Br) δ 6.95 (m, 6), 6.63 (m, 2), 2.24 (sept, 2, $CH_2CH(CH_3)_2$) 1.38 (s, 6, C*Me*$(CD_3)_2$), 1.18 (d, 4, $CH_2CH(CH_3)_2$), 1.01 (d, 12, $CH_2CH(CH_3)_2$); ^{13}C-NMR δ 147.5, 142.29, 125.8, 121.9, 119.4, 118.7, 81.5, 56.7, 30.8, 30.2 (m), 28.5. Anal. Calc. for $C_{28}H_{32}D_{12}N_2OZr$: C, 63.70; H, 8.40; N, 5.31. Found: C, 63.92; H, 8.69; N, 5.28.

[NON]Zr$(^{13}CH_2CHMe_2)_2$ was prepared by an analogous method.

4.3. Generation of cationic species

In a typical experiment a solution of metal complex (25 µmol) in C_6D_5Br (0.5 ml) was added to a solution of $[CPh_3][B(C_6F_5)_4]$ (25 µmol) in C_6D_5Br (0.5 ml) inside a glovebox using solutions that had been cooled to ca. −30°C in the glovebox refrigerator. The required amount of olefin and/or base was then added. The solution was quickly transferred into an NMR tube, which was capped, placed in a beaker filled with ice and transported to the NMR instrument.

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