ORGANOMETALLICS

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pubs.acs.org/Organometallics

Alternating α-Olefin Distributions via Single and Double Insertions in Chromium-Catalyzed Ethylene Oligomerization

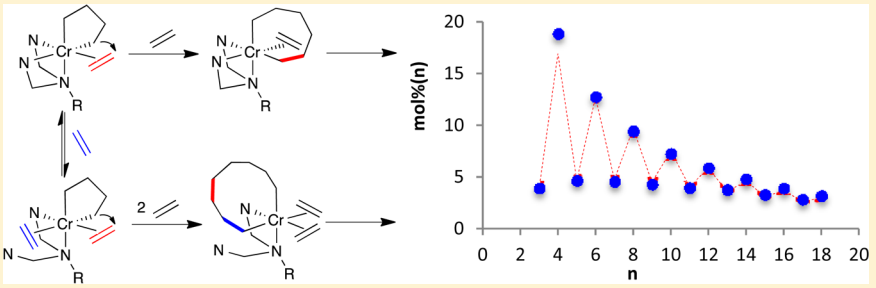
Atanas K. Tomov,[†] James D. Nobbs,[†] Juan J. Chirinos,[†] Prabhjot K. Saini,[†] Robert Malinowski,[†] Sarah K. Y. Ho,[†] Craig T. Young,[†] David S. McGuinness,[‡] Andrew J. P. White,[†] Mark R. J. Elsegood,[§] and George J. P. Britovsek*[,†]

[†]Department of Chemistry, Imperial College London, Exhibition Road, London, SW7 2AZ, U.K.

[‡]School of Physical Sciences−Chemistry, University of Tasmania, Private Bag 75, Hobart 7001, Australia

[§]Chemistry Department, Loughborough University, Loughborough, LE11 3TU, U.K.

Supporting Information



ABSTRACT: The catalytic oligomerization of ethylene with chromium-based complexes containing bis(benzimidazolemethyl)-amine (BIMA) ligands results in alternating distributions of linear α-olefins (LAOs). Extremely high activities are obtained (>100 000 g mmol^{-1} h^{-1} bar^{-1}) with *N*-alkyl-substituted BIMA ligands, whereas bulky groups on the central nitrogen or alternative central donors result in much lower activities. Variations in the ligand backbone, as well as methylation of the benzimidazole units, lead to reduction in activity. The alternating LAO distributions have been mathematically analyzed using second-order recurrence relations. The shape of the distributions is affected by ethylene pressure (1−4 bar) and by the cocatalyst to some degree. On the basis of the results and analysis presented herein, we propose that the alternating behavior originates from the ability of these chromium BIMA catalysts to undergo single as well as double ethylene insertion reactions. A minor second distribution (<5 wt %) of 2-ethyl-1-alkenes is obtained under certain conditions, resulting from incorporation of 1-butene. DFT studies (M06L) and experimental observations regarding the reaction between $AlMe_3$ and the *N*-methyl BIMA ligand **2** have shown that deprotonation of the benzimidazole N−H units can occur, which suggests a change in coordination of the BIMA ligand under oligomerization conditions.

INTRODUCTION

Linear α-olefins (LAOs) are important chemical intermediates for the production of detergents and lubricants and as co-monomers in linear low-density polyethylene (LLDPE).[1−4] Several commercial processes produce LAOs with different distributions of chain lengths. The Alfen process involves stepwise insertions of ethylene into the Al−C bonds of aluminum alkyls, resulting in a range of LAOs that follow a Poisson distribution. The Shell Higher Olefin Process (SHOP) oligomerizes ethylene with a nickel-based catalyst (see Figure 1),[5] where chain propagation competes with chain termination according to the Cossee mechanism,[6] resulting in LAOs with a Schulz−Flory distribution.[7,8] Several chromium complexes have been reported that oligomerize ethylene with high selectivity to 1-hexene or 1-octene, for example, those based on PNP ligands[9−12] and more recently with PNC═N and PC═N ligand systems.[13,14] The trimerization of ethylene to 1-hexene with a pyrrole/chromium-based catalyst is operated by the

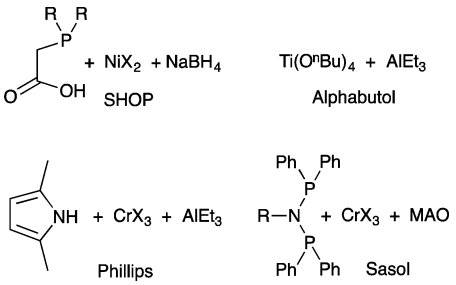


Figure 1. Examples of commercial ethylene oligomerization catalysts (X = appropriate anion).

Phillips Petroleum Company,[15] and Sasol has recently commercialized a tri/tetramerization technology based on

Received: August 22, 2016

DOI: 10.1021/acs.organomet.6b00671
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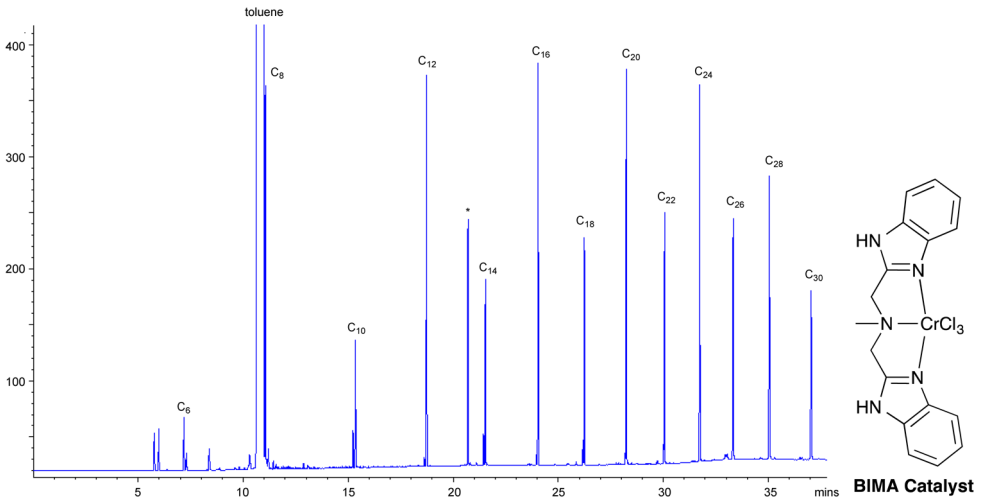

Figure 2. GC-FID analysis of an alternating olefin distribution obtained with chromium BIMA catalyst [Cr(**2**)Cl_3]/MAO (* = standard 2,2,4,4,6,8,8-heptamethylnonane).

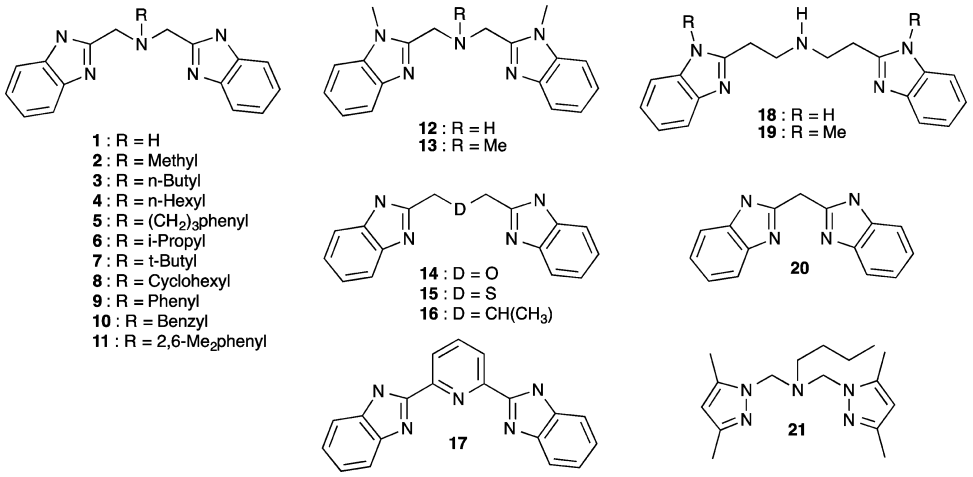

Figure 3. Overview of ligands **1**–**21**.

PNP/chromium catalysts for the production of 1-hexene and 1-octene.[16] Some examples of commercial oligomerization catalysts are collected in Figure 1. Deuterium labeling studies have shown that many chromium catalysts operate via a metallacyclic mechanism rather than a Cossee chain growth mechanism.[17−19]

In 2006, Tomov et al. reported a chromium bis(benzimidazolemethyl)amine (BIMA) complex that, in combination with methylaluminoxane (MAO) as the cocatalyst, generates a highly active ethylene oligomerization catalyst with activities of 100 000 g $mmol^{-1}$ h^{-1} bar^{-1}.[20] An unusual alternating distribution of LAOs was obtained that was very different from Schulz−Flory or Poisson distributions. The α-olefins formed from an odd number of ethylene units (n = 1, 3, 5, etc.) are significantly less abundant than the even-numbered oligomers such as 1-butene (n = 2), 1-octene (n = 4), and 1-dodecene (n = 6). An example of a chromatogram for a distribution obtained with a BIMA chromium catalyst is shown in Figure 2. Alternating distributions are still very rare and have been observed only with chromium-based catalysts, but are not exclusive to BIMA-type ligands.[21]

Here, we report a comprehensive study on these extremely active and remarkable chromium BIMA oligomerization catalysts. The effects of different ligands, the coordination geometry around chromium, reaction parameters such as pressure, and the nature of the cocatalyst on catalytic activity and product distribution have been investigated. Alternating distributions can be mathematically described by second-order recurrence relations, which are related to first-order recurrence relations, for example, the Schulz−Flory distribution.[22] Detailed analysis of the product distribution, including all side products, has led to a mechanistic proposal that involves a metallacyclic mechanism whereby both single and double ethylene insertion in the metallacycle are key steps in the oligomerization process.

RESULTS AND DISCUSSION

Ligand and Complex Synthesis. A series of nitrogen-based ligands **1**–**21** have been prepared, based on the original bis(benzimidazolemethyl)amine ligand **2** (see Figure 3). The synthesis and characterizing data of ligands **2**, **6**, **8**, **9**, **10**, **11**, **13**, and **16**,[23] as well as **4**, **5**, and **12**,[24,25] have been previously reported by us. The BIMA ligands **1**, **14**, and **15**,[26] as well as **17**,[27] **20**,[28] and **21**,[29] have been prepared by published methods, and our ^{1}H NMR values agree with those reported previously. The extended ligands **18** and **19** were prepared according to a published procedure by condensation of phenylenediamine with 3,3′-iminodipropionitrile, and our NMR data agreed with the data provided.[30,31] The new ligands

DOI: 10.1021/acs.organomet.6b00671
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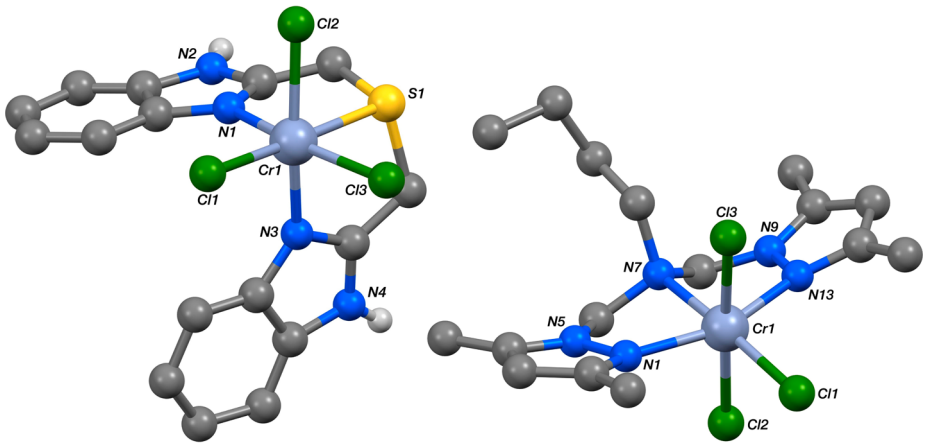

Figure 4. Molecular structures of the complexes *fac*-[Cr(**15**)Cl_3] and *mer*-[Cr(**21**)Cl_3].

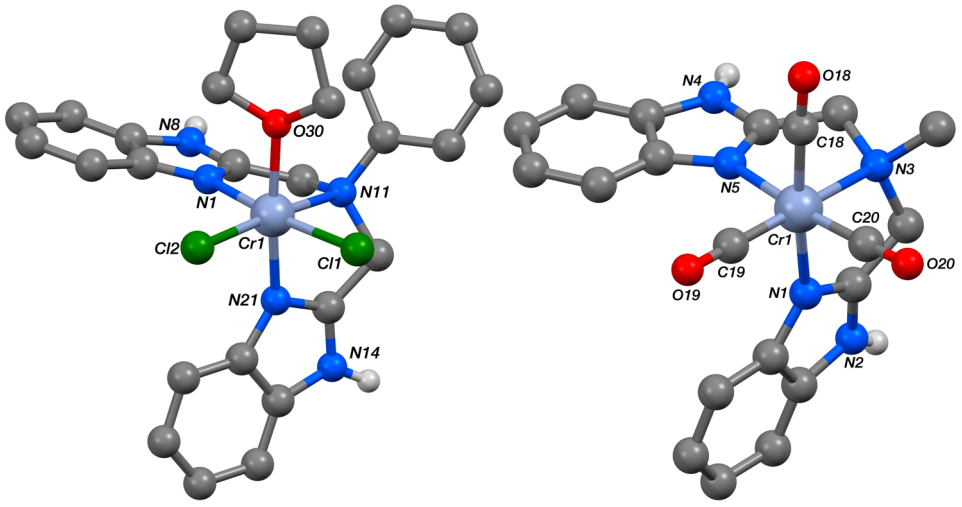

Figure 5. Molecular structures of the cationic complex *fac*-[Cr(**9**)Cl_2(thf)](SbF_6) (SbF_6^- anion has been omitted for clarity) and *fac*-[Cr(**2**)$(CO)_3$].

3 and **7** were prepared by conventional condensation of phenylenediamine with *N*-alkyliminodiacetic acid diethyl ester (see Experimental Section).

The syntheses and characterization of complexes [Cr(**2**)Cl_3][20] and [Cr(**17**)Cl_3][27,32] have been described previously. All other chromium trichloride complexes [Cr(**L**)Cl_3] were prepared by combining equimolar amounts of [$CrCl_3$(thf)$_3$] and the relevant ligand in tetrahydrofuran. The resulting paramagnetic Cr(III) complexes were insoluble in most common organic solvents and were analyzed by mass spectrometry, infrared spectroscopy, magnetic susceptibility measurements, and elemental analyses. X-ray analysis was carried out on crystals obtained from dimethylformamide (DMF) solutions for complexes [Cr(**3**)Cl_3], [Cr(**15**)Cl_3], and [Cr(**21**)Cl_3]. The structure of complex [Cr(**3**)Cl_3] is shown in Figures S15 and S16, whereas the latter two complexes are shown in Figure 4. In the case of ligand **5**, the ionic complex [Cr(**5**)Cl_2(dmf)]Cl crystallized from a DMF solution, rather than the neutral complex [Cr(**5**)Cl_3] (see Figure S21).

The poor solubility of the neutral complexes can be improved by their conversion into ionic complexes, for example with $AgSbF_6$. This enabled isolation and crystallization of the cationic complexes [Cr(**1**)$Cl_2(OH_2)$](SbF_6) and [Cr(**9**)Cl_2(thf)](SbF_6), the molecular structures of which can be found in Figure S20 and Figure 5, respectively. An alternative chromium source, [$Cr(CO)_6$], was also investigated, which gave access to complex [Cr(**2**)$(CO)_3$], which was characterized by NMR and X-ray diffraction (see Figure 5). Chromium(0) carbonyl complexes with phosphine ligands have been oxidized with silver salts to chromium(I) complexes and used as catalyst precursors in ethylene oligomerization.[33,34]

Bis(benzimidazole) ligands generally adopt a facial (*fac*) coordination mode around the chromium center, as seen previously in [Cr(**2**)Cl_3][35] and here in complexes [Cr(**3**)Cl_3], [Cr(**15**)Cl_3], and [Cr(**2**)$(CO)_3$], and in the cationic complexes [Cr(**5**)Cl_2(dmf)]Cl and [Cr(**9**)Cl_2(thf)](SbF_6). The chloro ligand *trans* to one of the benzimidazole units is substituted in these cationic *fac* complexes. Meridional (*mer*) coordination is less common and is seen with smaller ligands, for example in the bis(benzimidazole)amine complex [Cr(**1**)$Cl_2(OH_2)$](SbF_6) and the bis(pyrazole)butylamine complex [Cr(**21**)Cl_3], suggesting that the size of the ligands may affect the coordination mode. The chloro ligand *trans* to the central amine donor is substituted in the cationic *mer* complex. The difference between the *fac*/*mer* coordination modes appears to be rather subtle, as both can be obtained with seemingly similar ligands. For example, the *mer* geometry is observed for the bis(pyrazole) amine ligand **21** in [Cr(**21**)Cl_3], whereas a *fac* mode has been reported for the very similar *N*-methyl ligand.[36] Furthermore, the same ligand can show different coordination

DOI: 10.1021/acs.organomet.6b00671
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Table 1. Ethylene Oligomerization Results with [Cr(L)Cl_3]/MAO (L = 1−21)[a]

					solid PE		
run	catalyst (μmol)	activity	liquid wt % (LAO)	Schulz−Flory α	M_n	M_w	PDI
1	[Cr(**1**)Cl_3] (0.03)	15 000	18 (99)				
2	[Cr(**2**)Cl_3] (0.03)	102 000	21 (99)		1920	3530	1.8
3	[Cr(**3**)Cl_3] (0.03)	96 000	11 (97)		1240	4790	3.9
4	[Cr(**4**)Cl_3] (0.03)	97 000	6 (92)		1,250	5620	4.5
5	[Cr(**5**)Cl_3] (0.03)	39 000	12 (97)		2550	9400	3.7
6	[Cr(**6**)Cl_3] (0.03)	20 000	3 (98)		7710	127 710	16.6
7	[Cr(**7**)Cl_3] (0.03)	27 000	4 (99)		6310	131 130	20.8
8	[Cr(**8**)Cl_3] (0.03)	11 000	0		8890	158 700	17.9
9	[Cr(**9**)Cl_3] (0.03)	11 000	5 (99)		3930	92 830	23.7
10	[Cr(**10**)Cl_3] (0.03)	5000	17 (98)		2470	24 150	9.8
11	[Cr(**13**)Cl_3] (0.03)	320	nd				
12	[Cr(**14**)Cl_3] (0.3)	2200	11	0.95			
13	[Cr(**15**)Cl_3] (0.4)	75	46	0.79			
14	[Cr(**16**)Cl_3] (2)	770	92	0.55			
15	[Cr(**17**)Cl_3] (1)	2500	79 (99)	0.87	710[c]		
16	[Cr(**18**)Cl_3] (10)	44	20 (99)				
17	[Cr(**19**)Cl_3] (10)	21	9 (99)	0.62			
18	[Cr(**20**)Cl_3] (5)[b]	16	0				
19	[Cr(**2**)Cl_2(thf)](SbF_6) (0.03)	16,000	21 (98)		1200[c]		
20	[Cr(**9**)Cl_2(thf)](SbF_6) (0.03)	16 000	9 (99)		2800[c]		
21	[$CrCl_3$(thf)$_3$] (25)[d]	88	96 (99)	0.54			

[a]Conditions: 4 bar of ethylene pressure, 50 °C, MAO (5 mmol), toluene 200 mL, 1 h. Activity in g $mmol^{-1}$ h^{-1} bar^{-1}. [b]1 barg (bar gauge) of ethylene pressure. [c]Determined by ^{1}H NMR. [d]4 barg of ethylene pressure, 50 °C, MMAO-12 (500 equiv), toluene 100 mL, 1 h.

modes in different complexes; for example, ligand **2** coordinates in a *fac* mode in [Cr(**2**)Cl_3], but a *mer* coordination is observed in [Cr(**2**)Cl(acac)](SbF_6) when a bidentate acac ligand is employed.[20,35]

Ethylene Oligomerization Results. The chromium(III) complexes [Cr(**L**)Cl_3], where **L** = **1**−**21**, have been applied as catalysts for the oligomerization of ethylene (Table 1). The liquid fractions have been analyzed by FID-GC and the solid fractions by GPC in selected cases. For those catalysts that give an alternating olefin distribution, up to approximately 20 wt % of the total product collected is in the liquid phase, consisting of essentially pure C_4−C_{38} LAOs. The gas phase contains predominantly ethylene and butene, which were not quantified. Solid polyethylene (80−100 wt %) constitutes the remainder of the product spectrum, and the fraction with M_n values between 1000 and 2000 is the tail end of the overall LAO distribution. On the basis of several identical runs, the error in terms of activity and product selectivity values was estimated to be approximately 10% (see Table S1 and Figure S7).

Extremely high activities of approximately 100 000 g $mmol^{-1}$ h^{-1} bar^{-1} can be obtained with chromium BIMA complexes, for example, ligands **2**−**4** with *n*-alkyl substituents (Me, ^{n}Bu, or ^{n}Hex, runs 2−4). Catalytic activities are very sensitive to the nature of the substituent at the central amine. Complex [Cr(**1**)Cl_3], with a hydrogen substituent at the central nitrogen, is significantly less active at 15 000 g $mmol^{-1}$ h^{-1} bar^{-1}. More bulky substituents (^{i}Pr, ^{t}Bu, Cy, Ph, and Bz) at the central nitrogen donor in complexes [Cr(**6**)Cl_3]−[Cr(**10**)Cl_3] lead to a reduced catalytic activity, less toluene-soluble olefins, and higher molecular weight polyethylene. The 2,6-dimethylphenyl complex [Cr(**11**)Cl_3] was inactive under these conditions, and it is likely that the central amine is not coordinated in this case, as seen for an analogous cobalt(II) complex.[23] The cationic complex [Cr(**2**)Cl_2(thf)](SbF_6) shows a lower activity compared with [Cr(**2**)Cl_3] (runs 2 and 19),[20] whereas similar results are obtained for [Cr(**9**)Cl_2(thf)](SbF_6) versus [Cr(**9**)-Cl_3] (runs 9 and 20). The catalyst precursor [$CrCl_3$(thf)$_3$] without any additional ligand gives a Schulz−Flory distribution with very low activity (run 21). It appears that small alkyl substituents such as methyl or higher linear alkyls at the central nitrogen provide an optimal donor strength, both sterically and electronically, for high catalytic activity.

Substitution at the benzimidazole nitrogens reduces the activity dramatically. For example, complex [Cr(**13**)Cl_3] with methylated benzimidazoles shows an activity of 320 g $mmol^{-1}$ h^{-1} bar^{-1}. The related complex [Cr(**12**)Cl_3] with a central NH amine donor was inactive under the conditions used. Changing the central amine to other donors such as oxygen or sulfur in complexes [Cr(**14**)Cl_3] and [Cr(**15**)Cl_3] or a noncoordinating $CH(CH_3)$ unit in complex [Cr(**16**)Cl_3] reduces the activity significantly compared with [Cr(**2**)Cl_3]. Coordination of the central sulfur donor in [Cr(**15**)Cl_3] is confirmed by X-ray analysis (see Figure 4), but this coordination is weak judging from the long Cr−S distance of 2.415(3) Å. Coordination of the central oxygen donor in complex [Cr(**14**)Cl_3] is unlikely, considering the very long metal oxygen distances seen in other complexes with this ligand.[37,38] A strongly coordinating central donor appears to be essential for high catalytic activity, and only sp^3-hybridized amine donors result in an alternating olefin distribution. An sp^2-hybridized nitrogen donor, such as pyridine in complex [Cr(**17**)Cl_3], shows a significantly lower activity and, more importantly, gives a Schulz−Flory distribution of LAOs with α = 0.87.[39] A Schulz−Flory distribution is also observed for the distributions obtained with complexes [Cr(**14**)Cl_3]−[Cr(**16**)Cl_3], where α is 0.95, 0.79, and 0.55, respectively.

Extending the bridge between the central donor and the benzimidazole units with an extra methylene unit, as in [Cr(**18**)Cl_3], results in significantly lower activity compared with [Cr(**1**)Cl_3]. The activity is further reduced for [Cr(**19**)-

DOI: 10.1021/acs.organomet.6b00671
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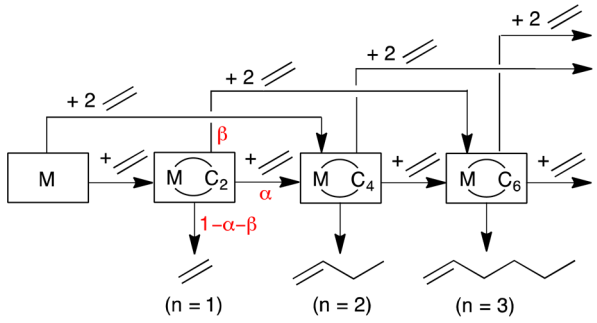
Cl_3], with *N*-methylated benzimidazole units, as seen for [Cr(**12**)Cl_3] versus [Cr(**1**)Cl_3]. Removal of the central donor in [Cr(**20**)Cl_3] or changing the benzimidazoles to pyrazole units in [Cr(**21**)Cl_3] results in very low polymerization activity. Similar activities have been reported for related chromium catalysts with bis(pyrazole)amine ligands,[40,41] whereas selective ethylene trimerization was reported with facially coordinating tridentate bis(pyrazolyl) ligands.[42]

Distribution Analysis. Chain growth in ethylene oligomerization can occur via different mechanisms, depending on the catalyst employed. For chromium complexes containing BIMA ligands, a metallacyclic mechanism is implicated based on deuterium labeling studies.[20] If chain growth proceeds via the coordination and insertion of single ethylene monomers, a Schulz–Flory distribution is obtained, as seen for example for the chromium complexes with ligands **14**–**17** and **19** (see Table 1). Schulz–Flory distributions can be mathematically described as *first-order linear homogeneous recurrence relations with a constant coefficient*, and the solution to this relation results in the typical Schulz–Flory equation: $\mathrm{mol}(n) = (1 - \alpha)\alpha^{n-1}R$, where n is the number of ethylene units in the oligomer and R is the total molar amount of oligomers produced within the reaction time. The term α is the probability of chain propagation, which is defined by the rate of propagation divided by the sum of the rate of propagation and termination. The term $1 - \alpha$ represents therefore the probability of chain termination. The mol % fraction for each oligomer equals $\mathrm{mol\%}(n) = \mathrm{mol}(n)/R = (1 - \alpha)\alpha^{n-1}$.[43]

Alternating LAO distributions, as obtained here with chromium complexes containing ligands **1**–**10**, **13**, and **18**, can be mathematically described as *second-order linear homogeneous recurrence relations with constant coefficients*.[43] Each oligomer fraction is related to the previous fraction *and* the one before by the parameters α and β, respectively, which are the probabilities of chain growth via single ethylene insertion (α) and double ethylene insertion (β) (see Scheme 1). The term $1 - \alpha - \beta$ represents the probability of termination.

Scheme 1. Ethylene Oligomerization Resulting in Alternating Distributions



The general solution to this recurrence relation takes the form $\mathrm{mol}(n) = c_1{r_1}^n + c_2{r_2}^n$, whereby $c_{1,2}$ and $r_{1,2}$ are related to α and β.[43] Experimental data obtained for an alternating distribution can be fitted to this equation to determine $c_{1,2}$ and $r_{1,2}$, and thereby α and β and $1 - \alpha - \beta$. Data fitting analysis is performed using the C_{10}–C_{34} LAO fraction (n = 5–17), and the goodness of fit is expressed by the R^2 values in the last column in Table 2. The C_4–C_8 oligomers are omitted because 1-butene (C_4) is too volatile for quantitative analysis and, as will be explained below, the experimental values for 1-hexene (C_6) and 1-octene (C_8) can sometimes deviate from the values calculated from the distribution analysis based on C_{10}–C_{34}. The analysis for a selection of distributions is collected in Table 2, and two graphical examples are shown in Figure 6. For example, data fitting analysis of the oligomerization results from C_{10}–C_{34} for complex [Cr(**4**)Cl_3] (run 4, Table 1) provides the equation $\mathrm{mol\%}(n) = 15.75(0.91)^n + 15.62(-0.80)^n$ for this particular distribution. The probabilities for single and double coordination are determined as $\alpha = 0.11$ and $\beta = 0.72$, and the probability for termination is $1 - \alpha - \beta = 0.17$. Other distributions can be found in the Supporting Information.

The relation $\mathrm{mol\%}(n) = c_1{r_1}^n + c_2{r_2}^n$ can be explained as an exponential decay function $c_1{r_1}^n$ with a positive decay parameter r_1, combined with an alternating, exponential decay function $c_2{r_2}^n$ with a negative parameter r_2. The relative importance of the various parameters $c_{1,2}$ and $r_{1,2}$ can be illustrated using the two examples shown in Figure 6. The r_1 and r_2 factors determine the steepness of the exponential decay functions. The degree of alternation is indicated by the weighting factors c_1 and c_2, and the ratio c_2/c_1 gives an indication of the extent of alternation. For example, for [Cr(**1**)Cl_3] the relatively small degree of alternation is indicated by the smaller value of $c_2/c_1 = 0.19$, whereas alternation is much more pronounced for [Cr(**4**)Cl_3], where $c_2/c_1 = 0.99$.

In many cases, differences are observed between the experimental amounts obtained for 1-hexene (C_6) and 1-octene (C_8) and those extrapolated from the C_{10}–C_{34} distribution. These minor deviations are attributed to differences in the probabilities for metallacycle growth (α and β) and termination ($1 - \alpha - \beta$) for smaller metallacycles early on in the oligomerization process. These differences become negligible for larger metallacycles beyond metallacyclononane (C_8), and the propagation and termination probabilities converge to constant values. The small deviations observed here for C_6 and C_8 with chromium BIMA catalysts are probably related to other chromium-based catalysts, where differences at the early stages of metallacycle growth lead to oligomerizations where 1-hexene or 1-octene become the major products of the distribution.[43] This is, for example, observed with chromium-based selective oligomerization catalysts.

Effect of Pressure. Ethylene oligomerization with catalyst [Cr(**17**)Cl_3], which contains a meridional ligand **17** with a

Table 2. Analysis of Alternating Distributions[a]

catalyst	$\sum$mmol(n)[b]	mol%(n) = $c_1{r_1}^n + c_2{r_2}^n$	α	β	$1 - \alpha - \beta$	β/α	c_2/c_1	R^2[c]
[Cr(**1**)Cl_3]	0.82	$18.77(0.89)^n + 3.64(-0.82)^n$	0.07	0.72	0.21	10.2	0.19	0.998
[Cr(**2**)Cl_3]	15.64	$25.16(0.90)^n + 23.06(-0.79)^n$	0.11	0.72	0.17	6.41	0.92	0.997
[Cr(**4**)Cl_3]	18.94	$15.75(0.91)^n + 15.62(-0.80)^n$	0.11	0.72	0.17	6.55	0.99	0.997
[Cr(**18**)Cl_3]	1.02	$13.28(0.92)^n + 5.58(-0.87)^n$	0.05	0.79	0.15	15.3	0.42	0.984

[a]Conditions: see Table 1. [b]Experimental total moles of LAOs from n = 3–17. [c]R^2 signifies the goodness of fit of the calculated values compared with the experimental data.

DOI: 10.1021/acs.organomet.6b00671
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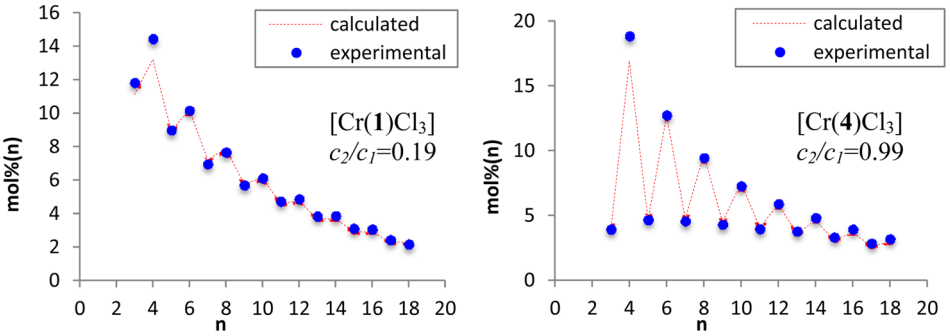

Figure 6. *Experimental* LAO distributions in mol%(n) versus n obtained with [Cr(**1**)Cl_3] (left) and [Cr(**4**)Cl_3] (right) together with *calculated* best-fit distributions (n = number of ethylene units in oligomer).

central pyridine donor, results in a Schulz−Flory distribution of LAOs.[39] The total oligomer yield obtained at different gauge pressures from 1 to 4 bar follows a first-order dependence on ethylene concentration (see Figure S2). The order in ethylene concentration for individual LAOs is conveniently determined from the slope in a ln(rate) versus ln[ethylene] plot,[44] whereby ethylene pressure is a reliable proxy for concentration in solution.[44,45] The rate can be approximated by the amount of LAO produced within a given time. A first-order dependence on ethylene pressure is observed for individual LAOs in this case, and the difference for example between the orders for 1-octene and 1-hexene formation is very close to zero (see Figure S5). The LAO distribution is characterized by α = 0.87, which is independent of ethylene pressure within the pressure range of 1−4 bar. Because α is equal to the rate of propagation divided by the rate of propagation plus the rate of termination, this suggests that both the rate of propagation and the rate of termination are affected in a similar manner by ethylene concentration and that therefore chain transfer to monomer must be the main termination pathway (rather than β-H elimination).

The effect of pressure on alternating distributions has been investigated for catalysts [Cr(**1**)Cl_3] and [Cr(**4**)Cl_3] at ethylene gauge pressures between 1 and 4 bar. The total yield of oligomers increases with a first-order dependence on ethylene pressure in both cases (see Figures S3 and S4). Figure 7 shows that the degree of alternation becomes more pronounced at higher pressure such that individual oligomers appear to have different orders in ethylene. Indeed, the

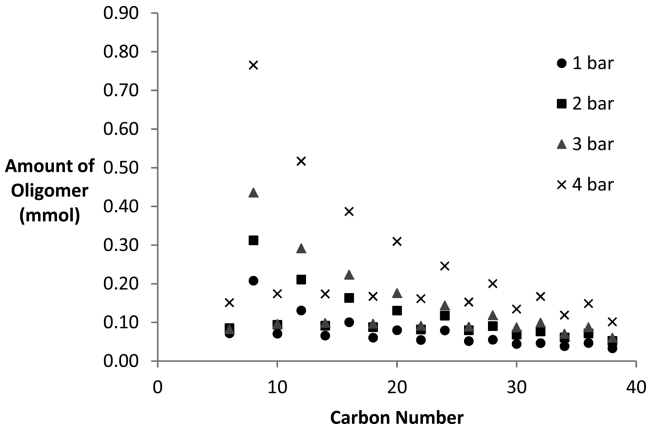

Figure 7. Pressure dependence of the LAO distribution with [Cr(4)Cl_3]. Conditions: see Table 3.

difference between the orders for 1-octene and 1-hexene formation is distinctly nonzero (see Figure S6). The higher order for the formation of 1-octene with respect to 1-hexene suggests a different mechanism involving both single and double insertions of ethylene in the case of 1-octene formation, whereas 1-hexene formation proceeds via single ethylene insertions only.

From Table 3 it appears that the ratio between the propagation probabilities for double versus single ethylene insertion (β/α) is pressure dependent. The increase in β/α shown in Figure 8 suggests that double insertion becomes more likely than single insertion at higher pressure. While the trend appears to be linear within this pressure regime, it is unclear at this stage whether this trend continues at higher or lower pressures.

Effect of Different Cocatalysts. Different cocatalysts have been evaluated in combination with BIMA catalyst [Cr(**2**)Cl_3]. All cocatalysts listed in Table 4 provide active catalyst systems, and the activities can vary considerably. MAO provides the best activity, but yields the lowest amount of oligomers in the liquid fraction. The combination of an alkylating reagent ($AlMe_3$) with several abstracting reagents ($B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, or $[PhNMe_2H][B(C_6F_5)_4]$) gives somewhat lower activities, but a larger oligomer fraction. Surprisingly, $AlMe_3$ without an abstractor also shows a reasonable activity with a comparable oligomer distribution. Experimental and calculated distributions can be found in Figures S8−12. While the differences between the distributions appear to be small, given the 10% error margin (see Table S1), we do believe they are significant. It appears that the nature of the cocatalyst can affect the oligomer distribution to some degree and that a trialkyl aluminum in general is an important aspect of the cocatalyst, something that will be discussed in more detail in the last section.

Side Products. The selectivity for the formation of LAOs obtained with chromium BIMA catalysts is generally very high, typically in excess of 95% (see Table 1). In addition to the main LAO distribution, a second minor distribution can sometimes be observed, depending on the reaction conditions. This minor distribution follows the opposite alternating pattern compared to the main distribution; that is, oligomers derived from an odd number of ethylene units are more abundant than those from an even number, as can be seen in Figure 2. Because 1-butene is the major product in these oligomerization reactions, the second minor distribution is generated from incorporation of 1-butene into the oligomerization reaction, as shown in eqs 1 and 2. This was confirmed by oligomerization experiments of ethylene with additional 1-butene, using catalyst [Cr(**2**)Cl_3] (Table 5). In the absence of 1-butene, the wt % ratio between

DOI: 10.1021/acs.organomet.6b00671
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Table 3. Pressure Dependence of the LAO Distribution with $[Cr(4)Cl_3]$/MAO[a]

P[b]	olig/mmol[c]	mol%(n)	α	β	$1-\alpha-\beta$	β/α	c_2/c_1	R^2[d]
1 barg	1.24	$13.23(0.92)^n + 9.93(-0.79)^n$	0.13	0.73	0.14	5.77	0.75	0.797
2 barg	1.88	$12.99(0.92)^n + 11.29(-0.81)^n$	0.12	0.74	0.15	6.22	0.87	0.993
3 barg	2.35	$13.79(0.92)^n + 14.18(-0.81)^n$	0.11	0.75	0.16	6.93	1.03	0.996
4 barg	4.07	$14.64(0.91)^n + 14.70(-0.81)^n$	0.10	0.74	0.16	7.06	1.00	0.996

[a]Conditions: $[Cr(4)Cl_3]$ 30 nmol, 50 °C, 1 h, 200 mL of toluene, MAO (5 mmol). [b]1 barg (bar gauge) = 2 bara (bar absolute) = 1 bar nitrogen + 1 bar ethylene. [c]Oligomers from n = 3−19. [d]R^2 signifies the goodness of fit of the calculated values compared with the experimental data.

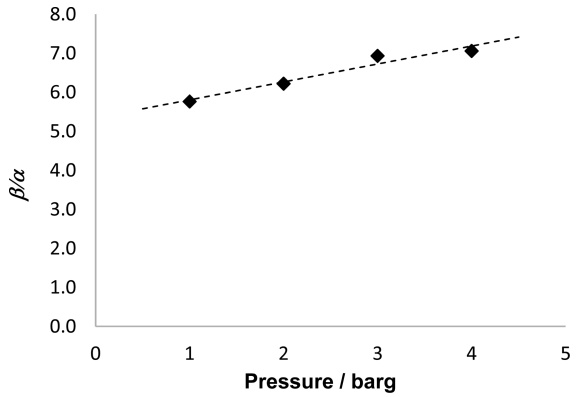
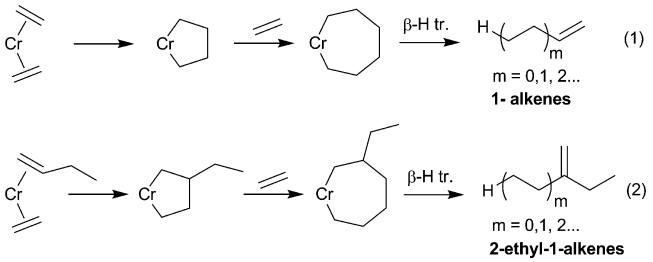


Figure 8. Dependence of β/α on ethylene gauge pressure. Trendline: linear (R^2 = 0.944). Conditions: catalyst $[Cr(4)Cl_3]$ (30 nmol), 50 °C, 1 h, 200 mL of toluene, MAO (5 mmol).



the major and minor fraction is approximately 17:1, which changes to 5:1 upon addition of an excess of 1-butene. The identity of the minor products was confirmed as a distribution of 2-ethyl-1-alkenes, based on NMR and GC analysis (see Figure S13) and comparison with an authentic sample of the C_6 product 2-ethyl-1-butene (m = 1 in eq 2). Co-oligomerization of ethylene with higher 1-alkenes is known to occur with chromium-type oligomerization catalysts that operate via a metallacyclic mechanism.[19,46−49]

The activity of the catalyst system $[Cr(2)Cl_3]$/MAO decreases significantly from 55 900 to 8400 g mmol^{-1} h^{-1} bar^{-1} upon addition of a large excess of 1-butene. Additional 1-butene is likely to slow down the rate of oligomerization due to coordination to the metal center, which will require substitution by ethylene before metallacycle growth can proceed. No oligomers due to the oligomerization of 1-butene alone are observed.

The distribution of the major 1-alkene fraction differs from the 2-ethyl-1-alkene fraction in that, aside from the opposite alternating behavior, the probability for termination ($1-\alpha-\beta$) is significantly higher for the latter, cf., 0.36 versus 0.22 (0.28 versus 0.22 with additional 1-butene). As a result, the amount of 2-ethyl-1-alkene isomer produced will decrease more rapidly than the amount of 1-alkene, and therefore the selectivity to 1-alkenes will increase across the product distribution. Termination via β-H transfer is expected to be faster for weaker tertiary C−H bonds in the 2-ethyl metallacyclic complex in eq 2. The addition of 1-butene affects the distribution in the 1-alkene and 2-ethyl-1-alkene fractions, as seen from the β/α ratios, which decrease from 5.89 to 3.99 and from 9.30 to 4.59, respectively. Different distributions for both fractions imply that 1-butene incorporation into the metallacycle affects the distribution, and 1-butene must therefore be incorporated *at the beginning of metallacycle formation and not at the end.* A stronger binding of 1-butene, but lower reactivity compared to ethylene provides an explanation for the observed behavior. These observations made here for 1-butene may also apply to other 1-alkenes and imply a general inhibition of the oligomerization reaction by the higher alkene products.

Mechanistic Considerations. *Single and Double Coordination Mechanism.* Chain growth in chromium-based BIMA catalysts proceeds via a metallacyclic mechanism.[39] A single coordination mechanism, i.e., coordination and insertion of a single ethylene unit at a time, results in a Schulz−Flory distribution, which is observed for example with chromium catalysts of ligands **14**−**17** that do not have a central amine donor. An alternating distribution is obtained via a double-insertion mechanism, whereby two ethylene monomers coordinate to the chromium center and insert sequentially.[43] In this case, the termination probability after the first insertion is zero, and the metallacycle effectively grows by two ethylene units at a time. The single- and double-insertion mechanisms can operate in parallel, and the extent of each is determined by the probabilities α and β, which are affected by the catalyst, ethylene pressure, temperature, and the coordinating properties

Table 4. Effect of Different Cocatalysts on the Oligomer Distribution with $[Cr(2)Cl_3]$

cocatalyst	activ[b]	liq wt %	mol%(n)	α	β	$1-\alpha-\beta$	β/α	R^2
MAO	18 500	8	$17.60(0.89)^n + 19.03(-0.77)^n$	0.12	0.69	0.20	5.92	0.994
$B(C_6F_5)_3$/$AlMe_3$	8000	32	$17.81(0.89)^n + 10.61(-0.76)^n$	0.13	0.68	0.20	5.39	0.998
$[Ph_3C][BAr^F]$/$AlMe_3$	12 000	35	$18.02(0.89)^n + 16.30(-0.74)^n$	0.15	0.66	0.19	4.49	0.999
$[PhNMe_2H][BAr^F]$/$AlMe_3$	13 200	46	$21.10(0.87)^n + 15.39(-0.79)^n$	0.09	0.69	0.22	8.00	0.998
$AlMe_3$	4800	32	$18.07(0.89)^n + 17.11(-0.72)^n$	0.16	0.64	0.20	3.91	0.996

[a]Conditions: catalyst $[Cr(2)Cl_3]$ 0.5 μmol, 4 barg, 1 h, 50 °C, 200 mL of toluene. [b]Activity in g mmol^{-1} h^{-1} bar^{-1}. Cocatalysts: MAO: 3 mmol (6000 equiv); $B(C_6F_5)_3$, $[Ph_3C][BAr^F]$, and $[PhNMe_2H][BAr^F]$: 0.5 mmol (1 equiv); and $AlMe_3$: 0.5 mmol (1000 equiv) $[BAr^F]^- = [B(C_6F_5)_4]^-$.

DOI: 10.1021/acs.organomet.6b00671
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Table 5. Effect of Addition of 1-Butene on the 1-Alkene and 2-Ethyl-1-alkene Distributions with [Cr(2)Cl$_3$]/MAO[a]

	activ[c]	wt%[d]	mol%(n)[e]	α	β	$1-\alpha-\beta$	β/α	R^2
1-alkenes[b]	55 900	17	21.04(0.88)^n + 20.58(−0.76)^n	0.11	0.67	0.22	5.89	0.996
2-ethyl-1-alkenes[a]		1	36.16(0.79)^n + 26.39(−0.73)^n	0.06	0.58	0.36	9.30	0.999
1-alkenes[b]	8400	29	22.45(0.87)^n + 24.85(−0.71)^n	0.16	0.62	0.22	3.99	0.996
2-ethyl-1-alkenes[b]		6	23.97(0.83)^n + 27.14(−0.71)^n	0.13	0.59	0.28	4.59	0.999

[a]Conditions: catalyst [Cr(2)Cl$_3$] (30 nmol), MAO (7 mmol), 4 bar, 1 h, 50 °C, 200 mL of toluene. [b]Conditions: [Cr(2)Cl$_3$] 150 nmol, MAO (7 mmol), 4 bar, 1 h, 50 °C, 200 mL of toluene, 1-butene (3.5 g) added. [c]Activity in g mmol^{-1} h^{-1} bar^{-1}, includes 1-alkenes, 2-ethyl-1-alkenes, and polymer. [d]Weight percentage of olefins in the liquid fraction, remainder is solid polyethylene. [e]1-Alkenes distribution: n = 1 is ethylene, n = 2 is 1-butene etc.; 2-ethyl-1-alkenes distribution: n = 1 is 1-butene, n = 2 is 2-ethyl-1-butene, etc.

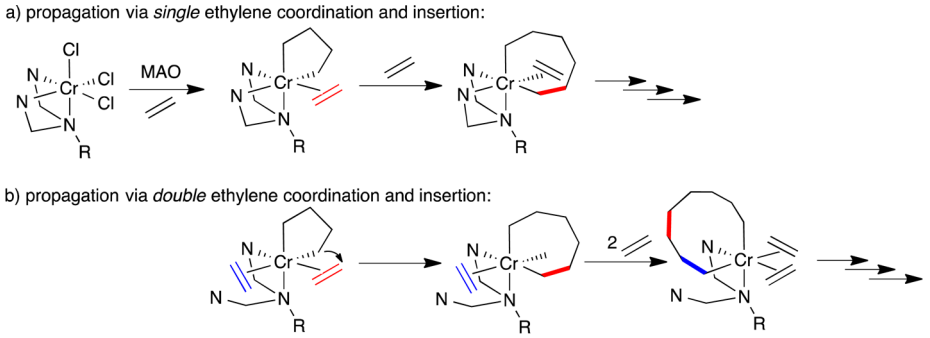
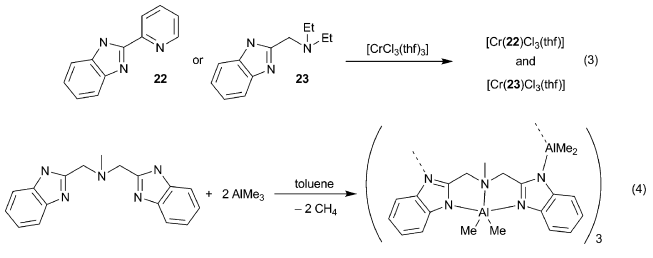


Figure 9. Metallacycle growth via (a) single and (b) double ethylene coordination and insertion.

of the solvent and the anion (cocatalyst). We have previously established a double-insertion route as the main mechanism in ethylene tetramerization with Cr-PNP catalysts.[22]

The growth of the metallacycle by single ethylene insertion requires a facial arrangement of the metallacyle and the ethylene monomer prior to insertion (Figure 9a). The insertion of two ethylene monomers requires double ethylene coordination. This arrangement can lead to the sequential insertion of two ethylene units *without* termination by β-H transfer after the first insertion. For each insertion step, the metallacycle and the ethylene monomer must be in facial orientation, as illustrated in Figure 9b.

Structural studies (*vide infra*) have shown that BIMA ligands can coordinate in a tridentate *fac* or *mer* fashion (see Figure 4), and a strong binding of the central donor was found to be essential for high catalytic activity. Coordination of two ethylene units to a chromium BIMA metallacyclic complex would generate a seven-coordinate complex, unless one of the donors dissociates. To explore this further, we investigated two related *bidentate* benzimidazole pyridine and benzimidazole amine ligands, **22** and **23** (see eq 3). Combination of these



ligands with [CrCl$_3$(thf)$_3$] is assumed to generate complexes of the type [Cr(**L**)Cl$_3$(thf)], as reported for similar bidentate nitrogen donor ligands.[49−51] Very low activities were observed for both catalysts (see Table 6). Similar reduction in catalytic activity was observed by McGuinness with tridentate versus bidentate pyridine carbene ligands.[49] The chromium complex with benzimidazole pyridine **22** resulted in a Schulz−Flory distribution of LAOs, similar to the oligomerization with the bis(benzimidazole) pyridine ligand **17** (see Table 1, run 15). The distribution obtained with ligand **23** showed alternating behavior (Table 6). Tridentate BIMA ligands clearly give a much better performance than the bidentate ligands **22** and **23**. Notwithstanding, partial dissociation of one donor during metallacycle growth to provide the necessary coordination sites for two ethylene monomers cannot be dismissed from these results.

The Nature of the Active Species. It is very likely that during the activation of the BIMA precatalyst with the cocatalyst, which contains AlMe$_3$, the benzimidazole NH functionalities become deprotonated to give anionic benzimidazolide ligands. This proposal is supported by a separate reaction carried out between BIMA ligand **2** and AlMe$_3$ according to eq 4. The reaction of **2** with two equivalents of AlMe$_3$ in toluene resulted in deprotonation of both benzimidazole NH groups, followed by trimerization to give a hexanuclear aluminum complex, [(AlMe$_2$)$_2$(**2′**)]$_3$, which was characterized by NMR spectroscopy and X-ray diffraction (see Figure S23). Related cyclic aluminum benzimidazole complexes have been reported previously.[52,53]

These observations suggest that the active species is generated upon reaction of the cocatalyst (AlMe$_3$) with the chromium trichloride precatalyst via deprotonation of the BIMA ligand. The requirement of AlMe$_3$ in the cocatalyst seen earlier is in agreement with this proposal. A polymerization reaction carried out using a combination of [(AlMe$_2$)$_2$(**2′**)]$_3$, [CrCl$_3$(thf)$_3$], and MAO resulted in a moderately active polymerization system, giving an alternating distribution of LAOs (see Table 6).

The possibility of partial ligand dissociation was also investigated by DFT calculations. The relative free energy profile for a series of potential intermediates formed upon reaction of BIMA complex [Cr(**2**)Cl$_3$] (**I**) with one or two equivalents of AlMe$_3$ is shown in Figure 10. Deprotonation by

DOI: 10.1021/acs.organomet.6b00671
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Table 6. Alkene Distributions with $[CrCl_3(thf)_3]$/22, $[CrCl_3(thf)_3]$/23, and $[CrCl_3(thf)_3]/[(AlMe_2)_2(2')]_3$[a]

	activ[b]	wt %[c]	mol%(n)[d]	α	β	$1-\alpha-\beta$	β/α	R^2
[Cr]/**22**	10	34	SF	0.62				0.999
[Cr]/**23**	13	17	$12.89(0.79)^n + 14.07(-0.63)^n$	0.16	0.50	0.34	3.12	0.964
$[Cr]/[(AlMe_2)_2(2')]_3$[e]	2066	20	$27.56(0.89)^n + 23.08(-0.80)^n$	0.09	0.71	0.21	8.32	0.996

[a]Conditions: catalyst [Cr] = $[CrCl_3(thf)_3]$: 25 μmol, ligand 1 equiv, MMAO-12 (12.5 mmol), 4 bar, 1 h, 50 °C, 100 mL of toluene. [b]Activity in g $mmol^{-1}$ h^{-1} bar^{-1}, includes polymer. [c]Weight percentage of α-olefins in the liquid phase. [d]SF = Schulz–Flory distribution. [e]$[CrCl_3(thf)_3]/[(AlMe_2)_2(2')]_3$: 100 nmol, MMAO-12 (24 mmol), 4 bar, 1 h, 50 °C, 200 mL of toluene.

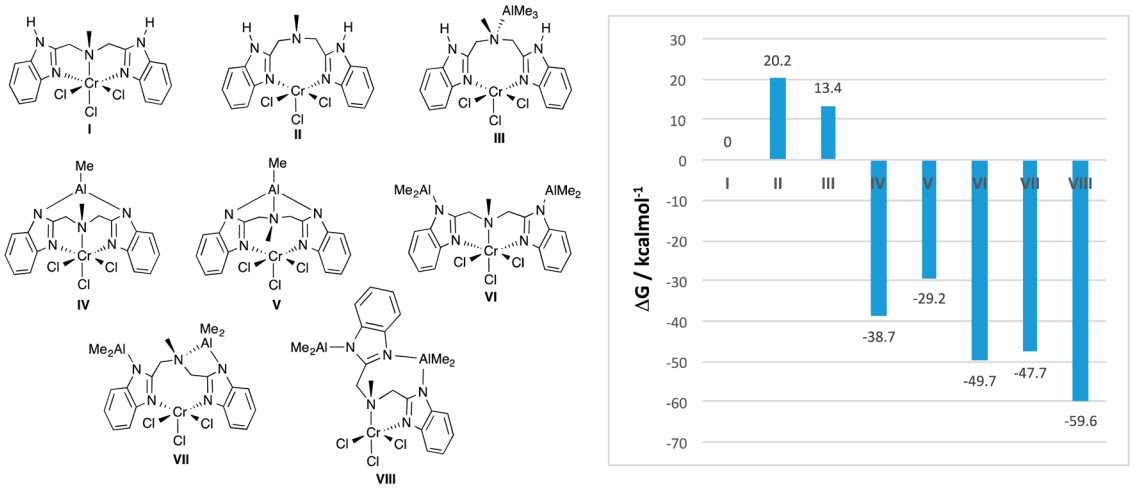

Figure 10. Relative Gibbs free energy profile of potential intermediates formed upon reaction of complex **I** with $AlMe_3$. All energies are balanced for $AlMe_3$ and, in the case of ligand deprotonation, CH_4 formation. See Supporting Information for details.

two $AlMe_3$ units (complexes **VI**–**VIII**) clearly shows a dramatic lowering of the relative energies, which suggests that a modifcation of the coordination environment around chromium upon addition of $AlMe_3$ is very likely. Further studies on the nature of the active species are under way.

In conclusion, chromium-based BIMA complexes are a class of ethylene oligomerization catalysts that, depending on the ligand, can give extremely high catalytic activities and either a Schulz–Flory or an alternating distribution of LAOs in the liquid fraction, together with a major solid polyethylene fraction. Schulz–Flory distributions are described by first-order linear homogeneous recurrence relations with a constant coefficient α, whereas alternating distributions are mathematically described by second-order linear homogeneous recurrence relations with constant coefficients α and β, which represent the probabilities for propagation via the insertion of one or two ethylene monomers, respectively. The β/α ratio increases with ethylene pressure within the range from 1 to 4 bar. A range of different cocatalysts can be used, which affect the catalytic activity and the LAO distribution. The presence of $AlMe_3$ appears to be essential, and it is believed to react with the facially coordinating BIMA ligand at the chromium center. Incorporation of the most abundant LAO, 1-butene, can occur during the oligomerization process, giving rise to a minor alternating distribution of 2-ethyl-1-alkenes with opposite alternating behavior. Further studies to understand this intriguing class of oligomerization catalysts and our search for new catalysts that will generate as yet unseen oligomer distributions continue.

EXPERIMENTAL SECTION

Synthesis of Ligands. *N-Bis((1H-benzimidazol-2-yl)methyl)-N-n-butylamine (**3**).* Compound **3** was synthesized using *o*-phenylenediamine (7.56 g, 70.6 mmol) and *N,N*-diethyl acetate-*N*-butylamine (8.66 g, 35.3 mmol). *o*-Phenylenediamine and the iminodiacetic acid ethyl ester were stirred at 190 °C for 4 h. The water byproduct was distilled from the reaction mixture, which was then allowed to cool to room temperature. The product was triturated with water (120 mL), filtered, washed with water (4 × 20 mL), recrystallized from hot methanol/water (1:30), and finally dried at 60 °C under vacuum for 2 days. Yield: 5 g (43%). ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 0.74 (t, 3H, $^3J_{HH}$ 7.2, CH_2CH_3), 1.18 (sept, 2H, $^3J_{HH}$ = 7.1, $CH_2CH_2CH_3$), 1.45 (quint, 2H, $^3J_{HH}$ 7.4, $CH_2CH_2CH_2$), 2.5 (overlapping with solvent signal, 2H, CH_2), 3.97 (s, 4H, NCH_2C_q), 7.13–7.17 (m, 4H, J_{HH} 3.1, Ar*H*), 7.53–7.56 (m, 4H, J_{HH} 3.1, Ar*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6, rt): δ 13.8 (CH_3), 19.8 (CH_2CH_3), 28.5 (CH_2CH_2), 52.1 (NCH_2C_q), 53.4 (NCH_2CH_2), 114.8 (ArC), 121.5 (ArC), 138.6 (ArC_{ipso}), 152.68 (ArC_q). Anal. Calcd for $C_{20}H_{23}N_5$ (FW 333.4): C 72.04, H 6.95, N 21.00. Found: C 71.87, H 7.07, N 20.83%. CI-MS (m/z): 334 $[M + H]^+$, 362.

*N-Bis((1H-benzimidazol-2-yl)methyl)-N-tert-butylamine (**7**).* Compound **7** was synthesized by an analogous procedure to that described for **3** using *o*-phenylenediamine (11.5 g, 106 mmol) and *N,N*-diethyl acetate-*N-tert*-butylamine (13 g, 53 mmol). Yield: 11.5 g (65%). ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 1.09 (s, $CH(CH_3)_2$), 4.00 (s, (NCH_2), 4.10 (s, NCH_2), 7.14 (broad m, Ar*H*), 7.53 (broad m, Ar*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6, rt): δ 26.1 (CH_3), 46.1 (NCH_2C_q), 54.4 ($NC(CH_3)_3$), 115.2 (ArC), 119.5 (ArC), 134.7 (ArC_{ipso}), 152.8 (ArC_q). IR (KBr, cm^{-1}): 3377 (NH, w), 3054 (Ar–H, s), 1683–1538 (ArC=C, C=N, m), 1456, 1436 (N–H, s), 1271 (CN, s), 749 (CH, s). Anal. Calcd for $C_{20}H_{23}N_5$ (FW 333.4): C 72.04, H 6.95, N 21.00. Found: C 72.28, H 6.83, N 20.91. CI-MS (m/z), 334 $[M + H]^+$.

Synthesis of Chromium Complexes. All Cr(III) complexes are paramagnetic, and no NMR spectra could be recorded.

*N,N-Bis((1H-benzimidazol-2-yl)methyl)amine Chromium(III) Chloride [Cr(**1**)Cl$_3$].* Equimolar quantities of **1** (1 g, 3.61 mmol) and $[CrCl_3(THF)_3]$ (1.35 g, 3.61 mmol) were stirred in 20 mL of THF for 12 h. The product was isolated by filtration, washed twice with THF (2 × 20 mL) and once with diethyl ether (20 mL), and dried under

DOI: 10.1021/acs.organomet.6b00671
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vacuum. Yield: 1.49 g, 95%. Anal. Calcd for $C_{16}H_{15}Cl_3CrN_5$ (FW 435.7): C 44.11, H 3.47, N 16.07. Found: C 44.25, H 3.74, N 15.84. IR (KBr, cm^{-1}): 3202 (NH, s), 3120, 3110 (Ar−H, s), 1622−1544 (ArC═C, C═N, m), 1497, 1477, 1456 (N−H, s), 1278 (CN, s), 743 (CH, s). UV−vis (DMF), λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 462 (138), 635 (93), 721 (shoulder). FAB(+) MS (m/z): 399 ([M − Cl]$^+$), 363 ([M − 2Cl]$^+$). μ_{eff} = 3.77 μ_B.

N,N-Bis((1H-benzimidazol-2-yl)methyl)-N-methylamine Chromium(III) Chloride [Cr(2)Cl$_3$]. Complex [Cr(**2**)Cl$_3$] was synthesized by an analogous procedure to that described for [Cr(**1**)Cl$_3$] using **2** (2 g, 6.87 mmol) and [$CrCl_3(THF)_3$] (2.57 g, 6.87 mmol). Yield: 2.87 g (93%). Anal. Calcd for $C_{17}H_{17}Cl_3CrN_5$ (FW 449.7): C 45.40, H 3.81, N 15.57. Found: C 45.35, H 3.76, N 15.66. IR (KBr, cm^{-1}): 3221 (NH, s),1622−1544 (ArC═C, C═N, m), 1497, 1477,1455 (N−H, s), 1274 (CN, s), 753 (CH, s). UV−vis (DMF), λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})): 464 (156), 659 (75), 723 (shoulder). FAB(+) MS (m/z): 413 [M − Cl]$^+$, 291 [M − $CrCl_3$]$^+$. μ_{eff} = 3.87 μ_B.

N,N-Bis((1H-benzimidazol-2-yl)methyl)-N-butylamine Chromium(III) Chloride [Cr(3)Cl$_3$]. Complex [Cr(**3**)Cl$_3$] was synthesized by a procedure analogous to that described for [Cr(**1**)Cl$_3$] using **3** (1 g, 3.03 mmol) and [$CrCl_3(THF)_3$] (1.13 g, 3.61 mmol). Yield: 1.49 g, 84%. Anal. Calcd for $C_{20}H_{23}Cl_3CrN_5$ (FW 491.8): C 48.85, H 4.71, N 14.24. Found: C 48.83, H 4.80, N 14.42. IR (KBr, cm^{-1}): 3440 (NH, m), 3229, 3077 (Ar−H, s), 1623−1549 (ArC═C, C═N, m), 1499, 1477, 1454, 1433 (N−H, m, s), 1276 (CN, m), 762, 748 (CH, s). FAB(+) MS (m/z): 455 [M − Cl]$^+$, 420 [M − 2Cl]$^+$. μ_{eff} = 3.89 μ_B.

N,N-Bis((1H-benzimidazol-2-yl)methyl)-N-hexylamine Chromium(III) Chloride [Cr(4)Cl$_3$]. Complex [Cr(**4**)Cl$_3$] was synthesized by an analogous procedure to that described for [Cr(**1**)Cl$_3$] using **4** (1 g, 2.8 mmol) and [$CrCl_3(THF)_3$] (1.05 g, 2.8 mmol). Yield: 1.35 g, 93%. Anal. Calcd for $C_{22}H_{27}Cl_3CrN_5$ (FW 519.8): C 50.83, H 5.24, N 13.47. Found: C 51.05, H 5.30, N 13.38. IR (KBr, cm^{-1}): 3502 (NH, m), 3228, 3073 (Ar−H, s), 1621−1542 (ArC═C, C═N, m), 1498, 1477, 1454, 1431 (N−H, s), 1273 (CN, m), 752 (CH, s). FAB(+) MS (m/z): 483 [M − Cl]$^+$, 448 [M − 2Cl]$^+$. μ_{eff} = 3.83 μ_B.

N,N-Bis((1H-benzimidazol-2-yl)methyl)-N-(3-phenylpropyl)amine Chromium(III) Chloride [Cr(5)Cl$_3$]. Complex [Cr(**5**)Cl$_3$] was synthesized by an analogous procedure to that described for [Cr(**1**)Cl$_3$] using **5** (1 g, 2.53 mmol) and [$CrCl_3(THF)_3$] (0.95 g, 2.53 mmol). Yield: 1.00 g (71%). Attempts to crystallize the complex from a solution in DMF resulted in crystals that were found to be the cationic complex [Cr(**5**)Cl_2(dmf)]Cl. Anal. Calcd for $C_{25}H_{25}Cl_3CrN_5$ (FW 553.9): C 54.21, H 4.55, N 12.64. Found: C 54.32, H 4.79, N 12.50. IR (KBr, cm^{-1}): 3231 (NH, s), 1622−1543 (ArC═C, C═N, m), 1498, 1477, 1454 (N−H, s), 1274 (CN, m), 752 (CH, s). FAB(+) MS (m/z): 517 [M − Cl]$^+$, 482 [M − 2Cl]$^+$. μ_{eff} = 3.87 μ_B.

N,N-Bis((1H-benzimidazol-2-yl)methyl)-N-(isopropyl)amine Chromium(III) Chloride [Cr(6)Cl$_3$]. Complex [Cr(**6**)Cl$_3$] was synthesized by an analogous procedure to that described for [Cr(**1**)Cl$_3$] using **6** (0.432 g, 1.35 mmol) and [$CrCl_3(THF)_3$] (0.51 g, 1.35 mmol). Yield: 1.20 g (84%). Anal. Calcd for $C_{19}H_{21}Cl_3CrN_5$ (FW 477.8): C 47.77, H 4.43, N 14.66. Found: C 47.87, H 4.35, N 14.46. IR (KBr, cm^{-1}): 3440, 3226 (NH, s), 3067 (Ar−H), 1622−1545 (ArC═C, C═N, m), 1496, 1478, 1455 (N−H, s, m), 1275 (CN, m), 752 (CH, s). UV−vis (DMF), λ_{max}/nm: 459, 704, 731 (shoulder). FAB(+) MS (m/z): 441 [M − Cl]$^+$, 406 [M − 2Cl]$^+$, 368 [M − 3Cl]$^+$, 320 [M − $CrCl_3$]$^+$. μ_{eff} = 3.46 μ_B.

N,N-Bis((1H-benzimidazol-2-yl)methyl)-N-(tert-butyl)amine Chromium(III) Chloride [Cr(7)Cl$_3$]. Complex [Cr(**7**)Cl$_3$] was synthesized by an analogous procedure to that described for [Cr(**1**)Cl$_3$] using **7** (1 g, 3.00 mmol) and [$CrCl_3(THF)_3$] (1.01 g, 3.00 mmol). Yield: 1.15 g (78%). Anal. Calcd for $C_{20}H_{23}Cl_3CrN_5$ (FW 491.8): C 48.85, H 4.71, N 14.24. Found: C 48.97, H 4.90, N 14.37. IR (KBr, cm^{-1}): 3463 (NH, m), 3192, 3066 (Ar−H, s), 1653−1559 (ArC═C, C═N, m), 1497, 1477, 1455 (N−H, m, s), 1275 (CN, m), 747 (CH, s). FAB(+) MS (m/z): 455 [M − Cl]$^+$, 420 [M − 2Cl]$^+$, 334 [M − $CrCl_3$]$^+$. μ_{eff} = 3.93 μ_B.

N,N-Bis((1H-benzimidazol-2-yl)methyl)-N-(cyclohexyl)amine Chromium(III) Chloride [Cr(8)Cl$_3$]. Complex [Cr(**8**)Cl$_3$] was synthesized by an analogous procedure to that described for [Cr(**1**)Cl$_3$] using **8** (1 g, 2.79 mmol) and [$CrCl_3(THF)_3$] (1.04 g, 2.79 mmol). Yield: 1.07 g (74%). Anal. Calcd for $C_{22}H_{25}Cl_3CrN_5$ (FW 517.8): C 51.03, H 4.87, N 13.52. Found: C 50.93, H 4.72, N 13.64. IR (KBr, cm^{-1}): 3252 (NH, s), 3060 (Ar−H, s), 1622−1538 (ArC═C, C═N, m), 1496, 1477, 1454 (NH, s, m), 1276 (CN, m), 749 (CH, s). UV−vis (DMF), λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 459 (160), 704 (65), 731 (shoulder). FAB(+) MS (m/z): 481 [M − Cl]$^+$, 446 [M − 2Cl]$^+$, 360 [M − $CrCl_3$]$^+$. μ_{eff} = 3.87 μ_B.

N,N-Bis((1H-benzimidazol-2-yl)methyl)-N-(phenyl)amine Chromium(III) Chloride [Cr(9)Cl$_3$]. Complex [Cr(**9**)Cl$_3$] was synthesized by an analogous procedure to that described for [Cr(**1**)Cl$_3$] using *N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-phenylamine (**9**) (0.20 g, 0.56 mmol) and [$CrCl_3(THF)_3$] (0.21 g, 0.56 mmol). Yield: 0.23 g (87%). Anal. Calcd for $C_{22}H_{19}Cl_3CrN_5$ (FW 511.8): C 51.63, H 3.74, N 13.68. Found: C 51.49, H 3.95, N 13.58. IR (KBr, cm^{-1}): 3503 (NH, s), 3224, 3065, 1622−1545 (ArC═C, C═N, m), 1497, 1478, 1454 (NH, s), 1275 (CN, s), 748 (CH, s). UV−vis (DMF), λ_{max}/nm: 484, 678, 705 (shoulder). FAB(+) MS (m/z): 475 [M − Cl]$^+$, 440 [M − 2Cl]$^+$, 354 [M − $CrCl_3$]$^+$. μ_{eff} = 3.95 μ_B.

N,N-Bis((1H-benzimidazol-2-yl)methyl)-N-(benzyl)amine Chromium(III) Chloride [Cr(10)Cl$_3$]. Complex [Cr(**10**)Cl$_3$] was synthesized by an analogous procedure to that described for [Cr(**1**)Cl$_3$] using **10** (0.63 g, 1.73 mmol) and [$CrCl_3(THF)_3$] (0.65 g, 1.73 mmol). Yield: 0.79 g (88%). Anal. Calcd for $C_{23}H_{21}Cl_3CrN_5$ (FW 525.8): C 52.54, H 4.03, N 13.32. Found: C 52.43, H 4.03, N 13.23. IR (KBr, cm^{-1}): 3255 (NH, s), 1617−1550 (ArC═C, C═N, m), 1496, 1477, 1454 (NH, s, m), 1276 (CN, s), 749 (CH, s). UV−vis (DMF, 298 K, λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})): 462 (162), 665 (75), 726 (shoulder). FAB(+) MS: (m/z) 489 [M − Cl]$^+$, 454 [M − 2Cl]$^+$. $\mu_{\mu eff}$ = 4.00 μ_B.

N,N-Bis((1H-benzimidazol-2-yl)methyl)-N-(2,6-dimethylphenyl)-amine Chromium(III) Chloride [Cr(11)Cl$_3$]. Complex [Cr(**11**)Cl$_3$] was synthesized by an analogous procedure to that described for [Cr(**1**)Cl$_3$] using *N,N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-(2,6-dimethylphenyl)amine (**11**) (0.20 g, 0.53 mmol) and [$CrCl_3(THF)_3$] (0.19 g, 0.53 mmol). Yield: 0.23 g (81%). Anal. Calcd for $C_{24}H_{23}Cl_3CrN_5$ (FW 555.9): C 53.40, H 4.29, N 12.97. Found: C 53.51, H 4.39, N 12.82. IR (KBr, cm^{-1}): 3252 (NH, m), 3189 (Ar−H), 1622, 1591, 1520 (ArC═C, C═N, m), 1466, 1451 (NH, s), 1273 (CN, s), 742 (CH, s). UV−vis (DMF), λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 482 (70), 678(58), 705 (shoulder). FAB(+) MS (m/z): 503 [M − Cl]$^+$, 468 [M − 2Cl]$^+$, 382 [M − $CrCl_3$]. μ_{eff} = 3.89 μ_B.

N,N-Bis((1-Me-benzimidazol-2-yl)methyl)amine Chromium(III) Chloride [Cr(12)Cl$_3$]. A slurry of 0.50 g (1.64 mmol) of *N,N*-bis(2-(1*Me*-benzimidazol-2-yl)methyl)amine (**12**) and 0.61 g (1.64 mmol) of [$CrCl_3(THF)_3$] in 20 mL of THF was stirred at reflux for 4 h. The obtained green solid was filtered, washed with THF (3 × 10 mL), and dried under reduced pressure. Yield: 0.39 g (51.0%). Anal. Calcd for $C_{18}H_{19}N_5CrCl_3$: C 46.62, H 4.13, N 15.10. Found: C 46.54, H 4.15, N 15.01. FT-IR, cm^{-1}: 3246 (s), 2857 (m), 1621 (m), 1541 (w), 1492 (m), 1474 (vs), 1465 (v.s), 1414 (m), 1382 (m), 1331 (m), 1272 (s), 1210 (w), 1147 (w), 1055 (s), 1003 (s), 981 (s), 944 (w), 919 (m), 977 (s), 752 (v.s), 702 (s), 654 (m), 558 (w), 518 (w), 510 (w), 431 (w), 418 (w). μ_{eff} = 3.91 μ_B.

N,N-bIs((1-Me-benzimidazol-2-yl)methyl)-N-(methyl)amine Chromium(III) Chloride [Cr(13)Cl$_3$]. A slurry of 0.50 g (1.56 mmol) of *N,N*-bis(2-(1-*Me*-benzimidazol-2-yl)methyl)-*N*-(methyl)amine (**13**) and 0.59 g (1.56 mmol) of [$CrCl_3(THF)_3$] in 20 mL of THF was stirred at reflux for 4 h. The obtained green solid was filtered, washed with THF (3 × 10 mL), and dried under reduced pressure. Yield: 0.64 g (85.8%). Anal. Calcd for $C_{19}H_{21}N_5CrCl_3$: C 47.77, H 4.43, N 14.66. Found: C 47.59, H 4.40, N 14.64. FT-IR, cm^{-1}: 3246 (v.s), 2857 (s), 1621 (m), 1595 (m), 1541 (w), 1492 (m), 1475 (v.s), 1462 (v.s), 1382 (m), 1382 (s), 1332 (m), 1272 (s), 1210 (w), 1146 (w), 1094 (w), 1055 (m), 1003 (s), 982 (s), 944 (w), 919 (m), 878 (s), 752 (v.s), 702 (s), 654 (m), 558 (w), 518 (w), 510 (w), 431 (w), 417 (w). μ_{eff} = 3.74 μ_B.

O-Bis((1H-benzimidazol-2-ylmethyl) Ether Chromium(III) Chloride [Cr(14)Cl$_3$]. Complex [Cr(**14**)Cl$_3$] was synthesized by a procedure

DOI: 10.1021/acs.organomet.6b00671
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analogous to that described for [Cr(**1**)Cl_3] using **14** (0.7 g, 2.5 mmol) and [$CrCl_3(THF)_3$] (0.94 g, 2.5 mmol) in 20 mL of THF. Yield: 0.96 g, 85%. Anal. Calcd for $C_{16}H_{14}Cl_3CrN_4O$ (FW 436.7): C 44.01, H 3.23, N 12.83. Found: C 44.19, H 3.38, N 12.70. IR (KBr, cm^{-1}): 3232 (NH, s), 1620−1540 (ArC═C, C═N, m), 1477−1454 (N−H, s), 1054−1043 (C−O, s), 749 (CH, s). FAB(+) MS (*m*/*z*): 400 [M − Cl]$^+$, 365 [M − 2Cl]$^+$, 329 [M − 3Cl]$^+$. μ_{eff} = 3.66 μ_B.

*S-Bis((1H-benzimidazol-2-yl)methyl) Thioether Chromium(III) Chloride [Cr(**15**)Cl_3].* Complex [Cr(**15**)Cl_3] was synthesized by a procedure analogous to that described for [Cr(**1**)Cl_3] using **15** (0.58 g, 1.96 mmol) and [$CrCl_3(THF)_3$] (0.73 g, 1.96 mmol). Yield: 0.75 g, 85%. Anal. Calcd for $C_{16}H_{14}Cl_3CrN_4S$ (FW 452.7): C 42.45, H 3.12, N 12.38. Found: C 42.59, H 3.22, N 12.27. IR (KBr, cm^{-1}): 3448 (Ar−H, s), 1622, 1593 (C═C, C═N, m), 1486, 1467, 1452 (N−H, s), 1277 (C−N, s), 1046 (CS, s), 744 (CH, s). FAB(+) MS (*m*/*z*): 416 [M − Cl]$^+$, 381 [M − 2Cl]$^+$. μ_{eff} = 3.89 μ_B.

*1,1-Bis(1H-benzimidazol-2-ylmethyl)ethane Chromium(III) Chloride [Cr(**16**)Cl_3].* Complex [Cr(**16**)Cl_3] was synthesized by a procedure analogous to that described for [Cr(**1**)Cl_3] using **16** (0.6 g, 2.07 mmol) and [$CrCl_3(THF)_3$] (0.78 g, 2.07 mmol). Yield: 0.86 g, 92%. Anal. Calcd for $C_{18}H_{18}Cl_3CrN_4$ (FW 448.7): C 48.18, H 4.04, N 12.49. Found: C 48.10, H 4.17, N 12.31. IR (KBr, cm^{-1}): ν 3384 (Ar−H, s), ν 1626−1560 (ArC═C, C═N, s), δ 1488, 1460 (N−H, s), ν 1222 (NC, s), δ 757 (CH, s). FAB(+) MS (*m*/*z*): 412 [M − Cl]$^+$, 377 [M − 2Cl]$^+$. μ_{eff} = 3.88 μ_B.

*N-Bis((1H-benzimidazol-2-yl)ethyl)amine Chromium Chloride [Cr(**18**)Cl_3].* Ligand **18** (0.20 g, 0.49 mmol), chromium(III) chloride tetrahydrofuran complex (0.246 g, 0.49 mmol), and 20 mL of dry THF were stirred and heated at 60 °C for 16 h under a nitrogen atmosphere. An insoluble solid formed, which was filtered off, washed with 10 mL of dry THF, and dried *in vacuo*. The product was obtained as a light brown, amorphous solid: 0.151 g (66%). IR ν_{max}/cm^{-1} (KBr): 3445 (m, N−H stretch), 3168, 2808 (s, aromatic and aliphatic C−H stretch), 1619, 1540 (m, C═N stretch), 1456, 1403 (s, aromatic C═C stretch and aliphatic C−H bending), 1260 (s, C−N stretch), 759 (s, aromatic C−H bending);. MS (LSIMS): *m*/*z* 427 ([M − Cl]$^+$, 15%) and 392 ([M − 2Cl]$^+$, 10%). Anal. Calcd for $C_{18}H_{19}N_5CrCl_3$: C 46.60, H 4.13, N 15.11. Found: C 46.69, H 3.91, N 14.91. μ_{eff} = 3.5 μ_B.

*N-Bis((1H-benzimidazol-2-yl)ethyl)-N-(methyl)amine Chromium Chloride [Cr(**19**)Cl_3].* Compound **19** (0.20 g, 0.60 mmol), chromium(III) chloride tetrahydrofuran complex (0.225 g, 0.60 mmol), and 20 mL of dry DCM were stirred and heated at 35 °C for 16 h under a nitrogen atmosphere. An insoluble solid formed, which was filtered off, washed with 10 mL of dry THF and 10 mL of dry DCM, and dried *in vacuo*. The product was obtained as a lilac, amorphous solid: 0.145 g (49%). IR ν_{max}/cm^{-1} (KBr): 3408 (m, N−H stretch), 3151, 2968 (s, aromatic and aliphatic C−H stretch), 1618, 1560 (m, C═N stretch), 1485, 1458 (s, aromatic C═C stretch and aliphatic C−H bending), 1274 (s, C−N stretch), 746 (s, aromatic C−H bending). MS (LSIMS): *m*/*z* 455 ([M − Cl]$^+$, 10%) and 420 ([M − 2Cl]$^+$, 5%). Anal. Calcd for $C_{20}H_{23}N_5CrCl_3$: C 48.83, H 4.72, N 14.24. Found: C 48.69, H 4.61, N 14.03. μ_{eff} = 4.2 μ_B.

*Bis(1H-benzimidazol-2-yl)methane Chromium(III) Trichloride [Cr(**20**)Cl_3].* The ligand **20** (0.626g, 2.5 mmol) and [$CrCl_3(THF)_3$] (0.943 g, 2.5 mmol) were combined in 30 mL of THF under nitrogen. The mixture was stirred for 3 days, and the intensely dark green suspension was filtered, washed with THF, and dried, to leave the product as a dark green powder (0.730 g, 78%). IR ν_{max}/cm^{-1} (KBr): 3126 (br, N−H stretch), 1624 (m, C═N stretch), 1595 and 1537 (m, aromatic C═C stretch and aliphatic C−H bending), 1467 (s, NH, bend), 1047 (m), 744 (s, aromatic C−H bending) 333 (s, N−Cr). MS (ESI): *m*/*z* 404 ([M + H + MeOH]$^+$, 15%). Anal. Calcd for $C_{15}H_{12}N_4CrCl_3$: C 44.30, H, 2.97, N 13.78. Found: C 44.42, H 3.16, N 13.59.

*N-Bis((3,5-dimethylpyrazol-1-yl)methyl)-N-(butyl)amine Chromium(III) Chloride [Cr(**21**)Cl_3].* A solution of 0.50 g (1.73 mmol) of *N*-bis((3,5-dimethylpyrazol-1-yl)methyl)-*N*-(butyl)amine (**21**) in 10 mL of dry THF was added to a suspension of 0.65 g (1.73 mmol) of [$CrCl_3(THF)_3$] in 10 mL of THF, and the reaction mixture was stirred at room temperature for 18 h. Shortly after the start the color of the reaction mixture changed from purple to green, and at the end of the reaction a green precipitate was formed. The solid was filtered off, washed with 5 mL of tetrahydrofuran and 3 × 10 mL of diethyl ether, and dried at room temperature under reduced pressure for 5 h. Yield: 0.72 g (93.4%). Anal. Calcd (found): C 42.92 (42.83), H 6.08 (6.17), N 15.64 (15.54). FT-IR (cm^{-1}): 574 (v.w), 600 (vw), 628 (w), 695 (w), 796 (s), 845 (m), 966 (w), 1031 (s), 1053 (v.s), 1119 (s), 1139 (w), 1258 (m), 1279 (s), 1300 (s), 1377 (vs), 1418 (v.s), 1422 (s), 1465 (v.s), 1492 (s), 1557 (vs), 2873 (m), 2932 (s), 2961 (vs), 3127 (w). μ_{eff} = 3.98 μ_B.

*N-Bis((1H-benzimidazol-2-yl)methyl)-N-(methyl)amine Chromium(0) Tricarbonyl [Cr(**2**)$(CO)_3$].* Freshly prepared [Cr$(CO)_3(NCMe)_3$] (0.08 g, 0.32 mmol), from [$Cr(CO)_6$] (2.00 g, 9.10 mmol) heated at reflux for 24 h in acetonitrile (60 mL), and **2** (0.09 g, 0.32 mmol) were stirred overnight in THF at room temperature. The product was isolated by filtration, washed with Et_2O (3 × 10 mL), and dried under vacuum. [Cr(**2**)$(CO)_3$] was obtained as an orange, air-sensitive solid. Recrystallization from a cold (−20 °C) THF solution gave crystals suitable for X-ray analysis. Yield: 0.12 g, 85%. Anal. Calcd for $C_{20}H_{17}CrN_5O_3$ (FW 427.4): C 56.21, H 4.01, N 16.39. Found: C 56.17, H 4.15, N 16.42. ^{1}H NMR (250 MHz, *J* = Hz, DMSO-d_6): δ 3.26 (s, 3H, NCH_3), 4.19 (dd, $^2J_{HaHb}$ = 16.90, CH_aH_b), 7.16 (m, 4H, $^nJ_{HH}$ = 7.33, Ar*H*), 7.34 (d, 2H, J_{HH} = 7.33, Ar*H*), 8.02 (d, 2H, J_{HH} = 7.93, Ar*H*). $^{13}C\{^1H\}$ NMR (62.9 MHz, DMSO-d_6): δ 25.1 (NCH_3), 60.1 (NCH_2C_q), 111.7 (Ar*C*), 118 (Ar*C*), 122.6 (Ar*C*), 134.0 (Ar*C*), 141.8 (ArC_{ipso}), 153.9 (ArC_q), 223.1 (C═O). FAB(+) MS (*m*/*z*): 427 [M]$^+$, 358 [M − 2(CO) − Me]$^+$, 343 [M − 3(CO)]$^+$.

Cationic Complexes. *trans-Dichloro(mer-N-bis((1H-benzimidazol-2-yl)methyl)amine)(tetrahydrofuran) Chromium(III) Hexafluoroantimonate [Cr(**1**)Cl_2(thf)]SbF_6.* Silver hexafluoroantimonate (0.24 g, 0.69 mmol) and complex [Cr(**1**)Cl_3] (0.3 g, 0.69 mmol) were stirred in THF (20 mL) at room temperature overnight. The solution was filtered, the solvent removed under reduced pressure, and the product washed twice with diethyl ether (2 × 20 mL) and dried under vacuum. Attempts to crystallize the complex from a THF solution resulted in blue crystals that were analyzed as [Cr(**1**)$Cl_2(OH_2)$]SbF_6, probably due to adventitious moisture in the system. Yield: 0.375 g (77%). Anal. Calcd for $C_{20}H_{23}Cl_2CrF_6N_5OSb$ (FW 708.1): C 33.92, H 3.27, N 9.80. Found: C 33.70, H 3.26, N 9.60. IR (KBr, cm^{-1}): 3202 (NH, m), 3164 (Ar−H), 1622−1544 (ArC═C, C═N, m), 1497, 1477, 1456 (N−H, s), 1278 (CN, s), 748 (CH, s), 660 (Sb−F, s). UV−vis (DMF), λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 440 (120), 647 (100), 726 (shoulder). FAB(+) MS (*m*/*z*): 401 [M − THF]$^+$, 364 [M − THF − Cl]$^+$, 328 [M − THF − 2Cl]$^+$. FAB(−) MS (*m*/*z*): 235 [SbF_6]$^-$. μ_{eff} = 4.10 μ_B.

*cis-Dichloro(fac-N-bis(1H-benzimidazol-2-ylmethyl)-N-(phenyl)-amine)(tetrahydrofuran) Chromium(III) Hexafluoroantimonate [Cr(**9**)Cl_2(thf)]SbF_6.* The procedure used was as described for [Cr(**1**)Cl_2(thf)]SbF_6, using ligand **9** (0.09 g, 0.18 mmol) and silver hexafluoroantimonate (0.06 g, 0.18 mmol) to afford [Cr(**9**)Cl_2(thf)]SbF_6 as a green solid. Yield: 0.10 g (72%). Anal. Calcd for $C_{26}H_{27}Cl_2CrF_6N_5OSb$ (FW 784.2): C 39.82, H 3.47, N 8.93. Found: C 39.72, N 3.58, N 8.73. IR (KBr, cm^{-1}): 3390 (NH, s), 3066 (Ar−H, s), 1623−1554 (ArC═C, N═C, m), 1498, 1479, 1454 (N−H, s), 1276 (CN, m), 1053 (C−O, m), 751 (CH, s), 665 (Sb−F, vs). UV−vis (DMF), λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 441 (118), 644 (103), 725. FAB(+) MS (*m*/*z*): 475 [M − (SbF_6) − THF]$^+$, 440 [M − (SbF_6) − THF − Cl]$^+$. FAB(−) MS (*m*/*z*): 235 [SbF_6]$^-$. μ_{eff} = 4.12 μ_B.

*Bis(benzimidazol-2-ylmethyl)methylamine(dimethyl)aluminum Trimer [($AlMe_2$)$_2$(**2′**)]$_3$.* A solution of trimethylaluminum in heptane (2 M, 1.7 mL, 3.4 mmol) was added to a suspension of 0.5 g (1.7 mmol) of bis(benzimidazol-2-ylmethyl)methylamine (**2**) in 20 mL of dry toluene, at −78 °C. The reaction mixture was stirred at −78 °C for 10 min, and the cooling bath removed. While warming up to room temperature, the solid gradually dissolved, forming a pale blue solution. The reaction mixture was stirred additionally for 2 h at room temperature, and then approximately 3/4 of the solvent removed under reduced pressure. The addition of 5 mL of dry *n*-heptane resulted in the formation of an off-white precipitate, which was filtered, washed with 5 mL of cold *n*-heptane, and dried under reduced

DOI: 10.1021/acs.organomet.6b00671
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pressure. Crystals suitable for X-ray analysis were obtained from a toluene/heptane solution. Yield: 0.55 g (80%). ^{1}H NMR (400 MHz, C_6D_6, 298 K), ppm: 7.08−7.55 (28H, Ar−H), 2.18−3.92 (21H, CH_2−N and CH_3−N), −0.88−1.58 (36H, CH_3−Al). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K), ppm: 153.9, 153.7, 153.5, 142.4, 142.0, 141.9, 139.4, 138.9, 138.8, 137.7, 129.3, 128.5, 125.6, 123.9, 123.6, 123.4, 122.8, 122.2, 117.3, 117.1, 116.9, 116.2, 115.8, 115.4, 58.2, 57.2, 44.9, 43.8, 21.7, −5.1, −5.7, −6.1, −6.5.

General Polymerization Procedure. Due to the insoluble nature of the chromium catalysts in the polymerization solvent, toluene, the complexes were first preactivated with the cocatalyst, methylaluminoxane. This solution was diluted with toluene in order to give a solution with a suitable catalyst concentration. The activated catalyst solution showed no significant loss of activity when stored at 5 °C for up to 2 weeks. In practice, catalyst solutions were freshly prepared by combining the precatalyst with the cocatalyst at room temperature, and the activated solutions were used within the same day. A mechanically stirred pressure reaction vessel was filled with toluene (200 mL) followed by addition of MAO as a moisture scavenger. The pressure reaction vessel was submerged in a water bath set to the desired polymerization temperature, and the solvent saturated with ethylene at a pressure of 1 bar. The polymerization was initiated by injection of an aliquot of the activated catalyst solution. Immediately after the injection the ethylene pressure was adjusted to the required pressure and kept constant over the reaction time. Reaction temperatures were measured inside the reactor. For highly active catalysts, nanomolar concentrations of catalyst were used in order to limit the rise in reaction temperature to less than 3 °C. After 1 h the reaction was terminated by turning off the ethylene supply and venting off excess unreacted monomer. A known amount of GC standard (nonane or 2,2,4,4,6,8,8-heptamethylnonane) was added to the reaction mixture, and then a small sample of the liquid phase was taken and passed through neutral alumina (Al_2O_3 microcolumn) to remove any catalyst and then analyzed by FID-GC. The remaining polymer product was precipitated by the addition of methanol (200 mL), followed by dilute HCl (20 mL).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00671.

NMR spectra, GC chromatograms, additional graphs, crystallographic details, and information regarding DFT calculations (PDF)

Crystallographic data (CIF)

Optimized Cartesian coordinates (XYZ)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: g.britovsek@imperial.ac.uk.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from INEOS Technologies is kindly acknowledged. We thank the Australian Research Council for financial support through grant FT100100609 to D.S.M. We thank the STFC for beam time at Daresbury Laboratory and Drs. Jonathan E. Warren and Timothy J. Prior for scientific support.

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