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Published on Web 09/12/2006

Hafnocene Catalysts for Selective Propylene Oligomerization: Efficient Synthesis of 4-Methyl-1-pentene by β-Methyl Transfer

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Abstract: A series of hafnocene complexes (η^5-$C_5Me_4R^1$)(η^5-$C_5Me_4R^2$)$HfCl_2$ with [R^1, R^2] = [H, H] (**1**), [Me, H] (**2**), [Me, Me] (**3**), [Et, Me] (**4**), [^{i}Pr, Me] (**5**), [SiMe$_3$, Me] (**6**), [^{t}Bu, Me] (**7**), [^{n}Bu, Me] (**8**), [^{i}Bu, Me] (**9**), [Et, Et] (**10**), [^{n}Bu, ^{n}Bu] (**11**), [^{i}Bu, ^{i}Bu] (**12**) was tested as catalyst precursors for propylene oligomerization. Upon activation with methylaluminoxane or $[Ph_3C][B(C_6F_5)_4]$/Al^{i}Bu$_3$, complexes **2**−**4** and **8**−**12** catalyzed the dimerization of propylene to produce 4-methyl-1-pentene with selectivities ranging from 23.9 to 61.6 wt % in the product mixture. The selectivity was dependent on the nature of the substituents R^1 and R^2, with the highest value found for (η^5-$C_5Me_4{}^i$Bu)$_2HfCl_2$ (**12**). Rapid deactivation was observed for **5**−**7**, whereas (η^5-$C_5Me_4H)_2HfCl_2$ (**1**) polymerized propylene. 4-Methyl-1-pentene is proposed to form by repeated 1,2-insertion of propylene into the hafnocene methyl cation, followed by selective β-methyl elimination. Detailed analysis of the byproduct distribution (isobutene, 1-pentene, 2-methyl-1-pentene, 2,4-dimethyl-1-pentene, 4-methyl-1-heptene, 4,6-dimethyl-1-heptene), determined by gas chromatography, was performed with the aid of a stochastic simulation involving rate constants for the propagation by insertion, β-hydride elimination, and β-methyl elimination. The rate of termination is dependent on the structure of the growing chain of the active species as well as on the bulkiness of the cyclopentadienyl ligands. The selectivity highly depends on the reaction conditions (pressure, temperature, concentration of methylaluminoxane). The rates of β-methyl elimination leading to 4-methyl-1-pentene were proportional to propylene pressure for **2**−**4** and **8**−**10** but practically independent from propylene pressure for the sterically bulkier derivatives **11**−**12**.

Introduction

Production of higher olefins by catalytic oligomerization of lower olefins such as ethylene or propylene as raw materials is an important process in the petrochemical industry.[1] Recent developments of homogeneous transition metal catalysts, such as the use of carefully designed ancillary ligands, have made the selective formation of linear α-olefins by dimerization,[2] trimerization,[3] or tetramerization[4] possible; in contrast, reportson the catalyzed synthesis of branched α-olefins have been limited. 4-Methyl-1-pentene is one of the branched α-olefins used for the production of (co)polymers with excellent optical, thermal, and electrical properties.[5] Currently, 4-methyl-1-pentene is manufactured by propylene dimerization promoted by heterogeneous catalysts based on alkali metals.[1d,6] There have been, to the best of our knowledge, only a small number of publications describing attempts at developing homogeneous catalysts based on transition metal metallocenes with Cp* ligands (Cp*: η^5-C_5Me_5) to produce 4-methyl-1-pentene.[7−10]

In 1990, Teuben et al. reported that cationic group 4 decamethylmetallocene complexes ($[Cp^*_2MMe(C_4H_8S)]^+BPh_4^-$; M = Zr, Hf; C_4H_8S: tetrahydrothiophene) catalyze the dimerization or trimerization of propylene to give mainly 4-methyl-1-pentene and 4,6-dimethyl-1-heptene.[9a,b] A mechanism consisting of primary (1,2-) insertions of propylene into the metal−

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Scheme 1. Proposed Mechanism for the Propylene Oligomerization by Metallocene Catalysts (M = Zr, Hf)

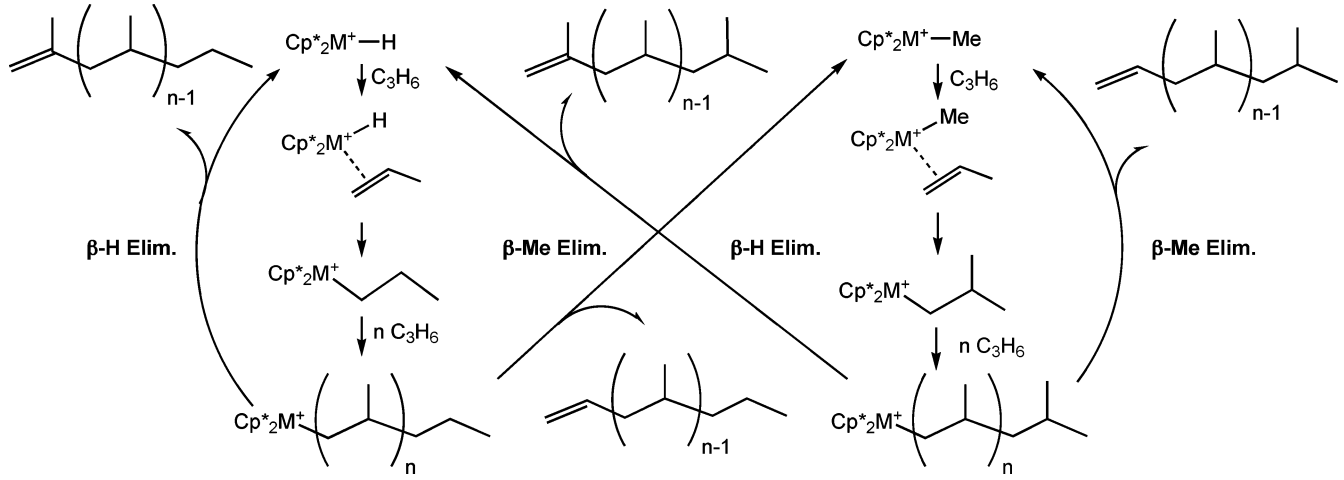
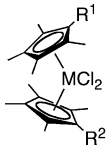


Chart 1



	1	2	3	4	5	6	7	8	9	10	11	12	13
R^1	H	H	Me	Et	^{i}Pr	SiMe$_3$	^{t}Bu	^{n}Bu	^{i}Bu	Et	^{n}Bu	^{i}Bu	^{i}Bu
R^2	H	Me	Me	Me	Me	Me	Me	Me	Me	Et	^{n}Bu	^{i}Bu	^{i}Bu
M	Hf	Hf	Hf	Hf	Hf	Hf	Hf	Hf	Hf	Hf	Hf	Hf	Zr

alkyl bond of the active species, followed by β-methyl elimination, was proposed to be crucial for the selective formation of the vinyl compounds.[9c]

At the same time, Yamazaki et al. reported that a combination of Cp*$_2$MCl$_2$ (M = Zr, Hf) and methylaluminoxane (MAO) catalyzed the oligomerization of propylene with high activity to produce mainly 4-methyl-1-pentene, as well as a considerable amount of byproducts.[10] The byproducts that contain up to 10 carbon atoms were identified, and a mechanism was proposed, consisting of insertion and β-methyl elimination (major) and β-hydride elimination (minor) pathways (Scheme 1).

Although it has been pointed out that sterically hindered ligands in the cationic metallocenes are essential for this catalysis, which is based on β-methyl elimination, there has been no further attempt at improving the catalysts for selective 4-methyl-1-pentene production. At the same time, β-methyl elimination remains a remarkable elementary step and is attracting considerable interest.[11−13] Although this reaction step has been studied in detail, much has remained unclear, especially with regard to the transition state.[12,13]

With the aim of controlling the selectivity of 4-methyl-1-pentene formation, we comprehensively studied the steric effects of hafnocene catalysts. Stochastic simulations to analyze kinetically controlled byproduct distributions according to the mechanism proposed in Scheme 1 were performed. We report here not only on our development of a significantly improved peralkylhafnocene catalyst but also on new insights into the process of homogeneously catalyzed propylene dimerization.

Results

Synthesis. Metallocene complexes **2**, **4**−**9**, **12**, and **13** (Chart 1) were prepared by the method used to synthesize **3**.[14] Lithium salts of the appropriate cyclopentadiene derivatives were reacted with Cp*HfCl$_3$ (for **2**, **4**−**9**) (eq 1) or with MCl$_4$ (M = Hf, Zr; for **12** and **13**) (eq 2) under reflux in xylene. The complexes were identified by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. Complex **6** was found to be relatively air-sensitive, while the others were air-stable.

$$\mathrm{Li(C_5Me_4R^1)} + \mathrm{Cp^*HfCl_3} \rightarrow \mathrm{Cp^*(\eta^5\text{-}C_5Me_4R^1)HfCl_2} + \mathrm{LiCl} \quad (1)$$

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$$2\ \mathrm{Li}(C_5Me_4R^1) + MCl_4 \rightarrow (\eta^5\text{-}C_5Me_4R^1)_2MCl_2 + 2\ \mathrm{LiCl} \quad (2)$$

Preliminary Screening. For the catalyzed reaction with propylene, hafnocene precatalysts (η^5-$C_5Me_4R^1$)(η^5-$C_5Me_4R^2$)-$HfCl_2$ were activated with MAO or $[Ph_3C][B(C_6F_5)]/Al^iBu_3$ and the products were analyzed by gas chromatography (GC) after aqueous workup and removal of polypropylene. Initial screening showed that complexes **1** and **5**−**7** had low productivity for the production of 4-methyl-1-pentene and were therefore unsuitable for further study (Table 1). The sterically less encumbered complex (η^5-$C_5Me_4H)_2HfCl_2$ (**1**) gave mainly atactic polypropylene, with low selectivity for 4-methyl-1-pentene, although the activity toward propylene was high (1027 g of polymer/(mmol of Hf · h)). Complexes **5**−**7** showed low productivities and, moreover, were found to lose their activities at the early stages of the reaction (Figure 1). It is interesting that irreversible deactivation occurred more rapidly for complexes **6** and **7** bearing the tertiary alkyl substituents $SiMe_3$ and ^{t}Bu than for **5** with the secondary alkyl substituent ^{i}Pr, while **4** with only primary alkyl substituents (Me and Et) did not undergo this deactivation step. This suggests that α-methyl groups of the substituents are involved in the deactivation. We propose that C−H activation occurs, followed by the formation of a Hf−C bond, to give a so-called "tucked-in" complex (Scheme 2).[15] The other complexes **2**−**4** and **8**−**13** were all stable enough to maintain their activities for at least an hour. The product distributions were not affected by the reaction time over this period under a constant propylene pressure. This observation indicates that the detected products are not consumed further during the catalysis.

Influence of Steric Effects on Selectivity. The product distributions and activities of complexes **2**−**4** and **8**−**13** were determined (Table 2). A run with decamethylhafnocene complex **3**/MAO gave, with slight deviations, results similar to those reported by Yamazaki et al.,[10] and in addition to 4-methyl-1-pentene (C_{6-1}, 31.1 wt %), a considerable amount of other byproducts also formed. Less than 0.3 wt % 2,4-dimethylpentane, which may be formed by alkyl transfer to aluminum, formed. The amount of higher oligomers obtained with Cp*-(η^5-$C_5Me_4H)HfCl_2$ (**2**) was significantly more than that obtained with $Cp^*_2HfCl_2$ (**3**), which has one methyl group more in the ligand sphere (**3**/MAO: 24.2 wt %, **2**/MAO: 48.8 wt %).[16] Conversely, a bulkier ligand prevented not only propylene polymerization but also the formation of isobutene (C_4), 2-methyl-1-pentene (C_{6-2}), 2,5-dimethyl-1-pentene (C_7), 4-methyl-1-heptene (C_8), and 4,6-dimethyl-1-heptene (C_{9-1}). In summary, the selectivity for 4-methyl-1-pentene (C_{6-1}) increases in the order of the bulkiness of the substituents [R^1, R^2]: [Me, Me] < [Et, Me] < [^{n}Bu, Me] ≈ [^{i}Bu, Me] ≈ [Et, Et] < [^{n}Bu, ^{n}Bu] ≈ [^{i}Bu, ^{i}Bu]; under the standard conditions up to 61.6 wt % C_{6-1} forms. The selectivity for 4-methyl-1-pentene (C_{6-1}) formation by zirconocene complex **13** was not as high as that of hafnocene congener **12**, in agreement with the results for the decamethylmetallocene complexes previously reported by Teuben et al. and Yamazaki et al.[9,10]

Table 1. Productivity of Production of 4-Methyl-1-pentene[a]

complex (R^1, R^2)	activator	productivity[b]	TOF (min^{-1})
1	MAO	20	7.9
(H, H)	$TrBAr_4$[c]	52	20.6
3	MAO	261	103.4
(Me, Me)	$TrBAr_4$	318	126.0
4	MAO	315	124.8
(Et, Me)	$TrBAr_4$	363	143.8
5	MAO	303	120.0
(^{i}Pr, Me)	$TrBAr_4$	100	39.6
6	MAO	12	4.8
($SiMe_3$, Me)	$TrBAr_4$	14	5.5
7	MAO	4	1.6
(^{t}Bu, Me)	$TrBAr_4$	2	0.8

[a] Conditions: Hf, 0.008 mmol; MAO, 2 mmol; $[Ph_3C][B(C_6F_5)_4]$, 0.009 mmol; Al^iBu_3, 0.25 mmol; toluene, 20 mL; propylene, 0.2 MPa; 50 °C, 30 min. [b] (g of 4-methyl-1-pentene)/(mmol of Hf · h). [c] $[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3.

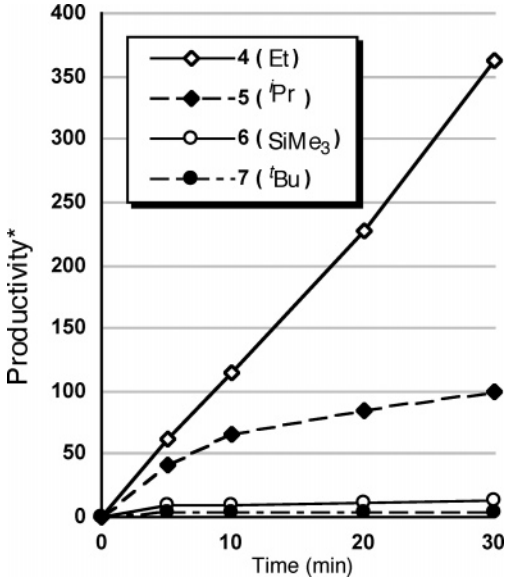
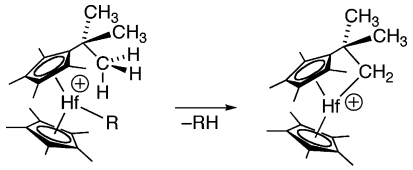


Figure 1. Production of 4-methyl-1-pentene catalyzed by complexes **4**, **5**, **6**, and **7**. Conditions: Hf, 0.008 mmol; $[Ph_3C][B(C_6F_5)_4]$, 0.009 mmol; Al^iBu_3, 0.25 mmol; toluene, 20 mL; propylene, 0.2 MPa; 50 °C; 30 min. * represents productivity in g of 4-methyl-1-pentene/(mmol of Hf · h).

Scheme 2. Proposed Mechanism of Catalyst Deactivation by C−H Activation of an α-Methyl Group on a Cyclopentadienyl Substituent (R = H or alkyl)



Rate Constants. To obtain more information from the selectivity of the oligomerization, ratios of rate constants for each of the elementary steps in the proposed mechanism (Scheme 3) were estimated. Values of k_4/k_5 and k_8/k_9 for the competitive β-methyl and β-hydride elimination reactions were

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(16) A similar observation made with Cp*(η^5-$C_5Me_4H)ZrCl_2$/MAO and (η^5-$C_5Me_4H)_2ZrCl_2$/MAO was mentioned in ref 10.

Table 2. Catalytic Oligomerization with Activated Metallocene Complexes[a]

complex (R^1, R^2, M)	activator	activity[b]	selectivity[c] (wt %) C_4	C_5	C_{6-1}	C_{6-2}	C_7	C_8	C_{9-1}	others
2	MAO	977	0.9	0.5	23.9	0.2	2.9	3.4	19.4	48.8
(H, Me, Hf)	$TrBAr_4$[d]	935	2.9	1.3	24.0	1.2	6.9	8.3	14.5	41.5
3	MAO	923	10.2	3.2	31.1	3.2	4.4	8.5	15.2	24.2
(Me, Me, Hf)	$TrBAr_4$	895	7.7	3.3	39.6	1.9	3.3	7.4	17.5	19.3
4	MAO	921	8.9	3.5	34.3	3.0	4.1	7.9	16.0	22.3
(Et, Me, Hf)	$TrBAr_4$	891	7.1	3.5	40.9	1.6	2.6	7.6	18.2	18.5
8	MAO	883	5.2	2.8	40.2	1.3	3.1	6.2	18.2	23.0
(^{n}Bu, Me, Hf)	$TrBAr_4$	862	4.2	3.3	50.7	0.7	1.8	4.7	20.7	13.9
9	MAO	860	5.0	2.8	41.5	1.0	2.5	6.2	19.7	21.3
(^{i}Bu, Me, Hf)	$TrBAr_4$	764	4.2	3.5	52.1	0.7	1.7	4.7	20.3	12.8
10	MAO	831	4.4	3.3	41.9	1.1	2.1	7.2	18.6	21.4
(Et, Et, Hf)	$TrBAr_4$	794	5.2	3.9	48.0	1.1	2.0	6.1	19.3	14.4
11	MAO	450	4.3	4.6	54.2	0.9	2.2	4.6	18.1	11.1
(^{n}Bu, ^{n}Bu, Hf)	$TrBAr_4$	432	4.4	5.1	58.3	0.7	1.5	3.9	18.3	7.8
12	MAO	311	3.8	4.9	58.5	0.8	1.7	4.4	16.6	9.3
(^{i}Bu, ^{i}Bu, Hf)	$TrBAr_4$	305	4.6	6.2	61.6	0.8	1.6	3.9	15.8	5.5
13	MAO	265	2.0	1.9	28.8	0.8	2.9	3.8	20.1	39.7
(^{i}Bu, ^{i}Bu, Zr)	$TrBAr_4$	237	3.9	3.3	34.3	1.2	2.5	4.1	21.4	29.3

[a] Conditions: catalyst, 0.008 mmol; MAO, 2 mmol, $[Ph_3C][B(C_6F_5)_4]$, 0.009 mmol; Al^iBu_3, 0.25 mmol; benzene, 19.5 mL; *n*-hexane, 0.5 mL; propylene, 0.2 MPa; 50 °C; 30 min. [b] (Sum of all the observed products in g)/(mmol of catalyst · h). [c] C_4: isobutene, C_5: 1-pentene, C_{6-1}: 4-methyl-1-pentene, C_{6-2}: 2-methyl-1-pentene, C_7: 2,5-dimethyl-1-pentene, C_8: 4-methyl-1-heptene, C_{9-1}: 2,4-dimethyl-1-heptene, others: higher oligomers; see Experimental Section. [d] $[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$.

calculated from the experimentally (GC) determined ratios (mol of C_{6-1})/(mol of C_7) and (mol of C_5)/(mol of C_{6-2}), respectively. Estimation of ratios of rate constants for the elimination steps (k_3, k_4, k_6, k_8) and propagation (k_1) required stochastic simulation[17] using an algorithm developed for this purpose, because the mechanism is far too complicated to be solved deterministically.[18] Despite the approximations adopted for the mechanism (viz, the rate constants k_1, k_4, and k_5 are kept constant regardless of the lengths of the growing chains), the simulation showed excellent agreement with the experimental results (Supporting Information).

During the simulation trials, we noticed that k_6/k_1 must be small for appropriate amounts of C_5 and C_8 to be obtained whenever a complex is sterically encumbered (e.g., $k_6/k_1 = 0$ for complex **12**, Table 3). The small k_6/k_1 value corresponds to the assumption that the extent of β-methyl elimination for the active species with an *n*-propyl chain is limited. This limitation impedes the regeneration of the methyl or isobutyl metal cation when the metal hydride cation is the initial active species. Ratios of the rate constants are summarized in Table 4.

As the bulkiness of the ligand increases, all ratios k_4/k_5, k_8/k_9, k_4/k_1, and k_8/k_1 increase; i.e., for the bulkier catalysts, β-methyl elimination is preferred to both β-hydride elimination and propagation, leading to higher selectivity for 4-methyl-1-pentene. Another important observation is that k_4/k_5 is always significantly larger than k_8/k_9, and k_4 is always considerably larger than k_8 for a given catalyst. As a result, C_5 formation is suppressed and more C_8 is formed.

It is also noteworthy that a critical point of polymerization/oligomerization change is found for complex **2**, where the ratio of elimination to propagation $(k_4+k_5)/k_1$ changes from 0.94 (MAO) to 1.36 ($[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$).

Pressure Dependence of Rate Constants. The oligomerization was investigated at various pressures (0.12−0.3 MPa) to determine whether the rate constants depend on propylene concentration (i.e., $k_{obs} = k$[propylene]), provided Henry's law is adhered to. Interestingly, only the bulkiest complexes **11**−**13** gave more of the higher oligomers at higher pressure. The other complexes **2**−**4** and **8**−**10** gave less C_4, C_5, C_{6-2}, C_7, and C_8 byproducts formed at higher pressure. Further analysis of the rate constants showed that k_1/k_4 (propagation and β-methyl elimination) was proportional to pressure for complexes **11**−**13**, while k_1/k_4 remained constant for the other complexes **2**−**4** and **8**−**10**. In contrast, values of k_4/k_5 (β-methyl elimination and β-hydride elimination) were constant for complexes **11**−**13** but proportional to pressure for the other complexes **2**−**4** and **8**−**10**. Typical examples are shown for complexes $Cp^*_2HfCl_2$ (**3**) and $(\eta^5\text{-}C_5Me_4{}^iBu)_2HfCl_2$ (**12**) with $[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ in Figure 2. The activity, considered to reflect the propagation rate constant k_1, was proportional to pressure for all complexes (Supporting Information). Therefore, the β-methyl elimination rate constant k_4 does not depend on propylene concentration for complexes **11**, **12**, and **13**. However k_4 values depend on propylene concentration for complexes **2**−**4** and **8**−**10**, while the rate constant for β-hydride elimination k_5 does not depend on propylene concentration for all complexes. The results suggest that the transition state for β-methyl elimination as the rate-determining step is associated with a propylene molecule, provided the catalyst's ligand sphere is sterically not too encumbered.

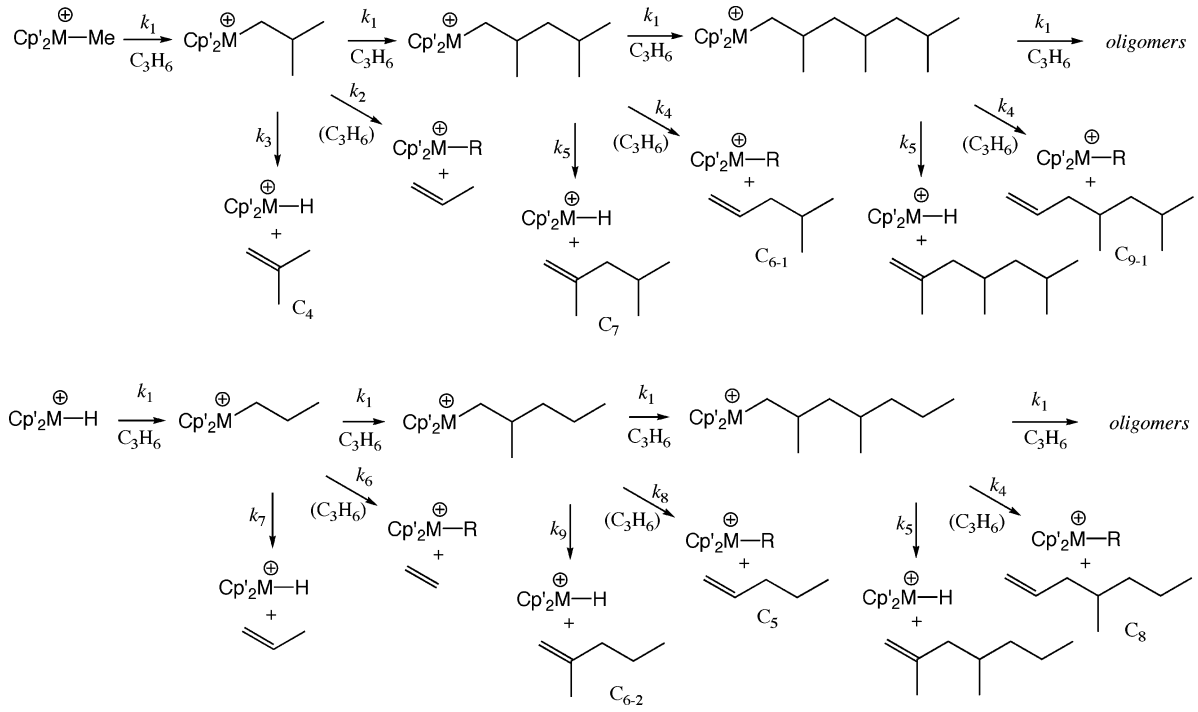
Temperature Dependence of Rate Constants. The oligomerization was also investigated in the temperature range 25−75 °C. The trend was similar for all complexes; i.e., more of the C_4, C_5, C_{6-2}, C_7, C_8 byproducts formed at higher temperatures at the expense of higher oligomers. A decrease in higher oligomers was previously reported for the decamethylmetallocene complexes.[8,9b] The increase of the byproducts (C_4, C_5, C_{6-2}, C_7, C_8) stemming from the increase of β-hydride elimination was unexpected, however, and the dependency differed from one complex to another. Analysis with regard to the rate constants clearly showed these dependencies (Figure 3 and Supporting Information). The activities were lower at higher temperature, e.g., 488 and 243 g/(mmol of Hf · h) at 25 and 75 °C, respectively, for complex **12**/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$), but other factors (e.g., increase in solubility or increased formation of propylene) precluded precise interpretation. The k_8/k_9 value was always lower than the k_4/k_5 value [$(k_8/k_9)/(k_4/k_5)$ was in the range of 0.10−0.35].

Influence of MAO Concentration. As shown in Table 2, $[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ is a slightly better cocatalyst than MAO with regard to the selectivity of 4-methyl-1-pentene.[19] As often discussed in the field of homogeneous olefin polymerization, MAO's performance is variable and simply changes with

(17) (a) Schaad, L. J. *J. Am. Chem. Soc.* **1963**, *85*, 3588−3592. (b) Connors, K. A. *Chemical Kinetics: The Study of Reaction Rates in Solution*; VCH: New York, 1990. (c) Flisak, Z.; Ziegler, T. *Macromolecules* **2005**, *38*, 9865−9872.

(18) When β-H elimination becomes negligible, the Flory−Schulz theory is applicable; see ref 9b.

Scheme 3. Definition of Rate Constants k_i[a]



[a] M = Zr, Hf; Cp′ = η^5-$C_5Me_4R^{1,2}$. R = Me (transfer to the metal) or R = ^{i}Bu (transfer to propylene). k_1: Propagation (insertion into alkyl−metal bond), k_2: β-methyl elimination from isobutyl−metal species, k_3: β-hydride elimination from isobutyl−metal species, k_4: β-methyl elimination from 2,4-dimethylpentyl (2,4,6-trimethylheptyl, etc.)−metal species, k_5: β-hydride elimination from 2,4-dimethylpentyl (2,4,6-trimethylheptyl etc.)−metal species, k_6: β-methyl elimination from *n*-propyl−metal species, k_7: β-hydride elimination from *n*-propyl−metal species, k_8: β-methyl elimination from 2-methylpentyl−metal species, k_9: β-hydride elimination from 2-methylpentyl−metal species.

Table 3. Results of Simulation for **12**/[Ph_3C][$B(C_6F_5)_4$]/Al^iBu_3

	selectivity[a] (wt %)							
k_8/k_1	C_4	C_5	C_{6-1}	C_{6-2}	C_7	C_8	C_{9-1}	others
1.63 (k_8/k_1)	4.8	1.7	67.7	0.2	1.7	1.3	16.5	6.1
0	4.7	4.4	62.7	0.6	1.6	3.7	16.2	6.1

[a] Formation of ethylene and propylene is excluded. C_4: isobutene, C_5: 1-pentene, C_{6-1}: 4-methyl-1-pentene, C_{6-2}: 2-methyl-1-pentene, C_7: 2,5-dimethyl-1-pentene, C_8: 4-methyl-1-heptene, C_{9-1}: 2,4-dimethyl-1-heptene.

Table 4. Ratios of Rate Constants

complex (R^1, R^2, M)	activator	k_4/k_5	k_9/k_9	$k_4/k_9/k_1$
2	MAO	9.9	3.3	0.85/0.10/1
(H, Me, Hf)	$TrBAr_4$[a]	4.0	1.3	1.09/0.12/1
3	MAO	8.3	1.2	1.86/0.37/1
(Me, Me, Hf)	$TrBAr_4$	13.9	2.0	2.27/0.48/1
4	MAO	9.9	1.4	2.02/0.45/1
(Et, Me, Hf)	$TrBAr_4$	18.2	2.6	2.34/0.49/1
8	MAO	14.7	2.5	2.16/0.48/1
(^{n}Bu, Me, Hf)	$TrBAr_4$	32.4	5.5	2.60/0.75/1
9	MAO	19.7	3.3	2.20/0.50/1
(^{i}Bu, Me, Hf)	$TrBAr_4$	35.2	5.9	2.75/0.80/1
10	MAO	23.3	3.5	2.27/0.59/1
(Et, Et, Hf)	$TrBAr_4$	27.7	4.2	2.65/0.72/1
11	MAO	30.0	6.2	3.32/1.10/1
(^{n}Bu, ^{n}Bu, Hf)	$TrBAr_4$	45.2	9.0	3.79/1.39/1
12	MAO	39.3	7.8	4.27/1.42/1
(^{i}Bu, ^{i}Bu, Hf)	$TrBAr_4$	46.2	9.2	4.84/1.63/1
13	MAO	11.6	3.1	1.05/0.35/1
(^{i}Bu, ^{i}Bu, Zr)	$TrBAr_4$	16.3	3.3	1.37/0.47/1

[a] [Ph_3C][$B(C_6F_5)_4$]/Al^iBu_3.

concentration.[20] The oligomerization was also strongly affected by the concentration of MAO in both activity and selectivity (Figure 4). The activities were improved as the concentration was increased and surpassed those with [Ph_3C][$B(C_6F_5)_4$]/Al-^{i}Bu_3. Surprisingly, k_4/k_5, which represents the dominance of β-methyl elimination over β-hydride elimination, concomitantly decreased from values comparable to those obtained with [Ph_3C]-[$B(C_6F_5)_4$]/Al^iBu_3, regardless of their dependence on propylene pressure (vide supra). Although the reason for this remains unclear, the tradeoff makes it difficult to apply MAO for the optimal conditions. At higher MAO concentration, k_1/k_4, which determines the average molecular weight of oligomers, increased only slightly (Supporting Information).

Discussion

The influence of steric effects on β-methyl elimination basically agrees with a model originally proposed by Teuben et al. (Figure 5).[9b] Steric repulsions between the substituents of the cyclopentadienyl ligands and the substituents in the β-position of the growing chain in the active species force the β-methyl group into an energetically more favorable position within the equatorial plane where the LUMO is located. However, this simple model requires modifications when the structure of the

(19) For complexes **1** and **2**, MAO suppresses β-hydride elimination more efficiently than [Ph_3C][$B(C_6F_5)_4$]/Al^iBu_3.
(20) Jüngling, S.; Mülhaupt, R. *J. Organomet. Chem.* **1995**, *497*, 27−32.

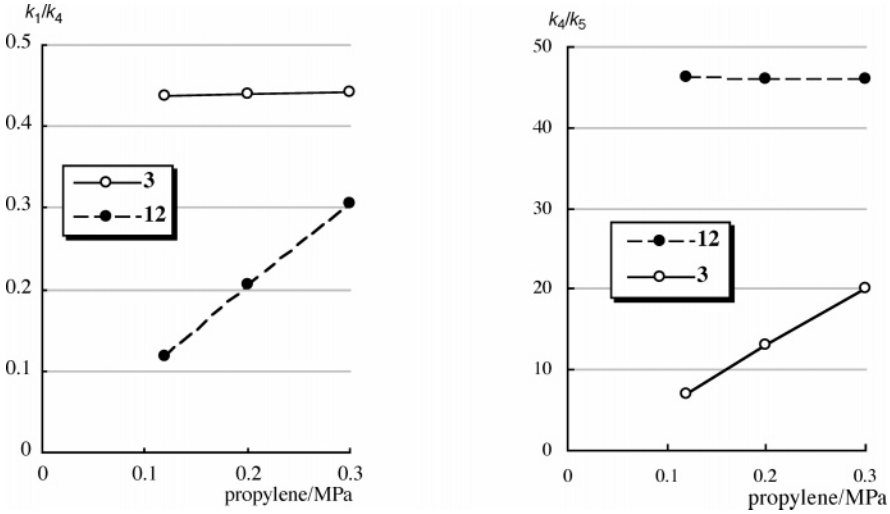


Figure 2. Pressure dependence of k_1/k_4 (left) and k_4/k_5 (right) for complexes $Cp^*_2HfCl_2$ (**3**) and (η^5-$C_5Me_4{}^iBu)_2HfCl_2$ (**12**). Conditions: Hf, 0.008 mmol; $[Ph_3C][B(C_6F_5)_4]$, 0.009 mmol; $^iBu_3Al$, 0.25 mmol; benzene, 19.5 mL; *n*-hexane, 0.5 mL; 50 °C; 30 min.

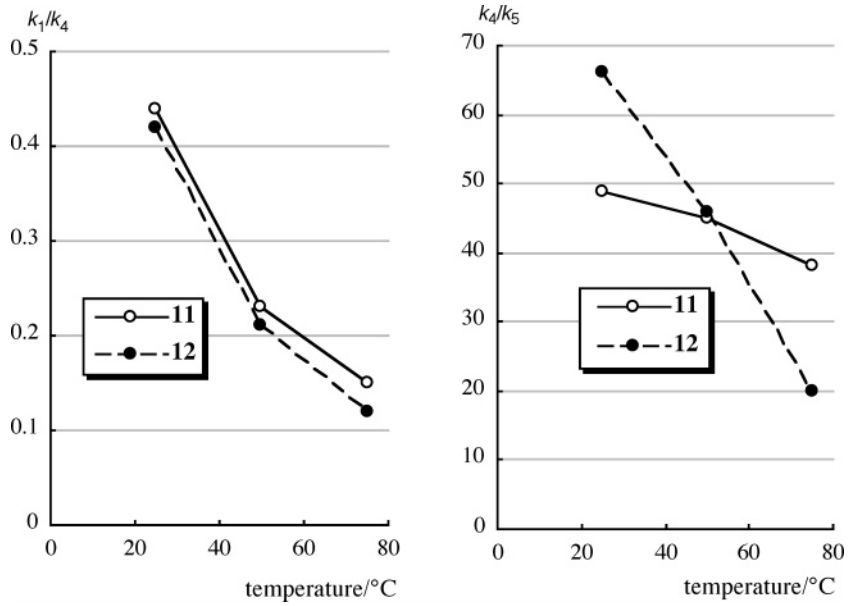


Figure 3. Temperature dependence of k_1/k_4 (left) and k_4/k_5 (right) for complexes (η^5-$C_5Me_4{}^nBu)_2HfCl_2$ (**11**) and (η^5-$C_5Me_4{}^iBu)_2HfCl_2$ (**12**). Conditions: Hf, 0.008 mmol; $[Ph_3C][B(C_6F_5)_4]$, 0.009 mmol; Al^iBu_3, 0.25 mmol; benzene, 19.5 mL; *n*-hexane, 0.5 mL; propylene, 0.2 MPa; 30 min.

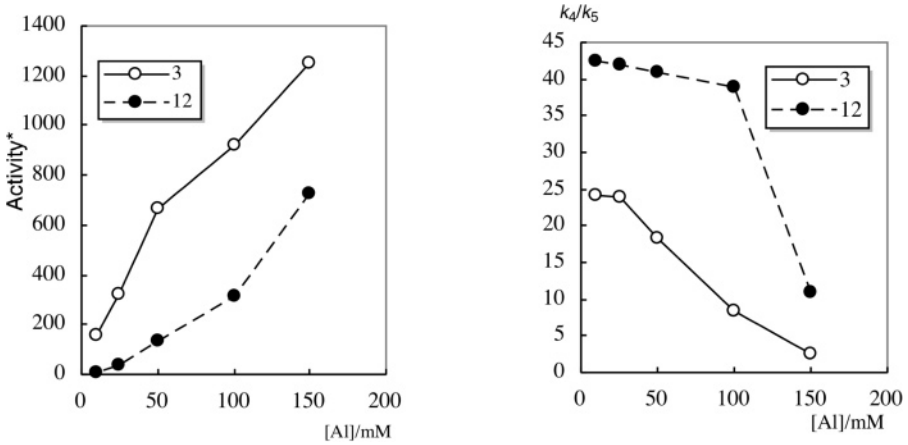
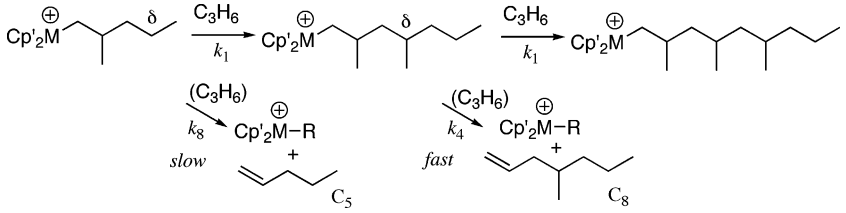


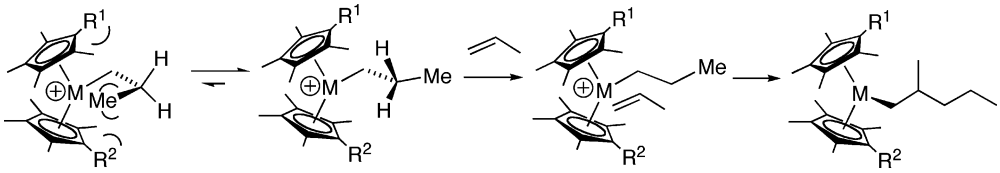
Figure 4. Influence of MAO concentration on activity (left) and k_4/k_5 (right) for complexes $Cp^*_2HfCl_2$ (**3**) and (η^5-$C_5Me_4{}^iBu)_2HfCl_2$ (**12**). Conditions: Hf, 0.4 mM; benzene, 19.5 mL; *n*-hexane, 0.5 mL; propylene, 0.2 MPa; 50 °C; 30 min. * represents (sum of observed products in g)/(mmol of Hf · h).

Scheme 4. Formation of C_8 Byproduct[a]

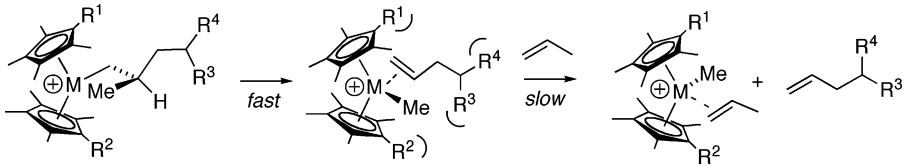


[a] R = Me (transfer to the metal) or R = ^{i}Bu (transfer to propylene).

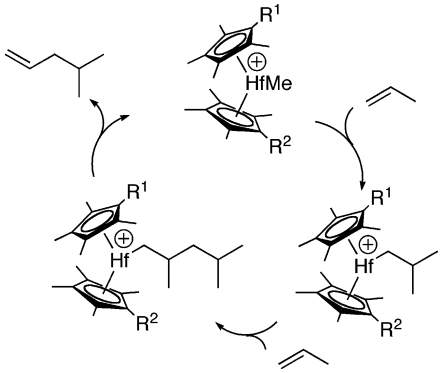
Scheme 5. Active Species with *n*-Propyl Growing Chain



Scheme 6. Resting State and Subsequent Associative Exchange of Olefins



Scheme 7. Idealized Catalytic Cycle for 4-Methyl-1-pentene Synthesis



growing chain is included. The relationship between the values of k_1, large k_4, and small k_8 to produce a very large amount of C_8 byproduct suggests that the growing chain with a secondary carbon in the δ-position influences the selectivity for β-methyl elimination effectively (Scheme 4). This steric effect of δ-substituents R^3 and R^4 is complimentary to that of the ring substituents R^1 and R^2 and weakened (i.e., k_4/k_8 becoming smaller) as the bulkiness of R^1 and R^2 increases.

In the case of the active species with an *n*-propyl growing chain, it is probable that the terminal methyl group is directed toward the outside of the wedge in the absence of another alkyl group in the geminal position. This accounts for the small k_6 values, in particular for the sterically encumbered complexes.

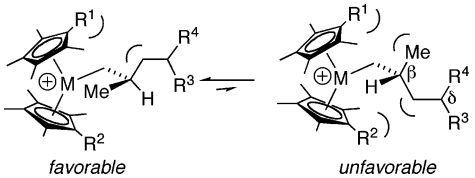


Figure 5. Steric effect of the ligands on β-methyl elimination.

This leads to facile coordination of propylene and subsequent insertion (Scheme 5).

Recently, Baird et al. proposed β-methyl transfer to the propylene monomer by a concerted mechanism for the zirconocene catalyzed propylene polymerization.[13] The pressure dependency of k_4 for complexes **2**−**4** and **8**−**10** is consistent with this proposal. The conformation model in Figure 5 can also be applied here, as long as the π-orbital of the incoming monomer is positioned in the equatorial plane of the metallocene. The requirement for a crowded transition state is in agreement with the results observed for the bulkier complexes **11**−**13**; direct β-methyl transfer to the metal center can be assumed when k_4 values are independent from pressure.

Another interpretation is that the β-methyl transfer to the metal is fast and the subsequent associative exchange of olefins constitutes the rate-determining step (Scheme 6). In this case, it is reasonable to assume that the steric bulk of substituents both on the cyclopentadienyl ligands and at the δ-position of the growing chain serve as the driving force for expelling the olefin by steric repulsion in the complexes **2**−**4** and **8**−**10**.

Finally, the data shown in Table 3 could be interpreted as that the selectivity is improved at the expense of activity. On one hand, it is possible that the bulkiness of the catalyst hinders propylene coordination and/or insertion to make the propagation rate small, resulting in a low activity. On the other hand, it is also possible that the catalytic activity is not strongly affected by the bulkiness. In the observed activity the rate for propylene formation is not included. The amount of propylene should be larger when the rate ratio of elimination to propagation is higher.

Conclusion

The introduction of bulky substituents in dhafnocene catalysts greatly improved the selectivity for the formation of 4-methyl-1-pentene, according to Scheme 7, and revealed some mechanistic details of the catalysis. The analysis of relative rates

showed that the bulkiness of the cyclopentadienyl ligands[22] as well as the structure of the growing chain significantly influence the selectivity. The dependence of the catalysis on the propylene pressure gave further information on the β-methyl elimination mechanism. We are continuing investigations aimed at catalyst development and at clarifying the mechanism in more detail.

Experimental Section

General. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique. Cp*$HfCl_3$,[21] 5-isopropyl-1,2,3,4-tetramethylcyclopentadiene,[23a] and 5-*tert*-butyl-1,2,3,4-tetramethylcyclopentadiene[23b] were prepared according to the literature. 5-*n*-Butyl-1,2,3,4-tetramethylcyclopentadiene and 5-isobutyl-1,2,3,4-tetramethylcyclopentadiene were prepared according to the literature[23a] with slight modifications (i.e., use of *n*-butyllithium/hexane and isobutylmagnesium chloride/Et_2O, respectively). Benzene, *n*-hexane, *n*-pentane, toluene, and xylene were dried and deoxygenated by distillation over sodium benzophenone ketyl under nitrogen. MAO (Aldrich Chemical Co.) was purchased as a 1.0 M toluene solution, and the remaining trimethylaluminum was evaporated under a vacuum to obtain a white powder. 2,4-Dimethyl-1-pentene (C_7) was purchased from TCI Europe N. V. 4-Methyl-1-heptene (C_8) and 4,6-dimethyl-1-heptene (C_{9-1}) were obtained according to the literature[10] and the references therein. Propylene (Aldrich Chemical Co.), $[Ph_3C][B(C_6F_5)_4]$ (Asahi Glass Co.), and other commercially available reagents were used as supplied. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were measured on a VARIAN-UNITY spectrometer at ambient temperature. Chemical shifts were referenced to the residual solvent resonances and reported relative to tetramethylsilane. Elemental analyses were performed by the Microanalytical Laboratory of the Johannes Gutenberg-University, Mainz, Germany.

Synthesis of Cp*(η^5-C_5Me_4H)$HfCl_2$ (2). In a Schlenk flask, a 2.5 M solution of Li^{n}Bu in hexane (0.44 mL, 1.1 mmol) was added to 1,2,3,4-tetramethylcyclopentadiene (122 mg, 1.0 mmol) in pentane (10 mL) at 0 °C. The mixture was stirred overnight at room temperature. The resulting white suspension was decanted, washed with pentane (2 × 10 mL), and dried under a vacuum to yield a white powder (125 mg, 0.975 mmol). Solid Cp*$HfCl_3$ (369 mg, 0.864 mmol) was mixed with Li(C_5Me_4H), xylene (15 mL) was added, and the suspension was refluxed for 2 days. All volatiles were removed under a vacuum. CH_2Cl_2 (50 mL) and 1 M hydrochloric acid (50 mL) were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined CH_2Cl_2 fractions were dried over Na_2SO_4 and filtered. The solvent was removed under a vacuum, washed with pentane (3 mL), and dried under a vacuum to give a pale yellow powder; yield: 269 mg (0.532 mmol, 62%). Recrystallization from hot hexane afforded colorless crystals. ^{1}H NMR ($CDCl_3$): δ 5.57 (s, 1H, $C_5(CH_3)_4H$), 2.07(s, 15H, $C_5(CH_3)_5$), 2.03 (s, 6H, $C_5(CH_3)_4H$), 1.85 (s, 6H, $C_5(CH_3)_4H$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 130.4, 121.4, 116.5, 109.1, 12.4, 12.3, 12.1. Anal. Calcd for $C_{19}H_{28}Cl_2Hf$: C, 45.12; H, 5.58. Found: C, 44.98; H, 5.58.

Synthesis of Cp*(η^5-C_5Me_4Et)$HfCl_2$ (4). The synthesis was carried out according to the procedure to prepare **2** using 5-ethyl-1,2,3,4-tetramethylcyclopentadiene instead of 1,2,3,4-tetramethylcyclopentadiene; yield: 45%. ^{1}H NMR ($CDCl_3$): δ 2.46 (q, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2-CH_3), 2.04 (s, 6H, $C_5(CH_3)_4Et$), 2.03 (s, 6H, $C_5(CH_3)_4Et$), 2.02 (s,15H, $C_5(CH_3)_5$), 0.94 (t, 3H, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 127.2, 122.1, 121.9, 120.9, 19.9, 14.4, 12.0, 11.9, 11.7. Anal. Calcd for $C_{21}H_{32}Cl_2Hf$: C, 47.24; H, 6.04. Found: C, 47.25; H, 6.10.

Synthesis of Cp*(η^5-$C_5Me_4{}^i$Pr)$HfCl_2$ (5). The synthesis was carried out according to the procedure to prepare **2** using 5-isopropyl-1,2,3,4-tetramethylcyclopentadiene instead of 1,2,3,4-tetramethylcyclopentadiene; yield: 39%. ^{1}H NMR ($CDCl_3$): δ 3.06 (septet, 1H, $^3J_{HH}$ = 7.1 Hz, $CH(CH_3)_2$), 2.05 (s, 15H, $C_5(CH_3)_5$), 1.98 (s, 6H, $C_5(CH_3)_4{}^i$Pr), 1.10 (d, 6H, $^3J_{HH}$ = 7.1 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 130.4, 122.8, 122.0, 121.2, 27.4, 21.9, 12.6, 12.0, 11.8. Anal. Calcd for $C_{22}H_{34}Cl_2Hf$: C, 48.23; H, 6.25. Found: C, 48.26; H, 6.13.

Synthesis of Cp*(η^5-$C_5Me_4SiMe_3$)$HfCl_2$ (6). The synthesis was carried out according to the procedure to prepare **2** using trimethyl-(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane instead of 1,2,3,4-tetramethylcyclopentadiene; yield: 35%. ^{1}H NMR ($CDCl_3$): δ 2.21(s, 15H, $C_5(CH_3)_5$), 2.03 (s, 6H, $C_5(CH_3)_4SiMe_3$), 2.02 (s, 6H, $C_5(CH_3)_4$-$SiMe_3$), 0.26 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 130.6, 124.7, 122.3, 121.9, 15.3, 12.0, 11.8, 2.1. Anal. Calcd for $C_{22}H_{36}Cl_2HfSi$: C, 45.72; H, 6.28. Found: C, 45.71; H, 6.20.

Synthesis of Cp*(η^5-$C_5Me_4{}^t$Bu)$HfCl_2$ (7). The synthesis was carried out according to the procedure to prepare **2** using 5-*tert*-butyl-1,2,3,4-tetramethylcyclopentadiene instead of 1,2,3,4-tetramethylcyclopentadiene; yield: 16%. ^{1}H NMR ($CDCl_3$): δ 2.26 (s, 6H, $C_5(CH_3)_4{}^t$Bu), 2.03 (s, 15H, $C_5(CH_3)_5$), 2.01 (s, 6H, $C_5(CH_3)_4{}^t$Bu), 1.33 (s, 9H, $C(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 135.7, 122.3, 121.2, 36.5, 31.8, 15.8, 12.1 (one resonance for methyl group and one resonance for Cp ring missing). Anal. Calcd for $C_{23}H_{36}Cl_2Hf$: C, 49.16; H, 6.46. Found: C, 49.17; H, 6.45.

Synthesis of Cp*(η^5-$C_5Me_4{}^n$Bu)$HfCl_2$ (8). The synthesis was carried out according to the procedure to prepare **2** using 5-*n*-butyl-1,2,3,4-tetramethylcyclopentadiene instead of 1,2,3,4-tetramethylcyclopentadiene; yield: 43%. ^{1}H NMR ($CDCl_3$): δ 2.43 (m, 2H, $CH_2CH_2CH_2$-CH_3), 2.02 (overlapped, s, 27H, $C_5(CH_3)_5$ and $C_5(CH_3)_4{}^n$Bu), 1.22−1.32 (m, 4H, $CH_2CH_2CH_3$), 0.90 (t, 3H, $^3J_{HH}$ = 6.7 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 126.3, 121.9, 121.8, 121.0, 32.4, 26.7, 23.1, 14.1, 12.0, 11.9, 11.8. Anal. Calcd for $C_{23}H_{36}Cl_2Hf$: C, 49.16; H, 6.46. Found: C, 49.20; H, 6.46.

Synthesis of Cp*(η^5-$C_5Me_4{}^i$Bu)$HfCl_2$ (9). The synthesis was carried out according to the procedure to prepare **2** using 5-isobutyl-1,2,3,4-tetramethylcyclopentadiene instead of 1,2,3,4-tetramethylcyclopentadiene; yield: 51%. ^{1}H NMR ($CDCl_3$): δ 2.35 (d, 2H, $^3J_{HH}$ = 7.5 Hz, $CH_2CH(CH_3)_2$), 2.04 (s, 6H, $C_5(CH_3)_4{}^i$Bu), 2.03 (s, 15H, $C_5(CH_3)_5$), 2.02 (s, 6H, $C_5(CH_3)_4{}^i$Bu), 1.60−1.79 (m, 1H, $CH(CH_3)_2$), 0.82 (d, 6H, $^3J_{HH}$ = 6.6 Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 125.6, 121.9, 121.4, 35.8, 29.7, 22.8, 12.6, 12.0 (one Cp ring resonance missing). Anal. Calcd for $C_{23}H_{36}Cl_2Hf$: C, 49.16; H, 6.46. Found: C, 49.14; H, 6.47.

Synthesis of (η^5-C_5Me_4H)$_2HfCl_2$ (1). The complex was mentioned in the literature without characterization.[24] In a Schlenk flask, a 2.5 M solution of Li^{n}Bu in hexane (1.8 mL, 4.5 mmol) was added to 1,2,3,4-tetramethylcyclopentadiene (549 mg, 4.50 mmol) in pentane (15 mL) at 0 °C. The mixture was stirred overnight at room temperature. The resulting colorless powder was washed with pentane (10 mL) and dried under a vacuum to give a white powder; yield: 461 mg (3.60 mmol, 80%). Solid $HfCl_4$ (576 mg, 1.80 mmol) was mixed with Li(C_5Me_4H), xylene (15 mL) was added, and the suspension was refluxed for 2 days. All volatiles were removed under a vacuum. CH_2Cl_2 (50 mL) and 1 M hydrochloric acid (50 mL) were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined CH_2Cl_2 fractions were dried over Na_2SO_4 and filtered. The solvent was removed under a vacuum to give a pale yellow powder; yield: 249 mg (0.50 mmol, 28%). Recrystallization from hot hexane

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afforded colorless crystals. ^{1}H NMR ($CDCl_3$): δ 1.79 (s, 12H, $C_5(CH_3)_4H$), 2.04 (s, 12H, $C_5(CH_3)_4H$), 5.23 (s, 2H, $C_5(CH_3)_4H$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 127.8, 118.4, 109.2, 13.7, 11.9. Anal. Calcd for $C_{18}H_{26}Cl_2Hf$: C, 43.96; H, 5.33. Found: C, 43.89; H, 5.21.

Synthesis of (η^5-$C_5Me_4Et)_2HfCl_2$ (10). This compound was mentioned in the literature without characterization data.[8] The synthesis was carried out in analogy to the procedure to prepare **1** using 5-ethyl-1,2,3,4-tetramethylcyclopentadiene instead of 1,2,3,4-tetramethylcyclopentadiene; yield: 43%. ^{1}H NMR ($CDCl_3$): δ 2.45 (q, 4H, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3), 2.02 (s, 12H, $C_5(CH_3)_4Et$) 2.01 (s, 12 H, $C_5(CH_3)_4$-Et), 0.92 (t, 6H, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 127.1, 122.2, 120.9, 20.0, 14.4, 12.0, 11.7. Anal. Calcd for $C_{22}H_{34}Cl_2$-Hf: C, 48.23; H, 6.25. Found: C, 48.24; H, 6.27.

Synthesis of (η^5-$C_5Me_4{}^n$Bu)$_2HfCl_2$ (11). The complex was mentioned in the literature without characterization.[8] The synthesis was carried out according to the procedure to prepare **1** using 5-*n*-butyl-1,2,3,4-tetramethylcyclopentadiene instead of 1,2,3,4-tetramethylcyclopentadiene; yield: 44%. ^{1}H NMR ($CDCl_3$): δ 2.41 (t, 4H, $^3J_{HH}$ = 7.1 Hz, $CH_2CH_2CH_2CH_3$), 2.01 (overlapped, s, 24H, $C_5(CH_3)_4{}^n$Bu), 1.07−1.39 (m, 8H, $CH_2CH_2CH_3$), 0.89 (t, 6H, $^3J_{HH}$ = 6.7 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 126.3, 122.0, 121.0, 32.4, 26.8, 23.1, 14.1, 12.0 (one methyl group resonance missing). Anal. Calcd for $C_{26}H_{42}$-Cl_2Hf: C, 51.70; H, 7.01. Found: C, 51.74; H, 7.09.

Synthesis of (η^5-$C_5Me_4{}^i$Bu)$_2HfCl_2$ (12). The synthesis was carried out according to the procedure to prepare **1** using 5-isobutyl-1,2,3,4-tetramethylcyclopentadiene instead of 1,2,3,4-tetramethylcyclopentadiene; yield: 43%. ^{1}H NMR ($CDCl_3$): δ 2.36 (d, 4H, $^3J_{HH}$ = 6.6 Hz, $CH_2CH(CH_3)_2$), 2.05 (s, 12H, $C_5(CH_3)_4{}^i$Bu), 2.02 (s, 12H, $C_5(CH_3)_4{}^i$-Bu), 1.58−1.79 (m, 2H, $CH(CH_3)_2$), 0.60 (d, 12H, $^3J_{HH}$ = 7.3 Hz, CH-$(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 125.6, 121.8, 121.4, 35.9, 29.7, 22.8, 12.6, 12.0. Anal. Calcd for $C_{26}H_{42}Cl_2Hf$: C, 51.70; H, 7.01. Found: C, 51.70; H, 6.98.

Synthesis of (η^5-$C_5Me_4{}^i$Bu)$_2ZrCl_2$ (13). The synthesis was carried out according to the procedure to prepare **12** using $ZrCl_4$ instead of $HfCl_4$; yield: 45%. ^{1}H NMR ($CDCl_3$): δ 2.31 (d, 4H, $^3J_{HH}$ = 7.3 Hz, $CH_2CH(CH_3)_2$), 1.96 (s, 12H, $C_5(CH_3)_4{}^i$Bu), 1.94 (s, 12H, $C_5(CH_3)_4{}^i$-Bu), 1.59−1.78 (m, 2H, $CH(CH_3)_2$), 0.81 (d, 12H, $^3J_{HH}$ = 6.6 Hz, CH-$(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 127.3, 123.6, 123.1, 36.0, 29.6, 22.8, 12.7, 12.1. Anal. Calcd for $C_{26}H_{42}Cl_2Zr$: C, 60.43; H, 8.19. Found: C, 60.45; H, 8.22.

Propylene Oligomerization Activated with MAO. Benzene (15.5 mL), *n*-hexane (0.50 mL, internal standard), and a 1.00 M solution of MAO in benzene (2.0 mL) were added via syringe into an argon filled autoclave (100 mL Büchi miniclave) equipped with an inlet/outlet for propylene/vacuum, an inlet with a septum, a thermocouple, a magnetic stirrer, and an oil bath. After the atmosphere was replaced by propylene, the mixture was heated to 50 °C and stirred for 10 min at 0.50 kgf/cm^2 (gauge pressure). The reaction was started with an addition of a solution of a metallocene complex in benzene (4 mM, 2 mL) via syringe, the septum was exchanged for a new one, and propylene was supplied at 1.00 kgf/cm^2 (gauge pressure) for 30 min. After stopping the propylene supply, water (0.1 mL) was added via syringe and the reactor was cooled to 10 °C and settled for 30 min. The reaction mixture was washed with 1.0 M HCl (20 mL) and then with water (20 mL). All volatiles are trapped in a flask cooled with liquid nitrogen under a vacuum (10^{-5} bar). The residue was weighed, and the trapped volatiles were thawed and analyzed by GC. GC analyses were carried out on a Shimadzu GC-2010A (FID) with a DB-1 column (60 m, J&W Scientific) and hydrogen carrier gas. Amounts of C_4, C_5, C_{6-1}, C_{6-2}, C_7, C_8, and C_{9-1} were estimated using the relative peak area of *n*-hexane as an internal standard and scaling factors referenced to the authentic compounds. Amounts of other higher oligomers were estimated on the assumption that the peak area is approximately proportional to the number of carbon atoms.

Propylene Oligomerization Activated with [Ph_3C][$B(C_6F_5)_4$]/Al^iBu_3. The above procedure was modified as follows: Benzene (14.5 mL), a 0.50 M solution of Al^iBu_3 in *n*-hexane (0.5 mL), and a 4 mM solution of a metallocene complex in benzene (2 mL) were added via syringe into an autoclave. After the atmosphere was replaced by propylene, the mixture was heated to 50 °C and stirred for 10 min at 0.50 kgf/cm^2 (gauge pressure). The reaction was started with an addition of a solution of [Ph_3C][$B(C_6F_5)_4$] in benzene (3 mM, 3 mL) via syringe.

Alteration of Reaction Conditions in Propylene Oligomerization. Propylene pressure, temperature, MAO concentration, and reaction time in the above procedures were varied to the designated value in order to investigate the influence of the reaction conditions. When the pressure was 2.00 kgf/cm^2, an inlet with a septum was exchanged for a screwed plug with a Viton O-ring after the reaction was started. The reaction was quenched after cooling at 10 °C for 2 min without a propylene supply. In the case of preliminary screening, toluene was used instead of benzene.

Stochastic Simulation. The program (SuzuKin.nb) was written in *Mathematica*[25] code and run on a Macintosh G4 (Apple Computer). Active species which appear in the plausible mechanism (Scheme 1) were indexed with the carbon number of an alkyl group attached to the metal (e.g., cat[0] for hydride species, cat[1] for methyl species, and so on). Because propylene insertion occurs only in a primary mode without resulting in regioisomeric structures, each intermediate species was uniquely defined by the index. The simulation started from cat[1] when activated with MAO or cat[4] with [Ph_3C][$B(C_6F_5)_4$]/^{i}Bu_3Al. After a generated random number was referred to, probabilities of possible competitive pathways were calculated on the basis of relative scales of rate constants, and an action was selected.[17c] If a propagation path was selected, cat[n] was changed to cat[n + 3]. If a β-methyl elimination path was selected, cat[n] was changed to cat[1] (or cat[4] in the case of β-methyl transfer to propylene). If a β-hydrogen elimination path was selected, cat[n] was changed to cat[0]. If no action was selected, cat[n] was not changed. To integrate first-order differential equations with good precision,[17a,b] these trials were applied to a large number of active species simultaneously (10 000) and for a large number of cycles (1000). Formation of olefins was estimated with the use of a history log of each active species. The algorithms in detail are described in the Supporting Information. Values of k_4/k_5 and k_8/k_9 were estimated from (mol of C_{6-1})/(mol of C_7) and (mol of C_5)/(mol of C_{6-2}), and k_1 was set to a constant (tentatively to 1). As for other rate constants, major pathways in the mechanism were considered first, and then minor pathways were adjusted subsequently. Values of k_4 and k_8 were tentatively set to (mol of C_{9-1})/(mol of C_{6-1}) and (mol of C_5)/(mol of C_8)*(mol of C_{9-1})/(mol of C_{6-1})*k_4. First k_4 was adjusted using the values of (wt % of C_{9-1})/(wt % of C_{6-1}) and a total of other higher oligomers with constraining {k_2, k_3, k_6, k_7, k_8} to {$2k_4$, k_5, k_4, $2k_5$, k_4} (the constant "2" stems from intuitive understanding that probability of β-elimination is proportional to the number of methyl or hydride substituents in the β-position), then k_8 was adjusted using the value of (wt % of C_8)/(wt % of C_5) with constraining {k_2, k_3, k_6, k_7} to {$2k_8$, k_9, k_8, $2k_9$}, then k_3 was adjusted using the amount of C_4 with constraining {k_2, k_6, k_7} to {$2k_8$, k_8, $2k_3$}, and finally k_6 was adjusted using the amount of C_5 and C_8. The remaining k_2 and k_7 were left as $2k_8$ and $2k_3$, respectively; in fact they do not influence the distribution of the observed products strongly. This procedure was repeated until the experimental result was well simulated.

Acknowledgment. We thank Ms. M. Kirch and Mr. Y. Kuzuba for the synthesis of the starting materials.

Supporting Information Available: Experimental details of simulation, oligomerization, algorithms (PDF), and a *Mathematica* notebook for simulation. This material is available free of charge via the Internet at http://pubs.acs.org.

JA063717G

(25) *Mathematica* 5.0; Wolfram Research, Inc. http://www.wolfram.com.