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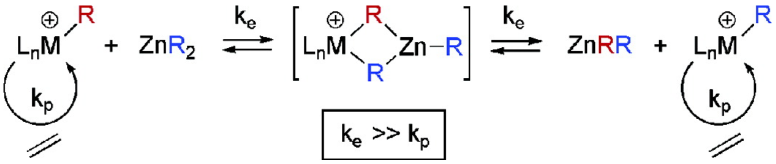

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Polyethylene Chain Growth on Zinc Catalyzed by Olefin Polymerization Catalysts: A Comparative Investigation of Highly Active Catalyst Systems across the Transition Series

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Abstract: Highly active transition metal ethylene polymerization catalysts across the transition series have been investigated for their ability to catalyze chain growth on zinc. In reactions of various catalysts with ZnEt$_2$, product distributions range from Schulz−Flory to Poisson, with several catalysts showing intermediate behavior. A statistical modeling program is introduced to correlate product distributions with the relative rates of propagation, chain transfer to zinc, and β-H transfer. Six regimes have been identified, ranging from Schulz−Flory to pure Poisson where chain transfer to metal is the only termination process, through to combined alkane/alkene distributions where β-H transfer is competitive with chain transfer to metal. It is concluded that, while catalyzed chain growth (CCG) is favored by a reasonable match between the bond dissociation energies of both the main group and transition metal alkyl species, the M−C bond energies of the bridging alkyl species, and hence the stabilities of any hetero-bimetallic intermediates or transition states, are key. The latter are strongly influenced by the steric environment around the participating metal centers, more bulky ligands leading to a weakening of the bonds to the bridging alkyl groups; CCG is thus usually more favored for sterically hindered catalysts.

Introduction

During the past decade there have been tremendous advances in the field of olefin polymerization catalysis, spurred initially by developments in single-site metallocene technology[1] and more recently by the discovery and development of highly active non-metallocene systems.[2] New catalysts are a key driver for the commercial exploitation of new materials as well as for improving the performance of existing polyolefin grades. While the rate of chain propagation is important for determining the productivity of the catalyst, the molecular weight of the product and chain-end functionalization are controlled by chain transfer processes. There are a number of chain transfer mechanisms that can operate during olefin polymerization using transition metal catalysts, but one of the most useful is "chain transfer to metal", which affords polymer chains end-functionalized by a metal fragment. The latter carry the potential to be converted to a variety of other functional groups by post-polymerization reactions.

The most common "chain transfer to metal" processes involve aluminum alkyls and have been observed in polymerization systems across the transition series, for example with early transition metal systems in the polymerization of ethylene,[3] propylene,[4] higher α-olefins,[4b,5] styrene,[6] and dienes[7] and in

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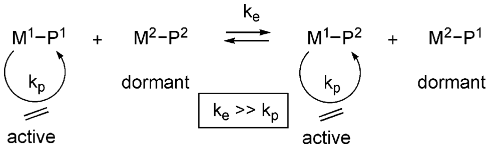
copolymerization reactions,[8] and for mid-to-late transition metal systems based on metals such as chromium,[9] iron,[10] and nickel.[11] Lanthanide[12] and actinide[13] systems have also been shown to engage in chain transfer to aluminum. Interestingly, on the evidence to date, it is generally found that the extent of chain transfer to aluminum is enhanced with increased steric hindrance at the polymerization-active metal center.[4a,8a,14] Other metal alkyls, including those based on beryllium, magnesium, boron, and zinc, have also been investigated as chain transfer agents.[14] Indeed, zinc alkyls of a type relevant to the studies reported here have been used to control (reduce) the molecular weight of polyolefins,[15] as well as to facilitate the formation of end-functionalized polypropylene.[16]

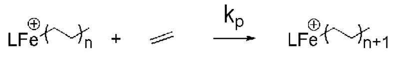
Catalyzed chain growth (CCG) is a special category of “chain transfer to metal” that may be viewed as a metal-catalyzed *Aufbaureaktion*.[17] It also falls within the general class of degenerative transfer polymerization processes, where propagating chains are transferred rapidly and reversibly between active and dormant species.[18] This is illustrated in eq 1 for an ethylene polymerization system. Here, each chain-lengthening step, i.e., insertion of olefin into a metal−carbon (alkyl) moiety, occurs at M^1. The chain is then transferred to a dormant metal, M^2, in a rapid and reversible alkyl exchange process, which leads to a commercially useful narrow (Poisson) distribution of polymer chains at the main group metal centers. When viewed from the perspective of M^2, the process displays characteristics of “living” polymerization, affording a narrow distribution (PDI ≤ 1.1) product, linear growth in molecular weight versus monomer conversion, and regrowth of polymer chains.



(1)

CCG, or degenerative transfer polymerization, provides a potentially powerful approach, not only to commercially useful Poisson distributions of α-olefins, but also to narrow distribution end-functionalized polyethylene (PE) oligomers and new materials containing narrow distribution PE segments.[18] It also provides a cost-effective method of generating narrow distribution polyolefin chains where a relatively cheap main group metal acts as a chain-carrying surrogate for a more expensive transition metal species. It is based on a symbiotic relationship between the transition metal catalyst, where the C−C bond-forming step occurs, and the main group species which acts as a storage vehicle for the “living” PE chains.

For a system to display true CCG behavior, the rate of exchange of the polymer chains between the transition metal and main group metal centers must typically be of the order of 100 times the rate of olefin insertion into the transition metal−carbon bond. It would seem to be a most severe challenge for a system to display such characteristics, yet over the past decade a growing number of these systems have been described. Samsel and Eisenberg disclosed a chain growth reaction on aluminum catalyzed by actinide metallocenes, the most active of which was $Cp^*_2ThCl_2$.[13] Mortreux and co-workers have shown that permethyllanthanocenes, for example $Cp^*_2Nd(\mu\text{-}Cl)_2Li(OEt_2)_2$, catalyze the chain growth reaction of ethylene on magnesium.[19] More recently a number of Cr-based systems have been reported to give CCG on aluminum.[9,20] We have recently reported an efficient catalyzed chain growth reaction on zinc using a bis(imino)pyridine iron(II) dichloride/methyl aluminoxane (MAO) catalyst system, the first time such a catalyzed chain growth reaction had been observed for zinc.[21] The key propagation and exchange processes are shown in eqs 2−4. We also examined a range of other metal alkyls using the iron catalyst system but found that only dialkyl zinc reagents afforded true CCG and, unlike many of the aluminum CCG systems, they maintained productivities comparable to those of the zinc-free system.[14] The question arises as to how general *catalyzed chain growth* is when zinc alkyl reagents are used. We have therefore undertaken a survey of the more active and commercially relevant catalyst systems (Scheme 1) across the transition series. To assist interpretation of the results, a statistical modeling



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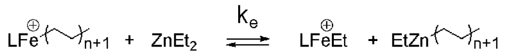

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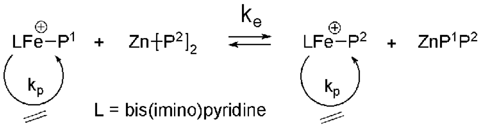

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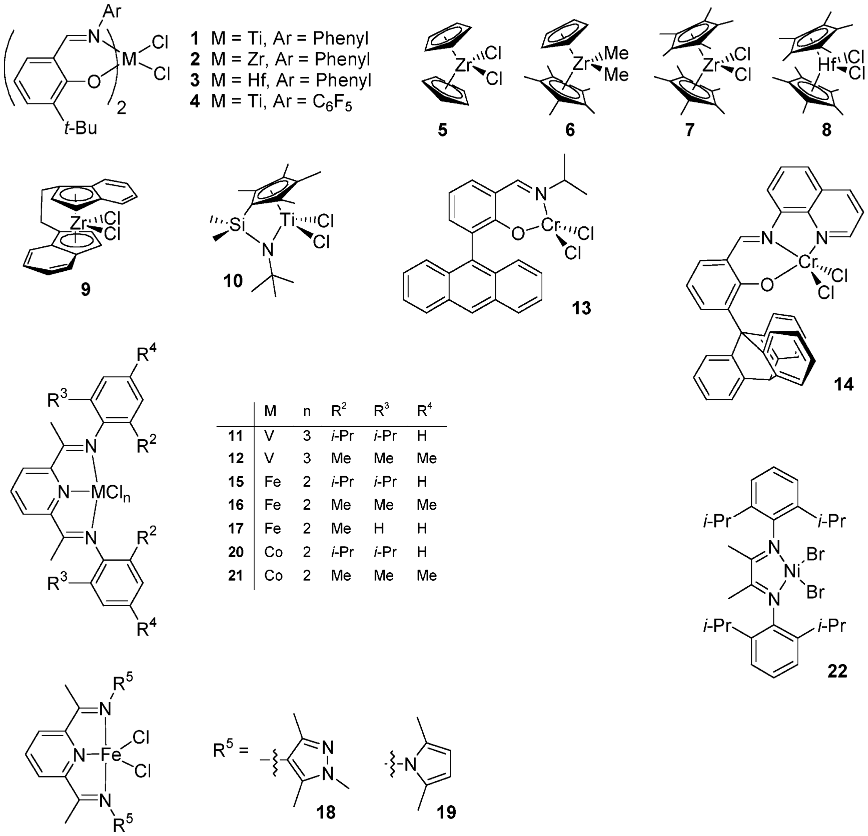
Scheme 1



	M	n	R^2	R^3	R^4
11	V	3	*i*-Pr	*i*-Pr	H
12	V	3	Me	Me	Me
15	Fe	2	*i*-Pr	*i*-Pr	H
16	Fe	2	Me	Me	Me
17	Fe	2	Me	H	H
20	Co	2	*i*-Pr	*i*-Pr	H
21	Co	2	Me	Me	Me

Table 1. Chain Transfer Experiments with $ZnEt_2$ and Group 4 Metal Phenoxyimine Catalysts[a]

run	precatalyst	$ZnEt_2$ (mmol (equiv))	yield[b] (g)	activity (g/mmol·h·bar)	M_n[c]	M_w[c]	PDI [c]	saturated chain ends [d]	unsaturated chain ends [d]	$(Zn–Et)_{ext}$ (mmol (%)) [e]
1.1	**1**	0	3.2	1300	247000	538000	2.2	1.1	0.2	
1.2	**1**	2.8 (550)	2.5	1000	1000	6500	6.5	24.4	0	2.5 (46)
1.3	**2**	0	4.1	1600	5500	128000	23.0	6.1	1.9	
1.4	**2**	2.8 (550)	4.1	1700	1000 [f]	1100 [f]	1.1 [f]	33.6	0.5	3.7 (68)
1.5	**3**	0	2.0	800	7000	65000	9.4	3.3	0.3	
1.6	**3**	2.8 (550)	2.3	900	800 [f]	900 [f]	1.1 [f]	51.3	0	4.4 (80)
1.7	**4**	0	2.2	900	1116000	1699000	1.5	0.5	0	
1.8	**4**	2.8 (550)	0.6	260	2500	9500	3.8	6.2	0	0.3 (5)

[a] Conditions: Schlenk flask test, 5 μmol of catalyst, 100 equiv of MAO, 1 bar ethylene, room temperature, 30 min, toluene solvent (50 mL). [b] Yield is total yield: solid polymer + oligomeric products (determined by GC). [c] Determined by GPC. [d] Determined by ^{1}H NMR, given per 1000 carbon atoms. [e] Defined as the number of ethyl groups that has been extended with at least one inserted ethylene, determined by GPC analysis of the polymer and GC analysis of the oligomers. [f] Contains also a small amount of high molecular weight polymer.

program has been developed to analyze the resultant product distributions, leading to conclusions which allow chain transfer regimes to be better understood and more readily categorized.

Results

The precatalysts studied in the following sections are collected in Scheme 1. For initial screens, the catalysts were typically activated with 100 equiv of MAO and tested in the presence of approximately 500 equiv of $ZnEt_2$ in toluene solvent under 1 atm ethylene pressure for 30 min. The solid polymer obtained from these experiments was analyzed by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy, while the toluene-soluble oligomer fraction was analyzed by gas chromatography (GC). The results of control experiments without diethyl zinc are presented for comparison of activity and polymer properties. Those catalysts that warranted a more detailed investigation were then tested with approximately 2000 equiv of diethyl zinc, and the evolution of the product distribution over time was followed by GC. The results are presented by Group of the Periodic Table, commencing with early transition metal catalysts and progressing to later transition metal systems.

Group 4: Metal Phenoxyimine Catalysts. The results of polymerizations using Group 4 metal phenoxyimine catalysts,[22] **1**−**4**, in the absence and in the presence of $ZnEt_2$, are collected in Table 1. It can be seen that the activities of the phenyl-substituted complexes **1**−**3** were not significantly affected by the presence of 550 equiv of diethyl zinc, but a decrease by a factor of 3 was found in the case of the pentafluorophenyl derivative **4**. In all cases, the resultant polymer was predominantly saturated, indicating that termination occurred preferentially via chain transfer to zinc. For all of the catalysts, the

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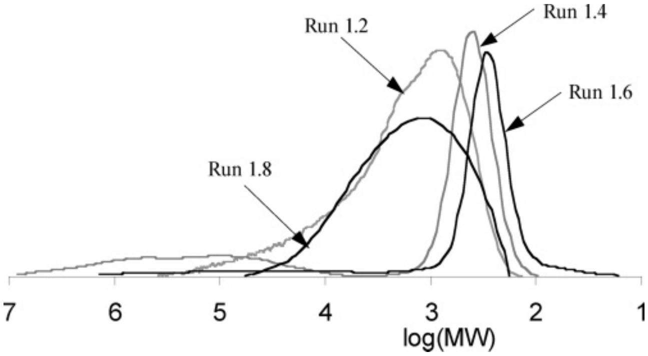

Figure 1. Effect of $ZnEt_2$ on the molecular weight distributions of PE products obtained using phenoxyimine complexes **1**−**4** (see Table 1).

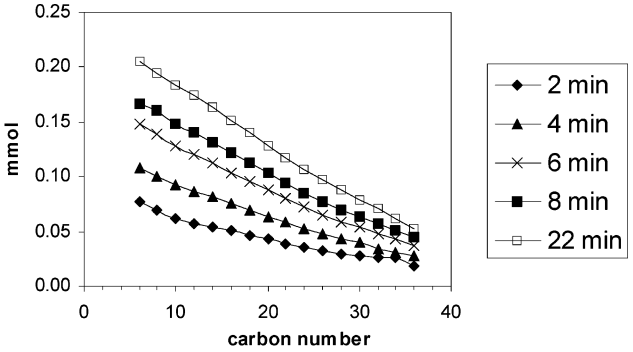

Figure 2. Molar distributions of linear alkanes obtained at different time intervals using precatalyst **1** (see Table S1).

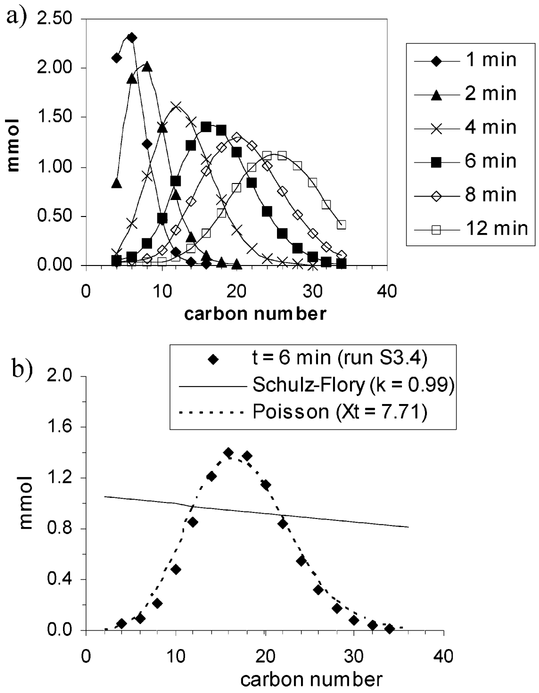

Figure 3. (a) Distribution of linear alkanes at different time intervals obtained with **3** and (b) curve fitting analysis showing best Poisson and Schulz−Flory fits for the distribution after 6 min (see Table S3).

presence of diethyl zinc resulted in a large reduction of the molecular weight, but closer inspection of the GPC traces showed distinct differences between the catalysts (Figure 1). Relatively broad distributions of low molecular weight resulted from titanium catalysts **1** and **4** (runs 1.2 and 1.8), while low molecular weight narrow distribution products, plus a small amount of high molecular weight polymer, were obtained when **2** (Zr) and **3** (Hf) were used. These narrow molecular weight distributions are indicative of CCG but, as we have shown previously, true CCG can be established only by determining the proportion of Zn−Et groups that have been extended and by monitoring chain growth over time.[14]

The number of Zn−Et groups that have actually engaged in chain transfer, and have therefore become chain extended, $(Zn-Et)_{ext}$, can be calculated using the formula given in eq 5, which takes into account both solid polymeric material and the toluene-soluble oligomers.[23] The closer the approach to the theoretical

$$(\mathrm{Zn-Et})_{\mathrm{ext}} = \frac{\mathrm{yield(polymer)}}{M_\mathrm{n}} + \sum \frac{\mathrm{yield(oligomer)}}{M(\mathrm{oligomer})} \quad (5)$$

maximum of 2 times the molar amount of diethyl zinc, the better diethyl zinc is acting as a chain transfer agent; $(Zn-Et)_{ext}$ divided by $(Zn-Et)_{available}$ gives the percentage $(Zn-Et)_{ext}$. As shown in the last column of Table 1, this value is high for **2** and **3** (68% and 80%, respectively), while it reaches only 46% for **1** and 5% for **4**. It is clear from these observations that diethyl zinc is a poor chain transfer agent for the fluorinated derivative **4**.

To determine how the Ti complex **1** differs from its Zr and Hf analogues **2** and **3**, chain growth was monitored over time. The alkane distributions obtained using **1** all follow Schulz−Flory distributions (Figure 2). During the course of the reaction, the amounts of all the oligomers increase but the distribution does not change significantly ($k = 0.92$, Table S1). The total number of alkane chains in the region C_6−C_{36} adds up to only half a chain per zinc center ($(Zn-Et)_{ext} = 23\%$). The remaining alkyl groups are either unreacted ethyl groups or longer alkyl chains that cannot be quantified by GC; however, the observation of insoluble polymer early on in the experiment is strongly indicative of the formation of longer alkyl chains.

During analogous experiments using **2** and **3**, an exothermic reaction occurred but no insoluble polymer was observed until well into the reaction (>10 min), indicating that oligomeric products were being produced selectively. The alkane distributions obtained over the course of the reaction using **3** are shown in Figure 3a (see Figure S2a for those obtained using **2**). They all follow a Poisson distribution, as demonstrated by the curve fitting analysis shown for the alkane distribution obtained after 6 min (Figure 3b). The maximum of the oligomer distributions shifts to higher carbon number with time, as expressed by an increase of the growth factor X_t (and consequently M_n) with time, supporting the "living" behavior of the chain growth reaction (see Tables S2 and S3). The percentage chain growth reaches a maximum of 93% for **2** and 100% for **3**, for growth factors around 6 and 8, respectively. Lower percentages are obtained for $X_t < 4$ and $X_t > 11$, due to the loss of ethane and higher oligomers ($> C_{34}$) from the molar mass balance, which cannot be determined by GC. All these observations imply that **2** and **3**, in combination with diethyl zinc, give rise to bona fide CCG on zinc.[14] Although relatively minor, we note that small amounts of oligomeric 1-alkenes were generated when **2** was used (~4 mol %, Figure S2b), while for **3** the amount was

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(23) These calculations are only a rough estimate as there is a relatively large error in the determination of M_n for low molecular weight polyethylene and, in addition, the small amounts of β-H transfer and chain transfer to aluminum due to TMA present in MAO are not taken into account.

Table 2. Chain Transfer Experiments with $ZnEt_2$ and Group 4 Metallocene and Half-Sandwich Catalysts[a]

run	catalyts	$ZnEt_2$ (mmol (equiv))	yield[b] (g)	activity (g/mmol·h·bar)	M_n[c]	M_w[c]	PDI[c]	saturated ends[d]	unsaturated ends[d]	$(Zn{-}Et)_{ext}$ (mmol (%))[e]
2.1	**5**	2.8 (550)	0	0	nd	nd	nd	nd	nd	
2.2	**6**	0	1.8	700	100000	331000	3.3	0.8	0	
2.3	**6**	2.6 (520)	4.2	1700	1100	18000	16	20.4	0	5.3 (100)
2.4	**6**	10.4 (2100)	4.3	1700	600	900	1.5	39.0	0	14.7 (71)
2.5[f]	**7**	0	2.0	1200	9300	72000	7.7	2.6	0	
2.6[f]	**7**	2.2 (440)	6.0	3600	1600	12000	7.7	14.9	0.1	4.0 (92)
2.7[f]	**7**	8.7 (1700)	5.4	3300	700	1500	2.2	37.5	0	10.8 (62)
2.8	**8**	0	1.2	470	9800	199000	20.3	2.9	0	
2.9	**8**	2.8 (550)	1.4	540	800	2700	3.3	28.0	0	5.3 (96)
2.10[g]	**9**	0	1.3	2500	91000	444000	4.9	0.5	0	
2.11[g]	**9**	2.8 (2800)	1.1	2300	700	1300	1.9	35.3	0	4.7 (86)
2.12	**10**	2.8 (550)	0	0	nd	nd	nd	nd	nd	

[a] Conditions: Schlenk flask test, 5 μmol of catalyst, 100 equiv of MAO, 1 bar ethylene, room temperature, 30 min, toluene solvent (50 mL). [b] Yield is total yield: solid polymer + oligomeric products (determined by GC). [c] Determined by GPC. [d] Determined by ^{1}H NMR, given per 1000 carbon atoms. [e] Defined as the number of ethyl groups that has been extended with at least one inserted ethylene, determined by GPC analysis of the polymer and GC analysis of the oligomers. [f] Run time of 20 min. [g] Using 1 μmol of precatalyst and 500 equiv of MAO.

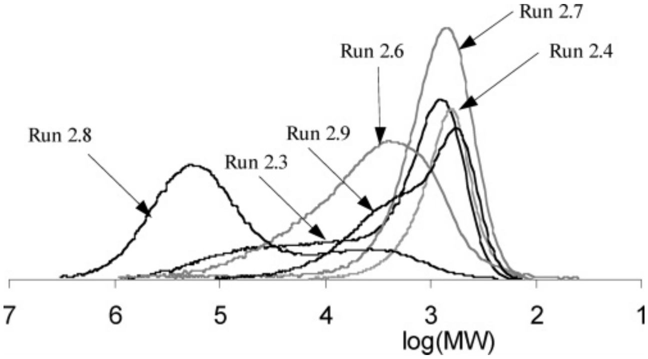

Figure 4. Effect of $ZnEt_2$ on the molecular weight distributions of PE products obtained using metallocene catalysts **6**−**8** (see Table 2).

negligible (<1 mol %). The significance of these 1-alkenes being produced and their effect on the product distribution will be discussed later.

Group 4: Metallocene and Constrained Geometry (Half-Sandwich) Catalysts. Previous observations of extensive chain transfer to aluminum in the polymerization of olefins using the metallocenes $Cp^*_2ZrCl_2$ (**7**),[3d,4b] *rac*-$Et(Ind)_2ZrCl_2$ (**9**),[3e,4c,e,j] and $Cp^*_2HfCl_2$ (**8**),[4b,24] in combination with MAO, led us to investigate the effect of $ZnEt_2$ on the polymerization of ethylene with the series of Group 4 metal complexes **5**−**10**. Cp_2ZrCl_2 (**5**) and the constrained geometry catalyst **10** did not afford active catalysts in the presence of $ZnEt_2$ (Table 2). For each of the other catalysts (**6**−**9**), comparable activities were obtained in the presence and in the absence of diethyl zinc. However, the addition of $ZnEt_2$ had a pronounced effect on the molecular weight of the polymer formed. Representative GPC traces are shown in Figure 4; the remaining GPC traces can be found in the Supporting Information (Figures S14−S17). In the case of $CpCp^*ZrMe_2$ (**6**) and $Cp^*_2ZrCl_2$ (**7**), polymer with a narrow molecular weight distribution was obtained only upon increasing the amount of $ZnEt_2$ to approximately 2000 equiv (runs 2.4 and 2.7). This increase in $ZnEt_2$ concentration resulted in an increase in the number of Zn−Et bonds that had been chain-extended, but a drop in the percentage chain growth (run 2.3 versus 2.4 and run 2.6 versus 2.7). The GPC trace for the polymer produced by $Cp^*_2HfCl_2$ (**8**) without diethyl zinc already contains a minor low molecular weight fraction (run 2.8), most probably arising from chain transfer to the aluminum of TMA (trimethylaluminum) present in MAO; Samsel has shown that TEA (triethylaluminum) is an efficient chain transfer agent for this system.[24]

From the analysis of the polymer end groups by ^{1}H NMR spectroscopy (Table 2), it can be seen that the products contain no (or very few) unsaturated end groups, indicating that virtually all the polymer chains are terminated via chain transfer to zinc. Furthermore, the last column shows that $ZnEt_2$ is a very efficient chain transfer agent for these metallocenes.

CCG requires all Zn−Et bonds to be involved in chain growth, but the observation of 100% chain growth with some of these catalysts is not proof alone of CCG unless accompanied by a Poisson distribution of alkanes. Inspection of the polydispersity index (PDI) data for the high zinc concentration runs shows values more consistent with Schulz−Flory distributions (PDI $\approx$ 2). However, the *k*-value increases over time (Figure S3b), indicating deviation from ideal Schulz−Flory behavior. Since half of the available Zn−Et bonds have been chain-extended within the first minute, the concentration of remaining Zn−Et groups decreases. Consequently, the probability of zinc alkyls other than ethyl being involved in chain transfer reactions increases. Since this process converts short oligomers into longer ones, it results in an increase in the *k*-value.

This effect is clearer for the bis(indenyl) complex **9**. The large amounts of zinc butyl and hexyl present after 4 min decrease during the experiment and have been mostly converted into higher zinc alkyls after 12 min (Figure 5a). As a result, the distributions start to deviate from Schulz−Flory toward a distribution that no longer has its maximum at the shortest chain length, and the average chain length increases during the experiment. These observations are still consistent with a pseudo-living process and can arise only if chain transfer to zinc is reversible. However, the product distribution is intermediate between Poisson and Schulz−Flory and cannot therefore be categorized as CCG (Figure 5b).

Group 5: Bis(imino)pyridine Vanadium Catalysts. Bis(imino)pyridine vanadium complexes show substantial amounts of chain transfer to aluminum when activated with MAO,[25] prompting us to study complex **11** for its ability to catalyze chain growth on zinc. **11** gave a substantially higher activity in the presence of the zinc reagent (1400 versus 560 g/mmol·h·

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(24) Samsel, E. G. (Ethyl Corp., USA). Patent EP 0539876, 1993.

(25) Reardon, D.; Conan, F.; Gambarotta, S.; Yap, G.; Wang, Q. *J. Am. Chem. Soc.* **1999**, *121*, 9318−9325.

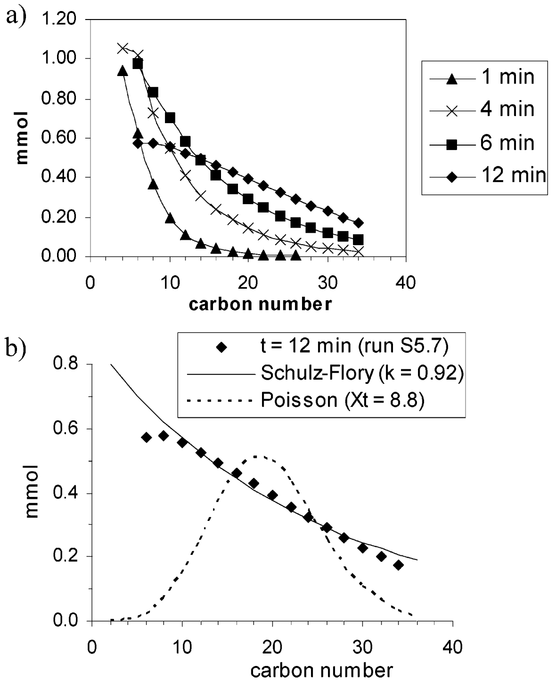

Figure 5. (a) Distribution of linear alkanes at different time intervals obtained with **9** and (b) curve fitting analysis showing best Poisson and Schulz−Flory fits for the distribution after 12 min (see Table S5).

bar) and produced polymer with a much lower molecular weight (runs 3.1 and 3.2, Table 3). The large PDI value is indicative of non-Poisson behavior, although the percentage chain growth on zinc reached 100%.

Analysis of samples taken during a chain growth reaction using precatalyst **11** and 2200 equiv of $ZnEt_2$ showed that 90% chain growth had been achieved after 10 min (Table S6), but the alkane distributions are intermediate between a Poisson and a Schulz−Flory distribution (Figure 6). Analysis of the polymer from run 3.2 by ^1H NMR spectroscopy showed that 2 mol % of the product contained vinyl end groups. Catalyst **12** gave similar alkane distributions, but with the formation of up to 14 mol % of 1-alkenes (Table S7 and Figure S4a,b).

Group 6: Chromium Catalysts Supported by Salicylaldiminato Ligands. The recent discovery of highly active chromium ethylene oligomerization and polymerization catalysts bearing salicylaldiminato ligands prompted us to test complexes **13** and **14** for their ability to perform CCG on zinc.[26] In the absence of $ZnEt_2$, **13** generates high molecular weight polyethylene with a broad molecular weight distribution, while in the presence of 550 equiv of $ZnEt_2$ a narrow molecular weight distribution of fully saturated alkanes is obtained (runs 3.3 and 3.4, Table 3). The toluene-soluble alkanes follow a distribution that more closely resembles Schulz−Flory than Poisson (Figure S5), and the PDI of the polymer is also closer to that expected for a Schulz−Flory distribution.

Complex **14**, bearing a tridentate salicylaldiminato ligand, produces low molecular weight, predominantly vinyl-terminated polymer in the absence of $ZnEt_2$ (run 3.5). The most striking effect of diethyl zinc with this catalyst is the narrowing of the molecular weight distribution to ca. 1.2 (run 3.6). Two molecules of alkane are generated for every zinc center $[(Zn-Et)_{ext} = 100\%]$ which, together with the low M_n and PDI, is suggestive of CCG. However, contrasting our observations on other CCG systems, chain transfer to zinc is not the only termination pathway in this case, since vinyl end groups are also observed in the ^1H NMR spectra of the products. From the GC traces, the alkane distributions exhibit the characteristics of a CCG system with the number of alkane chains per zinc close to 2 and Poisson-like distributions (Table S8 and Figure 7). However, an excess of short alkanes (C_6-C_{10}) remains as the reaction progresses to higher growth factors, whereas their amount is expected to tend to zero upon chain growth of the lower zinc alkyls (compare Figure 7 with Figure 3a). As a result, the alkane distributions show an increasing deviation from a Poisson distribution with increasing growth factors. The 1-alkene distribution changes during the reaction, but it does not follow Schulz−Flory or Poisson behavior (Figure 8), although the proportion of 1-alkenes increases steadily and constitutes ca. 25 mol % of the final product. The peak of the 1-alkene distribution is always at a lower chain length than that of the alkane distribution, and the ratio of 1-alkene to alkane is the highest for the shortest chain lengths.

Group 8: Bis(imino)pyridine Iron Catalysts. CCG on zinc and chain transfer reactions with other main group metal alkyls catalyzed by bis(imino)pyridine iron complex **15** in combination with MAO have been described previously.[14] Here, the study is extended to iron complexes containing other bis(imino)-pyridine ligands (**16**−**19**, Table 4). Substitution of the isopropyl groups for methyls (**16**) has little effect on the CCG behavior, and near-perfect Poisson distributions of alkanes are obtained with very high activities (run 4.4, Table S10 and Figure S7). Reducing the size to *o*-tolyl (**17**) is known to afford a highly active ethylene oligomerization catalyst;[27] however, in the presence of $ZnEt_2$, **17** is completely inactive (run 4.5). The addition of diethyl zinc to a solution of **17** after activation with MAO results in a color change from orange (the typical color of bis(imino)pyridine iron complexes when activated with MAO) to green with concomitant catalyst deactivation. This color change is different from the orange-to-yellow transformation that is observed with **15** or **16**, and may possibly be associated with the formation of a stable hetero-bimetallic adduct between iron and zinc. A similar deactivation has been observed when using large amounts of TMA or TIBAL (triisobutylaluminum) as a scavenger with bis(imino)pyridine iron oligomerization catalysts.[27]

For complexes **18** and **19** containing pyrazolyl and pyrrolyl imino substituents, the presence of diethyl zinc has virtually no effect on the molecular weight distribution of the resultant polymer (runs 4.6−4.9), but does result in the formation of approximately 15% fully saturated product for **18** and 30% in the case of **19**. Only 38% and 74% chain growth is achieved with these catalysts, and it can therefore be concluded that chain transfer to zinc acts alongside β-H transfer as a termination mechanism in these cases.

Group 9: Bis(imino)pyridine Cobalt Catalysts. Bis(imino)-pyridine cobalt complexes[20,21] typically produce lower molecular weight products than their iron relatives and show almost no chain transfer to aluminum (Table 4); at first sight they might

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Table 3. Chain Transfer Experiments with $ZnEt_2$ and Vanadium and Chromium Catalysts[a]

run	precatalyst	$ZnEt_2$ (mmol (equiv))	yield[b] (g)	activity (g/mmol·h·bar)	M_n[c]	M_w[c]	PDI [c]	saturated chain ends[d]	unsaturated chain ends[d]	$(Zn-Et)_{ext}$ (mmol (%))[e]
3.1	**11**	0	1.4	560	7500	31000	4.1	2.8	1.7	
3.2	**11**	2.8 (550)	3.6	1400	700	2200	3.3	34.5	1.6	5.8 (100)
3.3	**13**	0	0.5	220	14000	160000	11.1	2.1	0.2	
3.4	**13**	2.8 (550)	1.6	650	400 [f]	600 [f]	1.5 [f]	53.2	0.4	5.7 (100)
3.5	**14**	0	4.4	1800	900	1800	2.0	20.8	13.7	
3.6	**14**	2.8 (550)	3.5	1400	500	600	1.2	50.0	7.5	5.9 (100)

[a] Conditions: Schlenk flask test, 5 μmol of catalyst, 100 equiv of MAO, 1 bar ethylene, room temperature, 30 min, toluene solvent (50 mL). [b] Yield is total yield: solid polymer + oligomeric products (determined by GC). [c] Determined by GPC. [d] Determined by ^1H NMR, given per 1000 carbon atoms. [e] Defined as the number of ethyl groups that has been extended with at least one inserted ethylene, determined by GPC and NMR analysis of the polymer and GC analysis of the oligomers. [f] Contains also a small amount of high molecular weight polymer.

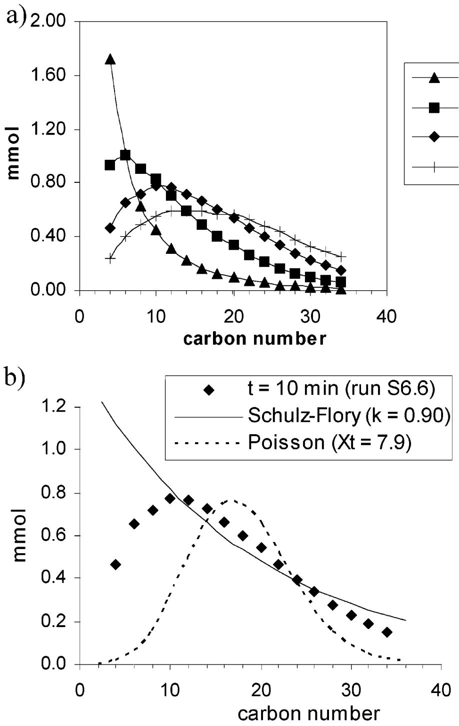


Figure 6. (a) Molar distributions of linear alkanes obtained at different time intervals using **11** and (b) curve fitting analysis showing best Poisson and Schulz−Flory fits for the distribution after 10 min (see Table S6).

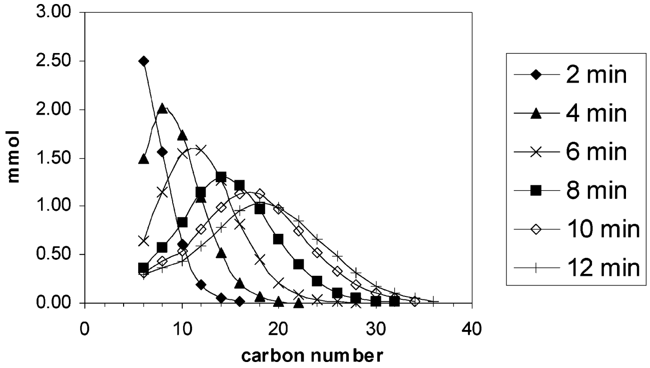


Figure 7. Molar distributions of linear alkanes obtained at different time intervals using precatalyst **14** (see Table S8).

therefore be expected to be less suited to CCG.[10a] However, when tested with 550 equiv of $ZnEt_2$, **20** afforded low molecular weight, largely saturated polymer (run 4.11), indicating that this complex does indeed undergo facile chain transfer to zinc. Since the polydispersity of the polymer is close to 2 and a large amount of diethyl zinc remained unreacted, this is an example of $ZnEt_2$ acting as a chain transfer agent rather than engaging in CCG.

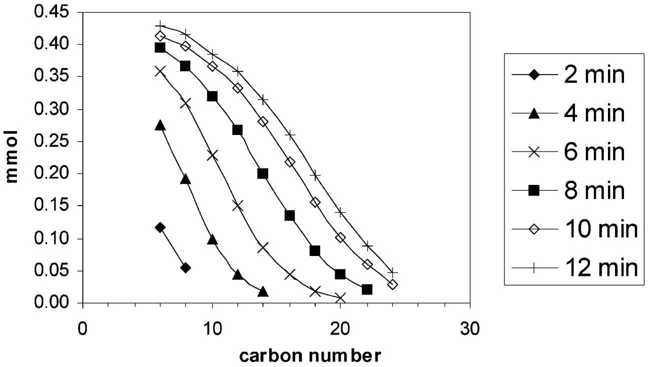


Figure 8. Molar distributions of linear 1-alkenes obtained at different time intervals using precatalyst **14** (see Table S8).

The narrow molecular weight distribution for the polymer obtained using **21** (PDI = 1.2, run 4.13) and the extension of 88% of Zn−Et groups could be the result of CCG, but the oligomers produced follow a Schulz−Flory distribution. The narrow molecular weight distribution of the isolated polymer is most likely a consequence of sampling the high molecular weight end of the Schulz−Flory distribution and accounts for only 40% of the weight and 9% of the molar mass balance. The formation of Schulz−Flory distributions was confirmed by analysis of samples taken during a chain growth experiment (Table S12, Figure S9). Insoluble polymer was formed almost instantaneously and 15 mol % of the oligomer fraction was 1-alkenes, in line with the relatively high level of vinyl end groups produced by this catalyst (run 4.13). In a similar experiment using **20**, Schulz−Flory distributions of alkanes were obtained (Table S11, Figure S8), but with a lower percentage chain growth (∼20%) and higher *k*-values (∼0.93), the latter being consistent with the effect of a bulkier bis(imino)pyridine ligand.

Group 10: α-Diimine Nickel Catalysts. The nickel complex **22**, containing a bulky α-diimine ligand, was tested in the presence of diethyl zinc (Table 5). Diethyl zinc reduces the molecular weight but leaves the polydispersity and branching levels unaffected, resulting in the formation of fully saturated, highly branched polymers of low to intermediate molecular weight. The molecular weight distributions are Schulz−Flory, and a maximum of 2% chain growth is obtained. Even in the presence of 1700 equiv of diethyl zinc, only polymer was obtained (run 5.4), showing that chain transfer to zinc is much slower than insertion. Because the conversion of diethyl zinc remained low (≤ 2%) and because **22** produced only polymer, the relative rate constants for propagation and chain transfer to

Table 4. Chain Transfer Experiments with $ZnEt_2$ and Bis(imino)pyridine Iron and Cobalt Catalysts[a]

run	catalyst	$ZnEt_2$ (mmol (equiv))	yield[b] (g)	activity (g/mmol·h·bar)	M_n[c]	M_w[c]	PDI[c]	saturated chain ends[d]	unsaturated chain ends[d]	(Zn–Et)$_{ext}$ (mmol (%))[e]
4.1	**15**	0	3.8	1500	10000	199000	19.1	2.3	0.6	
4.2	**15**	2.8 (550)	3.5	1400	700	800	1.1	38.7	0.2	5.0 (100)
4.3	**16**	0	5.0	2000	4700	45400	9.6	2.9	0.7	
4.4	**16**	2.2 (440)	5.1	2000	1000[f]	1100[f]	1.1[f]	25.5	0.8	5.1 (100)
4.5	**17**	2.8 (550)	0	0	nd	nd	nd	nd	nd	
4.6	**18**	0	3.7	1600	700	1500	2.2	21.9	18.0	
4.7	**18**	2.6 (520)	5.6	2200	700	1100	1.8	24.0	14.5	3.9 (74)
4.8	**19**	0	2.2	900	900	3400	3.6	16.9	14.0	
4.9	**19**	2.6 (520)	2.0	800	700	2000	2.9	26.4	11.0	2.0 (38)
4.10	**20**	0	2.0	800	3300	11000	3.2	4.7	3.1	
4.11	**20**	2.8 (550)	1.2	500	1500	2800	1.9	21.5	0.7	1.7 (30)
4.12	**21**	0	1.7	700	900	1900	2.2	10.9	7.2	
4.13	**21**	2.8 (550)	1.2	500	1000	1200	1.2	30.7	4.0	4.8 (88)

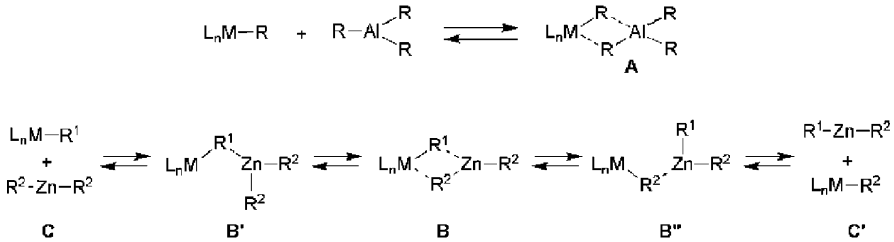
[a] Conditions: Schlenk flask test, 5 μmol of catalyst, 100 equiv of MAO, 1 bar ethylene, room temperature, 30 min, toluene solvent (50 mL). [b] Yield is total yield: solid polymer + oligomeric products (determined by GC). [c] Determined by GPC. [d] Determined by ^{1}H NMR, given per 1000 carbon atoms. [e] Defined as the number of ethyl groups that has been extended with at least one inserted ethylene, determined by GPC and NMR analysis of the polymer and GC analysis of the oligomers. [f] Contains also a small amount of high molecular weight polymer.

Table 5. Chain Transfer Experiments with $ZnEt_2$ and Nickel α-Diimine Precatalyst 22[a]

run	$ZnEt_2$ (mmol (equiv))	yield[b] (g)	activity (g/mmol·h·bar)	M_n[c]	M_w[c]	PDI[c]	(Zn–Et)$_{ext}$ (mmol (%))[d]	saturated ends[e]	methyl[e]	ethyl[e]	propyl[e]	butyl[e]
5.1	0	1.4	280	193000	435000	2.3		10	99.1	6	3.2	1.5
5.2	2.2 (440)	1.3	250	23000	67000	2.9	0.06 (1)	6.6	72.3	4.0	3.2	1.4
5.3	2.8 (550)	2.0	400	20000	36000	1.8	0.10 (2)	8.4	82.6	5.6	3.1	2.4
5.4	8.7 (1700)	1.5	300	4300	8400	1.9	0.35 (2)	12.9	89.7	6.1	3.5	3.1

[a] Conditions: Schlenk flask test, 5 μmol of **22**, 100 equiv of MAO, 1 bar ethylene, room temperature, 60 min, toluene solvent (50 mL). [b] Yield of precipitated polymer. [c] Determined by GPC. [d] Defined as the number of ethyl groups that has been extended with at least one inserted ethylene, determined by GPC analysis of the polymer. [e] Determined by ^{13}C NMR, given per 1000 carbon atoms.

Scheme 2



zinc can be determined from a Mayo plot.[28] Analysis of the polymer data from Table 5 showed that chain propagation is faster than chain transfer to zinc by a factor 200−300 (see Supporting Information). The branched polymer is a result of chain running, an isomerization process consisting of β-H transfer to Ni and re-insertion of the alkene.[29] Because the branching levels are unaffected by the presence of diethyl zinc, chain transfer to zinc does not affect the rate of chain running relative to propagation.

Discussion

Mechanistic Considerations. Catalysts affording active polymerization systems in the presence of diethyl zinc generally show activities comparable to those of their zinc-free counterparts. The three complexes that are inactive, Cp_2ZrCl_2 (**5**), the constrained geometry catalyst **10**, and the Fe oligomerization catalyst **17**, all have a relatively open coordination sphere which may favor stronger binding of the zinc alkyl reagent (vide supra); the activities of **5** and **17** are known to be affected negatively by the presence of TMA or other aluminum alkyls.[27,30] For metallocenes such as **5**, cationic hetero-bimetallic species of the type $[L_2M(\mu\text{-}R)_2AlR_2]^+$ have been observed and studied and are believed to be the resting state of the catalyst.[31] High concentrations of aluminum alkyls can have a detrimental effect on polymerization activity, particularly where CCG on aluminum is concerned, by shifting the equilibrium in Scheme 2 toward the resting state **A**.[20a,31c,32] We have previously proposed the involvement of related hetero-bimetallic species of general formula $[L_nM(\mu\text{-}R)_2ZnR]$ in CCG with zinc alkyls (**B** in Scheme 2); mono-bridged alkyl species (**B′** and **B″**) could also be relevant and may even be the propagating species since catalyst productivity is found not to be detrimentally affected by increasing dialkyl zinc concentration.[14]

The dissociation of **B**, or **B′** and **B″**, into dialkyl zinc and the active polymerization catalyst **C** can proceed in both

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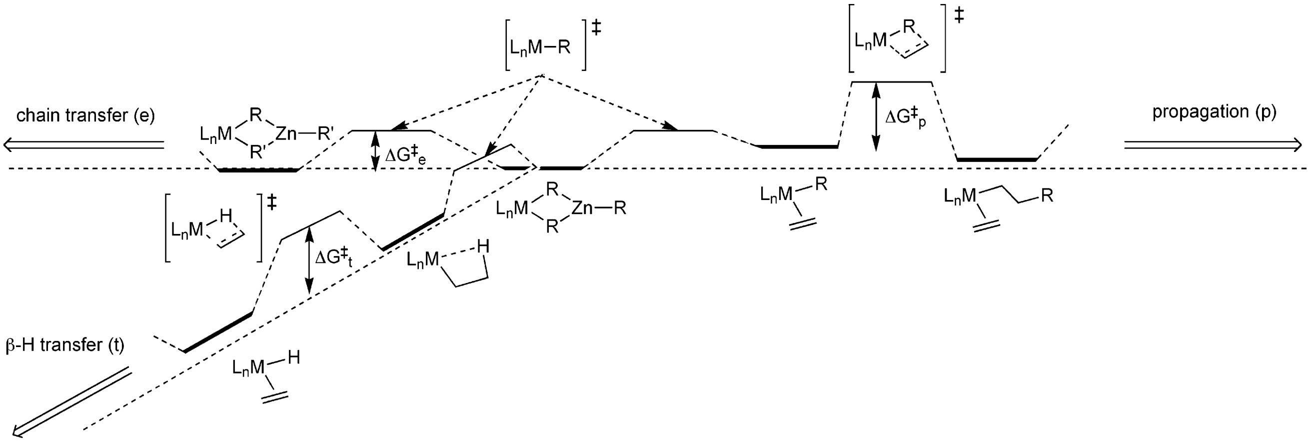
Scheme 3



directions, thereby constituting the mechanism for exchange of alkyl groups between free zinc alkyls and catalyst. In order for CCG to occur, these association and dissociation reactions have to be very rapid. The stabilities of **B**, **B′**, and **B″** are therefore crucial since it should be attainable yet not too stable. Stable hetero-bimetallic alkyl-bridged complexes involving zinc are, unlike their aluminum analogues, indeed very rare.[33] Our attempts to observe hetero-bimetallic adducts in ^{1}H NMR scale reactions between zirconocene alkyl cations, obtained from the reaction of Cp_2ZrMe_2 or $Cp^*_2ZrMe_2$ with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$, and zinc alkyls have been unsuccessful and hampered by the facile exchange of alkyl and aryl groups between zinc and boron.[34] Similarly, we were unable to isolate any hetero-bimetallic species of structure type **B** from reactions between bis(imino)pyridine iron complexes and zinc alkyls.

Those complexes that are active in the presence of diethyl zinc all undergo chain transfer to zinc. In some cases, chain transfer to zinc is the only termination pathway, affording fully saturated products; in other cases chain transfer to zinc and *β*-H transfer occur concurrently, affording both saturated and unsaturated products. The three reactions that a catalyst can undergo in the presence of diethyl zinc—propagation, *β*-H transfer, and chain transfer to zinc—are depicted in the qualitative, three-dimensional energy diagram shown in Scheme 3. For the sake of argument, here the resting state of the catalyst is assumed to be a hetero-bimetallic species $[L_nM(\mu\text{-}R)_2ZnR]$, and for any of the three reactions to occur, this species has to first dissociate to give either a mono-bridged alkyl species or $[L_nM-R]$. The latter is depicted here as a transition state.

The types of products and distributions obtained with each catalyst are governed by the relative heights of the activation barriers for insertion ($\Delta G^‡_p$), *β*-H transfer ($\Delta G^‡_t$), and chain transfer to zinc ($\Delta G^‡_e$). For some catalysts, the hetero-bimetallic species might be higher in energy than the metal alkyl species $[L_nM-R]$. In this case, the resting state of the catalyst is assumed to be a metal alkyl or alkyl olefin complex, and the hetero-bimetallic species is assumed to be a high-energy intermediate or transition state during chain transfer to zinc. The observation of unimpeded chain running with the nickel catalyst **22** in the presence of diethyl zinc favors this alternative energetic ordering. Irrespective of the identity of the resting state, the product distribution is still governed by the relative heights of the three activation barriers, $\Delta G^‡_p$, $\Delta G^‡_t$, and $\Delta G^‡_e$.

Determination of Relative Rates of Chain Transfer versus Chain Propagation. The molecular weight distributions of the products obtained using different catalysts vary widely. Bis(imino)pyridine iron complexes **15** and **16** and zirconium and hafnium phenoxyimine complexes **2** and **3** afford Poisson distributions of zinc alkyls, albeit with the formation of some 1-alkenes in the case of **2**. Titanium phenoxyimine complexes **1** and **4**, on the other hand, undergo chain transfer to zinc as a termination pathway, affording Schulz−Flory distributions of alkanes.

For the zirconium bis(indenyl) complex **9** chain transfer is reversible, but not sufficiently fast to give CCG on zinc, thereby producing alkane distributions that are intermediate between Poisson and Schulz−Flory distributions. To understand how different product distributions of alkanes and 1-alkenes can be obtained, we have exploited a statistical modeling program that enables us to correlate product distributions with relative rates (see Supporting Information). This model calculates alkane and 1-alkene distributions on the basis of the *relative rates* of the three reactions depicted in Scheme 3: propagation (p), chain transfer to zinc (e), and *β*-H transfer (t). For those complexes whose product distributions have been followed with time, the ratios of e/p and t/p that give the best fit between experimentally determined and calculated distributions are shown in Table 6.

On the basis of the t/p ratio determined for each complex, the $M_{n,th}$ that is expected to result in the absence of any chain transfer to zinc can be calculated. In Table 6 these values are reported together with the $M_{n,exp}$ taken from the control experiments without diethyl zinc. Generally, both values fall in the same range, although some deviations clearly exist. In many of the control experiments, *β*-H transfer is not the only, or even the main, termination pathway, as shown by the excess of saturated over unsaturated end groups present in the polymer. The presence of chain transfer to aluminum due to MAO results in a lowering of molecular weights, which may explain why for some complexes $M_{n,exp}$ is smaller than $M_{n,th}$. Also, for calculating $M_{n,th}$, single-site catalyst behavior with a Schulz−Flory polymer distribution is assumed, while several of the catalysts produce much broader distributions.

The reasonable correlation between $M_{n,th}$ and $M_{n,exp}$ suggests that the ratio of *β*-H transfer to insertion is not

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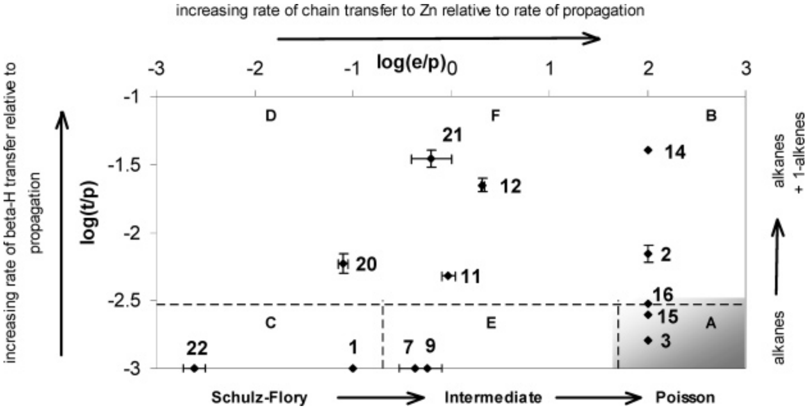

Figure 9. Classification of catalysts according to their rates of β-H transfer (t) and chain transfer to zinc (e) relative to propagation (p) (see Table 6).

Table 6. Relative Rates of Chain Transfer to Propagation (e/p) and β-H Transfer to Propagation (t/p) for Various Catalysts

complex	Table[a]	e/p[b]	t/p[b]	$ZnEt_2$ (mmol)[c]	$M_{n,th}$[d]	$M_{n,exp}$[e]
1	S1	0.1	<0.001	4.4	>28000	247000
2	S2	≥100	0.006−0.008	4.2	3600−4700	5500
3	S3	≥100	0.0016	4.6	18000	7000
7	S4	0.3−0.6	<0.001	4.4	>28000	9300
9	S5	0.4−0.8	<0.001	4.4	>28000	91000
11	S6	0.8−1.1	0.0048	4.4	5900	7500
12	S7	2−2.2	0.02−0.025	4.4	1200−1500	nd
14	S8	≥100	0.038−0.042	4.6	700−800	900
15	S9	≥100	0.0025	5.3	11000	10000
16	S10	≥100	0.003	4.0	9400	4700
20	S11	0.07−0.09	0.005−0.007	4.4	4100−5700	3300
21	S12	0.4−1	0.03−0.04	4.4	800−1000	900

[a] The experimentally obtained data used in each entry is that obtained from the experiment described in the specified table. [b] Relative rates that give the best fit of the experimentally obtained distributions with the distributions calculated through modeling (see Supporting Information). [c] Amount of $ZnEt_2$ used in the calculations. [d] M_n calculated from t/p for a control experiment without $ZnEt_2$. [e] M_n obtained in control experiment without $ZnEt_2$.

affected by the presence of diethyl zinc, nor by the rate of chain transfer to zinc. This implies that, concerning the alkane versus alkene selectivity, the best catalyst for CCG should be a catalyst that produces high molecular weight polyethylene in the absence of diethyl zinc. Following this reasoning, a living polymerization catalyst might be anticipated to be an ideal CCG catalyst, since it shows no β-H transfer at all. However, not only is a slow β-H transfer required but also a very fast chain transfer to zinc, a characteristic not normally associated with a living polymerization catalyst but one that should not be ruled out. The “living” polymerization catalyst **4** can no longer be termed living in the presence of diethyl zinc (run 1.8). However, chain transfer to zinc is even slower with this catalyst than with its nonliving analogue **1** (run 1.2), making it unsuitable for CCG. Little chain transfer to zinc has been seen when related fluorinated phenoxyimine titanium complexes have been used.[35]

Classification of Olefin Polymerization Systems. While the rate of β-H transfer can to some extent be predicted from the molecular weight distribution obtained in the absence of diethyl zinc, there seems to be no “hard and fast” rule to predict whether a catalyst will undergo efficient chain transfer to zinc. Catalysts that show chain transfer to aluminum are likely to undergo chain transfer to zinc, but even catalysts that show virtually no sign of chain transfer to aluminum can have a very fast chain transfer to zinc, as shown by Cr complex **14**. We found chain transfer to zinc to be sufficiently fast for CCG with **2**, **3**, and **14**−**16**. These complexes contain three types of ligands based on four different transition metals, ranging from early to late and first to third row (Zr, Hf, Cr, Fe) metals, disguising any obvious trend. The only similarity between these complexes is the presence of an imine functionality, but this is likely to be a coincidence. Comparison of the bis(imino)pyridine vanadium (**11**, **12**) and cobalt (**20**, **21**) catalysts shows that a small reduction in the size of the imine substituent results in a faster chain transfer to zinc and faster β-H transfer, both relative to insertion. For the corresponding iron complexes **15** and **16**, β-H transfer is also faster for the less sterically crowded **16**, but chain transfer for both catalysts is too fast to observe any difference between them. The more efficient chain transfer to zinc in the case of Zr (**2**) and Hf (**3**) phenoxyimine complexes compared with the Ti complexes (**1**, **4**) might result from the larger ionic radius of Zr^{4+} (0.86 Å) and Hf^{4+} (0.85 Å) relative to that of Ti^{4+} (0.75 Å). The covalent character of zinc−carbon bonds might also make them more compatible with the zirconium− and hafnium−carbon bonds than with the more polarized titanium−carbon bond.

To develop an overall classification of olefin polymerization catalysts according to their intrinsic rates of propagation, β-H transfer, and chain transfer to zinc, the relative rates of chain transfer to propagation (e/p) versus the relative rates of β-H transfer to propagation (t/p) are plotted in Figure 9. The catalysts can be assigned to six categories of product distributions according to the value/range of relative rates obtained from the simulations shown in Table 6.

A. Poisson distribution of alkanes (CCG): chain transfer has to be much faster than insertion (e/p > ∼100) and β-H transfer has to be much slower than insertion (t/p < ∼0.003). Catalysts in this category (shaded gray in Figure 9) include those derived from the Hf phenoxyimine complex **3** and the bis(imino)pyridine Fe complexes **15** and **16**.

B. Alkane distribution deviating from Poisson due to alkene formation: chain transfer is much faster than insertion (e/p > ∼100), but the rate of β-H transfer is sufficiently high (t/p > ∼0.003) to observe 1-alkenes and deviation from an ideal Poission distribution. Catalysts falling within this category are those derived from Zr phenoxyimine complex **2** and Cr salicylaldimine complex **14**.

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C. Schulz−Flory distribution of alkanes: the rate of insertion is faster than chain transfer to zinc and much faster than β-H transfer (e/p < ∼0.2 and t/p < ∼0.003). Catalysts in this category include Ni α-diimine **22** and Ti phenoxyimine derivatives **1** and **4**.

D. Schulz−Flory distributions of alkanes and 1-alkenes: the rate of insertion is faster than chain transfer to zinc (e/p < ∼0.2), but the rate of β-H transfer is significant (t/p > ∼0.003). Catalysts falling within this category include those derived from bis(imino)pyridine Co complex **20** and probably bis(imino)pyridine Fe complexes **18** and **19**.

E. Intermediate distribution of alkanes: the relative rates of insertion versus chain transfer (∼0.2 < e/p < ∼100) afford distributions intermediate between Poisson and Schulz−Flory; β-H transfer is low (t/p < ∼0.003). Catalysts in this category include those derived from metallocenes **6**−**9** and Cr salicylaldimine complex **13**.

F. Intermediate distributions of alkanes and 1-alkenes: the relative rates of insertion versus chain transfer (∼0.2 < e/p < ∼100) afford distributions intermediate between Poisson and Schulz−Flory, but the rate of β-H transfer (t/p > ∼0.003) is sufficiently high to give 1-alkenes. The catalysts in this category include those derived from bis(imino)pyridine V (**11** and **12**) and Co (**21**) derivatives.

Standard Schulz−Flory and Poisson distributions can be used to describe systems at the extremes, i.e., either slow (category **C**) or very fast (category **A**) chain transfer reactions, respectively. However, assigning boundaries between these extreme cases and intermediate situations is not straightforward, since the transition is continuous. We have selected a rather conservative value of e/p ≈ 100 for the lower boundary for CCG. For a ratio below 100, deviation from a Poisson distribution can be observed in GC traces. A much lower ratio (as low as 1) could suffice as a boundary if catalysts were classified solely on molecular weight distributions since polydispersities of 1.1 are attainable at this ratio. The upper level of e/p for Schulz−Flory distributions has been assigned to ∼0.2, since distributions with a fairly constant *k*-value can be expected below this value. Some of the catalysts that fall in the intermediate category (**E**) produce alkane distributions that actually obey Schulz−Flory distributions, but their *k*-values increase with time. We therefore classify them as intermediate cases. The upper boundary for the rate of β-H transfer has been assigned to a ratio of t/p ≈ 0.003. For higher amounts of 1-alkene formation, the alkane distribution can no longer be described as a true Poisson distribution (**B**).

Summary

A systematic study of chain transfer reactions between diethyl zinc and a series of homogeneous olefin polymerization catalysts containing metals across the transition series has been carried out. Complexes with little steric crowding around the metal center result in inactive systems, whereas all other catalysts show activities comparable to those obtained in the absence of diethyl zinc. The active catalysts all undergo chain transfer to zinc, but with largely differing rates, resulting in the formation of differing product distributions, some of which have not been described previously. A statistical modeling program has been exploited to understand and analyze the origin of these distributions: the relative rates of olefin insertion versus chain transfer to zinc, and versus β-H transfer, have been derived for each catalyst, allowing catalysts to be classified according to their relative rates of chain transfer to chain propagation. However, predicting which catalyst systems will afford bona fide CCG catalysts is not straightforward. While a reasonable match between the intrinsic bond dissociation energies of both the main group and transition metal alkyl species is clearly important, the M−C bond energies of the bridging alkyl species, and hence the stability of any hetero-bimetallic intermediates or transition states, are key. The latter are strongly influenced by the steric environment around the participating metal centers, more bulky ligands leading to a weakening of the bonds to the bridging alkyl groups and thus explaining why CCG tends to be more favored for sterically hindered catalysts.

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Supporting Information Available: Experimental details, formulas, and methods used for Schulz−Flory and Poisson distributions, C++ code for the modeling program, and additional GPC and GC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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