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Pressure Modulates Stereoregularities in the Polymerization of Propylene Promoted by *rac*-Octahedral Heteroallylic Complexes

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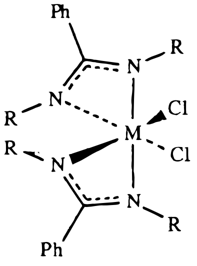
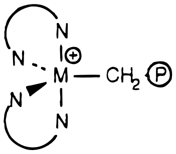
Summary: This communication reports the synthesis and activity of four racemic mixtures of bis(benzamidinate) group-4 complexes, cis-$[p\text{-}R'C_6H_4C(NR)_2]_2MX_2$ *(*$R' = CH_3$, $R = SiMe_3$, $M = Ti$, $X = Cl$ *(**1**);* $R' = CH_3$, $R = SiMe_3$, $M = Zr$, $X = Cl$ *(**2**);* $R' = H$, $R = i\text{-}pr$, $M = Zr$, $X = Cl$ *(**3**);* $R' = CH_3$, $R = SiMe_3$, $M = Zr$, $X = CH_3$ *(**4**)) as precatalysts for the stereoregular polymerization of propylene. These complexes catalyze the stereoregular polymerization of propylene only under pressure in* CH_2Cl_2*, producing polypropylene with very large isotacticities (mmmm % = ∼95−98), high melting points (140−154 °C).*

During the past decade an enormous advancement has been made in the design and synthesis of well-defined or "single-site" catalysts for the polymerization of olefins.[1−5] The majority of these catalysts belong to the metallocene ensemble, although some are known that contain one cyclopentadienyl ring and (for example) a pendant amido ligand.[6−8] Recently, however, complexes containing only chelating dialkoxide,[9−11] chelating diamido,[12−15] or chelating benzamidine[16−20] ancillary ligands have received attention as potential Ziegler−Natta catalysts. Previously, we and others have investigated the α-olefin polymerization chemistry catalyzed by several chelating bis(benzamidinate) complexes of group 4. The bis(benzamidinate) dichloride group 4 complexes (**A**) are obtained as a mixture of the racemic C_2-symmetry *cis*-octahedral structures, and when activated with methyl alumoxane (MAO), these complexes were found to be active catalytic precursors for the polymerization of ethylene, propylene, and the oligomerization of 1,5-hexadiene.[16,21,22]



A



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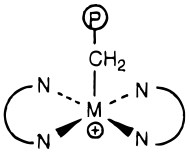

C

Interestingly, for propylene, performing the polymerization at atmospheric pressure produced polypropylene as an atactic oil, despite the expected isotactic polymer.[22,23] The resulting atactic polypropylene can be accounted for by two plausible mechanisms: (1) a "cationic" five-coordinated trigonal-bypyramid (**B**) or square-planar-pyramid intermediate (**C**) is formed, as the active complex, with no stereo-differentiation at the propene insertion;[24−26] (2) an intramolecular epimerization reaction of the growing polypropylene chain at the last-inserted monomeric unit is faster than the stereoregular insertion of propene (Scheme 1, vide infra).[27−29]

In this paper, we report the synthesis and characterization of non-Cp, racemic bis(benzamidinate) cationic

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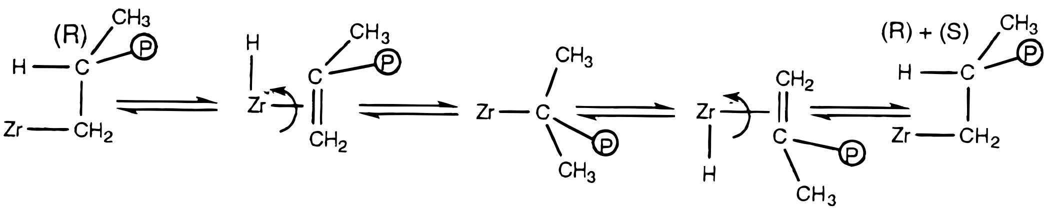
Scheme 1



I

octahedral complexes as new catalytic systems for the highly stereoregular polymerization of propylene, which can be modulated by pressure. To our knowledge, this is the first example when the stereoregular polymerization of an α-olefin catalyzed by early-transition-metal octahedral complexes is modulated by pressure (from atactic to isotactic through elastomers).[30−32]

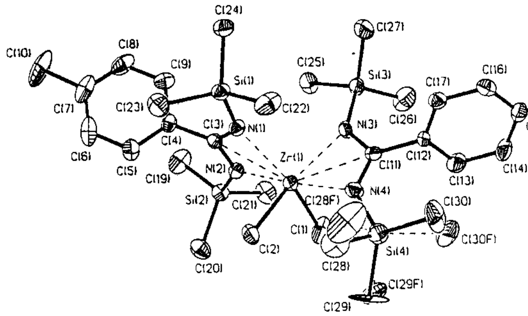
Reactions of $TiCl_4(THF)_2$ and $ZrCl_4(THF)_2$ with 2 equiv of $Li[p\text{-}R'C_6H_4C(NSiMe_3)_2]\cdot TMEDA$ (TMEDA = tetramethylethylenediamine) or $Li[C_6H_5C(NCH(CH_3)_2)_2]\cdot TMEDA$, respectively, afforded the disubstituted dichloro complexes **1**−**3** as orange (M = Ti) or yellow (M = Zr) crystalline solids (eq 1). The addition of 2 equiv of MeLi·LiBr to complex **2** in toluene at −78 °C yield the dimethyl complex **4** in 95% yield (eq 2). An X-ray study

$$2\ Li[p\text{-}R'C_6H_4C(NR)_2]\bullet TMEDA + MCl_4\bullet (THF)_2 \xrightarrow[\text{-2 LiCl, - TMEDA}]{\text{THF}} cis\text{-}[p\text{-}R'C_6H_4C(NR)_2]_2MCl_2 \quad (1)$$

1-3

1 M = Ti; R' = Me; R = $SiMe_3$
2 M = Zr; R' = Me; R = $SiMe_3$
3 M = Zr; R' = H; R = $CH(CH_3)_2$

$$\mathbf{2} \xrightarrow[\text{- 2 LiCl}]{\text{2 MeLi} \bullet \text{LiBr}}$$



(2)

4

of **4** shows that the central Zr atom is octahedrally surrounded by two chelating benzamidinate ligands and two terminal methyl groups. One carbon atom from the methyl group (C(1)) and one nitrogen atom of a chelate unit (N(1)) are in the axial positions, while the second C(2) atom and the remaining nitrogen atoms occupy the equatorial positions, producing a C_2-symmetric complex. As a result, the C−N bond lengths of the two chelate units are slightly different (1.32 and 1.34 Å). The Zr−N(1) to Zr−N(4) distances of 2.227, 2.320, 2.234, and 2.295 Å, respectively, are somewhat longer than in the dimeric zirconium benzamidinate $[C_6H_5C(NSiMe_3)_2ZrCl_3]_2$ (2.14 and 2.19 Å),[33] although similar to the monomeric complexes $C_6H_5C(NSiMe_3)_2ZrCl_2$ (2.20 and 2.24 Å)[16] and $C_6H_5C(NSiMe_3)_2ZrMe_2$ (2.24 and 2.31 Å).[22]

Special attention is given to the large torsion angle between the two planar $ZrCN_2$ rings, which are almost perpendicular with respect to each other (89.8°). This situation obviously minimizes repulsion between the bulky trimethylsilyl groups in the molecule.[23] Addition of $B(C_6F_5)_3$ to complex **4** in toluene-d_8 at room temperature yields a bright yellow solution. ^{13}C NMR spectra suggest that a cationic product is formed quantitatively, in which the methyl groups and the benzamidinate groups are inequivalent.[34] Noteworthy is the large downfield chemical shift change observed for the Zr−methyl group (44.6 ppm in the starting complex as compared to 62.3 ppm for the cationic complex), similar to those chemical shift changes obtained in cyclopentadienyl systems.[35−39] In the absence of excess monomer, attempts to spectroscopically identify the catalytically active species have been thwarted by the extreme reactivity of the catalytic system with chlorinated or aromatic solvents.

The elucidation of which of the two plausible mechanisms is responsible for the production of an atactic polypropylene was achieved by performing the reactions under pressure. For the first mechanism, no or small changes in the stereoregularity of the polymer would be predicted, respectively, whereas for the second mechanism a highly isotactic polymer would be expected. A summary of the polymerization results is shown in Table 1. The catalytic systems generate polymers with molecular weights similar to those obtained with chiral cyclopentadienyl systems, at the corresponding temperatures, with high stereoregularities and melting points. ^{13}C NMR analysis of the polymer-chain ends shows that the β-methyl transfer is the exclusive termination chain

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Table 1. Activity, Molecular Weight, and Melting Point Data for the Polymerization of Propylene by Bis(benzamidinate) Group 4 Complexes

entry	*T*, °C	catalyst	Al:M[a] ratio	solvent	pressure, atm	activity[b]	M_v[c]	mmmm %	mp, °C
1	25	**1**	400	CH_2Cl_2	7.2	1.1×10^4		57.0	120.4[e]
2	25	**3**	400	toluene	7.2	2.0×10^3 [d]	42 161	96.6	148.7
3	60	**3**	400	toluene	10.1	2.1×10^3 [d]	41 879	96.0	141.9
4	0	**3**	400	CH_2Cl_2	5.1	3.9×10^3	34 489	97.5	153.6
5	25	**3**	400	CH_2Cl_2	7.2	4.7×10^3	28 570	97.9	150.5
6	60	**3**	400	CH_2Cl_2	10.1	1.1×10^3	20 300	97.4	145.8
7	25	**3**	200	CH_2Cl_2	7.2	2.7×10^3	87 400	98.3	145.7
8	25	**4**	250	toluene	7.2	1.2×10^3	17 500	82.5	130.6[e]
9	0	**4**	250	CH_2Cl_2	5.1	1.3×10^3	39 000	58.5	151.4
10	25	**4**	250	CH_2Cl_2	7.2	2.4×10^4	26 740	92.3	146.5
11	50	**4**	250	CH_2Cl_2	10.1	1.9×10^5	22 670	96.3	138.7
12	25	**4**	400	CH_2Cl_2	7.2	8.2×10^4	42 470	95.5	147.6
13	25	**4**	1000	CH_2Cl_2	7.2	8.6×10^4	14 200	97.2	149.9
14	25	**4**	$B(C_6F_5)_3$	CH_2Cl_2	7.2	2.8×10^3	26 103	90.0	148.5

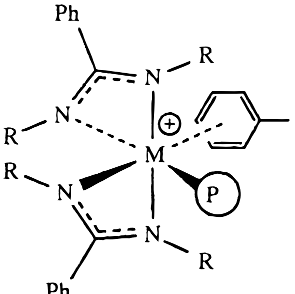
[a] Methylaluminoxane, solvent removed from a 20% solution in toluene (Schering) at 25 °C /10^{-6} Torr. [b] Grams of total polymer/mole of Zr·h. [c] By viscosimeter technique in 1,2,4-trichlorobenzene at 130 °C ($K = 1.37 \times 10^{-2}$; $\alpha = 0.7$). [d] An additional low molecular weight oily fraction was separated from the solid. [e] The polypropylene is obtained as an elastomer (Tg).

mechanism for these catalytic systems at either atmospheric or high pressure.[34,40]

This result is also in agreement with the epimerization mechanism (Scheme 1), which shows no intermediate detachment of the growing polymer chain (β-H elimination) from the Zr atom (the insertion of the Zr−H into the Zr−vinylidene complex is much faster as compared to the β-methyl transfer).[27−29]

An additional corroboration that the mechanism presented in Scheme 1 is responsible for the stereodefects in polypropylene obtained by C_2-symmetric octahedral complexes was obtained by reacting catalyst **2** with MAO and 1-octene. Since the polymerization rate is extremely low, a β-hydrogen elimination is expected to occur either from each of the methyl groups at the α-position in complex **I** (Scheme 1), causing no change in the alkene, or from the α-position at the chain, inducing the isomerization of the double bond. Thus, 1-octene was isomerized to a mixture of (*E*)-2-octene (25%), (*Z*)-2-octene (15%), (*E*)-3-octene (40%), and *trans*-4-octene (18%), giving strong evidence for the formation of the intermediate complex **I**.[41]

For complex **4**, a noticeable increase in activity, stereoregularity and hence melting points is observed for the polymerization performed in CH_2Cl_2 (compare entries 8 and 10). The polarity of CH_2Cl_2 may result in greater charge separation between the putative cationic benzamidinate alkyl complex and the MAO anion. This result argues for a competitive bonding of toluene to the cationic group 4 complex (**D**), impeding the insertion of the monomer (lowering the catalytic activity) though allowing the epimerization of the growing chain.



D

These types of interactions are possible given the low coordination number of these benzamidinate complexes and the spectroscopic observation of other group 4 and actinide cationic η^6-toluene complexes.[42−46] It is noteworthy to point out that the polypropylene obtained with complex **1** (entry 1) or other complexes[47] is obtained as an elastomer,[48] arguing for similar insertion and epimerization kinetics.

In summary, a new catalytic system for the highly stereoregular polymerization of α-olefins at high pressure and at room temperature or high temperatures has been introduced. The polymer stereoregularities can be modulated by pressure, allowing the formation of highly isotactic or elastomeric polymers. The large variety of readily synthesized heteroallylic, pentadienyl, or heteropentadienyl ligands are attractive incentives for the development of new octahedral catalysts for highly stereoregular or elastomeric types of materials.

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Supporting Information Available: Text giving the experimental procedures, tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates, and an ORTEP diagram for complex **4** (17 pages). Ordering information is given on any current masthead page.

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