$B(OH)_2$ was dissolved in ca. 200 mL of warm 3:1 THF/EtOH and concentrated to about 20 mL before using. The reaction mixture was heated for 6 h, during which a white precipitate formed. The white precipitate was isolated by filtration and extracted with hot CH_2Cl_2 followed by hot toluene, yielding a white powder weighing 0.98 g (69%): mp 415–422 °C; mass spectrum (EI) m/z 1302/1303. (1.0/0.64). Anal. Calcd for $C_{60}H_{12}F_{30}$: C, 55.32; H, 0.93; F, 43.76. Found: C, 54.30; H, 0.81; F, 45.08.

7F-TMS. This compound was synthesized using procedure A with 7.09 g (15.6 mmol) of **3F-B(OH)$_2$**, 2.85 g (7.09 mmol) of **1**, 0.49 g (0.42 mmol) of $Pd(PPh_3)_4$, 3.5 mL of 2 M Na_2CO_3, and 90 mL of 2:1 THF-EtOH/toluene. The reaction mixture was refluxed for 2 days and worked up by dilution with CH_2Cl_2 and H_2O. The aqueous and organic phases were separated, and the aqueous phase was washed with CH_2Cl_2. The organic phases were combined, washed with brine, dried over $MgSO_4$, and concentrated. The crude brown solid was chromatographed on 250 g of silica gel using hexane as the eluant. The resulting white solid was recrystallized from EtOAc/EtOH, yielding 6.85 g (75%): mp 198–202 °C; ^1H NMR ($CDCl_3$) δ 7.75 (bs, 7 H), 7.51 (bs, 2 H), 0.37 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 144.2 (d, J = 144 Hz), 142.7, 140.8 (d, J = 261 Hz), 139.8, 138.0 (d, J = 251 Hz), 132.1, 130.7, 130.1, 127.7, 127.1, 114.9 (t, J = 19 Hz), −1.10. Anal. Calcd for $C_{45}H_{18}F_{20}Si$: C, 55.91; H, 1.88; F, 39.31; Si, 2.91. Found: C, 55.85; H, 1.68; F, 38.96; Si, 3.22.

22F. This compound was synthesized using procedure A with 2.00 g (4.41 mmol) of **3F-B(OH)$_2$**, 0.429 g (0.55 mmol) of **4-Br$_6$**, 75 mg (0.065 mmol) of $Pd(PPh_3)_4$, 2 mL of 2 M Na_2CO_3, and 30 mL of 2:1 THF-EtOH/toluene. The reaction mixture was heated for 20 h, and the resulting mixture was worked up as above. The crude product (2.01 g) was chromatographed on 100 g of silica gel, beginning with 1:1 CCl_4/hexane and gradually changing to 2:1 CCl_4/hexane. The resulting white solid (1.04 g 68%) was analytically pure after pumping on it to remove traces of volatiles: mp 357–359 °C; ^1H NMR ($CDCl_3$) δ 7.96 (s, 3 H), 7.91 (d, J = 1.5 Hz, 6 H), 7.83 (t, J = 1.5 Hz, 3 H), 7.81 (bs, 12 H), 7.53 (bs, 6 H); ^{13}C NMR ($CDCl_3$) δ 144.2 (d, J = 248 Hz), 142.8, 142.0, 141.5, 140.9 (d, J = 273 Hz), 138.0 (d, J = 260 Hz), 131.1, 130.0, 127.9, 126.5, 126.1. Anal. Calcd for $C_{132}H_{30}H_{30}F_{60}$: C, 57.53; H, 1.10; F, 41.37. Found: C, 57.24; H, 1.26; F, 41.02.

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Registry No. 1, 17878-23-8; **3-TMS**, 128388-53-4; **3-B(OH)$_2$**, 128388-54-5; **3F-TMS**, 137897-05-3; **3F-B(OH)$_2$**, 137915-47-0; **4F**, 61371-30-0; **4-Br$_6$**, 29102-67-8; **7-TMS**, 128388-55-6; **7-B(OH)$_2$**, 128388-56-7; **7-B(OH)$_2$** (homopolymer), 137897-11-1; **10**, 137897-08-6; **10F**, 137897-06-4; **22**, 137897-09-7; **22F**, 137897-07-5; $PhB(OH)_2$, 98-80-6; $Pd(PPh_3)_4$, 14221-01-3; C_6F_5Br, 344-04-7; 1,3,5-tribromobenzene, 626-39-1; 3,5-dibromoacetylbenzene, 14401-73-1; N,N-dimethylacetamide, 127-19-5.

Olefin Polymerization at Bis(pentamethylcyclopentadienyl)zirconium and -hafnium Centers: Chain-Transfer Mechanisms

Luigi Resconi,*,† Fabrizio Piemontesi,† Giuseppe Franciscono,† Luigi Abis,‡ and Tiziana Fiorani‡

Contribution from the HIMONT Italia S.r.l., via Caduti del lavoro, 28100 Novara, Italy, and Istituto G. Donegani, via Fauser 4, 28100 Novara, Italy. *Received June 5, 1991*

Abstract: Chain transfer via β-CH_3 elimination by a homogeneous bimetallic Ziegler–Natta propylene polymerization catalyst is reported. Propylene is converted by $Cp^*_2MCl_2$/MAO catalysts (Cp^* = pentamethylcyclopentadienyl; M = Zr, Hf; MAO = methylalumoxane) to atactic propylene oligomers and low polymers. GC–MS and ^1H and ^{13}C NMR analyses of the oligomers obtained at 50 °C ($\bar{P}_n \approx 4.5$ for Zr, 3.4 for Hf) show these products to be mainly allyl- and isobutyl-terminated (1/1 ratio). The allyl/vinylidene ratio is 92/8 for Zr and 98/2 for Hf. No other unsaturated end groups could be detected. This end group structure is produced by first monomer insertion into the M–CH_3 bond and then chain transfer by β-CH_3 elimination. On the contrary, $Cp^*_2MCl_2$/MAO promotes 1-butene polymerization with the chain transfer being exclusively β-H elimination and transfer to Al: no β-ethyl elimination could be detected. The behavior of these catalysts toward propylene and 1-butene is compared with known Cp_2MCl_2/MAO catalysts.

Introduction

Homogeneous olefin polymerization by means of group 4 metallocene–methylalumoxane[1] systems is undoubtedly the most versatile route to polymers with controlled structures: the broad electronic and steric variability of Cp-type ligands allows the design of catalyst precursors that are able to direct the polyinsertion reaction to form regioregular (1,2 insertion[2]) and stereoregular (isotactic[3] or syndiotactic[4]) polyolefins with unprecedented selectivity. The present knowledge of the mechanistic details of the olefin insertion step has reached a high degree of accuracy thanks to extensive ^{13}C NMR analysis of the polymers, the use of model organometallic compounds, the elegant work of Grubbs[5] and Pino,[2c] and the calculations done by Corradini and Guerra.[6] The cationic nature of the active site, postulated as early as 1961,[7] has gained strong support from the synthesis of a now wide series of model cationic titanocene, zirconocene, and hafnocene alkyls and the proven ability of some of them to polymerize olefins in the absence of any added cocatalyst.[8]

Chain transfer normally occurs via facile β-H elimination,[9] which is the main reason for the much lower molecular weights

† HIMONT Italia.
‡ Istituto G. Donegani.

(1) Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390–392. For an early review, see also: Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 137–149.

(2) 1,2 insertion has been proved for a wide enough range of catalyst precursors that it can be assumed to be the normal insertion mode in this class of catalyst systems: (a) Ewen, J. *J. Am. Chem. Soc.* **1984**, *106*, 6355–6364. (b) Zambelli, A.; Ammendola, P.; Grassi, A.; Longo, P.; Proto, A. *Macromolecules* **1986**, *19*, 2703–2706. (c) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189–6191. (d) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*, 428–431. Isolated 2,1 propylene units (ca. 1%) have been so far detected only in isotactic polypropylenes prepared with ethylene bis-indenyl- or tetrahydroindenylzirconium dichlorides.[2e,f] (e) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617–622. (f) Cheng, H.; Ewen, J. *Makromol. Chem.* **1989**, *190*, 1931–1943.

(3) Ewen was the first to show that chiral stereorigid metallocenes can produce isotactic polypropylene by enantiomorphic site control.[2a] This breakthrough idea has been successfully developed into highly active polymerization catalysts:[3a–e] (a) Kaminsky, W.; Külper, K.; Brintzinger, H.; Wild, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507–508. (b) Ewen, J.; Haspeslagh, L.; Atwood, J.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544–6545. (c) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1989**, 1853–1856. (d) Herrmann, W.; Rohrmann, J.; Herdtweck, E.; Spaleck, W.; Winter, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1511–1512. (e) Röll, W.; Brintzinger, H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279–280.

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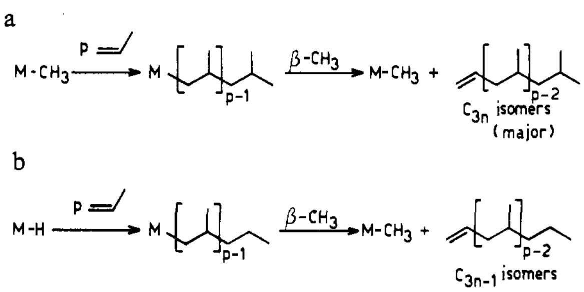
Table I. Propylene Polymerization[a]

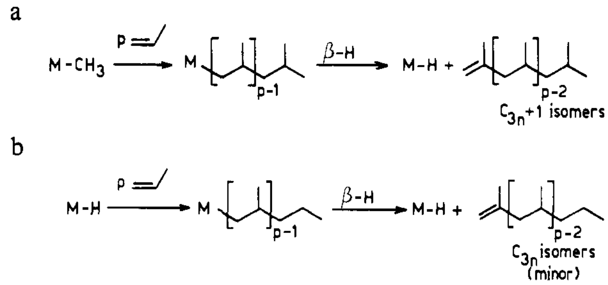
sample	metallocene, μmol	Al, mmol[b]	T, °C	t, h	yield, g	g/mmol·h
PP1	Cp_2ZrCl_2, 5.8	8.6	50	1	32.8	5655
PP2	Cp_2ZrCl_2, 6.9	8.6	0	4	22.9	830
PP3	Cp_2HfCl_2, 5.8	8.3	50	1	26.5	4570
PP4	Cp_2HfCl_2, 6.8	8.4	0	4	0.4	15
PP5	$Cp^*_2ZrCl_2$, 5.8	9.1	50	1	20.7	3570
PP6	$Cp^*_2ZrCl_2$, 11.4	9.3	0	4	20.5	450
PP7	$Cp^*_2HfCl_2$, 5.8	8.7	50	1	73.2	12620
PP8	$Cp^*_2HfCl_2$, 11.6	8.7	0	4	76.1	1640
PP9[c]	Cp_2ZrCl_2, 35.4	17.2	−50	4	3.0	20
PP10[c]	$Cp^*_2ZrCl_2$, 34.6	21.5	−40	4	0.1	1

[a] Polymerization conditions: Büchi 1-L stainless steel autoclave. Propylene, 300 g. [b] MAO Schering, solid powder. [c] Glass autoclave, 1/1 toluene/propylene.

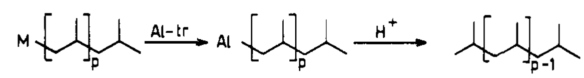
Scheme I



Scheme II



Scheme III



of the produced polymers, when a comparison with heterogeneous catalysts is made. Chain transfer to aluminum has also been detected as a minor chain-transfer mechanism.[10] Recently, Teuben[11] and ourselves[12] found that a different chain-transfer mechanism, namely, β-CH_3 elimination, becomes viable and is actually the most important mechanism in propylene polymerization when $Cp^*_2M^{IV}$-type complexes (Cp^* = pentamethylcyclopentadienyl; M = Zr, Hf) are used as catalyst precursors.[13-18]

Trying to evaluate the generality of this new (for group 4 metallocene alkyls) chain-transfer mechanism, we set out to study

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(7) Zefirova, A.; Shilov, A. *Dokl. Akad. Nauk SSSR* **1961**, *136*, 599. Dyachkovskii, F.; Shilova, A.; Shilov, A. *J. Polym. Sci. Part C* **1967**, *16*, 2333–2339.

(8) (a) Eisch, J.; Piotrowski, A.; Brownstein, S.; Gabe, E.; Lee, F. *J. Am. Chem. Soc.* **1985**, *107*, 7219–7221. (b) Jordan, R.; Bajgur, C.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410–7411. (c) Jordan, R. *J. Chem. Educ.* **1988**, *65*, 285–289 and references therein. (d) Taube, R.; Krukowka, L. *J. Organomet. Chem.* **1988**, *347*, C9–C11. (e) Hlatky, G.; Turner, H.; Eckman, R. *J. Am. Chem. Soc.* **1989**, *111*, 2728–2729. (f) Turner, H., Exxon. Eur. Pat. 0,277,004, 1988. (g) Bochmann, M.; Jaggar, A.; Nicholls, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780–782. (h) Xinmin, Y.; Stern, C.; Marks, T. *J. Am. Chem. Soc.* **1991**, *113*, 3623–3625.

(9) See for example: Kaminsky, W.; Ahlers, A.; Möller-Lindenhof, N. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1216–1218.

(10) Chien, J.; Wang, B. J. *Polym. Sci. Polym. Chem. Educ.* **1990**, *28*, 15–38. Resconi, L.; Bossi, S.; Abis, L. *Macromolecules* **1990**, *23*, 4489–4491.

(11) Eshuis, J.; Tan, Y.; Teuben, J.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277–287.

(12) Resconi, L.; Giannini, U.; Albizzati, E.; Piemontesi, F.; Fiorani, T. *ACS Polym. Prepr.* **1991**, *32(1)*, 463–464.

(13) Propylene polymerization with $Cp^*_2ZrCl_2$/MAO had been briefly investigated by Kaminsky,[14] who obtained a low molecular weight, atactic product. More recently, Watanabe et al.[15] disclosed the formation of 4-methyl-1-pentene and higher *vinyl-terminated* oligomers with both $Cp^*_2ZrCl_2$/MAO and $Cp^*_2HfCl_2$/MAO. Before the very recent findings by Teuben[11] and ourselves[12] that chain termination in propylene oligomerization at Cp^*_2M sites is due almost exclusively to β-CH_3 elimination,[16] both the low molecular weight and end group structure of the products were unexpected.[17]

(14) Kaminsky, W.; Külper, K.; Niedoba, S. *Makromol. Chem., Macromol. Symp.* **1986**, *3*, 377–387.

(15) Watanabe, M.; Kuramoto, M.; Tani, N., Idemitsu Kosan. JP 01,207,248, 1989; *Chem. Abstr.* **1990**, *112*, 78185.

(16) β-Alkyl elimination at transition-metal centers in a catalytic cycle was previously known only for lutetium[16a] and scandium.[16b,c] Interestingly, allyl-terminated polypropylene obtained with $TiCl_3$–$AlEt_3$ at high temperature had been reported long time ago,[16d] but allyl group formation was ascribed to allylic activation. A theoretical evaluation of the enthalpy of different β-alkyl elimination processes at Cp^*_2Zr-alkyl intermediates has been proposed.[16e] β-Me transfer has been observed for unsolvated Cp_2ZrMe^+ in the gas phase.[16f] (a) Watson, P.; Roe, C. *J. Am. Chem. Soc.* **1982**, *104*, 6471–6473. (b) Bunel, E.; Burger, B.; Bercaw, J. *J. Am. Chem. Soc.* **1988**, *110*, 976–978. (c) Burger, B.; Thompson, M.; Cotter, D.; Bercaw, J. *J. Am. Chem. Soc.* **1990**, *112*, 1566–1577; see ref 40. (d) Longi, P.; Mazzanti, G.; Roggero, A.; Lachi, A. M. *Makromol. Chem.* **1963**, *61*, 63–68. (e) Schock, L.; Marks, T. *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715. (f) Christ, C.; Eyler, J.; Richardson, D. *J. Am. Chem. Soc.* **1990**, *112*, 596–607.

(17) As far as molecular weight is concerned, if β-H elimination were the main chain-transfer mechanism, as observed so far for a number of related systems, one would expect an increase in polymer molecular weight on increasing alkyl substitution at the (freely rotating) Cp ligand, due both to the energy of the conformation needed for β-H elimination, which grows higher with increasing steric bulk around the metal (see discussion on 1-butene polymerization), and the decrease in metal acidity when the latter is bound to the π-basic Cp^* ligand.[18] As a matter of fact, Ewen reported a more than 2-fold $\bar{M}_n$ increase on passing from Cp_2ZrCl_2 to $Cp^*CpZrCl_2$ in propylene polymerization (β-H elimination being the main chain-transfer process in both cases),[2a] and a similar effect in ethylene polymerization has been observed by Kaminsky, who found that both $Cp^*_2ZrCl_2$ and $Cp^*CpZrCl_2$ produce HDPE with a much higher molecular weight than Cp_2ZrCl_2.[14] On the other hand, the structure of unsaturated propylene oligomers (vinyl-terminated) reported in the patent literature[15] is incompatible with the usual sequence of 1,2 polyinsertion/β-H elimination processes (Scheme IIb) and, of course, with 1,2 polyinsertion/Al transfer, which produces only saturated end groups upon hydrolysis (Scheme III). From these findings, it became clear that a chain-transfer mechanism other than β-H elimination or transfer to aluminum must be at work when $Cp^*_2MCl_2$ catalyst precursors were employed for propylene polymerization.

(18) For a discussion on Cp^* basicity, see: Bordwell, F.; Bausch, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 6188–6189. Gassman, P.; Macomber, D.; Herschberger, J. *Organometallics* **1983**, *2*, 1470–1472. The mechanism of β-H elimination (β-hydride shift) involves an electron-deficient, Lewis acidic metal center. Bercaw's measurements of β-H elimination rates at Cp^*_2ScR complexes (isoelectronic with group 4 metallocene alkyl cations) show positive charge buildup in the transition state.[16c] It is reasonable that the same mechanism would be operative in the case of group 4 metallocenes. Thus, electron-releasing (π-basic) Cp^* ligands will disfavor the β-hydride shift due to diminished electrophilicity at M.

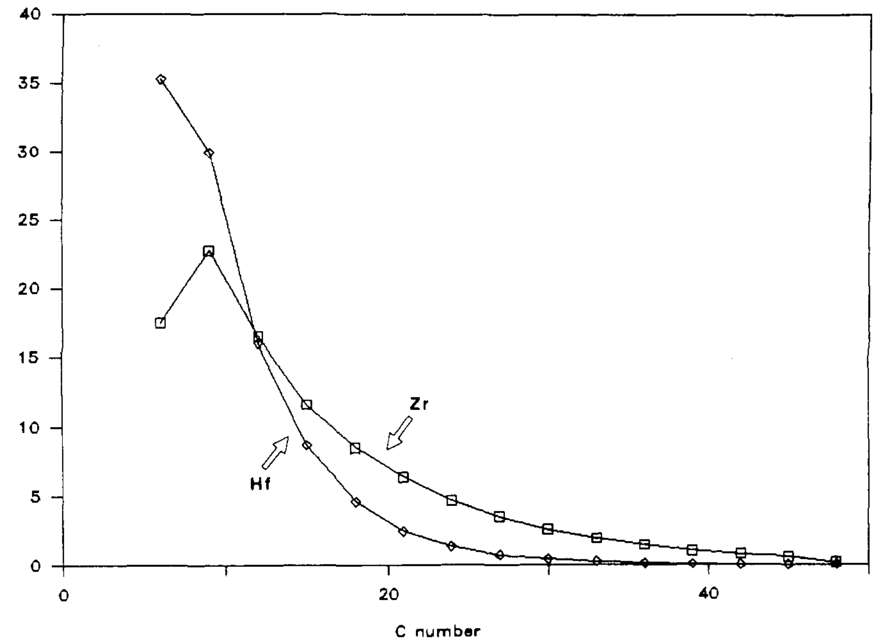


Figure 1. Experimental (GC) propylene oligomer distribution from $Cp^*_2ZrCl_2/MAO$ and $Cp^*_2HfCl_2/MAO$, 50 °C, liquid propylene.

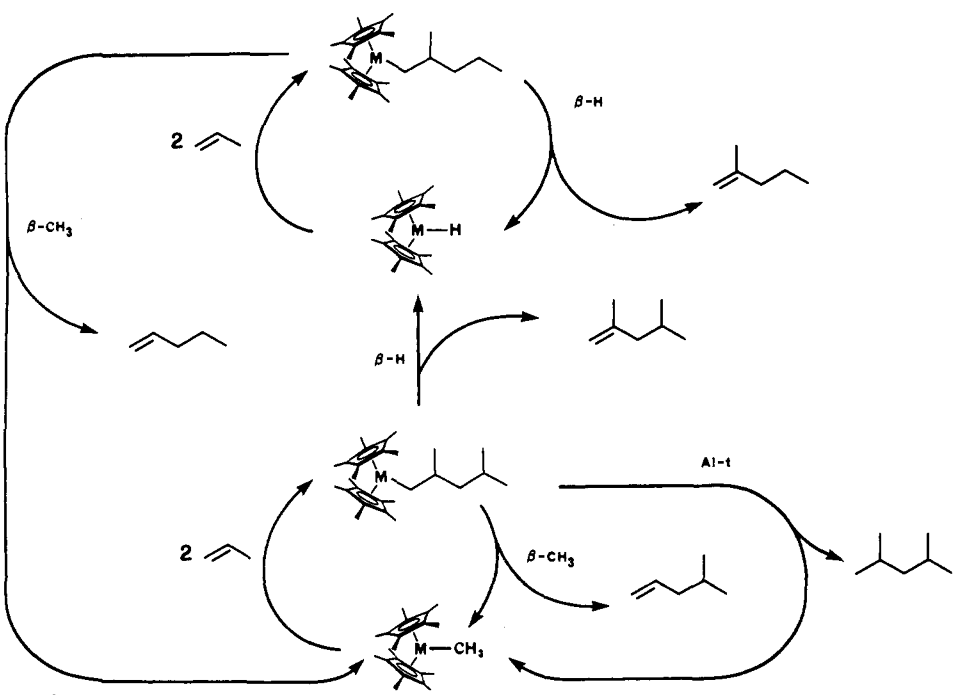


Figure 2. Catalytic cycles for propylene dimerization with $Cp^*_2MCl_2/MAO$ (M = Zr, Hf).

1-olefin polymerization with aspecific group 4 metallocenes in more detail. In this work we report on the different chain-transfer mechanisms operating in the polymerization of propylene and higher α-olefins with $Cp^*_2MCl_2/MAO$ (MAO = methylalumoxane) catalysts in comparison with Cp_2MCl_2/MAO (Cp = cyclopentadienyl) systems.

Results and Discussion

1. Propylene Polymerization. Propylene polymerization has been investigated at two different temperatures (0 and 50 °C) with four catalyst precursors (Cp_2ZrCl_2, Cp_2HfCl_2, $Cp^*_2ZrCl_2$, and $Cp^*_2HfCl_2$). To minimize monomer concentration effects, all polymerization tests have been carried out in liquid monomer at low monomer conversions. The physical consistency of samples obtained with Cp_2ZrCl_2 and Cp_2HfCl_2 ranges from viscous oils to sticky waxes, while samples obtained at 50 °C with $Cp^*_2ZrCl_2$ and $Cp^*_2HfCl_2$ are liquid and contain a considerable amount of distillable fractions. In addition, low-temperature polymerizations have been carried out with Cp_2ZrCl_2 (−50 °C) and $Cp^*_2ZrCl_2$ (−40 °C).[19] Polymerization data are reported in Table I.

A. GC–MS Analysis. Both samples PP5 ($Cp^*_2ZrCl_2/MAO$, 50 °C) and PP7 ($Cp^*_2HfCl_2/MAO$, 50 °C) consist of a mixture of oligomers from C_4 to C_{48}, enabling us to carry out a detailed GC–MS analysis.

In the dimer fraction, all detected isomers have been identified:[20] 1-pentene, 4-methyl-1-pentene, 2-methyl-1-pentene, 2,4-dimethylpentane, and 2,4-dimethyl-1-pentene, with 4-methyl-1-pentene being by far the major product in both samples. Trace

(19) $Cp^*_2ZrCl_2$ is inactive at −50 °C.

(20) The following compounds are listed in order of increasing GC retention times, MS m/e (relative intensities): 2-methyl-1-propene 56 ($M^{•+}$, 38), 55 (18), 41 (100), 39 (57); 1-pentene 70 ($M^{•+}$, 43), 55 (65), 42 (100), 41 (52), 39 (44); 4-methyl-1-pentene 84 ($M^{•+}$, 30), 69 (23), 56 (62), 43 (100), 42 (38), 41 (84), 39 (35); 2-methyl-1-pentene 84 ($M^{•+}$, 36), 69 (43), 56 (100), 55 (56), 41 (97), 39 (58), 29 (42); 2,4-dimethylpentane 100 ($M^{•+}$, 1), 85 (14), 57 (69), 56 (46), 43 (100), 42 (39), 41 (53), 39 (17); 2,4-dimethyl-1-pentene 98 ($M^{•+}$, 18), 83 (15), 70 (25), 56 (100), 55 (48), 43 (85), 41 (89), 39 (49); 4,6,8-trimethyl-1-nonene: 168 ($M^{•+}$, 0.1), 153 (0.2), 139 (0.2), 125 (6), 111 (13), 85 (31), 71 (69), 69 (46), 57 (76), 55 (28), 43 (100), 41 (70).

Table II. ^{13}C NMR Chemical Shifts of End Groups in Polypropylene

carbon[a]		end group[a]	chemical shift (configuration)[b] 1	2	3	4
PP1	Cp_2ZrCl_2	A	12.4_0		37.7_0, 37.9_3, 38.5_4, 38.7_2	28.3_6 (*r*), 28.4_5 (*m*)
		B	109.3_4	142.9_1, 142.8_3	20.5_6	
PP7[c]	$Cp^*_2HfCl_2$	C	20.5_9 (*m*), 20.7_7 (*r*)	23.6_9 (*r*), 23.7_4 (*m*)	21.4_7 (*r*), 21.6_8 (*m*)	46.1_8 (*rr*), 46.3_2 (*rm*)
		D	113.4_4	135.7_2	39.4_0 (*mm*), 39.6_0 (*mr*), 40.2_6 (*rr*), 40.4_5 (*rm*)	28.6_7 (*r*), 28.7_1 (*m*)

[a] Carbons labeled according to Scheme IV; δ HMDS = 0. [b] Configuration in terms of dyad (m, r) arrangement with next-neighbor unit. [c] Nondistillable fraction.

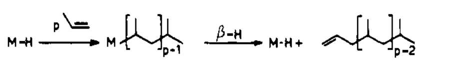
amounts of isobutene have also been detected. Unfortunately, given our experimental procedure (liquid propylene, low conversion), quantitative analysis of the dimers is spoiled by partial loss of the lower-boiling products. This problem is absent for higher fractions, for which GC peak separation allowed us to quantify both the molar fractions, χ_p, up to C_{48} (Figure 1) and, for each oligomerization degree p, the C_{3n}, C_{3n+1}, C_{3n-1} relative ratios up to C_{19}.

In these fractions, only the MS spectrum of 4,6,8-trimethyl-1-nonene[20] was found in a library of spectra. The remaining species have had their structures assigned on the basis of their molecular ions and fragmentation patterns (e.g., loss of ethyl in C_{3n-1}). Stereoisomer multiplicity is consistent with the following structure assignment: one isomer for $CH_2{=}CHCH_2CH(CH_3)CH_2CH(CH_3)_2$, $CH_2{=}C(CH_3)CH_2CH(CH_3)CH_2CH_2CH_3$, and $CH_2{=}C(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)_2$ ($CH_2{=}CHCH_2CH(CH_3)CH_2CH_2CH_3$ was hidden under the toluene peak), two for each of the tetramers, and four for each of the pentamers. In each group, diastereoisomers are thus present in the maximum theoretical number and in comparable amounts, as would be expected for aspecific propylene insertion into the M–C bond. Saturated oligomers are present in very low amounts (~1% for Zr, ~0.2% for Hf), thus showing transfer to Al to be negligible at 50 °C. Apparently, copolymerization of 4-methyl-1-pentene with propylene is rather limited, probably because of its lower reactivity and the very high propylene concentration.[21] The absence of other peaks indicates the absence of regioinverted propylene units, thus showing that insertion is highly regiospecific (see also NMR analysis).

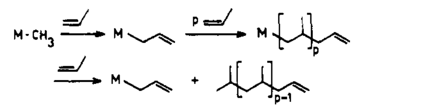
All of these findings are in agreement with the oligomerization mechanism being aspecific 1,2 insertion coupled with β-Me elimination as the main chain-transfer mechanism (Scheme I), with β-H elimination and Al transfer being minor pathways[11,12] (Schemes II and III). The catalytic cycles producing propylene dimers are sketched in Figure 2.[22,23]

(21) Smaller peaks with the same MS spectra as $CH_2{=}CHCH_2[CH(CH_3)CH_2]_2CH(CH_3)_2$ and $CH_2{=}CHCH_2[CH(CH_3)CH_2]_3CH(CH_3)_2$ but with lower retention times and peak multiplicity one-half (i.e., one and two respectively) have been detected. These amount to traces in the Zr system and to ~2% in the Hf system and have been tentatively assigned to the $CH_2{=}CHCH_2CH(iBu)CH_2CH(CH_3)_2$ and $CH_2{=}CHCH_2CH(iBu)CH_2CH(CH_3)CH_2CH(CH_3)_2$ species. The higher amount of these species in the Hf system is in accord with them being propylene–4-methyl-1-pentene co-oligomers: the higher activity of the Hf catalyst and the lower $\bar{P}_n$ of the produced mixture of oligomers both result in a higher concentration of 4-methyl-1-pentene, thus increasing the probability for its insertion. As a matter of fact, 4-methyl-1-pentene reacts with both $Cp^*_2ZrCl_2$/MAO and $Cp^*_2HfCl_2$/MAO in toluene to give oligomers in low yield; see text.

(22) In principle, two other mechanisms could explain both the low molecular weight and the presence of allylic groups, namely, 2,1 insertion/β-H elimination at the last methyl (mechanism 1) and 1,2 insertion allylic activation, as observed by Marks for propylene oligomerization at $Cp^*_2ThMe_2/MgCl_2$[23] (mechanism 2). Both mechanisms can be ruled out because they cannot account for the C_{3n-1} and C_{3n+1} isomers. In addition, allylic activation has been shown to produce inactive $Cp^*_2LuCH_2CH{=}CH_2$,[16a] and $Cp_2ZrCH_2CH{=}CH_2^+$ does not react with ethylene in the gas phase.[16f]



(1)



(2)

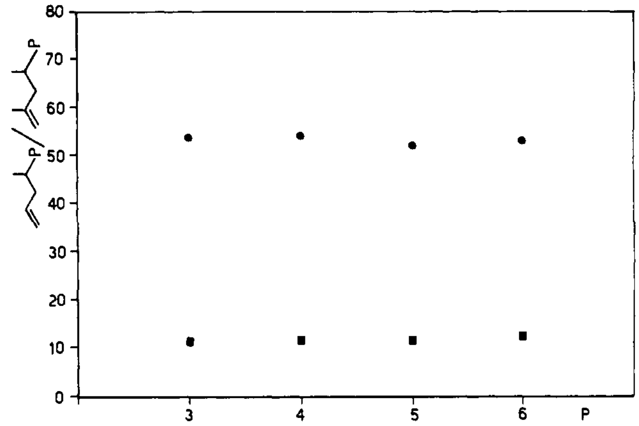


Figure 3. [Allyl]/[vinylidene] ratio vs degree of oligomerization p for propylene oligomers from $Cp^*_2ZrCl_2$/MAO (lower, average ratio 11.9) and $Cp^*_2HfCl_2$/MAO (upper, average ratio 53.3), 50 °C, liquid propylene.

Experimental oligomer distributions for PP5 and PP7 (Figure 1) follow the Schulz–Flory (or Most Probable) distribution,[24-26] $m_p = Ap\alpha^p$. In fact, the linear relationship log (m_p/p) = log A

(23) Finch, W.; Gillespie, R.; Hedden, D.; Marks, T. *J. Am. Chem. Soc.* **1990**, *112*, 6221–6232.

(24) Schulz, G. V. *Z. Physik. Chem.* **1939**, *B-43*, 25–46.

(25) m_p is the weight fraction with degree of polymerization p, $\alpha = R_p/(R_p + \sum R_{tr})$ is the probability of propagation, and the constant A depends on the normalization chosen. Normalizing $m_p = Ap\alpha^p$ over $p = 2, ..., \infty$, we obtain the Schulz–Flory distribution for oligomerizations:

$$\sum_{p=2}^{\infty} m_p = 1 \qquad \sum_{p=2}^{\infty} m_p = A\sum_{p=2}^{\infty} p\alpha^p$$

$$A = 1/\sum_{p=2}^{\infty} p\alpha^p$$

Bearing in mind that $\sum_{p=0}^{\infty} p\alpha^p = \alpha/(1-\alpha)^2$, it follows

$$\sum_{p=2}^{\infty} p\alpha^p = \sum_{p=0}^{\infty} p\alpha^p - \sum_{p=0}^{1} p\alpha^p = \alpha/(1-\alpha)^2 - \alpha = \alpha^2(2-\alpha)/(1-\alpha)^2$$

$$A = (1-\alpha)^2/\alpha^2(2-\alpha)$$

Hence,

$$m_p = [(1-\alpha)^2/\alpha^2(2-\alpha)]p\alpha^p \qquad \text{(eq 1)}$$

From this normalized distribution, we can derive the expression for the number-average oligomerization degree $\bar{P}_n$ as a function of α. Since

$$\bar{P}_n = 1/\sum_{p=2}^{\infty} m_p/p$$

$$\sum_{p=2}^{\infty} \alpha^p = \alpha^2 \sum_{p=0}^{\infty} \alpha^p = \alpha^2/(1-\alpha)$$

Using eq 1 and summing:

$$\sum_{p=2}^{\infty} m_p/p = [(1-\alpha)^2/\alpha^2(2-\alpha)]\sum_{p=2}^{\infty} \alpha^p = (1-\alpha)/(2-\alpha)$$

Thus, $\bar{P}_n = (2-\alpha)/(1-\alpha)$.

(26) Henrici-Olivé, G.; Olivé, S. *Adv. Polym. Sci.* **1974**, *15*, 1–30 and references therein.

Table III. ^{1}H and ^{13}C NMR Data for Polypropylene Samples

		^{1}H NMR		^{13}C NMR						
		unsatd end groups[b]		unsatd end groups[c]		satd end groups[c]		triad distribution		
sample	$\bar{P}_n$[a]	vinylidene	allyl	vinylidene	allyl	*n*-propyl	isobutyl	*mm*	*mr*	*rr*
PP1	18.7	100		50		50				
PP2	79.5	100		50		50		31.1	51.6	17.3
PP3	137.4	100		50		50		36.1	50.0	13.9
PP4		nd[e]	nd	nd	nd	nd	nd	44.1	47.0	8.9
PP5[d]	4.5	8	92							
PP6	95	8	92	nd	44	nd	56	17.4	48.3	34.3
PP7[d]	3.4	2	98							
PP8	27.4	3	97	nd	32	nd	68	15.3	47.2	37.5
PP9		nd	nd	nd	nd	nd	nd	42.0	49.0	9.0
PP10	24.5			nd	nd	nd	100			

[a] Number-average polymerization degree measured as propylene units per unsaturated end group. Higher than actual when Al-tr is present. [b] % of total unsaturated end groups. [c] % of total end groups. [d] GC–MS data for comparison. [e] nd = nondetectable.

$+ \, p \log \alpha$ is obeyed from $p = 3$ up to $p = 14$ with excellent correlation parameters ($R = 0.9995$ for Zr and 0.9992 for Hf), giving $\alpha_{Zr}(50\ °C) = 0.740$ and $\alpha_{Hf}(50\ °C) = 0.554$. The Schulz–Flory distribution holds if a single type of active center is present and all propagation centers are equally active toward propylene insertion. Thus, it follows that for these catalytic systems a single active species—disregarding growing chain length—is present (albeit nothing can be said about their fraction with respect to total transition metal) and that k_p's are equal for all active sites C^*R_p (i.e., bearing growing chains of degree of polymerization p) from $p = 2$ on. This conclusion is in agreement with previously studied homogeneous polymerization catalysts.[26]

Given the fairly constant [allyl]/[vinylidene] ratio for $p = 3$–6 (Figure 3) with

$$d[\text{allyl}]/dt = k_{\beta\text{-Me}}(\text{obsd})[C^*],$$
$$d[\text{vinylidene}]/dt = k_{\beta\text{-H}}(\text{obsd})[C^*]$$

it follows that

$$[\text{allyl}]/[\text{vinylidene}] = k_{\beta\text{-Me}}(\text{obsd})/k_{\beta\text{-H}}(\text{obsd}) = k_{\beta\text{-Me}}/k_{\beta\text{-H}}$$

assuming that both transfer reactions have the same dependence on monomer concentration. Thus, we could obtain both kinetic rate constant ratios: $k_{\beta\text{-Me}}/k_{\beta\text{-H}} = 11.9$ for Zr and $k_{\beta\text{-Me}}/k_{\beta\text{-H}} = 53.3$ for Hf.

In a first approximation, the number-average oligomerization degree $\bar{P}_n$ for PP5 and PP7 is obtained from GC oligomer distributions (Figure 1). If $\bar{P}_n = \sum_p(\chi_p p) = [\sum_p(m_p/p)]^{-1}$ and $\sum_p m_p$ ($p = 2, ..., 16$) = 1, we obtain $\bar{P}_n(\text{exp}) = 4.5$ (Zr) and $\bar{P}_n(\text{exp}) = 3.4$ (Hf). A better estimate for $\bar{P}_n$, which accounts for the lower than actual m_2 value and the undetected (by GC) oligomers above C_{48}, is obtained from the Schulz–Flory derived[25] expression $\bar{P}_n = (2 - \alpha)/(1 - \alpha)$, which gives 4.85 for Zr and 3.24 for Hf.

Such low molecular weights indicate a low $R_p/\sum R_{tr}$ ratio and thus a very low $k_p/\sum k_{tr}$. Assuming the usual kinetic equations $R_p = k_p[C^*][M]$ and $\sum R_{tr} = \sum k_{tr}[C^*] = (k_{\beta\text{-H}} + k_{\beta\text{-Me}})[C^*]$ to be valid with these catalysts and since $\alpha = R_p/(R_p + \sum R_{tr})$, one obtains $\alpha/(1 - \alpha) = R_p/\sum R_{tr} = [k_p/(k_{\beta\text{-Me}} + k_{\beta\text{-H}})][C_3H_6]$.

For PP5 and PP7 (liquid propylene, 50 °C), we have $[C_3H_6] = 10.57$ mol/L, $(k_{\beta\text{-Me}}/k_{\beta\text{-H}})_{Zr} = 11.9$, and $(k_{\beta\text{-Me}}/k_{\beta\text{-H}})_{Hf} = 53.3$; hence, the $k_p/k_{\beta\text{-Me}}$ ratios at 50 °C are readily obtained: $(k_p/k_{\beta\text{-Me}})_{Zr} = 0.25$ and $(k_p/k_{\beta\text{-Me}})_{Hf} = 0.12$. Thus, the reason for the low molecular weights obtained with $Cp^*_2MCl_2$/MAO-catalyzed propylene polymerization resides in $k_{\beta\text{-Me}}$ being higher than k_p.

B. NMR Analysis. The ^{1}H NMR spectra of PP1–3 show in the olefinic region two singlets at 4.65 and 4.73 ppm (vinylidene), while PP5–8 show the predominance of an allylic structure (5.78 ppm, multiplet, 1 H; 4.92–5.05 ppm, multiplet, 2 H) of the type $CH_2{=}CHCH_2R$, thus confirming the GC–MS analysis of PP5 and PP7.

The end group structure of atactic polypropylene prepared with aspecific Cp_2ZrCl_2/MAO has been already studied in detail.[2d] The ^{13}C NMR spectrum of sample PP1 prepared with said catalyst at 50 °C is shown in Figure 4a just for comparison. The end

Scheme IV

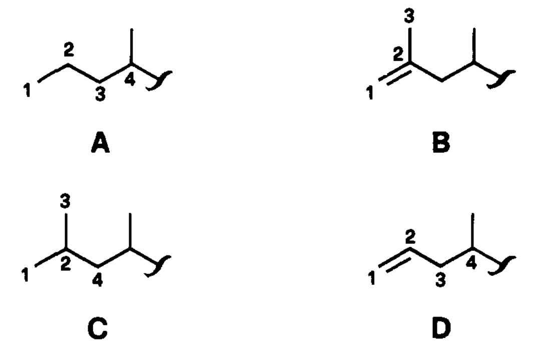


Table IV. Percent of Different Chain Transfer[a] Mechanisms in Polypropylene Samples[b]

sample	metallocene	T_p	β-H	β-Me	Al-tr
PP1	Cp_2ZrCl_2	50	100		
PP2	Cp_2ZrCl_2	0	100		
PP3	Cp_2HfCl_2	50	100		
PP5	$Cp^*_2ZrCl_2$	50	7.9	91.1	1
PP6	$Cp^*_2ZrCl_2$	0	7.1	81.8	11.1
PP10	$Cp^*_2ZrCl_2$	−40			100
PP7	$Cp^*_2HfCl_2$	50	2	98	traces
PP8	$Cp^*_2HfCl_2$	0	2.0	62.7	35.3

[a] Calculated from the relative intensities of different end groups (Table III): β-H = vinylidene, β-Me = allyl, Al-tr = (isobutyl-allyl)/2. [b] No end groups detectable in PP4 and PP9.

groups (Table II) consist solely of *n*-propyl and vinylidene in a 1/1 ratio. Both observations are consistent with aspecific 1,2 insertion/β-H elimination, with transfer to aluminum being negligible at this temperature (transfer to Al would produce isobutyl end groups, which are not detectable in this sample). The absence of signals at 15–18, 30.4, and 35.8 ppm characteristic of isolated 2,1 propylene units[2e] indicates that insertion is highly regioregular.

The ^{13}C NMR spectrum of the nondistillable fraction (0.2 mmHg, 70 °C) of PP7 ($\bar{P}_n \approx 9$) is shown in Figure 4b. Known assignments[2d,27] and DEPT experiments allow the assignment of the peaks due to end groups as labeled in Scheme IV and reported in Table II. We observe that end group signals are split into different resonances due to the different tactic arrangements of next-neighbor units. Their relative intensities are different because they reflect the *r* vs *m* dyad population ($r > m$).[28] Therefore,

(27) Cheng, H. N.; Smith, D. A. *Macromolecules* **1986**, *19*, 2065–2072.

(28) The methyl triad distribution for PP2–4 (Cp_2ZrCl_2 and Cp_2HfCl_2) shows a slight preference toward isotacticity, which is higher with Hf. This is not unexpected given the known ability of Cp_2TiPh_2 to polymerize propylene to isotactic polypropylene by chain end control.[2a] Surprisingly, PP samples made with both $Cp^*_2ZrCl_2$ and $Cp^*_2HfCl_2$ at 0 °C show a slight tendency toward syndiotacticity, with Hf being again more stereoregulatory than Zr. Enantioface selectivity in the polymerization of propylene and 1-butene with these catalysts will be reported in a forthcoming paper.

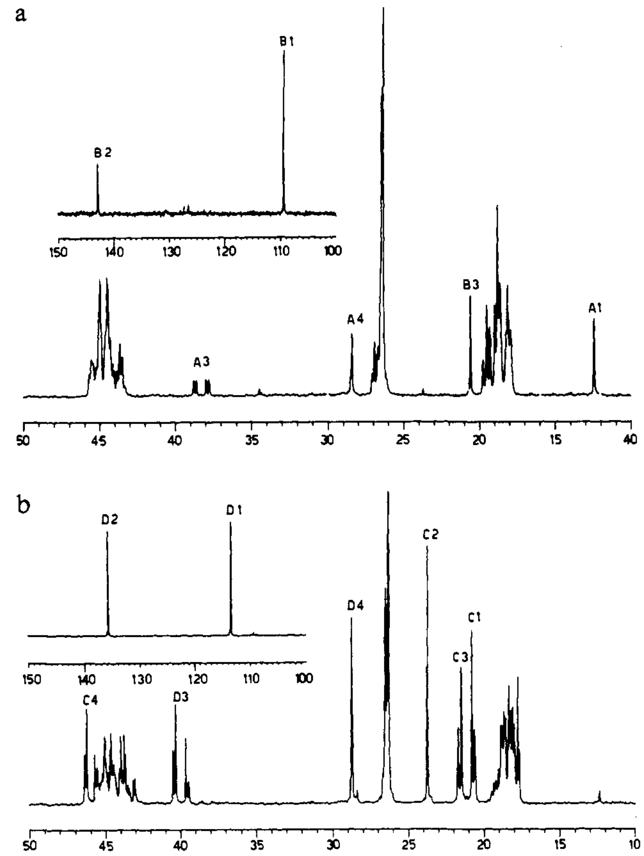


Figure 4. (a) ^{13}C NMR spectrum of PP1, $C_2D_2Cl_4$, 100 °C; (b) ^{13}C NMR spectrum of PP7 (undistillable fraction), $C_2D_2Cl_4$, 100 °C.

assignment to the respective stereosequences was possible.

Collective ^1H and ^{13}C NMR data for samples PP1–10 are reported in Table III. Owing to their low molecular weight, a precise pentad distribution analysis is prevented for most samples, as signals from end groups overlap with signals due to rr triads. From the NMR data of Table III and Schemes Ia, IIa, and III, the percentages of different chain transfers can thus be calculated (Table IV).

Trying to find the limits of β-Me transfer in propylene polymerization with metallocene/MAO catalysts, we synthesized and tested the following zirconocenes: $Me_2SiCp_2ZrCl_2$ (**1**), $(MeCp)_2ZrCl_2$ (**2**), Ind_2ZrCl_2 (**3**), and $Me_2Si(Me_4Cp)_2ZrCl_2$ (**4**).[29] None of these showed measurable amounts of allylic structure: only β-H elimination could be detected. $\bar{P}_n$ values calculated from vinylidenic signals in the ^1H NMR spectra (no Al-tr could be detected by ^{13}C NMR spectroscopy in any of the samples) reflect increasing steric crowding of the zirconocene precursor on going from **1** to **4**, such that $\bar{P}_n \propto k_p/k_{tr}$: **1**, $\bar{P}_n$ = 17.4, activity = 9100 $g_{PP}/mmol_{Zr}\cdot h$; **2**, $\bar{P}_n$ = 35, activity = 24 600 $g_{PP}/mmol_{Zr}\cdot h$; **3**, $\bar{P}_n$ = 109.5, activity = 18 000 $g_{PP}/mmol_{Zr}\cdot h$; **4**, $\bar{P}_n$ = 316, activity = 3700 $g_{PP}/mmol_{Zr}\cdot h$ (liquid propylene, 50 °C).

From the data for propylene polymerization reported in Tables I–IV, the following facts are worth noting. While Cp_2HfCl_2 is less active and gives higher molecular weights than Cp_2ZrCl_2 at both temperatures, $Cp^*_2HfCl_2$ is more active and gives lower molecular weights than $Cp^*_2ZrCl_2$. Also, $Cp^*_2HfCl_2$ displays a higher β-Me/β-H selectivity than $Cp^*_2ZrCl_2$. Seemingly, this different behavior is due to β-Me elimination at 50 °C and both β-Me and Al transfers at 0 °C being faster for $Cp^*_2HfCl_2$ than for $Cp^*_2ZrCl_2$. The higher activity of the former must be due to electronic factors,[3b] as the lower molecular weights produced (it is expected that $k_i > k_{p1}$) are not sufficient to explain a 3-fold difference in activities. Furthermore, the β-Me/β-H ratio appears to be temperature independent between 0 and 50 °C (compare PP5 and PP6, and PP7 and PP8 in Table III).

At 50 °C, the only observed chain-transfer mechanism in propylene polymerization with Cp_2ZrCl_2/MAO and Cp_2HfCl_2/MAO is normal β-H elimination, while β-Me is highly preferred in propylene oligomerization at Cp^*_2M catalyst centers. Both β-H and β-Me transfers require the overlapping of a σ_{C-H} or σ_{C-C} orbital with an empty d orbital on M. For this to occur, the first two chain carbons and the moving fragment (H or Me) must lay in the equatorial plane containing the metal, in between the two Cp rings.[16c] In the case of β-H transfer, this goes through the well-known β-C–H agostic interaction. We expect β-Me transfer to follow a similar reaction path; thus, a β-C–C agostic interaction is to be expected. To prove the existence of such an intermediate, we are pursuing the synthesis of $Cp^*_2ZrCH_2CR_3$ cationic complexes.

The preference for β-Me vs β-H elimination in propylene oligomerization at Cp^*_2M catalyst centers can be attributed on first analysis to the lower steric hindrance in transition state A vs transition state B shown in Figure 5. A similar effect has been observed in Cp^*_2ScEt and Cp^*_2Sc-nPr,[16c] where steric interaction between a Cp* ligand and the propyl CH_3 has been invoked to explain the absence of β-H agostic interaction in the latter.

The higher β-Me/β-H selectivity shown by Hf with respect to Zr could be rationalized by assuming a slightly lower covalent radius for Hf vs Zr (as observed in related complexes[3b]): the resulting shorter Cp*–Hf distance would result in an increase of the nonbonded interactions in transition state B.

Finally, β-Me elimination is faster (i.e., easier) at Cp^*_2M centers ($k_{\beta\text{-Me}} > k_p$) than is β-H elimination at Cp_2M centers, as we observe much lower molecular weights at 50 °C with the former catalysts (activities are in the same range, and similar amounts of active centers are expected in the two systems).

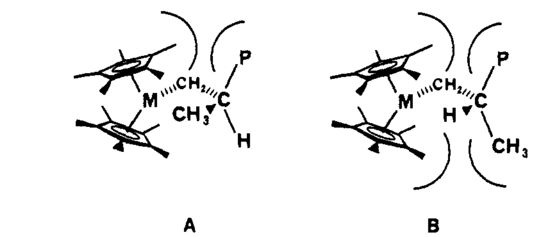


Figure 5. Proposed transition states for β-Me (A) and β-H (B) elimination at Cp^*_2MR centers showing nonbonded interactions disfavoring B.

Table V. 1-Butene Polymerization[a]

sample	metallocene, μmol	T, °C	t, h	yield, g	$1/f_{\beta\text{-H}}$[b]
PB1	Cp_2ZrCl_2, 4.3	0	4	10.3	114
PB2	$Cp^*_2ZrCl_2$, 4.2	0	4	1.6	222
PB3	$Cp^*_2ZrCl_2$, 4.3	50	2	1.4	19[c]
PB4	$Cp^*_2HfCl_2$, 4.2	0	4	7.5	141

[a] Polymerization conditions: 250-mL glass autoclave; 1-butene 20 mL, toluene 10 mL, MAO Schering, solid powder; 4.4 mmol as Al. [b] $f_{\beta\text{-H}}$ = frequency of β-H elimination (number of double bonds per propylene unit) as measured from vinylidene end groups by ^1H NMR. [c] Undistillable fraction (0.1 mmHg, 60 °C). The distillate contains trace amounts of 2-ethyl-1-hexene, 2-ethyl-4-methyl-1-hexene, and unidentified trimers.

2. 1-Butene Polymerization. In order to establish whether β-alkyl elimination is a general transfer mechanism in α-olefin polymerization with $Cp^*_2MCl_2$ catalyst precursors, we investigated 1-butene, 4-methyl-1-pentene, and allyltrimethylsilane polymerization. Poly(1-butene) samples show no detectable allylic patterns in the olefinic region of their ^1H NMR spectra, only the normal signal (two singlets at 4.71 and 4.76 ppm, $CDCl_3$) due to CH_2=C(Et)R vinylidene protons. Data for 1-butene polymerization are reported in Table V. So, while β-Me is the major

(29) The use of tied-back chelating permethylated cyclopentadienyl rings is a common trick to reduce the ring centroid–metal–ring centroid angle in order to release the steric bulk at the metal center without losing the well-established advantages of the Cp* ligand: Fendrick, C.; Mintz, E.; Schertz, L.; Marks, T. *Organometallics* **1984**, *3*, 819–821. Fendrick, C.; Schertz, L.; Day, V.; Marks, T. *Ibid.* **1988**, *7*, 1828–1838. Piers, W.; Shapiro, P.; Bunel, E.; Bercaw, J. *Synlett* **1990**, 74–84.

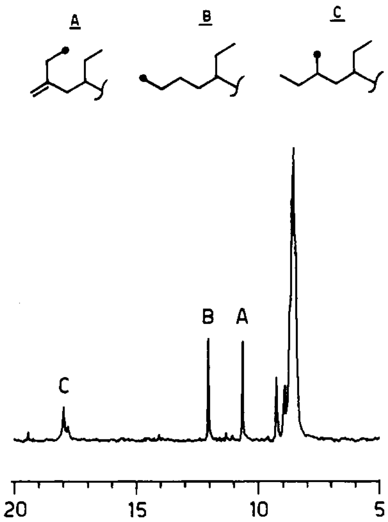


Figure 6. ^{13}C NMR spectrum of the methyl region of 1-butene oligomers (PB3) and structure of the end groups: A, 10.1 ppm; B, 11.9 ppm; C, 18.1, 17.8 ppm.

transfer reaction for propylene, β-Et transfer appears to be inaccessible to these catalyst systems.

From end group analysis[30] on PB3 (Figure 6), PB2, and PB4, the relative ratio of β-H vs Al transfer could be estimated as being about 75/25 at 50 °C (Zr) and 37/63 (Zr) and 77/23 (Hf) at 0 °C, while no Al-tr occurs at 0 °C with Cp_2ZrCl_2 (PB1).

It is worth noting that poly(1-butene)s made with $Cp^*_2MCl_2$ have a lower frequency of β-H elimination than the polymer made with Cp_2ZrCl_2 at the same temperature and a higher molecular weight than propylene oligomers obtained with $Cp^*_2MCl_2$. These findings reflect both the very slow (too slow to be detectable) β-Et elimination in 1-butene polymerization vs preferred β-Me elimination in propylene oligomerization and a more difficult β-H elimination in 1-butene polymerization at Cp^*_2M than at Cp_2M sites. This latter effect is easily ascribed to steric crowding in the conformation required in the transition state for β-H elimination (substitute methyl for ethyl in transition state B, Figure 5).

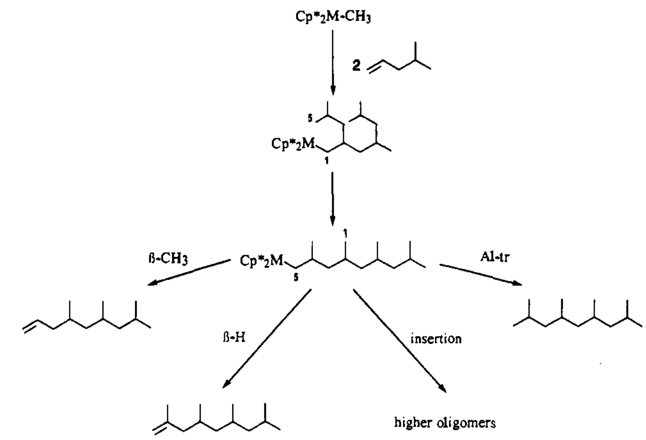
Likewise, the absence of β-Et elimination in 1-butene polymerization with $Cp^*_2MCl_2$/MAO indicates that its rate is far slower than the rate of β-H elimination. A possible explanation for this finding could be that an ethyl group is not easily accommodated in the reaction plane between the two Cp*'s while Me is (transition state A, Figure 5), although it could also be due to thermodynamic effects, as predicted by Marks.[16e]

3. 4-Methyl-1-pentene and Allyltrimethylsilane Polymerization. Poly(4-methyl-1-pentene) samples (PMP1: $Cp^*_2ZrCl_2$/MAO, Zr = 4.4 μmol, 0 °C, 4 h, 36.4% conversion, $\bar{P}_n \approx 210$; PMP2: $Cp^*_2HfCl_2$/MAO, Hf = 4.4 μmol, 0 °C, 4 h, 22.9% conversion, $\bar{P}_n \approx 94$, $\bar{P}_n \approx 32.2$ with Cp_2ZrCl_2/MAO under the same conditions) on the contrary show a preferred formation of allylic end groups (allyl/vinylidene ≈ 2/1 in both PMP1 and PMP2; ^1H NMR allyl 5.25 ppm (m, 1 H), 5.0 ppm (m, 2 H), vinylidene 4.7 ppm (s)) vs β-H elimination. $\bar{P}_n$ values comparable to those of PB2 and PB4 (see Table V) indicate that both transfer reactions are more difficult for 4-methyl-1-pentene than for 1-butene, in accord with increased steric encumbrance of the olefin substituent (k_p for 1-butene is obviously higher than k_p for 4-methyl-1-pentene). Actual $\bar{P}_n$ values might be lower due to undetectable (by ^1H NMR) Al transfer.

Reaction of allyltrimethylsilane with Cp_2ZrCl_2/MAO produces mainly the dimer, 2-[(trimethylsilyl)methyl]-5-(trimethylsilyl)-1-pentene (76.4% conversion, 16 h, 20 °C). As in the case of 4-methyl-1-pentene, reacting allyltrimethylsilane with $Cp^*_2ZrCl_2$/MAO resulted in higher oligomers ($\bar{P}_n$ = 4.7, 23.6% conversion, 22 h, 20 °C), which are mainly allyl-terminated (^1H NMR 5.75 ppm (m, 1 H), 4.8 ppm (m, 2 H), 75% of total olefinic protons).

(30) Longo, P.; Grassi, A.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1987**, *20*, 1015–1018. Locatelli, P.; Tritto, I.; Sacchi, M. C. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 495–499; see also ref 2b.

Scheme V



At least two different mechanisms can be invoked to explain the allylic end groups in the products, the first one being (in analogy to the propylene case) β-alkyl elimination.[31] However, this mechanism would be rather peculiar when compared to the absence of β-Et elimination in 1-butene polymerization.

Another mechanism that could explain the observed allyl groups in both the poly(4-methyl-1-pentene) and allyltrimethylsilane oligomers is sp^3 C–H activation, in analogy to Watson's tetramethylsilane and methane C–H activation with Cp^*_2LuMe.[32,33]

In order to ascertain which transfer mechanism is at work in the case of 4-methyl-1-pentene, we carried out a low-conversion oligomerization test with $Cp^*_2HfCl_2$/MAO at 50 °C and analyzed the dimer fraction by GC–MS. Curiously enough, in addition to the expected 4-methyl-1-pentene dimers—2,8-dimethyl-4-methylenenonane, 2,4,8-trimethylnonane, and 2,4,6,8-tetramethylnonane (2 diastereoisomers)—we also detected a $C_{11}H_{22}$ isomer, 4,6,8-trimethyl-1-nonene (2 diastereoisomers) and 2,4,6,8-tetramethyl-1-nonene (2 diastereoisomers): linear propylene tetramers from 4-methyl-1-pentene dimerization!

To explain this rather surprising dimer composition, we tentatively propose an *intramolecular* sp^3 C–H activation (insertion of a methyl C–H bond from the iBu side group of the last inserted unit into the M–C bond, resulting in chain isomerization) after the second insertion, followed by competitive β-Me, β-H, Al-tr, and insertion processes (Scheme V).

Supporting our hypothesis, the β-Me/β-H ratio obtained from the 4,6,8-trimethyl-1-nonene/2,4,6,8-tetramethyl-1-nonene ratio is 98/2, the same as that obtained for propylene oligomerization under the same conditions (PP7). Furthermore, the trimer fraction contains $C_{17}H_{34}$, $C_{18}H_{36}$, and $C_{19}H_{38}$ isomers, where at least formation of the $C_{17}H_{34}$ isomer requires β-Me elimination. However, a deeper investigation is needed to confirm our hypothesis and elucidate the mechanism for allyl group formation in allyltrimethylsilane oligomerization.

Conclusions

Unambiguous evidence for β-Me elimination as the preferred chain-transfer reaction in propylene oligomerizations with $Cp^*_2ZrCl_2$/MAO and $Cp^*_2HfCl_2$/MAO has been presented. $Cp^*_2HfCl_2$ produces oligomers with lower $\bar{P}_n$ values and displays a higher β-Me/β-H selectivity than $Cp^*_2ZrCl_2$. Chain transfer to aluminum has also been observed, and the relative amounts of β-Me, β-H, and Al-tr reactions for Cp_2ZrCl_2, Cp_2HfCl_2, $Cp^*_2ZrCl_2$, and $Cp^*_2HfCl_2$ have been determined at 0 and 50 °C.

(31) β-CH_2Si agostic interaction has been reported for $(MeCp)_2Zr(L)$-$CH_2CH_2SiMe_3^+$: Wang, Y.; Jordan, R.; Bradley, P.; Baenziger, N. *ACS Polym. Prepr.* **1991**, *32(1)*, 457–458. Examples of Si–C agostic interaction are available in the literature: Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 108–112 and references therein. Van der Heijden, H.; Schaverien, C. *Organometallics* **1989**, *8*, 255–258.

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β-Me elimination appears to be restricted to the presence of *two* Cp* ligands on the metal. On the contrary, 1-butene polymerization with $Cp^*_2ZrCl_2$/MAO and $Cp^*_2HfCl_2$/MAO shows only β-H elimination (and Al-tr) as with the nonsubstituted metallocenes. In the polymerization of 4-methyl-1-pentene with $Cp^*_2MCl_2$/MAO, the presence of allylic end groups is attributed to chain isomerization (through intramolecular C–H activation) followed by β-Me elimination.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere, using standard Schlenk tube techniques. Toluene (Carlo Erba) was purified by refluxing over Al-i-Bu_3 and subsequent distillation under nitrogen. Methylalumoxane (30% w/w toluene solution, Schering) was dried in vacuo to a white, free-flowing powder (4 h, 50 °C, 0.1 mmHg) in order to remove the major part of unreacted $AlMe_3$ (~25% in the starting solution, ~5% in the isolated solid). Cp_2ZrCl_2 (Aldrich), Cp_2HfCl_2, $Cp^*_2ZrCl_2$, $Cp^*_2HfCl_2$ (Strem), and polymerization grade propylene were used as received. Zirconocene dichlorides were found to be over 99% pure (by ^1H NMR). $Cp^*_2HfCl_2$ contained ~4.5% $Cp^*_2ZrCl_2$. 1-Olefins were distilled over CaH_2 prior to use. $Me_2SiCp_2ZrCl_2$,[34] $(MeCp)_2ZrCl_2$,[35] Ind_2ZrCl_2,[36] and $Me_2Si(Me_4Cp)_2ZrCl_2$[37] were synthesized according to known procedures.

GC–MS analyses were performed on a Finnigan Mat INCOS 50 quadrupole mass analyzer interfaced with a HP-5090 gas chromatograph carrying an SPB-5 capillary column (length 30 m, film thickness 0.25 mm). The following conditions were employed: electron energy 70 eV; scan range from *m/z* 33 to 500 in 1.3 s; ion source temperature 150 °C; transfer line temperature 250 °C; injector temperature 250 °C; column temperature 40 °C for 10 min, then 5 °C/min to 300 °C; carrier gas He at flow rate 1 mL/min.

^1H and ^{13}C NMR spectra were run on an AM 300 Bruker spectrometer operating at 300 MHz for proton (5-mm probe) and 75.43 MHz for carbon (10-mm probe) spectroscopy. Quantitative end group analysis was obtained by recording ^{13}C NMR spectra in Inverse Gated Decoupling (IGD) mode. In this technique proton broad band decoupling is applied only during the acquisition step to avoid the onset of the nuclear Overhauser effect (NOE). The following experimental conditions were adopted: 90° pulse = 24 μs, sweep width = 20000 Hz, recycle delay = 20 s to allow complete recovery of the longitudinal magnetization, acquisition time = 0.819 s, number of transients = 3300. A 50/50 mixture of $C_2D_2Cl_4/C_2H_2Cl_4$ was used as a solvent for ^{13}C spectra, while neat $C_2D_2Cl_4$ was used for proton spectra. All spectra were recorded at 373 K.

Propylene polymerizations: In a 1-L stainless steel autoclave (Büchi) washed with a dilute solution of $AlEt_3$ in *n*-hexane and dried at 50 °C in vacuo were subsequently placed 300 g of propylene, 150 mg of MAO in 10 mL of toluene and, after stirring this mixture at the polymerization temperature for 10 min, the metallocene/MAO solution in 15 mL of toluene, previously aged 5 min at room temperature. Polymerizations were quenched by introducing 5 mL of CH_3OH, cooling down the autoclave to 0 °C, and slowly venting the monomer. Oligomer mixtures obtained from $Cp^*_2MCl_2$/MAO catalysts were filtered to remove catalyst residues and kept at low temperature to minimize the loss of low-boiling oligomers. 1-Butene polymerizations were carried out in a 250-mL glass autoclave with magnetic stirring; 4-methyl-1-pentene and allyltrimethylsilane were polymerized in a Schlenk tube. After methanol quenching, dissolution in benzene, and filtration, all products were thoroughly desiccated (0.1 mmHg, 60 °C, 1 day).

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Registry No. Cp_2ZrCl_2, 1291-32-3; Cp_2HfCl_2, 12116-66-4; $Cp^*_2ZnCl_2$, 54039-38-2; $Cp^*_2HfCl_2$, 85959-83-7; $H_2C{=}CHCH_3$, 115-07-1; $H_2C{=}CHCH_3$ (homopolymer), 9003-07-0; $H_2C{=}CHCH_2CH_3$, 106-98-9; $H_2C{=}CHCH_2CH$ (homopolymer), 9003-28-5; $H_2C{=}CHCH_2CH(CH_3)_2$ (homopolymer), 25068-26-2; $H_2C{=}CHCH_2CH(CH_3)_2$, 691-37-2; $H_2C{=}CHCH_2Si(CH_3)_3$, 762-72-1; $H_2C{=}C(CH_2Si(CH_3)_3)(CH_2)_3Si(CH_3)_3$ (homopolymer), 88266-74-4; $H_2C{=}C(CH_2Si(CH_3)_3)(CH_2)_3Si(CH_3)_3$, 16153-25-6.

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