Mechanistic Aspects of the Ziegler-Natta Polymerization

Thesis by

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Para Angeles.
Por todos aquellos momentos
que hiciste brillar el sol en mi mente
cuando todo era tormenta.
Por el optimismo que me inspiraste
cuando no salían bien los experimentos.

Acknowledgements

I would like to thank Bob Grubbs for the opportunity he gave me to do some organometallic chemistry, as well as for his financial support. I am also grateful to Conacyt (México) for partial financial support.

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Finally, my most sincere and especial thanks to my wife, Angeles, for her love, encouragement and understanding during the past years, without which this work would not have been possible.

Abstract

The isotope effect on propagation rate was determined for four homogeneous ethylene polymerization systems. The catalytic system $Cp_2Ti(Et)Cl + EtAlCl_2$ has a $k_p^H/k_p^D = 1.035 \pm 0.03$. This result strongly supports an insertion mechanism which does not involve a hydrogen migration during the rate determining step of propagation (Cossee mechanism). Three metal-alkyl free systems were also studied. The catalyst $I_2(PMe_3)_3Ta$(neopentylidene)(H) has a $k_p^H/k_p^D = 1.709$. It is interpreted as a primary isotope effect involving a non-linear α-hydrogen migration during the rate determining step of propagation (Green mechanism). The lanthanide complexes $Cp_2^*LuMe \cdot Et_2O$ and $Cp_2^*YbMe \cdot Et_2O$ have a $k_p^H/k_p^D = 1.46$ and 1.25, respectively. They are interpreted as primary isotope effects due to a partial hydrogen migration during the rate determining step of propagation.

The presence of a precoordination or other intermediate species during the polymerization of ethylene by the mentioned metal-alkyl free catalysts was sought by low temperature NMR spectroscopy. However, no evidence for such species was found. If they exist, their concentrations are very small or their lifetimes are shorter than the NMR time scale.

Two titanocene(alkenyl)chlorides (hexenyl <u>1</u> and heptenyl <u>2</u>) were prepared from titanocene dichloride and a THF solution of the corresponding alkenylmagnesium chloride. They do not cyclize in solution when alone, but cyclization to their respective titanocene(methyl(cycloalkyl))chlorides occurs readily in the presence of a Lewis acid. It is demonstrated that such cyclization occurs with the alkenyl ligand within the coordination sphere of the titanium atom. Cyclization of 1 with $EtAlCl_2$ at 0^oC occurs in less than 95 msec (ethylene insertion time), as shown by the presence of 97% cyclopentyl-capped oligomers when polymerizing ethylene with this system. Some alkyl exchange occurs (3%). Cyclization of 2 is slower under the same reaction conditions and is not complete in 95 msec as shown by the presence of both cyclohexyl-capped oligomers (35%) and odd number α-olefin oligomers (50%). Alkyl exchange is more extensive as evidenced by the even number n-alkanes (15%).

Cyclization of $2\text{-}d_1$ (titanocene(hept-6-en-1-yl-1-d_1)chloride) with $EtAlCl_2$ demonstrated that for this system there is no α-hydrogen participation during said process. The cyclization is believed to occur by a Cossee-type mechanism. There was no evidence for precoordination of the alkenyl double bond during the cyclization process.

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List of Abbreviations used in this thesis.

Al	alkylaluminum dihalide species, $Al(R)Cl_2$
Al:bipy	$Al(R)Cl_2$:bipy adduct
bipy	2,2'-bipyridine
br	broad
Cp	η^5-cyclopentadienyl
Cp*	η^5-(pentamethyl)cyclopentadienyl
d	doublet
dist	distorted
equiv	chemical equivalent
Et	ethyl
Et_2O	diethyl ether
GC/MS	gas chromatography-mass spectrometry
m	multiplet
Me	methyl
q	quartet
R	alkyl
s	singlet
t	triplet
THF	tetrahydrofuran
UV	ultraviolet

CHAPTER 1

Isotope Effects on Propagation Rates of Ethylene Polymerization

Introduction

One of the most important discoveries in catalysis during the past 30 years is the Ziegler-Natta catalyst.[1] Despite the heavy industrial and academic research, the mechanisms that operate during the polymerization when such catalysts are used are only vaguely known. The main drawback for the study of such systems has been their heterogeneity, which makes difficult a detailed analysis of the intermediates involved in such reactions.

A major breakthrough came in 1957 when Natta[2] and Breslow[3] reported the use of the homogeneous catalytic system bis(cyclopentadienyl)-titanium dichoride + diethylaluminum chloride for the polymerization of ethylene. However, it becomes heterogeneous when polyethylene is formed. It is also ineffective for the polymerization of propylene.

Long and Breslow[4] made a spectroscopic study of the same system and inferred the presence of bis(cyclopentadienyl)ethyltitanium chloride in the mixture as well as a Ti(III) species.

The homogeneous system bis(cyclopentadienyl)ethyltitanium chloride + ethylaluminum dichloride became popular and thorough kinetic studies were performed by Henrici-Olivé and Olivé[5] and by Meyer and Reichert.[6] They concluded that the active species of this catalytic system is formed extremely rapid and its concentration depends on the ratio Al/Ti, with excess aluminum component ($Al/Ti > 1$) acting as deactivator. The propagation rate constant was estimated to be 15 $M^{-1}s^{-1}$ at 10^oC.

Although the exact nature of the active species is still unknown, it was suggested[5a] that the tetrahedral configuration of the bis(cyclopentadienyl)ethyltitanium chloride (titanocene(ethyl)chloride) was changed to an octahedral environment upon complexation with the co-catalyst. By this procedure, the Ti-Et bond comes under the trans-influence of the bridged aluminum and presumably will be weakened. This weakening will be responsible for both polymerization and reduction of the Ti(IV) to Ti(III).

The idea of such rearrangement was objected to by Fink[7] when he showed by means of low temperature ^{13}C-NMR that the signals of the titanocene(ethyl)chloride/ethylaluminum dichloride system were shifted downfield from those of the original components, this meaning that there was no electron donation into the Ti-C bond, but rather a pronounced electron withdrawal. Katz[8a] also presented evidence that even in the fixed tetrahedral configuration of 1,1'-methylenetitanocene dichloride, ethylene could be polymerized after addition of 2 equivalents of diethylaluminum chloride to the ansa-metallocene derivative. A MO-SCF calculation was done by the CNDO semi-empirical method[8b] and favored the retention of bent structure of the Cp_2Ti fragment by about 2eV for the titanium-aluminum complex, and by 1eV when an ethylene molecule was included in the coordination environment of the titanium.

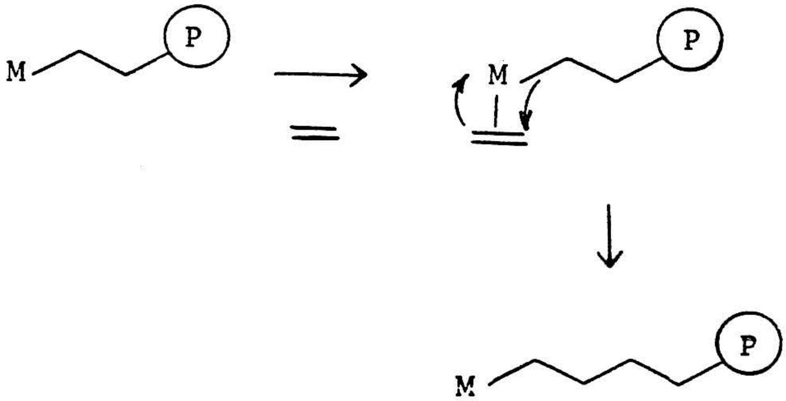
It was also proposed[9] that coordination of the monomer to the open site of the active center would provoke a strong destabilization of the vicinal Ti-C bond. In fact, addition of non-polymerizable olefins, like 1-octene and 2-octenes, showed that the reduction rate of the system increases with the increasing coordination ability of the olefins.

Again, Fink's NMR studies[7] had no evidence for precoordination of ethylene even at 200°K.

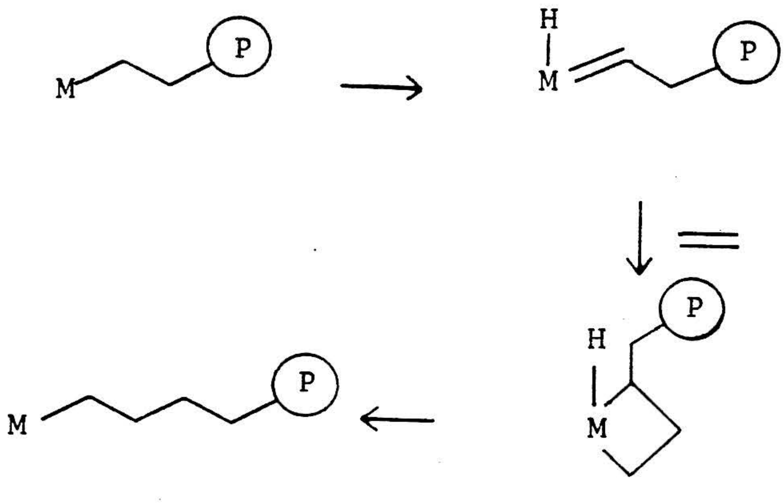
Aluminum alkyls are reducing agents and therefore a reduction Ti(IV) → Ti(III) inevitably takes place when the catalyst components are brought together. The question of the valency of the titanium in the catalytically active species was answered by magnetic susceptibility as well as ESR experiments.[5a] Since the polymerization rate clearly decreases with increasing aging time of the catalyst, and because the Ti(III) concentration increases with aging, this precludes Ti(III) species from being responsible for catalytic activity. Addition of small amounts of oxygen to solutions containing such Ti(III) compounds reactivates the catalyst for polymerization, while at the same time ESR signals for Ti(III) decrease. Use of chlorinated solvents in the reaction gives more active systems,[10] and it is thought that the same phenomenon of reoxidation to Ti(IV) is occurring.

Water has a similar behavior in Ziegler-Natta polymerizations. Adding small and controlled amounts of water to the catalyst increases dramatically the polymerization rate.[11] Aluminoxanes of the general type $-(\mathrm{AlR{-}O})-_n$ were suspected in the reaction mixtures. Use of titanocene derivatives with authentic samples of aluminoxanes[12] corroborated their likely existence in the water-containing reactions, as extremely active systems were obtained.

Although much has been done to understand the actual mechanism of monomer insertion into the growing polymer chain, the phenomenon is still very obscure and only a few clearly defined proposals exist to date: the direct four-center olefin insertion mechanism of Cossee and Arlman[13] (Eqn. 1) and the carbene-to-metallacycle mechanism of Green and Rooney[14,15] (Eqn. 2).

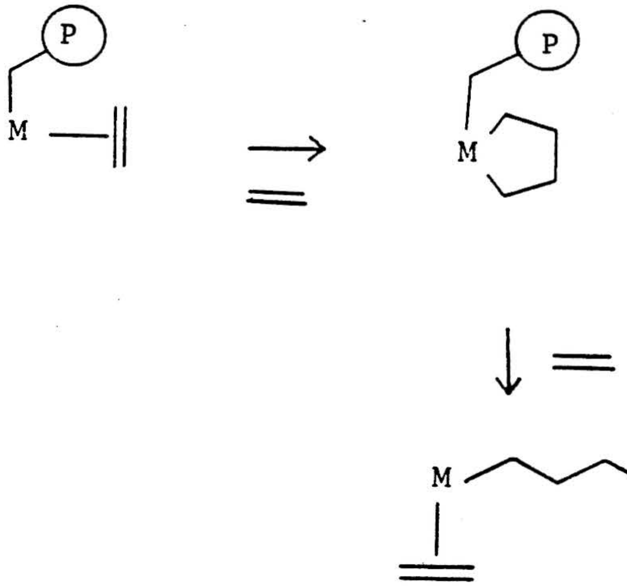


(1)



(2)

A proposal by McKinney[16] (Eqn. 3) lacks strength because it claims a chain growth of two monomer units at a time, while the actual increment is one monomer per turnover[17] (vide infra).



(3)

The difference between the above hypotheses resides in the hydrogen migration in the Green-Rooney mechanism, which is absent in Cossee's mechanism. This should lead to a large primary kinetic isotope effect on chain propagation in (2) but not in (1). In this chapter the isotope effects on propagation for a Ziegler-Natta catalyst and two metal-alkyl free systems are discussed, as well as some NMR studies on the polymerization of ethylene with the two last systems.

Results and Discussion

The catalytic system titanocene(ethyl)chloride 1 / ethylaluminum dichloride has been used extensively for multitude of studies related to the polymerization of ethylene,[18] so it was chosen for the experiments described in this thesis. The polymerization reactions were done in a quench flow apparatus, similar to the one described by Fink[17] (see Experimental Section). Relatively short contact times were required to obtain oligomers in the molecular weight range that allowed accurate yet simple analysis and calculations. Typically, contact times of 0.7 sec gave reasonable amount of oligomers in the range C_nH_{2n+2} (n=12,14,16... .,30). Appendix I describes some parameters of the quench flow reactions.

Mathematical Model. It is necessary to relate the molecular weight of the oligomers formed in the reaction with the average number of deuterated units $\langle n \rangle$ to define the numerical value of the isotope effect on the propagation rate. A model will be described where it is assumed that a 1:1 mixture of ethylene-d_0 and ethylene-d_4 is polymerized and that the isotope effect for the complexation step of ethylene is equal or near 1.

Consider an equal number of units containing ethylene-d_0 and ethylene-d_4 fragments as the last entered in the growing polymer. Each of these units can add another monomer at a rate k_c. If there is an isotope effect the new monomer will add at different rates into the deuterated and undeuterated metalated chain end, therefore the system will behave as a distillation with enrichment according to the number of deuterated monomers in the chain end and the number of monomers added per unit of time. This is represented in Scheme 1.

It can be shown that the average number of deuterated units <n> in the oligomer is related to the total number of inserted monomer units N by the expressions:[19]

$$\langle n\rangle = (N-1)\left[\frac{c\alpha}{1 + c\alpha}\right] + \frac{c}{1 + c} \qquad (4)$$

where

$$c = \frac{k_c^D\,[C_2D_4]}{k_c^H\,[C_2H_4]} \qquad (5)$$

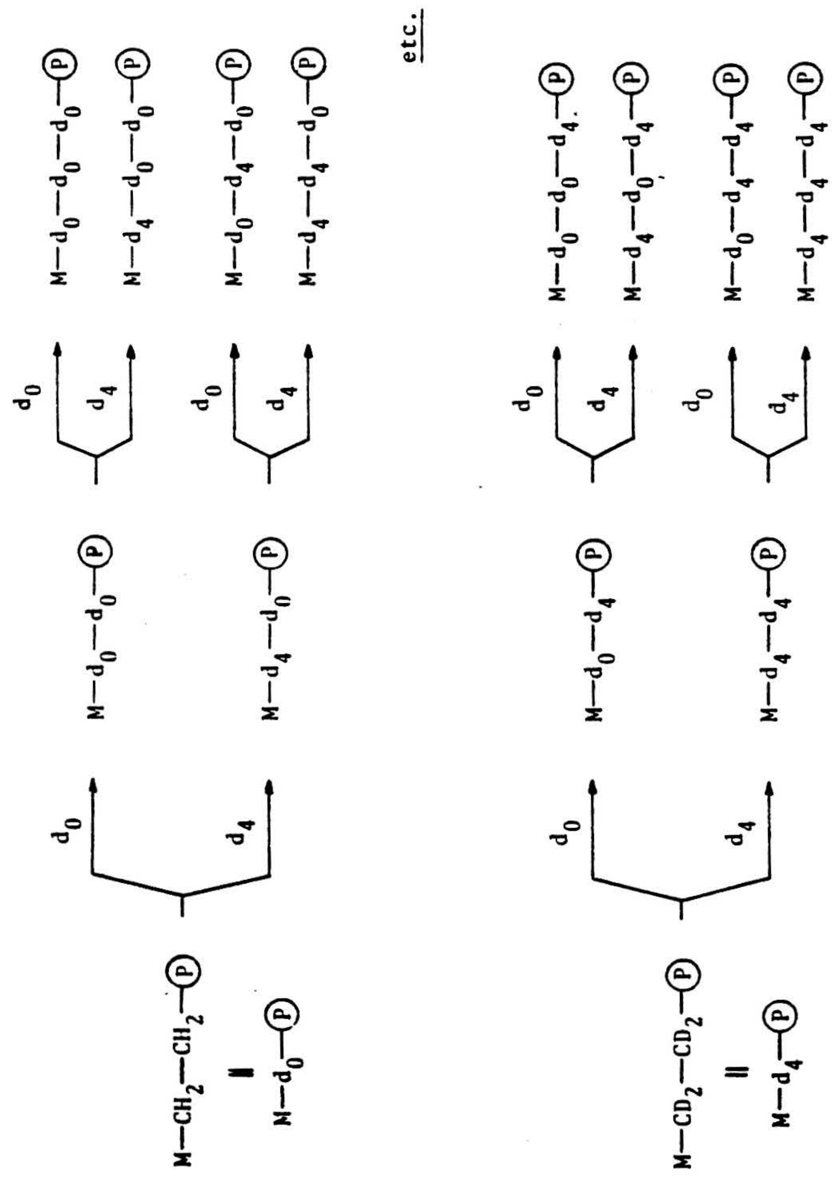
and

$$\alpha = \frac{k_p^D}{k_p^H} \qquad (6)$$

with k_c being the rate of complexation and k_p the rate of propagation.

Spectrometric Analysis and Data Interpretation. The analysis of the final products of the polymerizations was done by GC/MS-CI (chemical ionization). The advantage of this technique over the EI (electron impact) mode is that the CI enhances the molecular ions dramatically, thus allowing a direct and precise quantitative determination of the different isotope components in a mixture. However, it does not have the sensitivity of the EI technique and more concentrated samples are required for the analysis. This limitation brought along some problems for the analysis of some of the samples obtained from various polymerizations.

Scheme 1


M—CH2—CH2—P
M—d0—P
M—CD2—CD2—P
M—d4—P
d0
d4
M—d0—d0—P
M—d4—d0—P
M—d0—d4—P
M—d4—d4—P
M—d0—d0—d0—P
M—d4—d0—d0—P
M—d0—d4—d0—P
M—d4—d4—d0—P
M—d0—d0—d4—P
M—d4—d0—d4—P
M—d0—d4—d4—P
M—d4—d4—d4—P
etc.

It is well known that in MS-CI analysis[20] the relative sizes of the molecular ions, as well as the fragmentation generated from the parent molecule, depend not only on the chain length of the hydrocarbon, but also on the pressure of the ionizing gas and the type of gas used for the analysis, e.g. isobutane is a softer ionizing gas than methane. To understand the ionization pattern from the various oligomers obtained in this work, the molecular ion region of a C_{22} oligomer is used as an example (Fig. 1).

Alkanes are characterized by the presence of the $(M-H)^+$, $(M)^+$ and $(M+H)^+$ ions in MS-CI, and the relative abundance of these ions will depend on the CI conditions operating during the analysis. The polymerization of a mixture of ethylene-d_0 and ethylene-d_4 with $Cp_2Ti(Et)Cl$ + $EtAlCl_2$ will give oligomers of the type $C_nH_{2n+2-m}D_m$ (m=0,4,8...2n-4). Because of the presence of deuterium in the oligomers, a $(M-D)^+$ ion was also observed (except when m=0). No H-D exchange occurs between the ionizing gas and the sample, as confirmed by a study[20] using labeled hydrocarbons and unlabeled ionizing gas or vice versa. Only traces of olefin were formed in the polymerization reaction.[21]

Titanocene(alkyl)chloride/ethylaluminum dichloride systems. Proper conditions were developed to obtain oligomers in the C_{12} to C_{30} molecular weight range according to Eqn. 7. The plot of <n> versus (N-1) for the system $Cp_2Ti(Et)Cl$/ethylaluminum dichloride is shown in Fig. 2. It has excellent agreement with Eqn. 3 (correlation factor 0.9995) with a slope of 0.49 which corresponds to a $k_p^H/k_p^D = 1.04 \pm 0.03$. Appendix 2 exemplifies the determination of <n> for a particular oligomer.

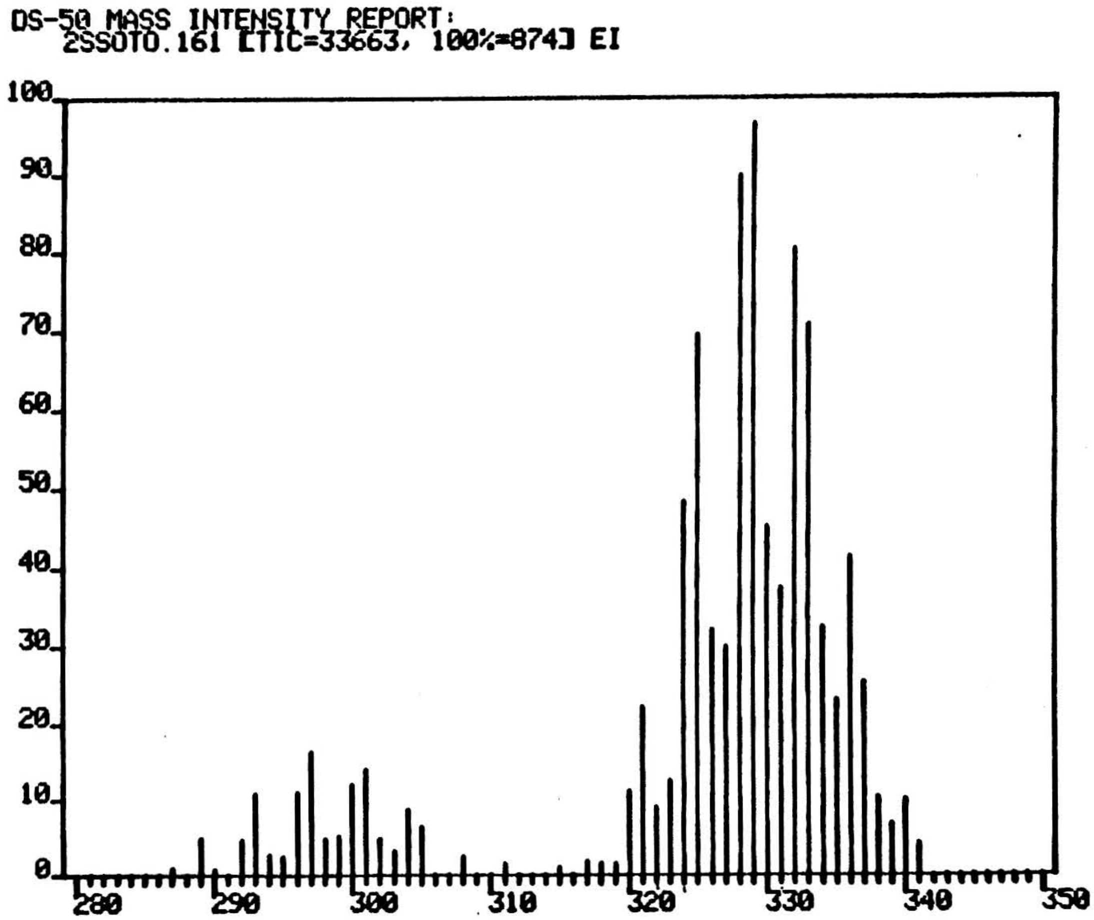


Fig.1. Mass spectrum (CI methane) of the molecular ion region of $C_{22}H_{46-m}D_m$ (m=0,4,8...40) oligomers with M.W. 310,314...350. See text.

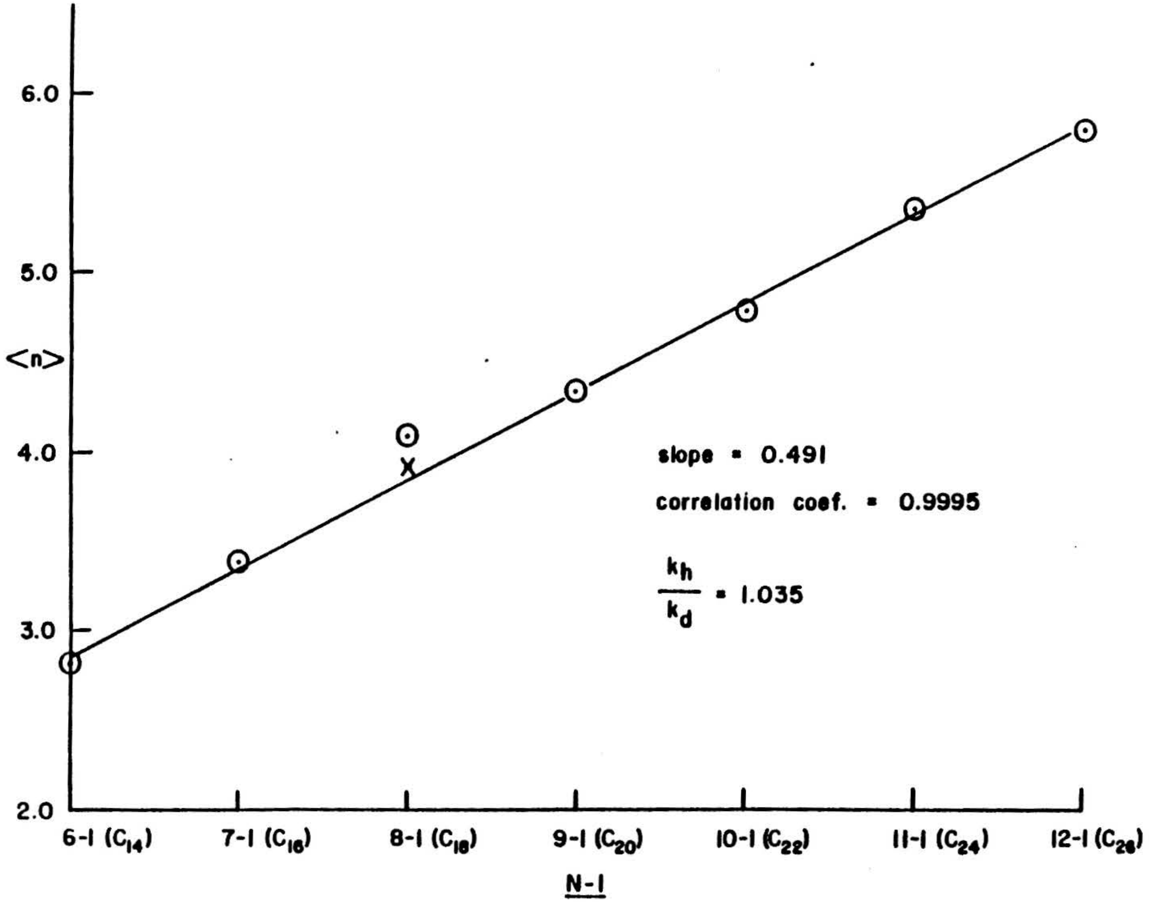


Fig. 2. Average number of C_2D_4 units, $\langle n \rangle$, as a function of total number of monomer units, N, in an oligomer for the system $Cp_2Ti(Et)Cl + EtAlCl_2$.

$$\mathrm{CD_2{=}CD_2 + CH_2{=}CH_2 + Cp_2Ti(Et)Cl} \xrightarrow[\text{2) HCl}]{\text{1) EtAlCl}_2\text{, 0.7 sec}} \mathrm{C_nH_{2n+2-m}D_m} \quad (m=0,4,8...2n-4) \tag{7}$$

The assumption that the complexation step for ethylene is close to 1 is strengthened by the fact that the recovered unreacted ethylene mixture after the polymerization has the same original relative amounts of ethylene-d_0 and ethylene-d_4. It showed no deuterium scrambling.

There was no difference in the isotope effect on the propagation rate between a polymerization system from which water was excluded and one to which small controlled amounts of water had been added. However, the propagation rate was dramatically increased with the addition of water.[11]

These results strongly support an insertion mechanism which does not involve a hydrogen migration as the rate determining step of propagation.[22,23]

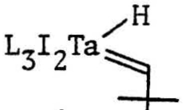
Similar polymerization reactions were carried out using titanocene(neopentyl)chloride 2 and titanocene(benzyl)chloride 3 with ethylaluminum dichloride as cocatalyst and ethylene-d_0 as monomer. For these systems, only small amounts of oligomers were formed, Nevertheless, it was possible to detect by GC/MS-CI the presence of the alkyl from the titanocene derivative as the end group in the oligomers. There was no evidence for hydrocarbons formed by alkyl exchange.

The formation of small amounts of oligomers may be due to the fact that the bulkiness of the neopentyl (or benzyl) ligand hinders the entrance of the cocatalyst to generate the active center. However, once it is formed, the reaction should proceed at about the same rate as the system titanocene(ethyl)chloride/ethylaluminum dichloride.

When the 1:1 mixture of ethylene-d_0/ethylene-d_4 was polymerized using 2 + $EtAlCl_2$, only small amounts of oligomers were obtained (the concentration of the oligomers "spreads" into the various labeled hydrocarbons), and it became extremely difficult to obtain good data for the determination of the isotope effect on propagation for this system. Only a few attempts were made to determine the isotope effect because the data obtained gave fairly scattered points on the <n> versus (N-1) plot. The propagation steps for this system should be the same as those for the titanocene(ethyl)chloride reaction once the polymerization has started, i.e. when the bulky ligand has been removed away from the active center, so a similar isotope effect should be expected. No attempt was made to determine the isotope effect on propagation for the titanocene(benzyl)chloride system because it leads to even smaller amounts of oligomers.

Metal-alkyl free catalysts.[24] These types of catalysts have been used for a while (e.g. the Phillips catalyst) because they represent an advantage over the more elaborated two component catalysts. The homogeneous systems known are sluggish. A homogeneous system that could polymerize ethylene and maybe other olefins at a reasonable rate, and still be free of alkylaluminum halides or other type of cocatalysts, would represent a tremendous advantage for the study of the mechanisms involved during the polymerization. Two of such systems were developed recently by Schrock[25] and Watson.[26] These novel catalysts were subjected to the studies described below.

Schrock's group synthesized a tantalum(V)neopentylidene-hydride complex 4 that can polymerize ethylene readily under mild conditions.[25b]

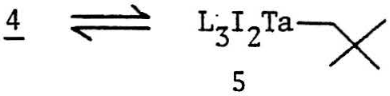


4

L= $P(CH_3)_3$

This molecule is a good model to test the Green-Rooney mechanism.

The compound 4 exists in rapid equilibrium with its tantalum(III)-neopentyl analog 5.[27] Using magnetization spin saturation transfer experiments, Turner obtained evidence of such reversible α-hydrogen elimination.



5

(8)

However, the presence of 5 was not detected by variable temperature NMR spectroscopy.

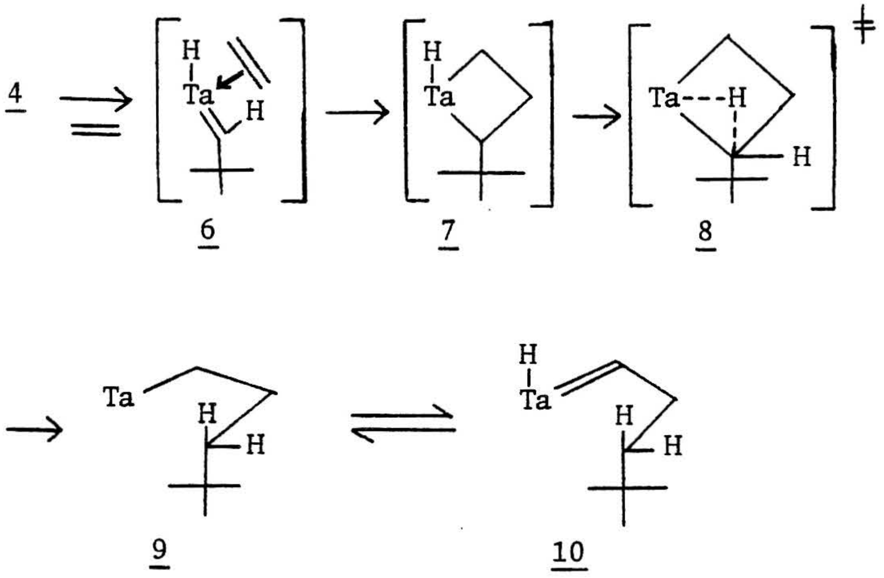
A toluene solution of 4 was used to polymerize the ethylene-d_0/ethylene-d_4 mixture. The reaction is slow compared to the Ziegler-Natta system, but gives a fairly large amount of oligomers with few interfering by-products. The oligomers obtained had the neopentyl fragment as the end group.[28] Again, there was no scrambling of the original ethylene mixture composition. Precipitation of the living polymer does not affect the rate of polymerization appreciably during the early stages of the reaction.

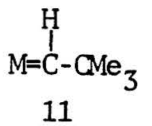
The isotope effect on propagation for this system was $k_p^H/k_p^D=1.709$ (correlation factor 0.991). This does not correspond to a secondary isotope effect, but seems too small for a primary isotope effect. It can be rationalized if we take into account two things.

First, there is evidence[29] that the alkylidene complex $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ has a large Ta-C(1)-C(2) angle (161.2^o), which may be explained partially by the steric crowding of the CMe_3 group. The $Ta-C_\alpha-H_\alpha$ angle is only 84.8^o and the Ta•••H(1) distance of 2.119 Å is less than the sum of van der Waals radii and only ~0.35 Å longer than the average terminal Ta-H distance (1.774 Å) in Cp_2TaH_3. For $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$, ${}^1J_{CH}=101$ Hz, and this extraordinarily low value can be rationalized if we take into account the C(1)-H(1) bond distance of 1.131 Å which is longer than the average value of 1.083 Å for a $C(sp^3)$-H(s) bond. It is still slightly longer than that (1.120 Å) predicted for a bond between a carbon pure p orbital and a hydrogen 1s orbital.[30] In the case of our model molecule <u>4</u>, ${}^1J_{CH}=71$ Hz. This low value suggests that this neopentylidene ligand is highly distorted toward a neopentylidyne ligand. For the growing living polymer like <u>10</u>, ${}^1J_{CH}=90$ Hz indicates that the relative geometry of the $Ta-C_\alpha-H_\alpha$ atoms is almost invariable. Therefore we may have the valence bond descriptions <u>11</u>, <u>12</u> or even <u>13</u> for our molecules <u>4</u> and <u>10</u> (see Scheme 2).

Second, primary isotope effects for reactions with non-linear transition states are small.[31] Therefore, we should not expect a large

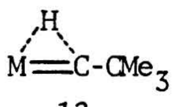
Scheme 2





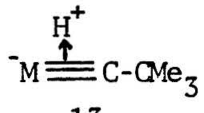
$M{=}\overset{\overset{H}{|}}{C}\text{-CMe}_3$

11



$\overset{H}{M{=}C}\text{-CMe}_3$

12



$^{-}\overset{H^+}{M{\equiv}C}\text{-CMe}_3$

13

primary isotope effect for this system if it is going through an intermediate like 8 during the rate determining step. The existence of a metallacycle like 7 has been proposed as an intermediate in the reaction[25b] but was not observed by variable temperature NMR spectroscopy.

It is concluded that the isotope effect observed for this system is derived from α-hydrogen migration through a non-linear transition state and accommodates in the general pattern of Green's mechanism.

In an attempt to detect the presence of intermediates during the polymerization, a low temperature reaction between 4 and 1,2-^{13}C-ethylene (90% ^{13}C atom) was followed by ^{1}H- and ^{13}C-NMR. Formation of small amounts of oligomers is evident at -40°C by the presence of a new $Ta=\underline{C}HR$ resonance at δ-0.75, but the reaction is extremely slow until the solution is warmed up to -20°C. At this temperature, a $^{13}C(^{1}H)$ NMR spectrum (Fig. 3) shows the C_{α} from the growing oligomers at δ208.7 and the $-(CH_2CH_2)_{\overline{n}}$ chains centered at δ31.3. The ethylene signal is unperturbed from its original position,[32] so insertion to obtain 10 must be very fast, as none of the other species were observed. The signal at δ116.8 comes from $\underline{C}H_2=CHR$, maybe formed by chain transfer from 9; the corresponding $CH_2=\underline{C}HR$ signal very likely is buried in the solvent peak at δ139. Turner reported the presence of 5% of t-butyl-capped α-olefins by GC for this system.[25b]

To get a better idea on the nature of the species present during the reaction, a series of experiments were done where 4 was used to polymerize either ethylene-d_0 or ethylene-d_4 and the mixture was hydrolyzed with HCl or DCl. The results are shown in Table 1. Unfortunately no conclusion could be drawn from the data; even Reaction 1 gives an unexpected result.

Watson's lanthanide model molecules[26] 14 and 15 are very efficient catalysts for ethylene polymerization and will oligomerize propylene.

$Cp^*_2LuMe.Et_2O$ 14

$Cp^*_2YbMe.Et_2O$ 15

Both mechanisms, McKinney and Green, require oxidative additions in order to generate the active metallacyclic or carbenoid intermediate.

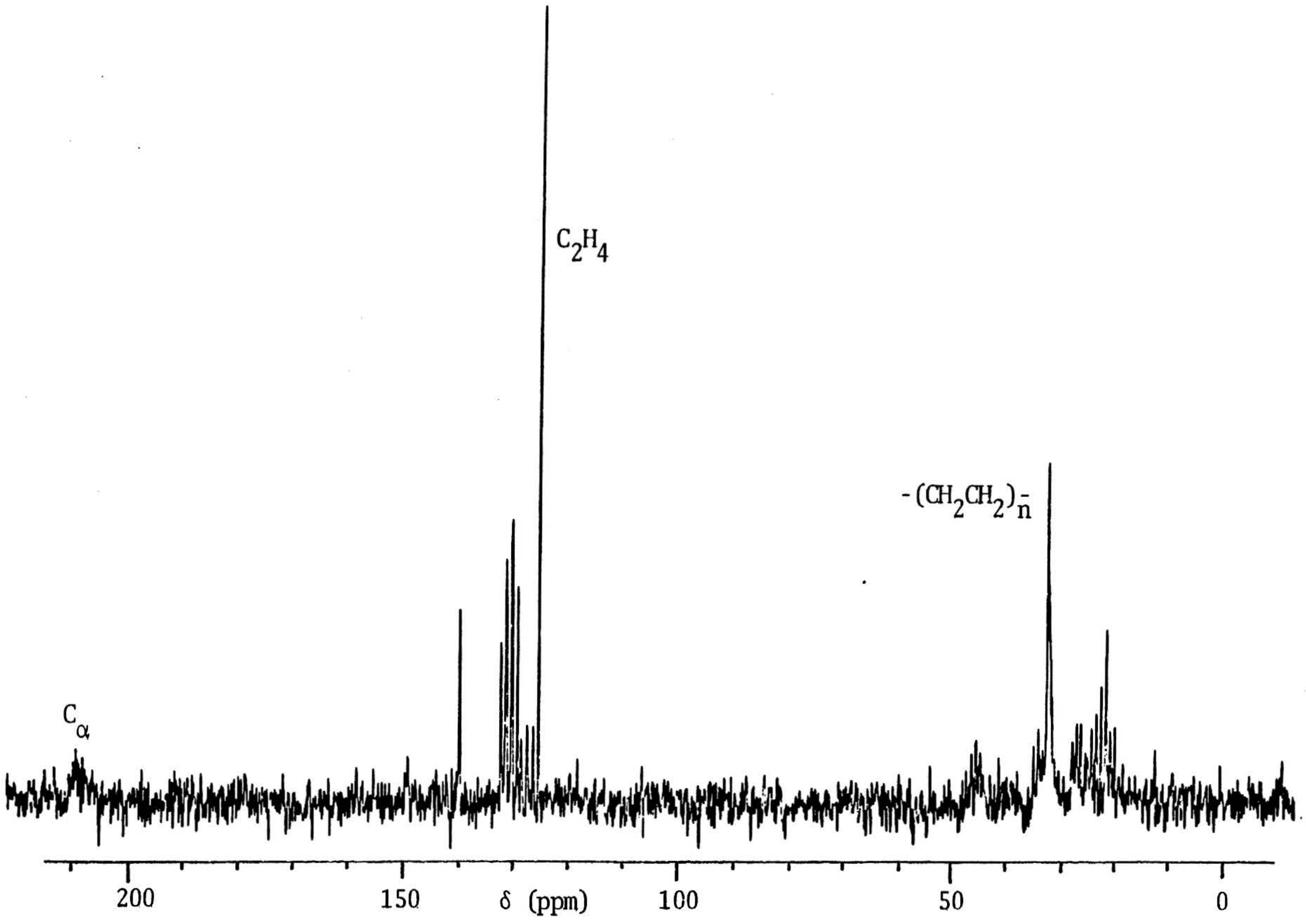


Fig. 3. ^{13}C(^{1}H)-NMR spectrum of 4 + 1,2-^{13}C-ethylene at -20°C.

Table 1

Analysis of Hydrolysis Products from 4 + ethylene-d_n

Reaction	Ethylene	Hydrolyzed with	Expected Product[a]	Observed Product
1	---	DCl	Neopentane-d_2	Neopentane-d_1
2	d_0	DCl	d_1-oligomers from 9a d_2-oligomers from 10a	d_1-oligomers [b]
3	d_4	HCl	h_{12}-oligomers from 9a h_{13}-oligomers from 10a	mostly h_{12}-oligomers, maybe some h_{13}-oligomers[c]
4	d_4	DCl	h_{11}-oligomers from both 9a and 10a	h_{11}-oligomers

a) The expected products shown assume fast incorporation of 2 equivalents of HCl(or DCl) into the living polymer analogous to 9 or 10, i.e. 9a or 10a.

b) Compare with reaction 1.

c) Reproducibility of the analysis was not good enough to establish the presence of small amounts of h_{13}-oligomers.

However, these routes are not reasonable for the lanthanide elements where reversible two-electron couples are generally precluded by the lack of accesible oxidation states.

The system looked promising for the determination of the isotope effect on propagation. However, two problems were encountered during the analysis of the hydrolysis products. First, there were only very small amounts of oligomers formed during the reaction, but this could be overcome partially by concentrating the samples. The major problem, though, was the elution of large amounts of by-products in the region where oligomer concentration maximized, i.e. pentadecane to nonadecane. These by-products were coming from the Cp* ligands of 14 (or 15) as verified by hydrolysis of 14 alone. Lower molecular weight oligomers were inaccessible because of overlapping with the solvent peak, and higher carbon number oligomers than $C_{21}H_{44}$ were scarce. Treatment of the samples with bromine (in carbon tetrachloride, after removal of the solvent under vacuum) helped to remove the by-products, but clean spectra were not yet obtained.

In spite of these problems, an isotope effect on propagation rate was determined for each 14 and 15. The results in Table 2 show right away the problems involved in the analysis, resulting only in fair correlation factors. The data show a small isotope effect on the propagation rate which is not due to a different "complexation" rate of the monomers with the catalyst (cf. previous systems). We may invoke a partial α-hydrogen migration during the rate determining step to explain the results. Such transient species may not be as distorted as 8 and its lifetime should be small since it is not observed by NMR. A similar α-hydrogen participation has been observed for unsaturated complexes.[15]

Table 2

Isotope Effects on Propagation for Ethylene Polymerization by <u>14</u> and <u>15</u>

Catalyst	k_p^H/k_p^D	Correlation Factor
<u>14</u>	1.46	0.983
<u>15</u>	1.25	0.984

A low temperature reaction between <u>15</u> and 1,2-^{13}C-ethylene was followed by NMR spectroscopy in order to search for possible intermediate species during the polymerization. At -90°C there is already a peak growing in at δ116.8 ($CH_2\underline{C}HR$, peak A) and a trace of a new set starts to grow at δ42.0, 41.3 and 40.5 (peaks B, C and D respectively). Warming up the solution to -70°C shows the consumption of about 35% of the original ethylene, with only a slight increase of the other signals (Fig. 4).

At -60°C ethylene was consumed completely in the time it took to obtain the spectrum and peaks A, B, C and D have increased but not proportionally to such consumption. There are also new small signals at δ139.0 ($\underline{C}H_2CHR$, peak E), δ120 and 118, as well as a medium size peak at δ20.3. The sample was warmed up to room temperature and after centrifuging the polymer formed from the solution, another $^{13}C(^1H)$-NMR spectrum was obtained (Fig. 5). It still had peaks A thru E and a

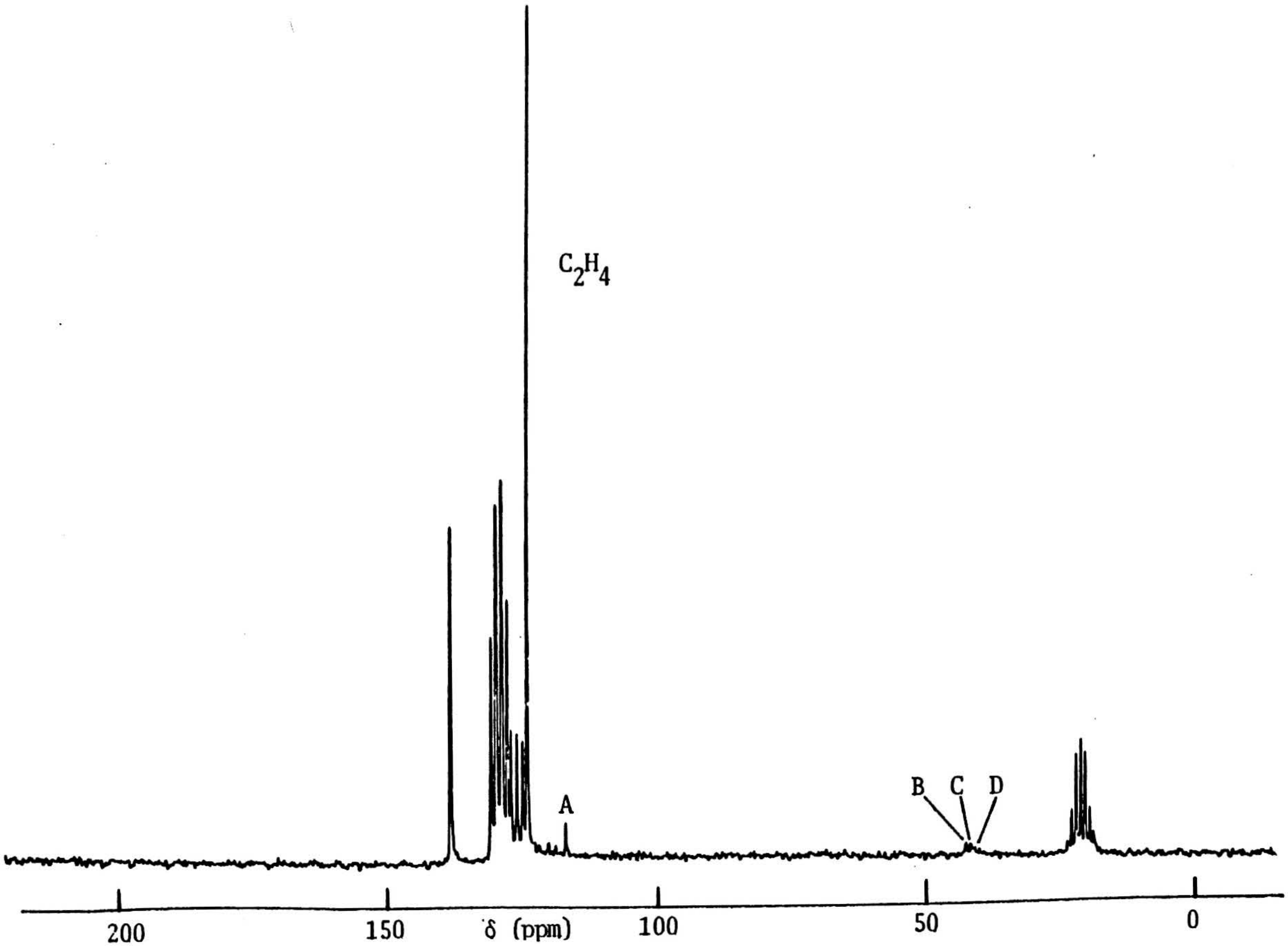


Fig. 4. $^{13}C(^1H)$-NMR spectrum of 15 + 1,2-^{13}C-ethylene at -70°C.

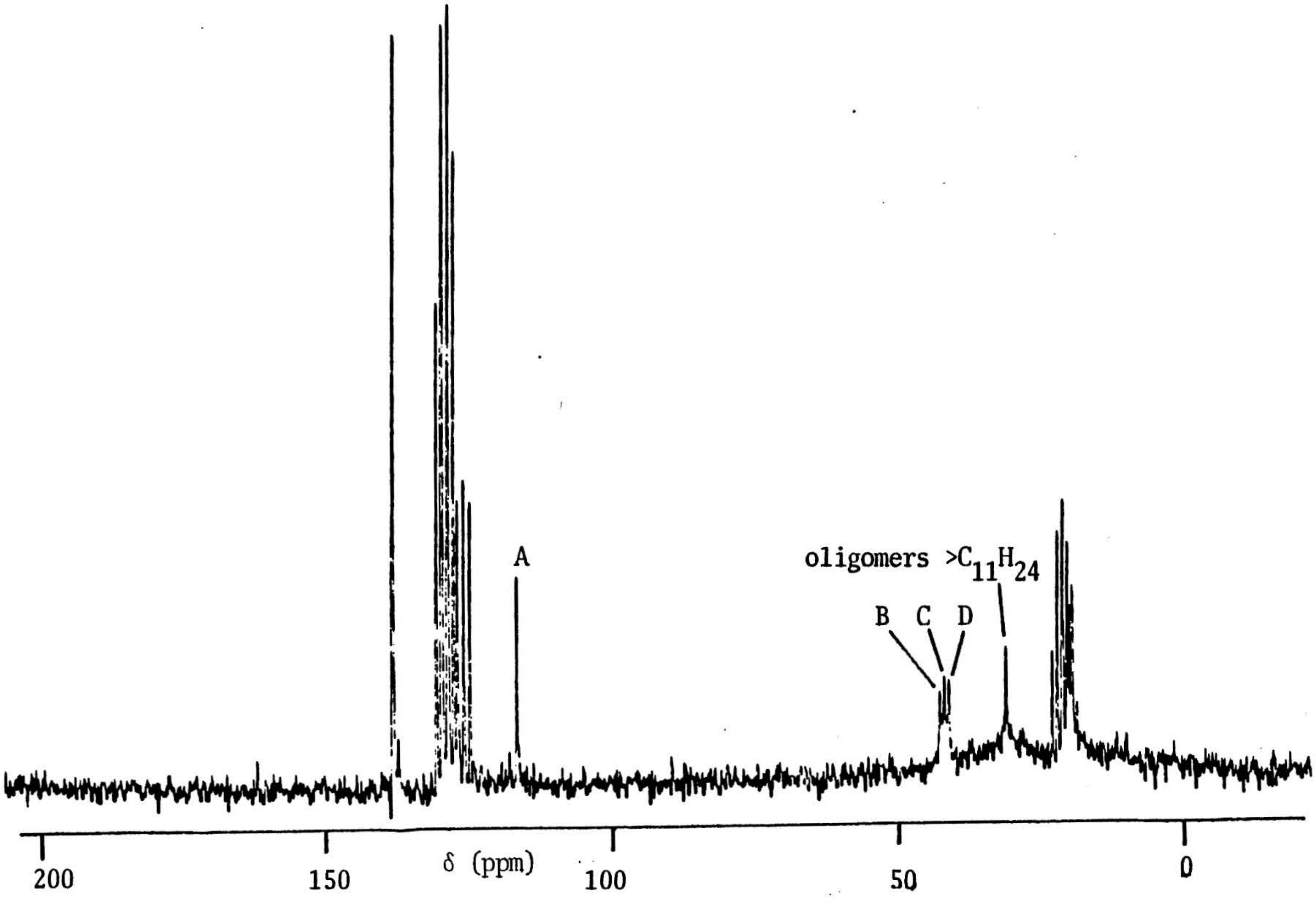


Fig. 5. $^{13}C(^{1}H)$-NMR spectrum of 15 + 1,2-^{13}C-ethylene at +25°C.

new medium size peak at δ30.5 (oligomers larger than $C_{11}H_{24}$), while the other signals had disappeared.

The ^{1}H-NMR spectrum of the same sample was ill-defined and no attempt was made to make assignments to it. When the sample was warmed up to room temperature (Fig. 6), the presence of terminal olefinic protons was evident at δ4.95-5.2 and δ5.6-5.9. The presence of free and coordinated diethyl ether was also notorious (peaks FDE and CDE respectively). Unidentified peaks occurred at δ1.56(td,J=1.5,6.3 Hz), 1.78 and 1.72, these last two maybe derived from new Cp* signals bonded to new organometallic species. There was still some ethylene in solution as shown by a sharp singlet at δ5.26 with large ^{13}C-satellites at δ6.12 and 4.40 ($^1J_{CH}$= 153.8 Hz).

There was no evidence for a precoordination of the monomer to the catalyst,[33] and if such species exists, its concentration is well below the NMR sensitivity or insertion is faster than the NMR time scale. It is interesting to compare at this point the three systems already discussed with regard to this reaction, because none of them shows evidence for the existence of a precoordination species before polymerization begins.

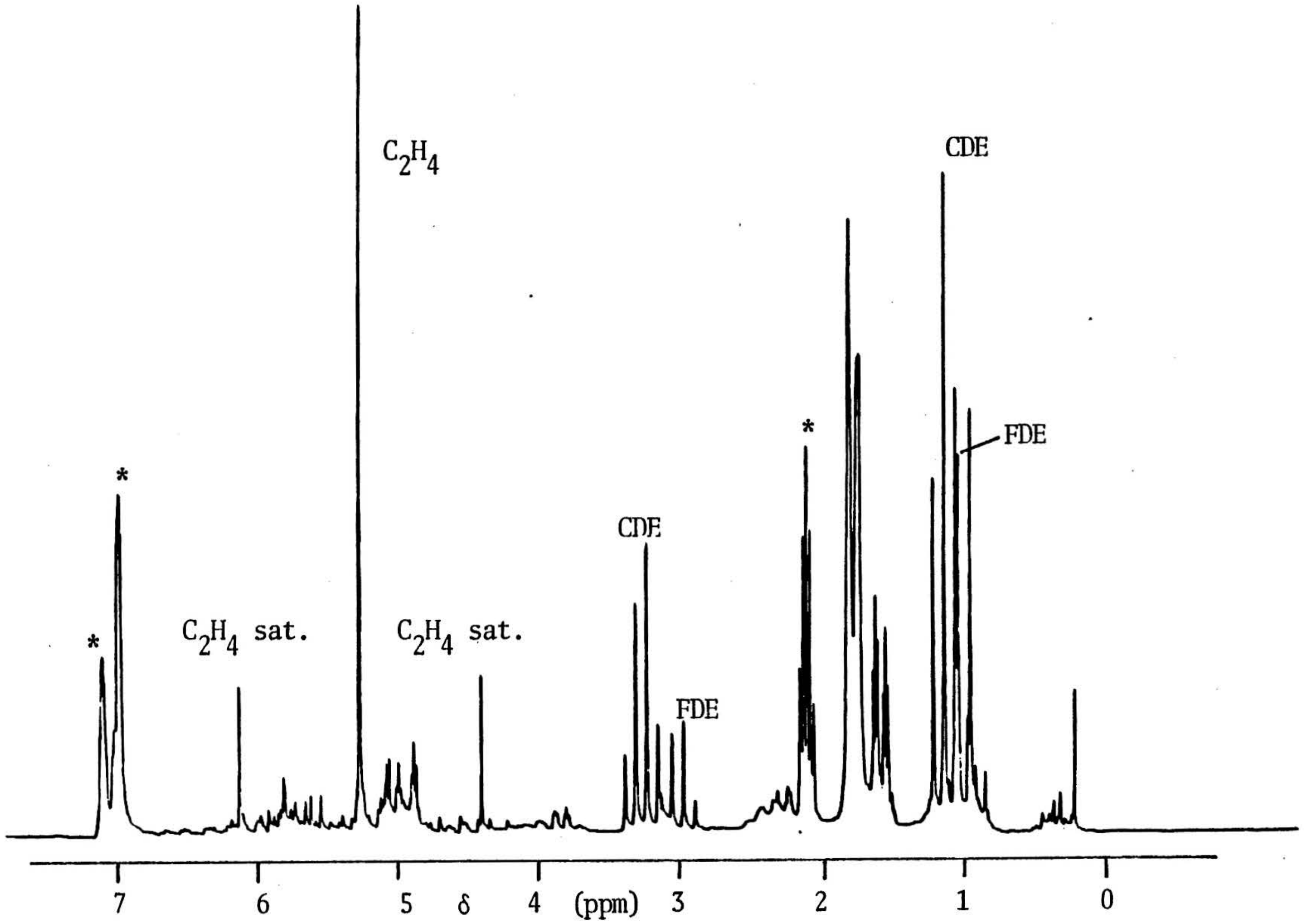


Fig. 6. ^{1}H-NMR spectrum of <u>15</u> + 1,2-^{13}C-ethylene at +25°C. *=solvent.

Experimental Section

General. All manipulations of air and/or moisture sensitive compounds were performed using a Vacuum Atmospheres dry box (nitrogen) or standard high vacuum line Schlenk techniques. Argon used in Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. NMR spectra were recorded with a Varian EM-390 (90 MHz ^1H) or a Jeol FX-90Q (89.6 MHz ^1H, 22.53 MHz ^{13}C). Capillary gas chromatographic analyses were performed on a Shimadzu GC Mini-2 (30m SE30 column, hydrogen used as carrier gas) equipped with a Hewlett-Packard 3390A integrator. GC/MS analyses were done with a Perkin-Elmer Sigma-1 instrument (2.4m 3% SE30 on 100/120 GCQ, helium used as carrier gas) coupled to a Kratos MS25 spectrometer. The ion source temperature was set at 150°C and the ionizing gas (methane or isobutane) pressure was $2X10^{-4}$torr. The total pressure in the ion source was about $2.1X10^{-4}$torr (ionizing gas + sample). The data acquisition was done with a Data General NOVA 3 computer. High resolution mass spectra were obtained using a Dupont MS9.

Materials. Pentane and THF were dried stirring over CaH_2, then filtered and transferred onto sodium benzophenone ketyl in tetraglyme where they were degassed. Diethyl ether and toluene were poured directly onto sodium benzophenone ketyl in tetraglyme and degassed. Dichloromethane was stirred over P_2O_5 and degassed. The above solvents were vacuum transferred into dry vessels equipped with teflon screw valves and stored under argon. CD_2Cl_2 (KOR Isotopes) was dried over P_2O_5 and deoxygenated by several freeze-pump-thaw cycles. C_6D_6 (Merck, Sharp and Dohme) and toluene-d_8 (KOR Isotopes) were dried and deoxygenated by stirring over sodium benzophenone ketyl after several freeze-pump-thaw cycles.

Titanocene dichloride (Strem or Boulder Scientific) was purified by Soxhlet extraction with dichloromethane. Ethylmagnesium chloride (3M in diethyl ether) was purchased from Apache Chemicals. Ethylaluminum dichloride (1.8M in toluene), benzyl chloride, tantalum pentachloride and (iodomethyl)trimethylsilane were purchased from Aldrich. Neopentyl chloride was purchased from Pfaltz and Bauer. Ethylaluminum dichloride (neat) was purchased from Alfa Products and was purified by sublimation. Calcium carbide was purchased from J.T.Baker. Ethylene was purchased from Matheson and 1,2-^{13}C-ethylene (90 atom% ^{13}C) from Isotope Labeling Corporation and were used as received. Trimethylphosphine was purchased from Strem and was deoxygenated by several freeze-pump-thaw cycles and kept under vacuum in a measuring tube equipped with a teflon screw valve. Hydrocarbons used as standards for GC and MS work were purchased from Sigma.

Ethylene-d_4,[34] $Cp_2Ti(R)Cl$ (R=ethyl, neopentyl and benzyl),[35] and $L_3I_2Ta(H)$(neopentylidene) (L=PMe_3)[36,37] were prepared by established procedures.

Typical Quench Flow Reaction. The quench flow apparatus (QFA) used for the short time polymerizations is shown in Fig. 7. The reactions were done as follows.

Separate toluene solutions (50 mL each) of titanocene(ethyl)-chloride (248 mg, 1 mmole) and the cocatalyst ethylaluminum dichloride

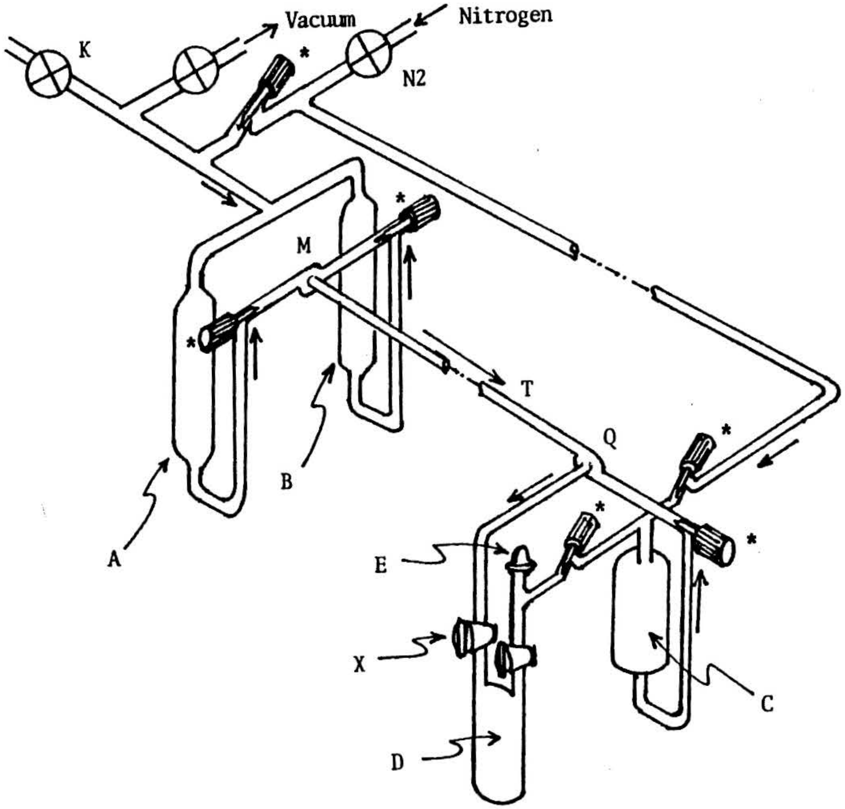


Fig. 7. Quench flow apparatus (see text for description).

(1.27g, 10mmole) were saturated with monomer[38] at ice-bath temperature. No polymerization occurs in these solutions during the saturation period (30 minutes).

The QFA was purged by evacuating the apparatus and the filling it with purified nitrogen. The quenching mixture (HCl conc./MeOH/toluene= 2/30/80, v/v/v) was placed in reservoir C (inlet port not shown) and all the needle valves marked with an asterisk were set to give suitable flow rates for the different solutions.

The catalyst solutions were transferred via syringe separately to containers A and B (inlet ports not shown) which were kept cooled down at 0°C by circulating iced-water through their jackets (not shown). Stopper E was removed prior to starting the reaction to allow a vent for the nitrogen excess pressure.

With everything set, nitrogen valve N2 was opened at once, pressurizing the system and forcing the solutions of reservoirs A, B and C to flow through the apparatus. In mixing cell M the catalysts started the polymerization and then flowed along the reaction tube T. Upon reaching the second mixing cell Q, the reaction was quenched immediately with the solution delivered from C. Finally, the mixture was collected in flask D.

To avoid polymer formation by the polymerization mixture left behind in reactor tube T, the apparatus was backflushed with the quenching mixture left in C by closing valve X and opening valve K at the end of the reaction.

The solution obtained from the reaction was washed with water followed by a 10% NaOH aqueous solution to remove the acid and most of the methanol. It was then subjected to capillary GC and GC/MS analyses. For the GC/MS analysis it was found useful to concentrate the sample about 10-50X, depending on the final concentration of the oligomers. Because the oligomers of interest for the analysis are of high boiling point (160°C and higher), the solvent could be removed by pumping off the solvent using the vacuum line, without fear of losing any precious products.

Polymerization reactions with metal-alkyl free catalysts. The polymerization of ethylene was not as fast when these catalysts were used, so they were done using regular Schlenkware.

a) $Ta(H)(CHCMe_3)(PMe_3)_3I_2$ (4). In an argon purged Schlenk tube, 50 mg of 4 (68.2 μmole) were dissolved in 4 mL of toluene. The solution was cooled to 0°C in an ice-bath and about 10 equivalents of monomer were admitted to the tube after partial evacuation of the same. The living polymer started to fall out of the solution after about 4 minutes of reaction. The tube was partially evacuated again after 10 minutes and HCl(g) was added to hydrolyze the organometallics. The solution was then washed with water followed by a 10% $NaHCO_3$ aqueous solution until the acidity was completely removed. The organic layer was then separated and dried with sodium sulfate (anhydrous). Before analysis the solution was concentrated ca. 10X.

b) $Cp^*_2LuMe.Et_2O$ (14) and $Cp^*_2YbMe.Et_2O$ (15). In an argon purged Schlenk tube, 40 mg of either 14 or 15 (75 μmole) were dissolved in 2 mL of toluene. The solution was cooled to 0°C and the tube was partially evacuated, followed by admission of about 10 equivalents of monomer. After only 20 seconds of reaction, living polymer begins to precipitate out of the mixture. It was hydrolyzed with a 1:1 mixture of HCl conc./MeOH after 30 seconds of total reacting time. Afterwards, it was washed with water followed by a 10% $NaHCO_3$ aqueous solution until all the acidity had been removed. The organic layer was separated and dried with anhydrous sodium sulfate. To remove the impurity that was eluting together by GC with the oligomers, the solvent was pumped off under vacuum and the resulting semi-solid mixture was treated with 5% Br_2 in carbon tetrachloride for 10 minutes at room temperature. Excess bromine was then eliminated by washing the resulting mixture with 10% $Na_2S_2O_3$ (aq.). The organic layer was separated and filtered to remove suspended sulfur. Volatiles were removed under vacuum and then ca. 0.3 mL of fresh toluene were added for the corresponding GC and GC/MS analyses.

Reaction of $(PMe_3)_3I_2Ta(H)$(neopentylidene) (4) and 1,2-^{13}C-ethylene. 40 mg (55 μmole) of 4 were carefully placed as close as possible to the bottom of an NMR tube and then 0.5 mL of toluene-d_8 were added, washing down any trace of catalyst remaining on the walls. The catalyst was dissolved by gently swirling the tube (should not be shaken). This precaution should be taken to avoid polymerization of ethylene by the catalyst left on the walls of the tube, as only the bottom part of it is actually cooled down while in the probe (the top half is always close to room temperature). Afterwards, about 4 mL of 1,2-^{13}C-ethylene (ca. 3 equiv.) were condensed into the evacuated tube by keeping the mixture at liquid nitrogen temperature. The NMR tube was sealed and kept at -196°C. With the NMR probe temperature at -90°C, the sample was rapidly placed in it, and after thermal equilibrium had been attained, a ^{1}H-NMR spectrum was taken. The probe was warmed up by 10°C increments until reaction was evident by the presence of the new alkylidene protons (δ-0.73) derived from the various oligomers formed. Then, ^{13}C-NMR spectra were taken alternating with ^{1}H-NMR spectra at various increasing temperatures.

Reaction of $Cp_2^*YbMe.Et_2O$(15) and 1,2-^{13}C-ethylene. Compound 15 is a very active polymerization catalyst for ethylene, so the same precautions described above should be followed. 20 mg (38 μmole) of 15 were placed at the bottom of an NMR tube and were carefully dissolved in 0.5 mL of toluene-d_8. About 5 mL of 1,2-^{13}C-ethylene (ca. 6 equiv.) were condensed at liquid nitrogen temperature into the evacuated tube. The NMR tube was sealed and kept at -196°C. The sample was rapidly placed in the -90°C NMR probe and after thermal equilibrium was reached, a ^{13}C-NMR spectrum was taken. Since it was noticed that even at that low temperature there was already some reaction, only a few more spectra were taken at intervals of 10°C before ethylene was depleted. A single ^{1}H-NMR spectrum was taken when the sample was warmed up to room temperature.

Appendix 1

The contact time for the reactions in the quench flow reactor was calculated by knowing the reaction tube dimensions:

diameter (d) = 3.15 mm I.D. (precision bore tubing)

length (l) = 116 cm

area (cross section) (A) = $7.79\text{X}10^{-2}$ cm^2

therefore, the reactor volume (V_r) is 9.04 cm^3.

A total volume of 100 mL of solution (V_1) flowed through the reactor tube (50 mL from each reservoir A and B, Fig. 7). We also timed the pass of the solutions through the tube by means of a stop-watch (t_1). Although t_1 varied slightly for different reactions, it was usually 7 sec.

Therefore, the flow rate is defined by

$$V' = \frac{V_1}{t_1} = \frac{100\text{ mL}}{7\text{ s}} = 14.3\text{ mL s}^{-1}\ (\sim 14.3\text{ cm}^3\text{ s}^{-1})$$

The contact time is then

$$t = \frac{V_r}{V'} = \frac{9.04\text{ cm}^3}{14.3\text{ cm}^3\text{ s}^{-1}} = 0.632\text{ s}$$

We can also calculate the stream velocity ω

$$\omega = \frac{V'}{A} = \frac{14.3\text{ cm}^3\text{ s}^{-1}}{7.79\text{X}10^{-2}\text{ cm}^2} = 183.6\text{ cm s}^{-1}$$

as well as the Reynolds number R_e which gives an idea of the mixing of the solution (R_e<3000 implies laminar flow, R_e>3000 for turbulent flow)

$$R_e = \omega \frac{d}{\nu}$$

ν is the kinematic viscosity of the solvent, given as

$$\nu(\text{stoke}) = \text{g s}^{-1}\ \text{cm}^{-1} \cdot \text{g}^{-1}\ \text{cm}^{3} \quad \text{(this last term is density}^{-1}\text{)}$$

and

$$R_e = (183.6\ \text{cm s}^{-1})(0.315\ \text{cm})\left[\frac{0.884\ \text{g cm}^{-3}}{7.7\text{X}10^{-3}\ \text{g s}^{-1}\ \text{cm}^{-1}}\right] = 6636$$

which shows that we have a well mixed solution.

Appendix 2

The calculation of the average number of deuterated units per oligomer <n> was performed using the data system of the GC/MS. The cross scan (XSCAN) subroutine from the display editor (DISP) program was used.

When the data are processed using the DISP program, a trace of the total ion current (TIC) is seen on the screen and quantitatively represents the total amount of ions generated by each of the individual components in the mixture. Therefore, this trace is similar in some aspects to a GC plot. To get the highest accuracy in the analysis one should obtain large TIC values.

For example, let us consider the determination of <n> for a $C_{19}H_{40}$ oligomer from the ethylene polymerization by 4. To exactly pinpoint the beginning and the end of the eluting oligomer, a XSCAN was done as follows. For this particular alkane the mass range would be from m/e=267 for the $(M-H)^+$ ion of the d_0-alkane (M.W. 268), up to m/e=297 for the $(M+H)^+$ ion of the d_{30}-alkane (M.W. 296). The general formula for the 2,2-dimethylalkanes derived from polymerizations with 4 is $C_nH_{2n+2-m}D_m$ (m=0,4,8...2n-10).

After defining these low and high mass limits, the XSCAN subroutine was executed and a second TIC trace (actually XSCAN:267-297) would appear on the screen. The beginning and the end of such XSCAN defined the elution of the different C_{19} labeled hydrocarbons and was expanded for precision. Having established where all the 2,2-dimethylheptadecanes were, individual XSCANs were executed for each labeled 2,2-dimethylheptadecanes, i.e. for the d_0-alkane we will execute XSCAN:267-269, masses that correspond to the $(M-H)^+$, $(M)^+$ and $(M+H)^+$ ions; for the d_4-alkane will be the XSCAN:270-273, for the $(M-D)^+$, $(M-H)^+$, $(M)^+$ and $(M+H)^+$ ions, and so on up to the d_{28}-alkane with XSCAN: 294-297., and a hard copy was made of each one. The peaks were cut with scissors and were weighed. After normalization of the TICs to the smallest TIC of the series and multiplication by their respective weights, we had the relative amounts of every labeled 2,2-dimethylheptadecane.

Finally, <n> was obtained by multiplying the percentage of the different labeled alkanes by their deuterium content, i.e. d_0 percentage multiplied by 0 (=0), d_4 percentage by 4, up to d_n percentage by n, adding up all these numbers (which represent the average deuterium content of the alkane) and dividing by 4 (maximum number of deuteriums per inserted unit). Two corrections had to be made to obtain the real <n>: a) the ethylene-d_0/ethylene-d_4 mixture was not exactly 1:1 but $d_0/d_4 = 1/1.033$, so the value of <n> obtained by the above procedure was multiplied by 1.033; b) the alkyl fragment derived from the starting catalyst was "subtracted" to get the correct value of N (for example, the 2,2-dimethylheptadecane C_{19} is considered a tetradecane C_{14} after the neopentyl C_5 from the original catalyst is subtracted).

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15. a) Two papers relevant to Green's mechanism were recently published where they discuss the bonding interaction between titanium and a β-C-H in Ti$(Me_2PCH_2CH_2PMe_2)EtCl_3$ and the bonding of the Ti-H-C (methyl) in Ti$(Me_2PCH_2CH_2PMe_2)MeCl_3$. Reactions of these compounds are not reported. Dawoodi,Z.;Green,M.L.H.;Mtetwa,V.S.B.;Prout,K. J.Chem.Soc.,Chem.Commun.(1982),802; Dawoodi,Z.;Green,M.L.H.;Mtetwa, V.S.B.;Prout,K. Ibid.(1982),1410; b) Lappert described the compound $(Cp_2YbMe)_2$ and it is important to notice the asymmetry of the C-H methyl distances: 0.86, 0.93 and 1.15Å. Even though these values are still within "normal" distances, once a polymerization starts with one of these catalysts, the system can be perturbed to allow for the existence of partial α-hydrogen participation during the propagation steps. Holton,J.;Lappert,M.F.;Ballard,D.G.H.;Pearce,R; Atwood,J.L.;Hunter,W.E. J.Chem.Soc.,Dalton Trans.(1979),54.

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19. If we assume that catalyst activation is fast[7] and chain transfer is slow[21] relative to chain propagation, then the probability of producing (in the given reaction time) a polymer chain N units long, n of which are deuterated, is proportional to

$$F(N,n) = \frac{(ck^D)^{n-1}(k^H)^{N-n-1}}{(k^H + ck^D)^{N-1}} \left\{ k^H \left[\frac{c}{1 + c}\right]\left[\frac{N!}{(n-1)!(N-n-1)!}\right] + \left[\frac{1}{1 + c}\right](ck^D)\left[\frac{(N-1)!}{n!(N-n-1)!}\right] \right\}$$

Then $\langle n \rangle$ is given by

$$\langle n \rangle = \frac{\sum_n F(N,n)}{\sum F(N,n)} = (N-1)\left[\frac{c\alpha}{1 + c\alpha}\right] + \frac{c}{1 + c}$$

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21. Lack of chain transfer was demonstrated by: a) polymerizing pure ethylene-d_0 and ethylene-d_4 which resulted in no detectable alkenes (capillary GC); b) from the polymerization of ethylene-d_4 only those oligomers of formula $C_nH_6D_{2n-4}$ were produced. None of the H_1 or H_5 isomers were observed by GC/MS.

22. As a first approximation, Green's mechanism is inaccessible because the titanium atom has a d^0 configuration and further oxidation to reach the alkylidene-hydride complex is precluded. See also Ref. 15a.

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27. An attempt was made to synthesize the methyl substituted analog of 4, $(PMe_3)_3I_2Ta(H)(CMe(CMe_3))$ in order to observe its effects on such equilibrium, as well as its catalytic properties. However, it was not possible to isolate its precursor $Cl_4Ta(CHMe(CMe_3))$ using the same procedure reported for the synthesis of 4.[36] The dipinacolyl zinc used for such synthesis was obtained by transforming pinacolyl alcohol into the corresponding chloride, forming the Grignard and subsequent treatment with zinc chloride.[36] The fuming liquid product has a b.p. 90°C at 20 mmHg, $\rho=0.86$ and was obtained in 6.4% yield overall.

28. Isobutane was used as the ionizing gas because methane affords a large $(M-CH_3)^+$ fragment (CH_3 from the neopentyl group), which overlaps badly with its own molecular ions for oligomers larger than $C_{15}H_{32}$.

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32. For $Ta(CHCMe_3)(C_2H_4)(R)L_2$ (R=ethyl,neopentyl) and $Ta(C_2H_4)_2(C_2H_5)L_2$ ($L=PMe_3$) the ^{13}C-NMR chemical shifts of the bound C_2H_4 molecules are upfield at δ28.8, 33.6 and 36.4 respectively.[22a]

33. Precoordination of the monomer prior to insertion into the growing chain would had generated inequivalent ethylene carbons (one coming close to the metal, the other to the oligomer) and an AB doublet should had been observed to the sides of the free ethylene signal, forming a pseudo-triplet.[7]

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    b) Wood,C.D.;McLain,S.J.;Schrock,R.R. Ibid. (1979),101,3210;
    c) Fellman,J.D.;Turner,H.W.;Schrock,R.R. Ibid. (1980),102,6608.

37. The product ratio on the reaction $Cl_4Ta(CHDCMe_3) \rightarrow L_3Cl_2Ta(H)(CDCMe_3)$ 16 + $L_3Cl_2Ta(D)(CHCMe_3)$ 17 ($L=PMe_3$) was 16/17=1.43, by ^1H-NMR spectroscopy. The iodo derivative was obtained by halide metathesis and the ratio changed to 16-I_2/17-I_2=1.18. Even though this reflects the isotope effect for the formation of the mentioned compounds, it is not clear if the change observed in the ratio of these compounds is of thermodynamic nature and therefore depends on the halide bound to the molecule.

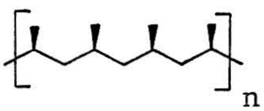
38. The monomer mixture was analyzed by high resolution mass spectrometry: ethylene-d_0/ethylene-d_4= 1/1.033.

CHAPTER 2

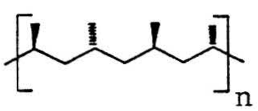
Intramolecular Cyclization of Titanocene(Alkenyl)Chlorides with Lewis Acids

Introduction

When α-olefins are polymerized with Ziegler-Natta catalysts, a new stereocenter is produced with each monomer addition. Three types of stereopolymers may be obtained: isotactic 1, syndiotactic 2 and atactic 3. These are exemplified for polypropylene.



1



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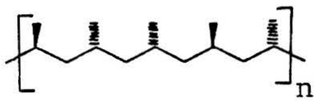
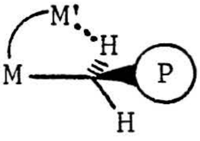


3

The stereoregularity of the polymer obtained depends on the catalyst used as well as the polymerization conditions. Isotactic polypropylene is of major practical importance because of its physico-mechanical properties.

The explanation of the stereochemistry for both mechanisms, Cossee and Green, lies on the fact that the entering monomer will orient itself as to minimize steric repulsions with the growing polymer (Scheme 1).

During the polymerization of α-olefins, there is also the possibility of an α-hydrogen participation to control such stereochemistry. The α-hydrogen participation is well documented for other systems.[1] If existent, this interaction can be either of bimetallic 4 or monometallic 5 type. It is known that when such participation exists, there



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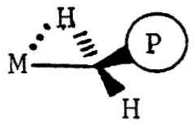
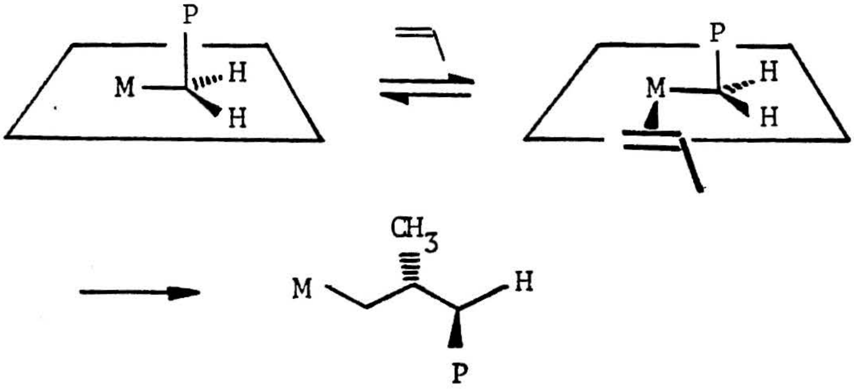
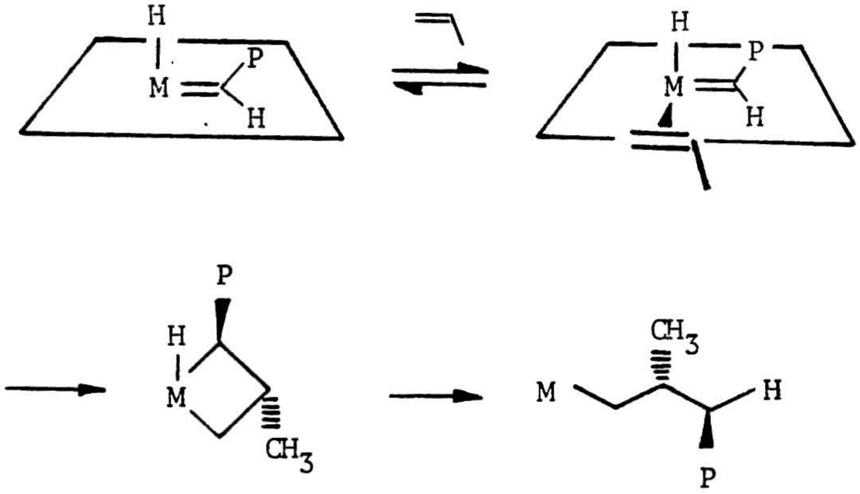


5

Scheme 1



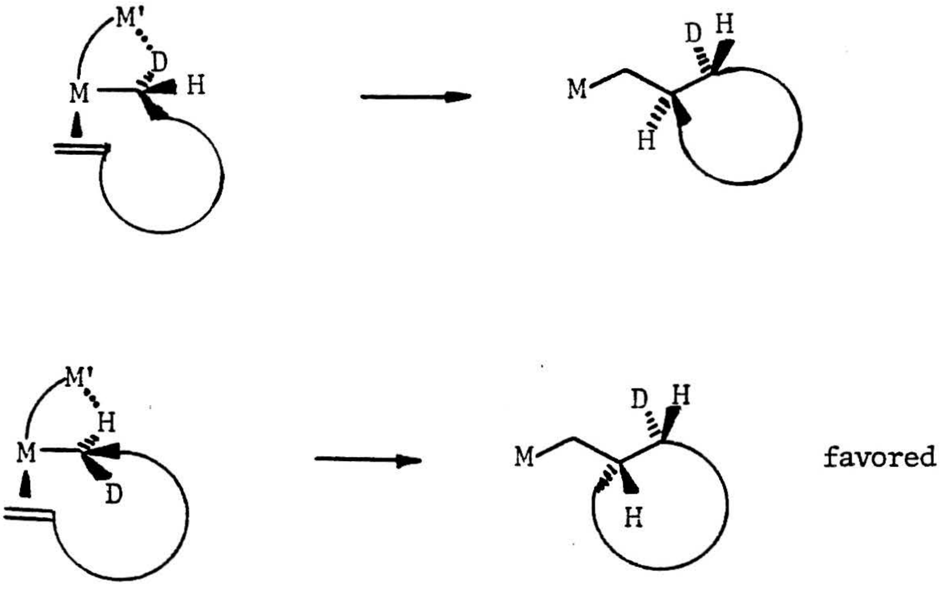
Cossee explanation of stereochemistry



Green explanation of stereochemistry

is a preference for a M···H-C interaction over a M···D-C interaction.[1i] If there is a structure like 4 or 5 during the polymerization, then, by having an alken-1-yl-1-d_1 chain, there could be a preference for the formation of some stereoisomers as shown in Scheme 2.

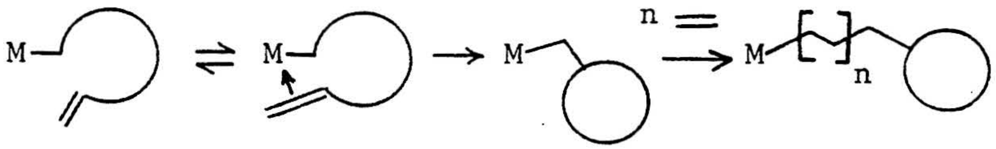
Scheme 2



A system that brings these two concepts together was developed, along with two non-deuterated analogs, and their behaviour is described in this chapter.

Results and Discussion

The problem can be approached by designing a metal alkyl system that will insert only one olefin. A very convenient way of doing this is by having an alkyl chain containing a pendant olefin which is appropriately situated for intramolecular insertion. This technique provides an artificially high local olefin concentration while providing only one olefin per metal alkyl. Once cyclization had occurred, if free ethylene was admitted to the system, polymerization would occur according to Eqn. 1.



(1)

Such interaction between a π-electron system and a metal atom has been shown to yield some stable complexes with transition metals and it has been established that these complexes play an extremely important role in the stereochemically controlled reaction of these systems.

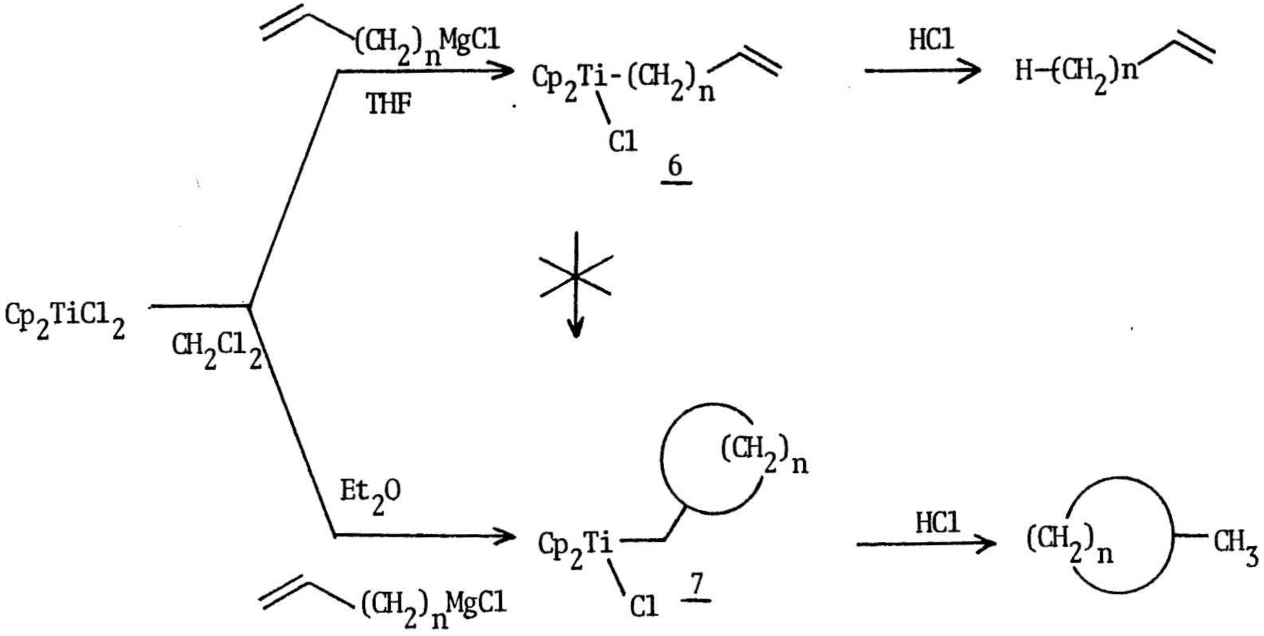
The intramolecular metal-π-electron interaction has been suggested in 3-butenyllithium,[2] several hexenyl-metal derivatives,[3] in some alkenyl-aluminum derivatives[4] and for some Grignard reagents arising from unsaturated species.[5] This type of interaction has also been postulated as the initial step in the intramolecular cyclization processes observed for the corresponding hex-5-en-1-yl derivatives. These reactions are depicted as occurring <u>via</u> an internal addition across the double bond with the ease of reaction shown to be a function of chain length.[6] No cyclization occurs when using 5-carbon or 8-carbon and larger olefins. In fact, ring opening of cyclobutylmethylmagnesium compounds occurs[5b] as an intramolecular analog to the reverse of the addition step during a polymerization. Only partial cyclization is evident for the 7-carbon olefin (0.9% methylcyclohexane vs. 99.1% n-heptane), while the 6-carbon olefin affords almost entirely cyclized product (97.6% methylcyclopentane vs. 2.4% n-hexane). The ease of cyclization of the hexenyl metal derivatives follows the order Al>Mg>Li>Zn>>Hg=0.[7]

The target molecules were prepared by similar routes (Scheme 3). The systems were studied to determine if, in the presence of a Lewis acid, cyclization of 6 into 7 would occur, if such cyclization was faster than free monomer insertion (polymerization) and the stereoselectivity of such cyclization.

Preparation of 6a and 7a. An attempt was made to synthesize 6a by slow addition of a diethyl ether solution of hex-5-en-1-ylmagnesium chloride to titanocene dichloride suspended in dichloromethane at -35°C.[8] After isolating the product, though, it unexpectedly proved to be 7a instead, as shown by the absence of both, vinylic protons in the ^{1}H-NMR spectrum and olefinic carbons by ^{13}C-NMR. The hydrolysis product derived from the new compound was methylcyclopentane and not 1-hexene, as shown by GC analysis with authentic standards.

A possible source of the problem (cyclization) was believed to be light, so a second reaction was done in complete darkness. However, another (fortunate) variable was also introduced. The initiation of the Grignard reaction had been difficult, so the magnesium used for

Scheme 3



n	compound	
4	6a	7a
5	6b	7b

the synthesis of new hex-5-en-1-ylmagnesium chloride was activated by treatment with a small amount of ethyl bromide. The ethylmagnesium bromide formed was removed by washing the magnesium repeatedly with dry THF. Afterwards, THF was poured into the flask to cover the magnesium and the corresponding alkenyl chloride was added to prepare the Grignard reagent. (Even after this activation, sometimes the formation of the Grignard reagent would not start immediately and the mixture had to be refluxed for a few hours. The key to the synthesis of 6a, though, was the use of the stronger coordinating solvent THF, as described below.)

The new reaction to obtain 6a was done protecting the mixture from light (which latter was shown not to be responsible for the cyclization) exactly under the same conditions as the previously described. Finally, 6a was isolated as a thick, dark red, thermally and light stable oil that had characteristic vinylic proton and olefinic carbon signals in the ^{1}H- and ^{13}C-NMR spectra. The ^{1}H-NMR of 6a is shown in Fig. 1. Compound 6a does not cyclize to 7a at room temperature in toluene solution, even after several days of exposure to light. Hydrolysis with HCl of a toluene solution of 6a was analyzed by GC and showed the presence of 1-hexene while methylcyclopentane was not detected (Scheme 3).

Being readily soluble in hexane, the UV spectrum of 6a was recorded and for the first time the wavelengths for the $\sigma \rightarrow d^*$ and the $\pi \rightarrow d^*$ transitions were observed in a titanocene system (Fig. 2). Compare it with the UV spectrum of titanocene(dodecyl)chloride[9] (Fig. 3). It should be noticed that both UV spectra are very similar therefore discarding the possibility of an intra- or intermolecular metal-double bond coordination

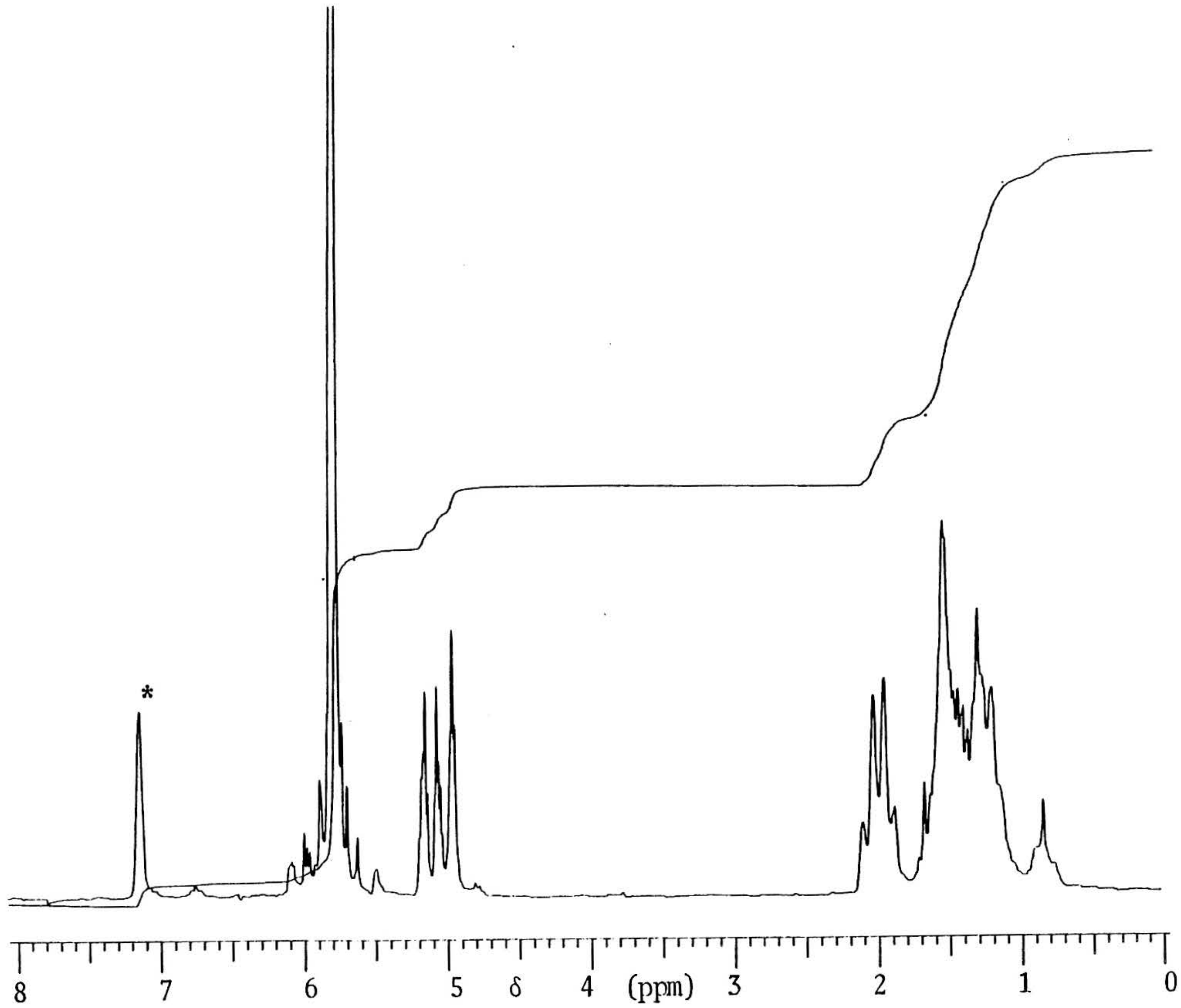


Fig. 1. ^{1}H-NMR spectrum of Cp_2Ti(hex-5-en-1-yl)chloride; * = solvent (C_6D_6).

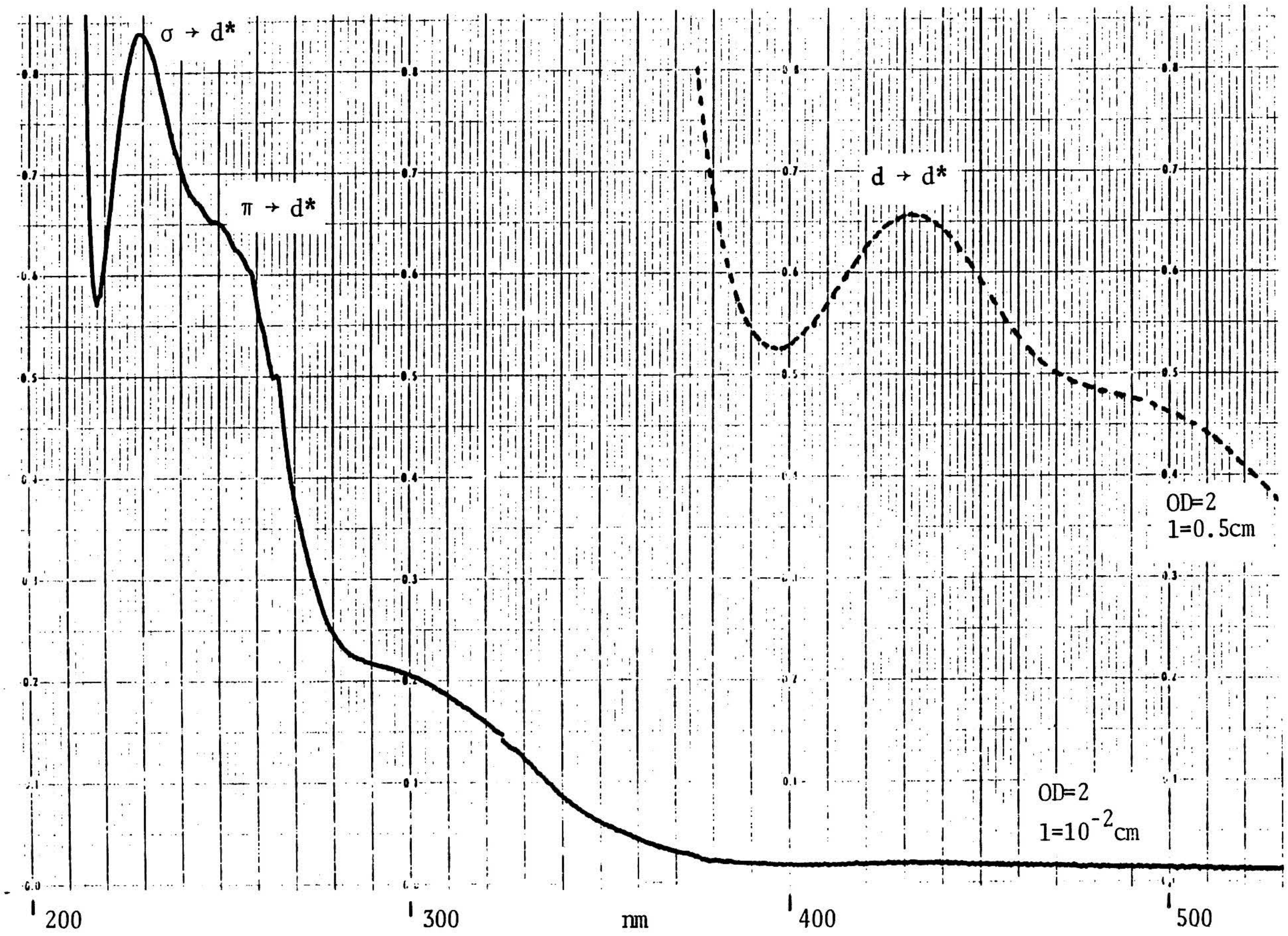


Fig. 2. UV spectrum of Cp_2Ti(hexenyl)chloride in hexane. OD=optical density.

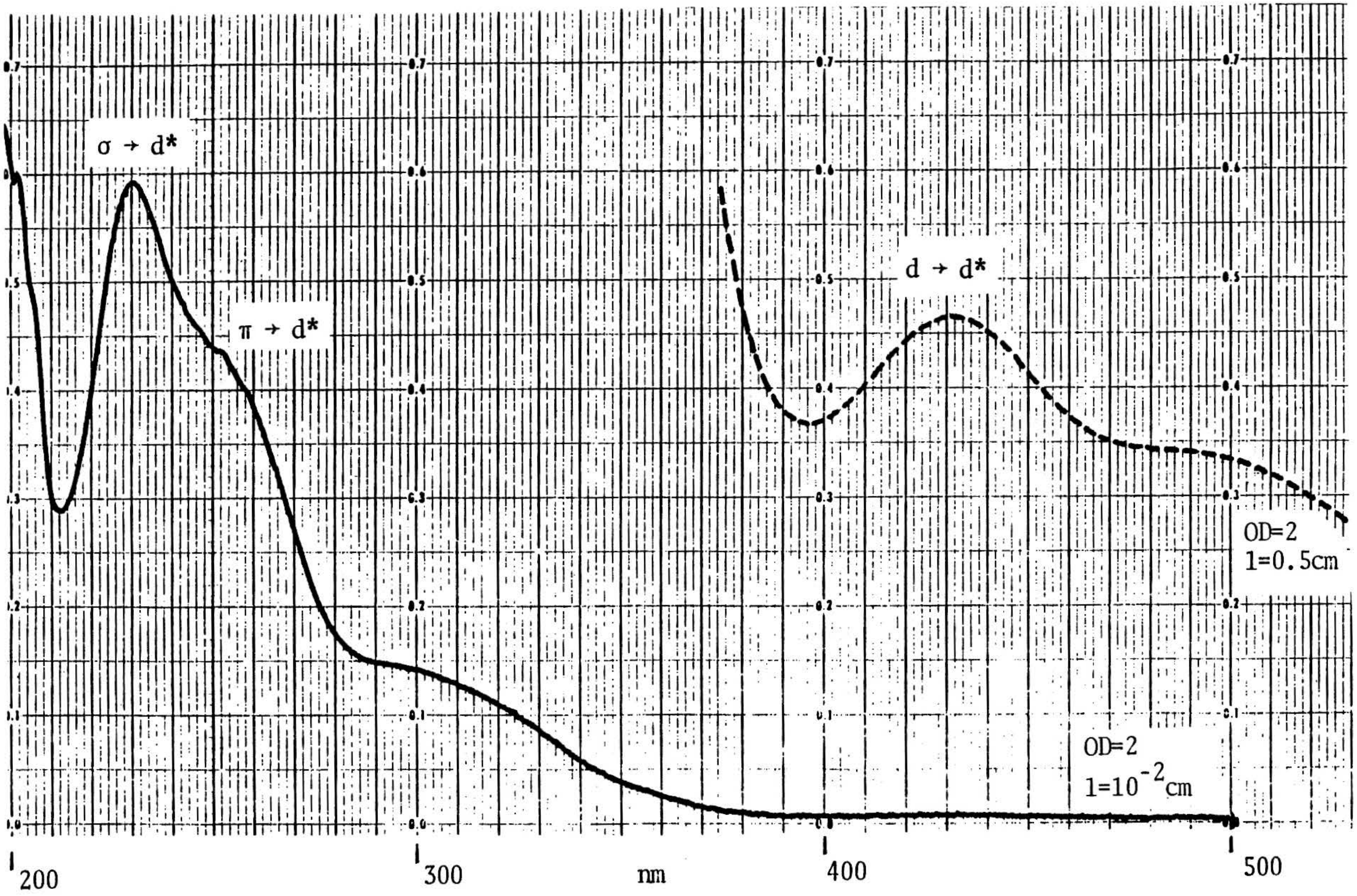


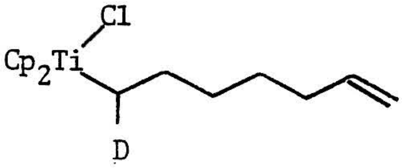
Fig. 3. UV spectrum of Cp_2Ti(dodecyl)chloride in hexane. OD=optical density.

of 6a. If there had been a coordination of the double bond, a new energy level would had formed by mixing metal d orbitals and olefin π^* antibonding orbitals.[10] This new orbital would be sufficiently below the energy level of the original metal 3d orbitals so that an electron from the metal-carbon σ-bond could easily be excited into it, i.e. the $\sigma \rightarrow d^*$ transition should had been observed at a longer wavelength, which was not the case. The absence of such coordination is also evident from the ^{1}H- and ^{13}C-NMR spectra were the chemical shifts of the vinylic protons and carbons are essentially the same as those of the free olefin: $\Delta\delta \simeq 0.15$ ppm downfield from free olefin for the vinylic protons; $\Delta\delta \simeq 0.06$ ppm downfield from free olefin for the terminal vinyl carbon and $\Delta\delta \simeq 0.4$ ppm upfield from free olefin for the internal vinyl carbon. The chemical shift of the α-H is the same as that of a titanocene(alkyl)-chloride.[3b,4b,4e]

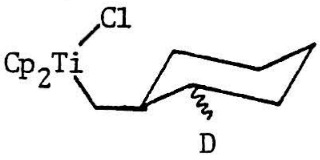
Preparation of 6b and 7b. When a THF solution of hept-6-en-1-yl-magnesium chloride was added to titanocene dichloride suspended in dichloromethane at -35°C and the reaction was not protected from light, the product obtained from the reaction was the anticipated 6b, as shown by ^{1}H- and ^{13}C-NMR spectroscopy and GC of its hydrolysis products.

Compound 7b was prepared using a diethyl ether solution of (cyclohexyl)methylmagnesium chloride under the same conditions as those used to prepare 6b. Analysis of 7b by NMR spectroscopy and GC of its hydrolysis products verified its authenticity. 6b does not cyclize to 7b in toluene solution at room temperature even upon exposure to light for a few days (Scheme 3).

Preparation of 6b-d_1. An attempt was made to synthesize 6b-d_1 before knowing the importance of the coordinating power of the solvent used in the reaction. A diethyl ether solution of hex-5-en-1-yl-1-d_1-magnesium chloride was used first, but the product obtained resulted in a mixture of 6b-d_1/7b-d_1 = 1/1. Note that cyclization in this case was not complete, versus 100% cyclization of 6a to 7a under the same reaction conditions.



6b-d_1



7b-d_1

Comparison with previous experiments showed that the coordination ability of the ether used for the Grignard solutions was playing a very important role in the reaction. Repeating the reaction, but using a THF solution of the Grignard reagent, afforded pure 6b-d_1.

It was evident that the cyclization of the titanocene(alkenyl)-chlorides was effected by one or both of the Grignard reagent and the magnesium chloride formed during the reaction. These magnesium compounds may behave as Ziegler-Natta cocatalysts because of their slight Lewis acidity.[11] Depending on the coordination ability of the ether present during the reaction, the Lewis acid sites will be more or less accessible to the titanocene derivative for the formation of an active species for cyclization (vide infra). A relatively poor coordination solvent like diethyl ether leaves those sites readily available for the formation of such species. However, when THF is used, the Lewis acidity is suppressed because of its stronger coordinating and solvating power.[4b]

Reaction of 6a with $EtAlCl_2$. A toluene solution of 6a (0°C) was treated with $EtAlCl_2$ and the mixture was kept at 0°C, and protected from light. It was hydrolyzed with HCl after 20 sec of reaction and the products were analyzed by GC. Three peaks were observed: ethane, methylcyclopentane and an unidentified peak (probably CpH, as it also appears with the same retention time when 6a itself is hydrolyzed with HCl). This unknown had a different retention time than 1-hexene, which was not detected. The reaction was very clean otherwise, and as will be discussed later, the cyclization occurs with the alkenyl ligand within the coordination sphere of the titanium atom.

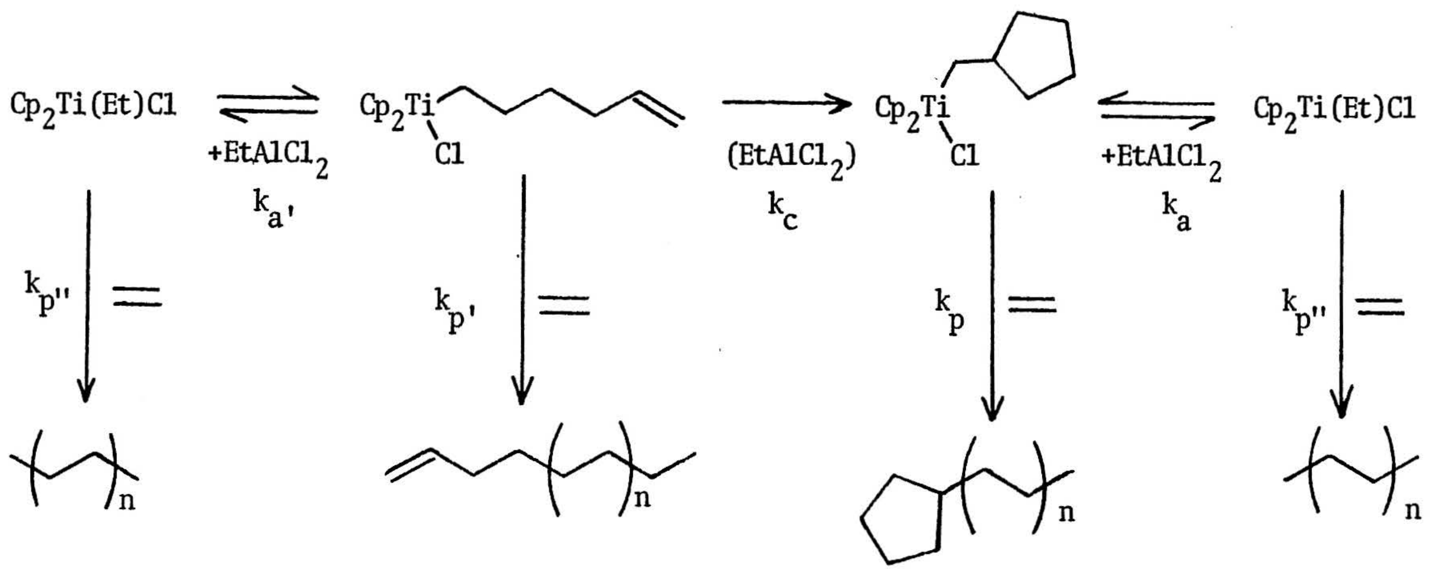
Reaction of 6b with $EtAlCl_2$. Upon treatment of a 0°C toluene solution of 6b with $EtAlCl_2$, cyclization of the heptenyl ligand is not complete after 20 sec of reaction (0°C). The hydrolysis products from the reaction were analyzed by GC and the ratio of methylcyclohexane to 1-heptene was ca. 4/1, showing that the cyclization of 6b is slower than that of 6a. This behaviour was further analyzed by polymerizing ethylene with 6a or 6b using $EtAlCl_2$ as cocatalyst.

Polymerization of ethylene using 6a and $EtAlCl_2$. A qualitative comparison was made between the rates of cyclization and polymerization of 6a and 6b. Cyclization of 6a was shown to be complete in 20 sec or less at 0°C. It is well known that the active species for this type of polymerization systems (titanocene(alkyl)halide + $EtAlCl_2$) is formed extremely fast[12] and the time for one ethylene insertion to the Ti-C bond of the system titanocene(hexyl)chloride + $EtAlCl_2$ is only 95 msec after mixing the reactants.[13] The question was if cyclization was faster than ethylene insertion.

The reaction of the system 6a + $EtAlCl_2$ with ethylene gave mostly cyclopentyl-capped oligomers (97%), with only a minor amount of oligomers derived from alkyl exchange (3%), but there were no α-olefins present derived directly from 6a (Fig. 4). The presence of the cyclopentyl group on the oligomers was confirmed by GC/MS and by coinjection with a solution of oligomers resulting from ethylene polymerization by 7a. Oligomers derived from alkyl exchange (even number n-alkanes) were confirmed with authentic standards.

The only way to justify the absence of α-olefins is by having a cyclization of 6a to 7a faster than the first ethylene insertion, i.e. occurring in less than 95 msec. Alkyl exchange is also a relatively fast process, and could be seen to take place between titanocene(hexyl)-chloride and $EtAlCl_2$ at 0°C in 0.29 sec.[13a] In the present case, the polymerization rate is faster than the alkyl exchange rate, and therefore the principal constituents of the reaction mixture are cyclopentyl-capped oligomers (Scheme 4). The direct alkyl exchange between 6a and $EtAlCl_2$ is hindered because $k_c >> k_{a'}$, and the cyclization reaction for this system is irreversible.[14] When an authentic sample of 7a was used to polymerize ethylene, alkyl exchange occurred only in small amounts, showing again that $k_p > k_{a'}$.

Scheme 4



$k_c >> k_p (\approx k_{p'}) \approx k_{p''} > k_a \approx k_{a'}$

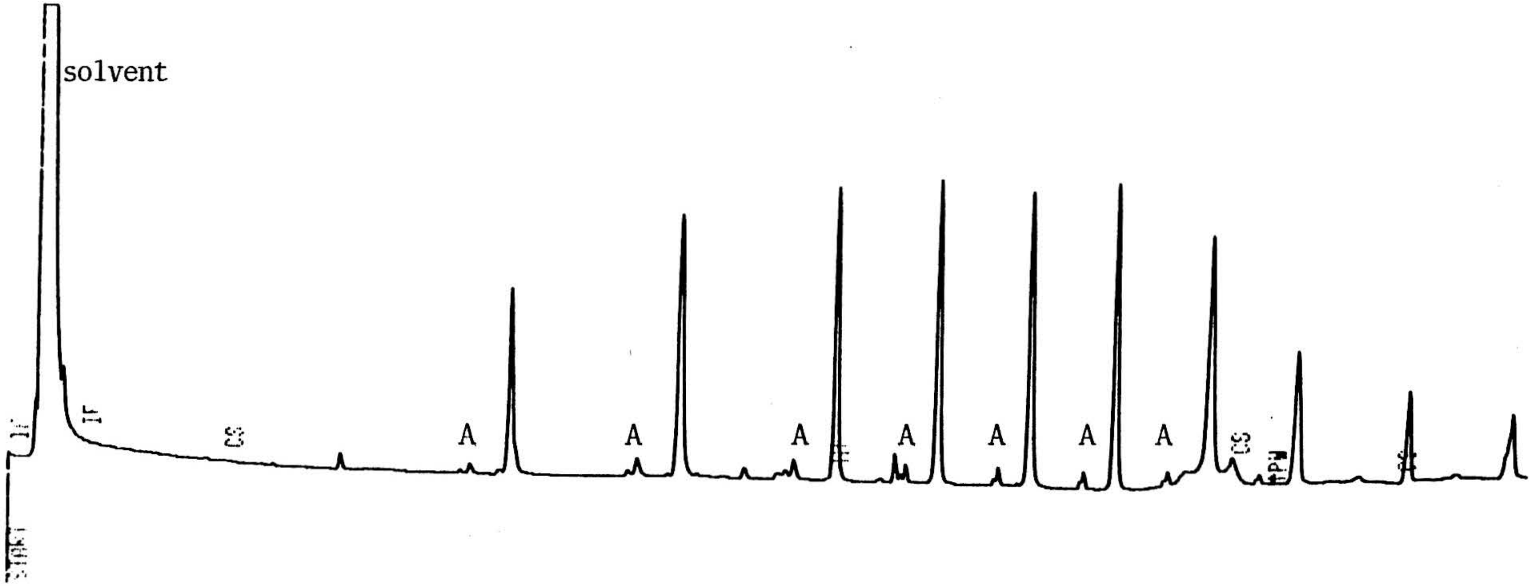


Fig. 4. Hydrolysis products from 6a + $EtAlCl_2$ + ethylene. Major peaks are odd number cyclopentyl-capped alkanes, A=even number n-alkanes(alkyl exchange).

Polymerization of ethylene using 6b and $EtAlCl_2$. The polymerization of ethylene by 6b and $EtAlCl_2$ gave a completely different result. There were all three types of oligomers expected: n-alkanes derived from alkyl exchange, cyclohexyl-capped oligomers formed from the newly generated 7b and α-olefin oligomers formed from the original 6b in a ratio of ca. 1/2/3, respectively (Fig. 5). All of these were confirmed by capillary GC using authentic standards.

For this system, the cyclization rate is slightly slower or equal to the polymerization rate, while the alkyl exchange rate is definitely slower as can be seen from the smaller amounts of n-alkanes formed during the reaction (Scheme 5). We can then derive the relative order $k_p \geqslant k_c > k_a$, but it seems that k_p would not be more than an order of magnitude larger than k_a.

Reaction of 6b-d_1 with $EtAlCl_2$. A Lewis acid is necessary to promote the cyclization of the alkenyl ligand in 6a and 6b. To determine if there was an α-hydrogen participation during said cyclization, 6b-d_1 was treated with $EtAlCl_2$ exactly under the same conditions as 6b (no ethylene present), except that the mixture was allowed to react for 60 sec to insure complete cyclization of the alkenyl ligand. After hydrolysis of the final mixture, a GC trace showed that cyclization had been complete, as no 1-heptene was detected. The product was separated from the solvent and an unidentified compound by preparative GC. The ratio of methylcyclohexane-d_1/unknown = 4/1. It was not possible to collect enough of the unknown compound to allow possible identification by NMR spectroscopy. A ^{13}C-NMR spectrum of the

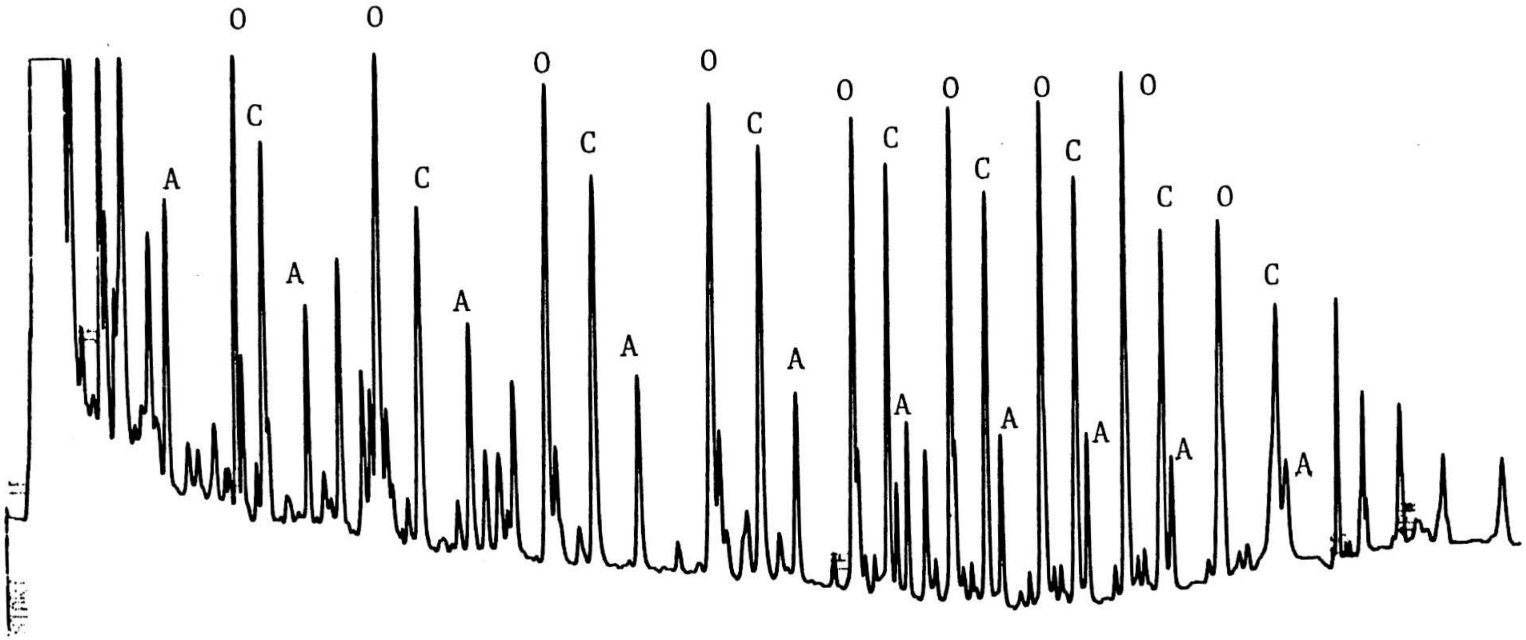
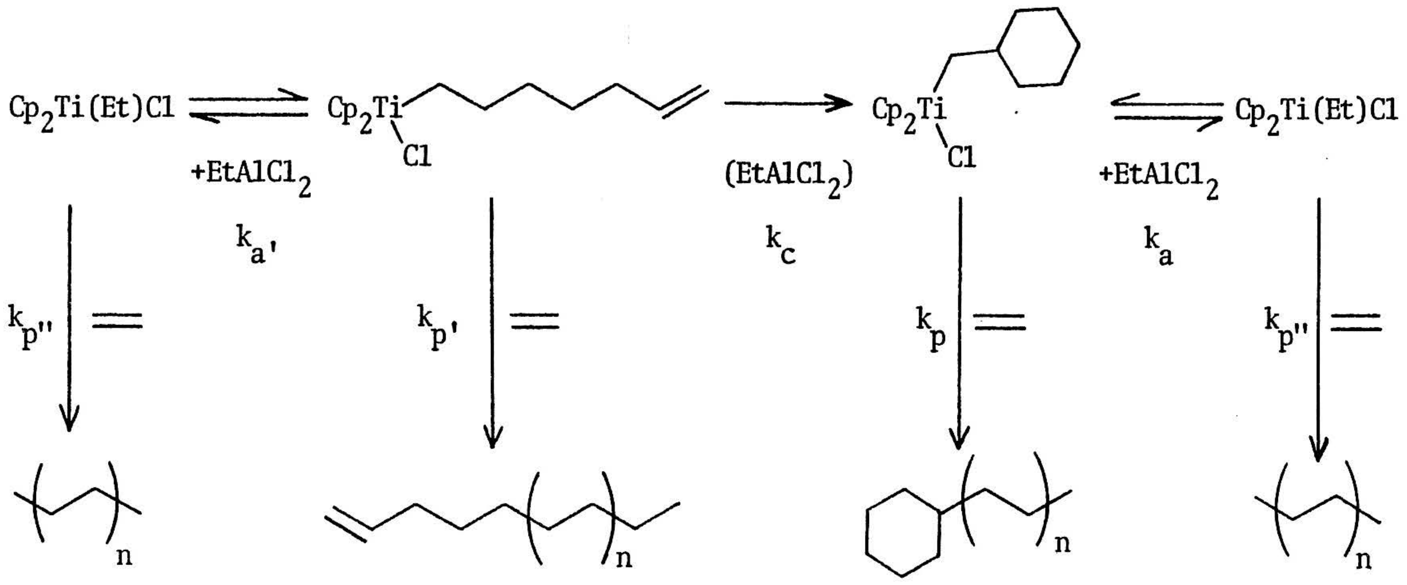


Fig. 5. Hydrolysis products from <u>6b</u> + $EtAlCl_2$ + ethylene. O=odd number α-olefins, C=odd number cyclohexyl-capped n-alkanes, A=even number n-alkanes (alkyl exchange).

Scheme 5



$k_p \simeq k_{p'} \simeq k_{p''} \geqslant k_c > k_a \simeq k_{a'}$

eluted product showed that methylcyclohexane was the major component in the mixture. By capillary GC it proved to be 70% methylcyclohexane plus two unidentified peaks close to it (12% and 18%).

A ^{2}H-NMR (13.76 MHz) spectrum of the labeled methylcyclohexane[15] (in toluene-d_0, benzene-d_6 as internal reference) showed two singlets at δ0.83 and 1.6, with an area ratio of 1.7 to 1.0, respectively. They were assigned to cis-methylcyclohexane-2-d_1 (2 ax.) 8 and trans-methylcyclohexane-2-d_1 (2 eq.) 9 , respectively. Upon close inspection of the spectrum, it was noticed that the upfield signal was somewhat broad, so the sample was analyzed by ^{2}H-NMR (77 MHz). This time the upfield signal was split into two singlets at δ0.80 from 9 and δ0.87 from an unidentified compound 10. Their integrated areas were about 1:1. No vinylic or allylic deuteriums were present.

It was noticed on the preparative GC trace that there was a shoulder trailing the methylcyclohexane peak. To insure that the signal observed on the ^{2}H-NMR spectrum at δ0.87 was derived from the first peak compound(s) and not from the shoulder compound, the sample was passed again through the preparative GC column and the products were collected as leading (major peak) and trailing (shoulder) halves. The ^{2}H-NMR spectra of these fractions were essentially identical, so the shoulder compound was not the cause of the unidentified signal. It was possible that the presence of such signal was due to the presence of (methyl-d_1)cyclohexane in the product. An authentic sample of this hydrocarbon was prepared by hydrolysis of titanocene(methyl(cyclohexane))chloride with DCl. Surprisingly, the deuterium signal of the standard grew up at

$\delta 0.84$ in between the other peaks (Fig. 6). The nature of <u>10</u> remains uncertain and is still under investigation. There was no cycloheptane formed (^{1}H-NMR $\delta 1.52$), nor cis- or trans-2-heptene (GC).

The ratio <u>8</u> / <u>9</u> = 1.01 shows that there is no α-hydrogen participation during the cyclization step. The analogous compound <u>6a-d_1</u> reacts with $EtAlCl_2$ to give a mixture of cis- and trans-methylcyclopentane-2-d_1 in a ratio cis/trans = 1.0 ,[16] and strenghtens the above observation.

<u>Polymerization of ethylene using</u> <u>6b-d_1</u> <u>and $EtAlCl_2$</u>. It was possible that the presence of the unknown compound <u>10</u> generated during the reaction of <u>6b-d_1</u> and $EtAlCl_2$ was caused by the relatively long contact time between the reactants (60 sec). If formation of <u>10</u> was slow compared to ethylene insertion, it would be possible to avoid it by polymerizing ethylene with this system, thus removing the heptenyl ligand from the active center after a very short time (95 msec,[13b] <u>vide supra</u>).

It was known that not all of the heptenyl ligands would have time to cyclize and because of that, some 7-d_1-α-olefins were going to be formed in about 50% excess over the cyclohexyl-capped oligomers (see Fig. 5). The chemical shift of the deuterated methylene unit derived from such olefins would be at about $\delta 1.2$-1.3. Therefore, if formation of <u>10</u> was slow, it was expected that the ^{2}H-NMR spectrum of the oligomer mixture would have three peaks at about $\delta 1.6$(oligomers from <u>8</u>), ca. 1.25 (oligomers derived directly from <u>6b-d_1</u>) and 0.8 (oligomers from <u>9</u>), with ratios of about 1:3:1.

The ^{2}H-NMR spectrum of the actual mixture (in toluene-d_0, benzene-d_6

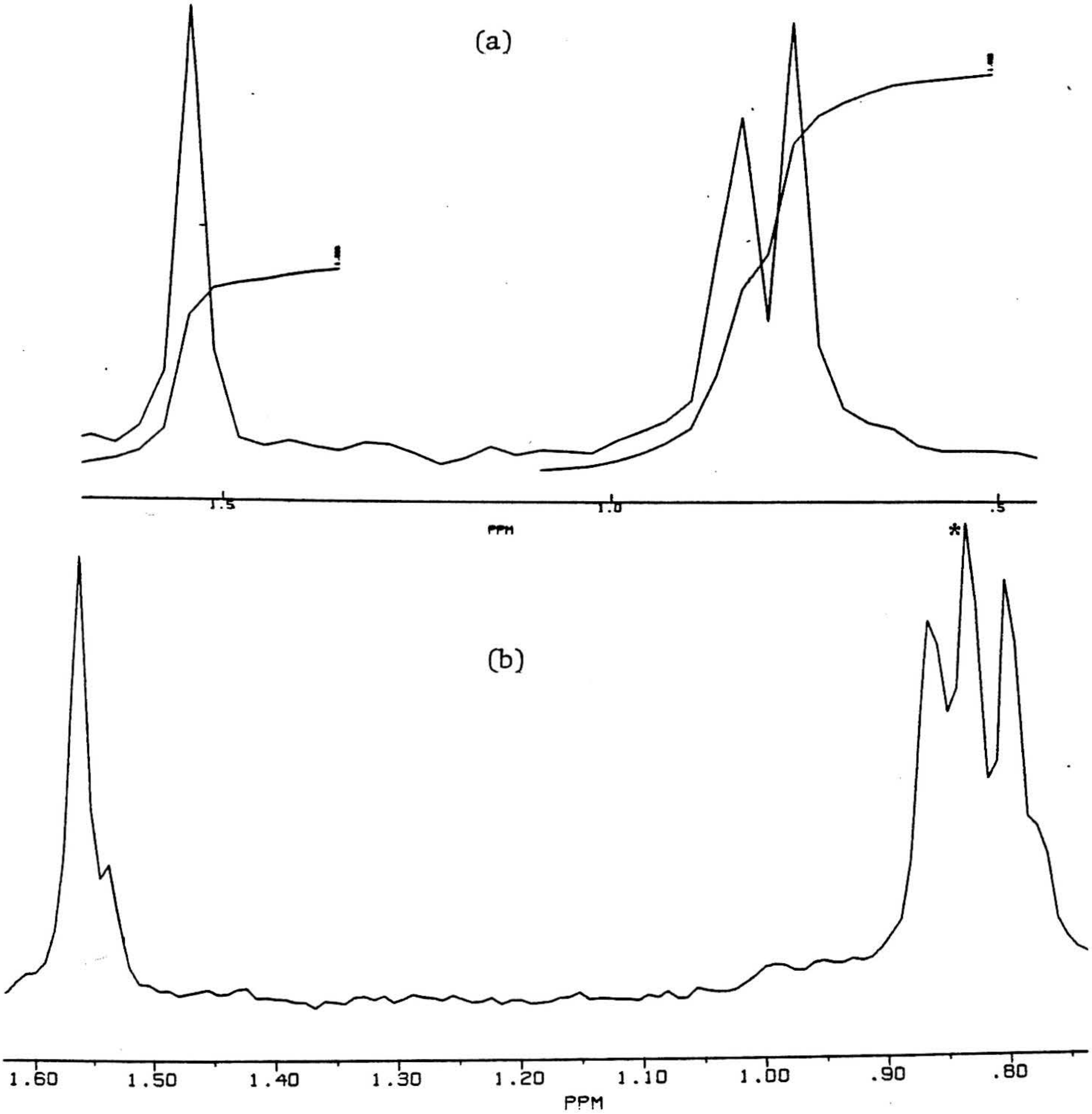


Fig. 6. ^{2}H-NMR (77 MHz) spectrum of the cyclization products from $\underline{6b\text{-}d_1}$ + $EtAlCl_2$: a) original spectrum; b) after addition of (d_1-methyl)cyclohexane (*).

as internal reference) is shown in Fig. 7. A pattern similar to the one predicted is clearly seen, plus an extra peak at δ1.18. The signal at δ1.25 was assigned to the deuterated methylene unit from the α-olefin oligomers by comparison with the ^{1}H-NMR spectrum of the same sample. The source of the signal at δ1.18 is unknown and may be related to the unidentified compound 10 previously described. There were no vinylic deuteriums present in the mixture and no allylic deuteriums were detected either, and this last observation excludes the possibility of β-alkyl elimination.[17]

Room temperature reaction of 6a with $EtAlCl_2$. Treating 6a with 1 equivalent of $EtAlCl_2$ in benzene at room temperature gives a light green solution immediately. A ^{1}H-NMR spectrum of the solution shows the disappearance of the Cp signal, as well as the vinylic protons. There are two new medium size broad peaks at δ2.17 and 4.96. When 1 equivalent of bipy is added to the solution, it turns green-yellow and after centrifuging the solution, a dark blue oil collects at the bottom of the sample tube (Al:bipy adduct). A yellow solution is left and displays the same NMR spectrum as before. Reduction of 6a took place extremely fast at this temperature. The presence of methylcyclopentane was shown by GC analysis.

Low temperature reaction of 6a with $EtAlCl_2$. Because of the problem of fast reduction of 6a at moderate temperatures, a reaction was done at -80°C. The ^{1}H-NMR spectrum of the cold dark red-brown mixture of 6a + 1 equivalent of $EtAlCl_2$ was somewhat broad. There is still evidence for vinylic protons (δ5.1) but, even though integration

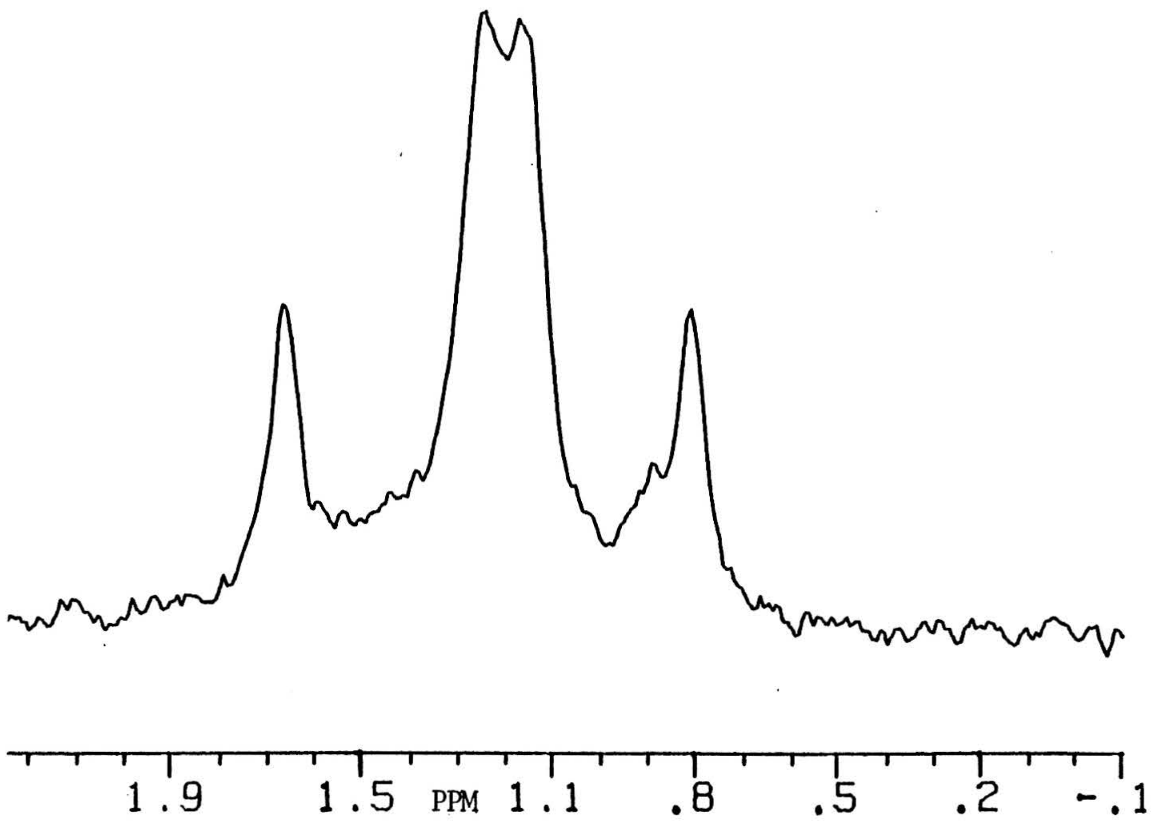


Fig. 7. ^{2}H-NMR (77 MHz) spectrum of the oligomers formed by reacting 6b-d_1 + EtAlCl$_2$ + ethylene at 0^{o}C.

is precluded because of broadened and overlapping signals, it is noticed that 6a has already started to cyclize. A ^{13}C-NMR spectrum of the same sample does not give much information either. Small signals were seen at δ117.8, 114.8, 36.9, 34.5, 25.2, 9.31 and 5.41 (these last two from $EtAlCl_2$) with a medium size peak at δ116.2.[18] No signal is observed for the C_α. There was no evidence for a metal-double bond interaction.[13b]

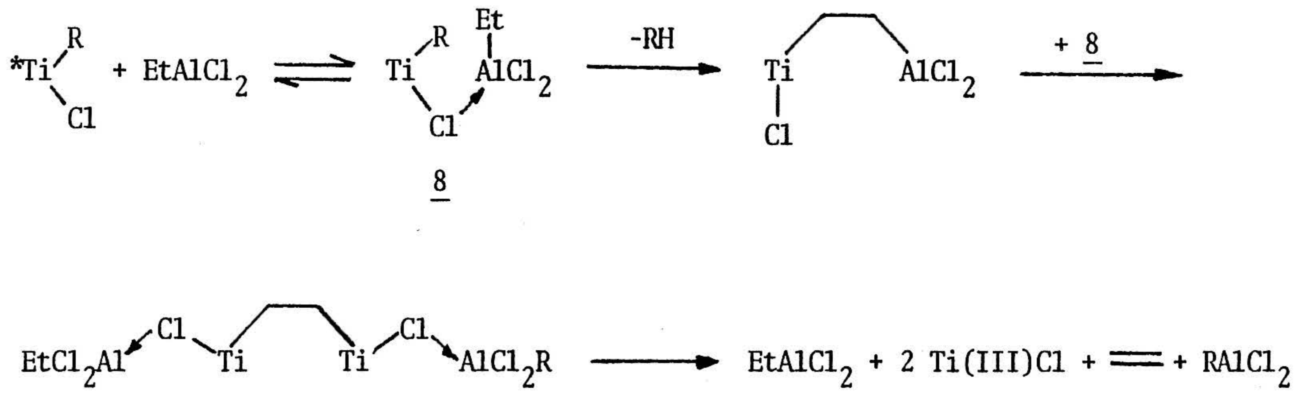
After 1.5 h at -80°C, 1 equivalent of bipy/Al was added to the reaction. The solution stays red and the ^1H-NMR signals sharpen up somewhat. There is a large Cp signal at δ5.64 that does not correspond to either 6a or 7a. Upon warming the solution to room temperature, a ^1H-NMR spectrum shows a sharp signal at δ5.80 (7a), a broad signal with sharp singlets protruding at δ1.62 and 1.57, a small broad lump with a singlet at δ0.82 (Me-cyclopentane), but no vinylic protons are observed. The Al:bipy adduct was removed from the mixture and the supernatant was separated in two fractions: a) volatiles, which showed the presence of free methylcyclopentane but not 1-hexene (GC); b) residue, which upon hydrolysis with HCl gave methylcyclopentane but not 1-hexene (GC). No ethane was seen in the hydrolysis products of the residue, therefore alkyl exchange did not occur between $EtAlCl_2$ and 6a (or the newly formed 7a) at -80°C.[13b,19]

Low temperature reaction of 6b with $EtAlCl_2$. The reaction of 6b and 1 equivalent of $EtAlCl_2$ at -80°C was similar in some aspects to the above reaction. However, the starting mixture was dark green-brown instead of dark red. The ^1H-NMR signals were very broad, but the presence of vinylic protons was shown by a broad peak at δ5.1. Even the ^{13}C-NMR spectrum was broadened with only two medium size signals visible at δ118.8 and 117.8.[18] Addition of bipy to the -70°C solution turns it dark red again. However, broadness of the NMR signals persist up to -20°C and no change is observed on them. The solution had to be warmed up to room temperature to obtain sharp signals. The ^1H-NMR spectrum shows both 6b and 7b in a ratio of ca. 1:1 (Cp signals). The presence of residual vinylic protons from 6b is seen at δ4.96, 5.08 and 5.15. A broad multiplet occurs at δ0.8-1.9 with a sharp singlet at δ0.84 (Me-cyclohexane). The ^{13}C-NMR spectrum verifies the presence of both 6b and 7b by their C_α at δ72.4 and 82.1 (ratio 1:1) and their Cp carbons at δ115.6 and 115.4 (ratio 1.2:1), respectively. The rest of the carbon atoms could also be accounted for, as well as small amounts of free methylcyclohexane. No alkyl exchange occurred between $EtAlCl_2$ and 6b or 7b, as no $Ti-\underline{C}H_2-CH_3$ was observed (δ64.5 [13b]).

Both 6a and 7a cyclize at low temperature with no alkyl exchange. This proves that cyclization occurs with the alkenyl ligand within the coordination sphere of titanium.

The formation of free methylcycloalkanes can be explained by the reduction of the Ti(IV) compounds. The first step of the reduction is the transfer of a β-hydrogen atom from one alkyl group to the other (in this case from the ethyl group of $EtAlCl_2$ to the methyl(cycloalkyl) ligand) with formation of metal-CH_2-CH_2-metal structures. Such β-hydrogen atom-transfer was first proposed by de Vries[20] for the reduction of

Scheme 6



* Cp rings have been omitted for clarity.

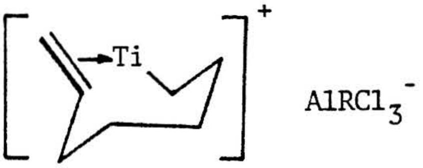
Titanium as Ti(IV) unless otherwise stated.

Ti(IV) compounds by $EtAlCl_2$. The ethylene that should be formed was not found, probably because it had polymerized (Scheme 6, after de Vries[20]).

Cyclization mechanism. It has been shown that cyclization of the alkenyl ligand of 6a and 6b occurs fast under mild conditions in the presence of a Lewis acid. At this stage the exact nature of the cyclization mechanism is unknown, but some of them are briefly discussed.

A free radical[21] or a cage radical mechanism can be discarded because the rate constant of cyclization of the hept-6-enyl radical ($k_c = 4 \times 10^3\ s^{-1}$ at 25°C [22]) is much faster than the rate constant of ethylene polymerization of the analogous system Cp_2Ti(hexenyl)chloride + $EtAlCl_2$ ($k_p = 47\ M^{-1}s^{-1}$ at 10°C, $(C_2H_4) = 0.22$ M [13b]). These rate constants suggest that a radical process will give mostly cyclohexyl-capped oligomers from the system 6b + $EtAlCl_2$, which is not the case.

Formation of an ion pair like the one proposed by Dyachkovskii[23] and Shilova,[24] i.e. $(Cp_2Ti(R))^+(AlRCl_3)^-$, is a better alternative (Cossee-type mechanism). The species $(Cp_2Ti(R))^+$ could then cyclize the alkenyl ligand, possibly going through an intermediate like 11 (intramolecular interaction shown only to identify Ti-olefin spatial arrangement; Cp rings omitted for clarity).



11

Models also show that the conformation of such intermediate is more favorable to accommodate the alkenyl double bond close to the titanium atom when R=hexenyl than for R=heptenyl, which explains the faster cyclization of 6a compared with that of 6b. The chloride ligand from the titanocene derivative does not have to be removed by the cocatalyst, but positive polarization of the titanium atom is required to effect the cyclization.

Experimental Section

General. All manipulations of air and/or moisture sensitive compounds were performed using a Vacuum Atmospheres dry box (nitrogen) or standard high vacuum line Schlenk techniques. Argon used in Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. NMR spectra were recorded with a Jeol FX-90Q (89.6 MHz ^1H, 22.53 MHz ^{13}C, 13.76 MHz ^2H) or a Bruker WM-500 (76.76 MHz ^2H). Gas chromatographic analyses were performed on a Varian 1400 (FID) using a 10 ft Durapak column (70-150°C, 4°C/min, initial time 4 min) or a Shimadzu GC Mini-2 with a 30m SE30 capillary column (90-250°C, 10°C/min, hydrogen used as carrier gas) equipped with a Hewlett-Packard 3390A integrator. Preparative gas chromatography was performed on a Varian Aerograph Model 920 using a 10 ft Durapak column isothermally at 90°C. UV spectra were recorded with a Varian Cary 219 spectrophotometer. GC/MS analyses were done with a Perkin-Elmer Sigma-1 chromatograph (2.4m 3% SE30 on 100/120 GCQ, helium used as carrier gas) coupled to a Kratos MS25 spectrometer. The ion source temperature was set at 150°C and methane was used as the ionizing gas (CI) with a pressure of $2X10^{-4}$torr. Data acquisition was done with a Data General NOVA 3 computer.

Materials. Pentane and THF were dried stirring over CaH_2, then filtered and transferred onto sodium benzophenone ketyl in tetraglyme where they were degassed. Diethyl ether and toluene were poured directly onto sodium benzophenone ketyl in tetraglyme and degassed. Dichloromethane was stirred over P_2O_5 and degassed. The above solvents were vacuum transferred into dry vessels equipped with teflon screw valves and stored under argon. Benzene-d_6 (Merck, Sharp and Dohme) and toluene-d_8 (KOR Isotopes) were dried and deoxygenated by stirring over sodium benzophenone ketyl after several freeze-pump-thaw cycles.

Titanocene dichloride (Boulder Scientific) was used as received (new batch, already recrystallized). Ethyl aluminum dichloride (purified by sublimation) and 6-heptenoic acid were purchased from Alfa Products. Cyclohexylmethanol was purchased from Aldrich. Ethylene (C.P. 99.5% min.) was purchased from Matheson and was used as received. 1-Chloro-5-hexene, heptylcyclohexane and nonylcyclohexane were purchased from Wiley Organics. The other hydrocarbons used as standards for GC work were purchased from Sigma.

1-Chloro-6-heptene was prepared by lithium aluminum hydride reduction of 6-heptenoic acid in diethyl ether, followed by reaction of the 6-heptenol obtained with mesyl chloride in dichloromethane, and finally treating the 6-heptenyl-mesylate with lithium chloride in refluxing acetone. 1-Chlorohept-6-ene-1-d_1 was prepared by oxidation of 6-heptenol with pyridinium dichromate in dichloromethane[25] to the corresponding aldehyde, and then reducing the aldehyde with lithium aluminum deuteride to hept-6-en-1-ol-1-d_1. The alcohol was transformed to the tosylate and finally, treatment with lithium chloride in refluxing acetone gave the desired product. (Cyclohexyl)methyl chloride was obtained from the corresponding alcohol via its mesylate. The authenticity of the alkenyl magnesium chlorides obtained was verified by hydrolyzing an aliquot of their solutions and analyzing the resulting hydrocarbons by GC. In all cases, the alkenyl magnesium chlorides analyzed as 100% alkenyl, 0% methylcycloalkyl. To avoid cyclization of the titanocene(alkenyl)chlorides prepared, the Grignard reagents must be used as THF solutions (see Results and Discussion).

Synthesis of Titanocene(5-hexenyl)chloride (6a). To 2 g (8mmole) of titanocene dichloride suspended in 30 mL of dichloromethane at -35°C, 7 mL of a 1.35M THF solution of 5-hexenylmagnesium chloride (1.35 g, 9 mmole) were added dropwise in 10 min and the reacting mixture was protected from light. The mixture was allowed to warm up to +5°C (2 h) and the solvents were removed in vacuo. Up to this point the flask was kept from light. The product was extracted from the residue with toluene (2X25 mL) and the solution was filtered through celite to remove magnesium salts. The solvent was pumped off and the red oily residue was redissolved in pentane (100 mL) and was cooled down to -50°C. A dark red oil was obtained, and after removing the excess solvent in vacuo, it was kept at -40°C protected from light. It solidified after several weeks at -40°C. Yield: 1.6 g (67%). ^{1}H-NMR(C_6D_6), shifts relative to C_6D_5H at δ7.15: δ1.0-1.8 (m,br,4H), 1.5 (s,br,2H, α-$\underline{CH_2}$), 2.0 (q,2H,$\underline{CH_2}$-CH=), 4.97 (m,1H, cis $\underline{CH_2}$=CH-), 5.12 (dm,J=7 Hz, 1H, trans $\underline{CH_2}$=CH-), 5.85 (s,10H, Cp's), 5.6-6.0 (m,1H, -$\underline{CH}$=CH_2); ^{13}C(^{1}H)-NMR (C_6D_6), shifts relative to $\underline{C_6}D_6$ at δ128.0: δ33.7, 34.5 (C_2 and C_3), 37.2 (C_4), 72.1 (C_1), 114.4 (C_6), 115.6 (Cp's), 139.6 (C_5); UV (hexane), λ_{max} (ε): 229 (27,700), 250 (sh), 431 (440), 500 (sh).

Synthesis of Titanocene(methyl(cyclopentyl))chloride (7a).[26] A suspension of 12.5 g (50 mmole) of titanocene dichloride in 130 mL of dichloromethane at -35°C was treated with a diethyl ether solution of 5-hexenylmagnesium chloride (7.16 g, 50 mmole). The mixture was allowed to warm up to room temperature (3 h). The solvents were removed in vacuo and the product was dissolved with as small amount as possible of toluene, and the solution was filtered through celite. Part of the solvent was removed under vacuum until the product started to precipitate; then the solution was layered with 2 volumes of pentane and the mixture was cooled down to -50°C. The supernatant was separated from the dark red solid. The product was then dried in vacuo to yield 11.2 g (75%). ^{1}H-NMR (C_6D_6), shifts relative to C_6D_5H at δ7.15: δ1.3-1.7 (br,9H), 1.66 (d,J= 5.6 Hz,2H, α-$\underline{CH_2}$), 5.81 (s,10H, Cp's); ^{13}C-NMR (C_6D_6), shifts relative to $\underline{C}_6D_6$ at δ128.0, gated decoupled: δ25.3 (t,$^1J_{CH}$=125.9 Hz, C(3) and C(4) of cyclopentyl), 37.2 (t,$^1J_{CH}$= 131.8 Hz, C(2) and C(5) of cyclopentyl), 48.3 (d,$^1J_{CH}$=127, C(1) of cyclopentyl), 82.5 (t,$^1J_{CH}$=125 Hz, C_α), 115.5 (d,$^1J_{CH}$=174 Hz, Cp's).

Synthesis of Titanocene(6-heptenyl)chloride (6b). This compound was prepared by dropwise addition of 5 mL of a 1.27M THF solution of 6-heptenylmagnesium chloride (1.0 g, 6.4 mmole) to 0.63 g (2.5 mmole) of titanocene dichloride suspended in 20 mL of dichloromethane at -45°C. The mixture was allowed to warm up to room temperature (3 h) and the solvents were removed under vacuum afterwards. The residue was extracted with pentane (4X10 mL) and filtered through celite. The red solution was concentrated down to its saturation point. Cooling the solution overnight at -50°C afforded a dark-red mass. After separating the supernatant, it was noticed that the solid consisted of dark red needles (55 mg) on top of a dark red solid. Both were kept in separate vials, even though their ^{1}H-NMR spectra were almost identical. Yield: 465 mg (60%). ^{1}H-NMR (C_6D_6), shifts relative to C_6D_5H at δ7.15: δ1.0-1.9 (m,br,6H), 1,57 (s,br,2H, α-C$\underline{H_2}$), 2.04 (q,2H, -C$\underline{H_2}$-CH=), 4.97 (m,1H, cis C$\underline{H_2}$=CH-), 5.12 (d,J=7 Hz,1H, trans C$\underline{H_2}$=CH-), 5.78 (s,10H, Cp's), 5.7-6.0 (m,1H, -CH=CH$_2$); ^{13}C(^{1}H)-NMR (C_6D_6), shifts relative to $\underline{C_6}D_6$ at δ128.0: δ28.9, 34.4, 34.9 (C(2), C(3) and C(4)), 37.8 (C(5)), 72.6 (C(1)), 114.4 (C(7)), 115.6 (Cp's), 139.4 (C(6)).

Synthesis of Titanocene(methyl(cyclohexyl))chloride (7b). To 3.17 g of titanocene dichloride (12.7 mmole) suspended in dichloromethane at -30°C it was added 15 mL of a diethyl ether solution of (cyclohexyl)methylmagnesium chloride (2.0 g, 12.8 mmole). The solution was allowed to warm up slowly to -5°C (2.5 h). The solvents were then removed under vacuum and the dark red residue was extracted with pentane (6X15 mL) and filtered through celite. Slight concentration of the solution gives a fine red precipitate. The solid was removed and the solution was set at -50°C to crystallize. Dark-red crystals of 7b were collected and dried under vacuum. Yield: 2.0 g (50%). ^{1}H-NMR (C_6D_6), shifts relative to C_6D_5H at δ7.15: δ0.8-1.9 (br multiplets,11H), 1.52 (overlapping d,2H, α-C$\underline{H_2}$), 5.81 (Cp's); ^{13}C(^{1}H)-NMR (C_6D_6), shifts relative to $\underline{C_6}D_6$ at δ128.0: δ26.8 (C(4), cyclohexyl), 27.4 (C(3) and C(5), cyclohexyl), 37.2 (C(2) and C(6), cyclohexyl), 46.0 (C(1), cyclohexyl), 82.5 (Cα), 115.5 (Cp's).

Synthesis of Titanocene(hept-6-en-1-yl-1-d_1)chloride (6b-d_1). 4 mL of a THF solution of hept-6-en-1-yl-1-d_1-magnesium chloride (1,25g, 7.9 mmole) were added dropwise to a suspension of 1.99 g (8.0 mmole) of titanocene dichloride in 50 mL of dichloromethane at -30°C. The mixture was allowed to warm up to -5°C (2 h) and the solvents were removed under vacuum. The residue was washed with pentane repeatedly (5X25 mL) and the solution was filtered through celite. After concentrating the solution to about 30% of its original volume, it was cooled to -50°C. The product was recovered as dark-red crystals (550 mg) on top of a dark-red semi-solid (650 mg). The latter was shown to be impure $\underline{6b\text{-}d_1}$ by ^{1}H-NMR spectroscopy. After removing *in vacuo* the excess solvent from each fraction, they were saved in separate vials at -40°C. Yield: ca.1.2 g (48%). ^{2}H-NMR (C_6H_6), shift relative to $C_6D_5CD_3$ at δ6.99: δ1.57.

Reaction of 6a with ethylaluminum dichloride. 10 mg of *6a* (32 µmole) were dissolved in 1 mL of toluene (solution A). In a separate Schlenk tube, 40 mg (320 µmole) of ethylaluminum dichloride were dissolved in 1 mL of toluene (solution B). Both solutions were then cooled down to 0°C. The solutions were rapidly mixed *via* syringe (the order of addition is not important) and the brown-green mixture was allowed to react for ca. 20 sec, after which a mixture of HCl conc./methanol=1/1 was added at once to hydrolyze the organometallic species in solution. After removing the acidic aqueous layer, the toluene solution was treated with 10% NaOH (aq.) until basic, and then the organic layer was separated and dried with anhydrous sodium sulfate. The organic products were then analyzed by gas chromatography. It was found that by cooling the solution to -40°C before hydrolysis helped to avoid losing the volatile organic products because of the highly exothermic reaction that takes place with the $EtAlCl_2$.

Reaction of 6b with ethylaluminum dichloride. A similar procedure to the one described for 6a was followed.

Polymerization of ethylene using 6a and ethylaluminum dichloride. A solution of 6a (31 mg, 0.1 mmole) in toluene (5 mL) was saturated with ethylene at 0°C (solution A). Separately, ethylaluminum dichloride (127 mg, 1 mmole) was dissolved in 5 mL of toluene, and the solution was also saturated with ethylene at 0°C (solution B). Solution A was added rapidly (<1 sec) to the vigorously stirred solution B. The dark green-brown solution was treated with a 1:1 mixture of HCl conc./MeOH after ca. 15 sec of beginning the reaction. After removing the acidic aqueous layer, the orange colored toluene solution was basified with a 10% NaOH aqueous solution. The organic layer was then separated and dried with anhydrous sodium sulfate and the clear solution was concentrated ca. 20-fold to obtain a reasonable concentration of oligomers. The analysis was done by capillary GC. For this reaction only, a GC/MS analysis was performed.

Polymerization of ethylene using 6b and ethylaluminum dichloride. A similar procedure to the one described for 6a was followed.

Polymerization of ethylene using 6b-d_1 and ethylaluminum dichloride. A similar procedure to the one described for 6a was followed. The mixture was then separated into two fractions: volatiles and residue (oligomers) which were analyzed by capillary GC and ^{2}H-NMR.

Reaction of 6b-d_1 with ethylaluminum dichloride. For this reaction, slightly more concentrated solutions were used to simplify the separation of the final organic product. 6b-d_1 (105 mg, 0.34 mmole) was dissolved in 2 mL of toluene (solution A). Ethylaluminum dichloride (420 mg, 3.31 mmole) was dissolved in 2 mL of toluene in a separate Schlenk tube (solution B). Both solutions were cooled down to 0°C. Solution B was added rapidly to solution A, and the mixture color turned dark green immediately. To insure complete cyclization, the solution was vigorously stirred for 60 sec before hydrolysis with HCl conc. CAUTION: because the solution is very concentrated in ethylaluminum dichloride, a highly exothermic reaction occurs; to avoid loss of material it is recommended to cool the mixture below -40°C before the HCl is added. The semi-jellified mixture resulting after the hydrolysis was immersed in an ice-bath and was treated with 2 mL of water to separate the organic layer, which was further washed with 10 mL of water and then 10 mL of a 15% NaOH (aq.) solution. It was finally dried with a small amount of anhydrous sodium sulfate. A GC trace showed methylcyclohexane as the major product of the reaction. It was separated from the solvent by preparative GC and it was redissolved in a small amount of toluene (400 µL) to which 1 µL of C_6D_6 had been added as internal reference. The sample was then analyzed by ^{2}H-NMR.

Low temperature reaction of 6a with ethylaluminum dichloride. A NMR tube was loaded with 6a (30 mg, 0.10 mmole) and 400 µL of toluene-d_8. The red solution was cooled down to -80°C. Separately, $EtAlCl_2$ (14 mg, 0.11 mmole, ca. 1 equiv) was dissolved in 300 µL of toluene-d_8

and the solution was cooled to -40^{o}C (below that temperature it crystallizes). While keeping the solution of 6a at -80^{o}C, the cold $EtAlCl_2$ solution was rapidly added to it via microsyringe through the rubber septum on the NMR tube. The solution turned dark red-brown (cf. with brown-green solutions formed at 0^{o}C). The tube was rapidly placed in the -80^{o}C NMR probe and both ^{1}H- and ^{13}C-NMR spectra were recorded. Afterwards, a -30^{o}C solution of 2,2'-bipyridine (17 mg, 0.11 mmole, 1 equiv/Al) in toluene-d_8 (200 μL) was added to the above mixture, which was kept at -80^{o}C. There was no noticeable change in the solution color. ^{1}H- and ^{13}C-NMR spectra were recorded and then the mixture was warmed up to room temperature, and another set of ^{1}H- and ^{13}C-NMR spectra were obtained. The oily Al:bipy adduct precipitates and does not interfere with the analysis. After removing said adduct, the solution was separated into two fractions: a) volatiles, which were analyzed by GC (methylcyclopentane, present; 1-hexene, absent); b) red residue, analyzed by ^{1}H-NMR (vinyl protons absent) and GC of hydrolysis products (methylcylclopentane, present; 1-hexene, absent).

Low temperature reaction of 6b with ethylaluminum dichloride. A NMR tube was loaded with 6b (80 mg, 0.27 mmole) and 350 μL of toluene-d_8. The red solution was cooled to -80^{o}C and a -40^{o}C solution formed by dissolving $EtAlCl_2$ (32.5 mg, 0.26 mmole, ca. 1 equiv) in 200 μL of toluene-d_8 was rapidly added to it. The sample was then placed in the -80^{o}C NMR probe. The solution was dark green-brown and the ^{1}H-NMR spectrum recorded at that temperature was extremely broad. The probe temperature was increased to -70^{o}C, but the ^{1}H-NMR spectrum obtained was still broad, so a -30°C solution of 2,2'-bipyridine (42 mg, 0.27 mmole, 1 equiv/Al) in toluene-d_8 (200 μL) was added. The solution turned dark red immediately. However, broadening of spectra persisted up to -20°C, so the sample was warmed up to room temperature and both ^{1}H- and ^{13}C-NMR spectra were recorded.

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9. Titanocene(dodecyl)chloride was synthesized for other experiments according to the method described by Waters[8]: ^{1}H-NMR (C_6D_6), shifts relative to C_6D_5H at δ7.15: δ0.9(dist. t,3H, $C\underline{H}_3$), 1.33 (br m,20H, -$C\underline{H}_2$-), 1.62(dist t,2H, Ti-$C\underline{H}_2$-), 5,82(s,10H, Cp's); ^{13}C(H)-NMR (C_6D_6), shifts relative to $\underline{C}_6D_6$ at δ128.0: δ14.4(C_{12}), 23.1(C_{11}), 29.8(C_9), 30.3($C_{4,5,6,7,8}$), 32.3(C_{10}), 35.6(C_3), 38.2 (C_2), 73.2(C_1), 115.7(Cp's); UV (hexane), $\lambda_{max}(\varepsilon)$: 230(27,100), 255(sh), 426(433), 500(sh).

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14. If the cyclization occurs through the insertion of the double bond via a Cossee-type mechanism, it is well known that such process is irreversible for Ziegler-Natta catalysts. If on the other hand the cyclization was occurring via a radical mechanism, it is also known that the methylcyclopentyl radical will not revert to the starting 1-hexenyl radical.[20d]

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18\. Some of these signals may be due to the primary complex generated between the reaction of the titanocene(alkenyl)chloride and $EtAlCl_2$.[12b]

19\. A similar experiment was also done with Cp_2Ti(neopentyl)chloride and $EtAlCl_2$ at -50°C. The dark green solution formed upon mixing the reagents was allowed to react for 1 h at -50°C; then 1 equiv bipy/Al was added to the mixture. After separating the oily Al:bipy adduct, a ^{1}H-NMR spectrum of the red-violet solution showed the presence of the starting Cp_2Ti(neopentyl)chloride but no $Cp_2Ti(Et)Cl$ was detected because alkyl exchange did not occur.

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