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# Structure/Properties Relationship for Bis(phenoxyamine)Zr(IV)-Based Olefin Polymerization Catalysts: A Simple DFT Model To Predict Catalytic Activity

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**S** Supporting Information

**ABSTRACT:** The productivity of a number of bis-(phenoxyamine)Zr(IV)-based catalysts (bis(phenoxyamine) = N,N'-bis(3-R<sub>1</sub>-5-R<sub>2</sub>-2-O-C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>)-N,N'-(R<sub>3</sub>)<sub>2</sub>-(NCH<sub>2</sub>CH<sub>2</sub>N)) in ethene and propene polymerization was evaluated for different R<sub>1</sub>/R<sub>2</sub>/R<sub>3</sub> combinations. In previous studies on this class we demonstrated that the cations that form upon precatalyst activation (e.g., by methylalumoxane) adopt a "dormant" *mer-mer* geometry, and an endothermic isomerization to the active *fac-fac* geometry is the necessary



first step of the catalytic cycle. Herewith we report a clear correlation between catalyst activity and the DFT-calculated energy difference  $\Delta E_i$  between the active and dormant state. The correlation only holds when the calculations are run on ion pairs, which is less obvious than it may appear because the anion in these systems is not at the catalyst front. This finding provides a comparatively simple and fast method to predict the activity of new catalysts of the same class.

# INTRODUCTION

The history of olefin polymerization is tightly liaised with serendipity since the very beginning, with the polyethylene breakthroughs in 1935 and 1953.<sup>1</sup> Methylaluminoxane (MAO, the preferred activator for new-generation catalysts<sup>2</sup>) represents a more recent but similarly paradigmatic case of fortuitous discovery.<sup>3</sup> Last but not least, the vast majority of olefin polymerization catalysts have been found by trial-and-error, an approach now boosted by the introduction of high throughput experimentation/screening (HTE/HTS) tools and methods,<sup>4,5</sup> particularly in industrial discovery programs.<sup>6,7</sup>

Catalyst design has often been claimed as a feasible option,<sup>8</sup> but the obvious prerequisite is a reliable model of structure/ properties relationships.<sup>9</sup> The discovery of group 4 metallocene systems offered the first realistic modeling opportunities for well-defined active species,<sup>10</sup> and since then several important aspects of catalyst performance (e.g., the enantio- and regioselectivity in the insertion of prochiral monomers, the relative rates of the accessible chain transfer pathways, and even—to some extent—the rate balance of the latter with chain propagation) have been more or less successfully quantified with computational methods (primarily density functional theory (DFT) based<sup>11</sup>). In spite of this remarkable progress, however, understanding of the quintessential relation, that is the one between catalyst structure and activity, remains elusive.

Among the published approaches, some comprehensively examined the 3-dimensional interaction between the monomer and the catalyst active pocket;<sup>10a-c</sup> others focused on specific supposedly key aspects, such as e.g. the energy of ion pair separation vs ligand cone angle.<sup>10d</sup> Moderate success has been achieved in ranking catalysts with ligand frames featuring limited structural diversity within prototypical classes. However, it is fair to admit that the picture remains poorly defined as soon as one looks at novel structures, particularly in the rapidly growing and widely differentiated area of "post-metallocene" catalysis.<sup>12,13</sup>

An interesting case is that of [bis(phenoxyamine)]Zr(IV)based catalysts (bis(phenoxyamine) =  $N_{,N'}$ -bis(3-R<sub>1</sub>-5-R<sub>2</sub>-2-O-C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>)- $N_{,N'}$ -(R<sub>3</sub>)<sub>2</sub>-(NCH<sub>2</sub>CH<sub>2</sub>N), Scheme 1; short notation, ONNO),<sup>14</sup> for which we recently elucidated an unusual polymerization mechanism (Figure 1 and Scheme 2).<sup>13</sup> In spite of the tetradentate nature of the ligand, which may suggest a certain stereorigidity, the first step entails the endothermic rearrangement of the Zr–alkyl cation from the *mer-mer* conformation **C2x** (the lowest energy isomer for an [ONNO]-Zr(R)( $\square$ )<sup>+</sup> species;  $\square$  = coordination vacancy) to the *fac-fac* 

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#### Scheme 1. Numbering of Complexes





Figure 1. DFT-calculated propene insertion profile for a model of [ONNO]Zr(IV) catalyst ( $R_1 = CMe_2Ph$ ,  $R_2 = R_3 = Me$ ).

#### Scheme 2. Geometrical Isomers of [(ONNO)ZrX<sub>2</sub>] Complexes



conformation C2, passing through an intermediate *fac-mer* conformation C1.<sup>15</sup> C2 in turn is the most stable isomer whenever a Lewis base, and in particular the olefin, saturates the Zr coordination sphere<sup>15</sup> and can undergo monomer insertion according to the classical Cossee–Arlman scheme.<sup>16</sup> Polymer microstructure analysis<sup>14d</sup> and DFT studies of the reaction path<sup>13b,14d</sup> consistently point to it as the active species; microstructure analysis also rules out propagation at the C1 conformation.<sup>14f</sup>

In this paper, we disclose a simple and quantitative correlation between catalyst activity and the DFT-computed energy difference  $\Delta E_i$  between ion pairs featuring **C2x** and **C2** cations, which—we believe—can be used as a convenient tool

to predict the activity of new catalysts within this family, thus opening the door to *in silico* catalyst prescreening.

# RESULTS AND DISCUSSION

The precatalyst structures considered for this investigation are shown in Scheme 1 (P1–P10). They were chosen so as to ensure a wide steric and electronic diversity for the  $R_1/R_2$  substituents and some variation on  $R_3$  as well. All neutral [ONNO]ZrX<sub>2</sub> precursor complexes had X = benzyl (previous studies demonstrated, not surprisingly, that catalytic activity is basically independent of the nature of X when X = alkyl<sup>15</sup>).

When exploring quantitative relationships between catalyst structure and performance, one should use reliable and truly comparable data. In order to minimize effects possibly arising from different materials and protocols, we decided to test *ex novo* all catalysts, even where previous literature results were available. The precatalysts were activated with MAO/2,6-di-*tert*-butylphenol (TBP) mixtures<sup>17</sup> in toluene, and tested in ethene and propene polymerization at 25 °C under similar conditions, as described in the Experimental Section. The observed productivities for polyethylene ( $R_E$ ) and polypropylene ( $R_p$ ), expressed as kg (polymer) mol (Zr)<sup>-1</sup> [ $C_nH_{2n}$ ]<sup>-1</sup> h<sup>-1</sup>, are summarized in Table 1; in general, the agreement with pre-

Table 1. Average Productivities for Polyethylene  $(R_E)$  and Polypropylene  $(R_P)^a$  in Toluene at 25 °C for Catalysts Obtained from Precursors P1–P10 upon Activation with MAO/TBP

	PE: $R_{\rm E}$	PP: $R_{\rm P}$		PE: R <sub>E</sub>	PP: $R_{\rm P}$
P1	$2.7 \times 10^{2}$	6.2	P6	$5.6 \times 10^{5}$	$1.2 \times 10^4$
P2	$4.0 \times 10^{2}$	2.5	<b>P</b> 7	$5.8 \times 10^{4}$	$6.2 \times 10^{2}$
P3	$4.6 \times 10^{3}$	76	P8	$4.6 \times 10^{2}$	1.0
P4	2.0	0.2	P9	$4.2 \times 10^{4}$	$2.6 \times 10^{2}$
P5	$2.4 \times 10^{3}$	7.4	P10	$2.9 \times 10^{3}$	33
<sup><i>i</i></sup> In kg (polymer) mol $(Zr)^{-1} [C_n H_{2n}]^{-1} h^{-1}$ .					

existing data is good.<sup>14f</sup> In most cases, the catalysts featured moderate activity ( $R_{\rm E} < 4000$ ;  $R_{\rm P} < 100$ ), e.g., compared with typical zirconocenes under similar conditions.<sup>18</sup> Notable exceptions are those derived from precursors **P6**, **P7**, and **P9**; the former, in particular, is more active than many competent zirconocenes.

Altogether, the *R* values in Table 1 span a range of more than 6 orders of magnitude and should therefore represent a valid set to benchmark models of structure-activity relationship. At first sight it is not easy to come up with simple qualitative interpretations. For polyethylene,  $R_{\rm F}$  clearly tends to increase with increasing size of the frontal R<sub>1</sub> substituents. A conceptually similar trend was reported for metallocenes and traced to a progressive loosening of the ion pairing;<sup>10b</sup> in the present case, however, the same interpretation looks questionable because we demonstrated that the anion is not at the catalyst front.<sup>11,13</sup> For polypropylene, in turn, no clear relationship of  $R_p$  with  $R_1$  size can be seen.<sup>19</sup> For both monomers, as already noted, the productivity has a dramatic maximum for  $R_1 = 9$ -anthracenyl (P6), a large but flat moiety that in the proper orientation leaves the catalyst "mouth" as open as with  $R_1$  = methyl (P1) (for a visual comparison see Figure 2). An interesting trend was observed when replacing methyl groups with practically isosteric Cl atoms as R1 and/or  $R_2$ : substitution at  $R_1$  (P1 vs P9) resulted in a large increase of productivity (from 270 to 42 000 for  $R_{\rm E}$ ; from 6.2 to 260 for



Figure 2. Optimized geometries of ion pairs M1\_C2x, M1\_C2, M6\_C2x, and M6\_C2. Hydrogen atoms are omitted for clarity.

 $R_{\rm p}$ ); a smaller but still very significant effect was associated with substitution at R<sub>2</sub> (**P1** vs **P10**), ending up with  $R_{\rm E}$  = 2900 and  $R_{\rm P}$  = 33; changing methyl for Cl at both R<sub>1</sub> and R<sub>2</sub> (**P7**) yielded the largest productivities in the subset ( $R_{\rm E}$  = 58 000,  $R_{\rm P}$  = 620). A truly surprising and puzzling effect was observed upon replacing R<sub>3</sub> = methyl with the slightly larger ethyl group; this caused a vertical drop of productivity (by roughly 3 orders of magnitude; compare **P3–P4** and **P7–P8**). Although not unprecedented in coordination catalysis, it is rather uncommon that a fragment remote from the active pocket impacts so strongly on the activity.

Searching for a key to interpret this picture, it is worth noting that according to the polymerization mechanism of Figure 1 the largest contribution to the activation enthalpy of the polymerization comes from the initial isomerization of C2x to C2, even though the rate-determining step can be monomer insertion (as seems to be the case for propene).<sup>13b</sup> Therefore, it seemed a reasonable working hypothesis that decreasing the enthalpy difference between C2x and C2 should speed up the overall reaction, and in this work we test this hypothesis.

We recently reported a <sup>1</sup>H-EXSY NMR methodology to measure this isomerization rate.<sup>13a,15</sup> The drawback of this procedure is that it requires the synthesis and isolation of the ion pair, which is a delicate job due to the high reactivity of this moiety. The EXSY study was undoubtedly very useful to get insight into the **C2x–C2** equilibrium, including the activation parameters, but it cannot be proposed as a practical way to predict catalyst activity because once a given ion pair is actually available testing it in catalysis is definitely faster than carrying out the EXSY measurements. Moreover, the spectroscopic approach has a limited window of applicability: in particular, if the isomerization is very fast—as it should be for a "good" catalyst—EXSY cannot be used because the peaks broaden and coalesce already at low temperature. On the other hand, assuming that the mechanism of Figure 1 is general for [ONNO]Zr(IV)-based catalysts (which based on current knowledge looks like a plausible hypothesis), estimating the relative stabilities of **C2x** and **C2** for a given ligand frame by means of DFT can represent a convenient predictive tool in alternative to experiment.

With this in mind, we studied computationally model catalyst ion pairs M1-M10 with the same ancillary ligand frames as precatalysts P1-P10. In all cases, the cation featured an isobutyl group (to mimic a growing polypropylene chain) and a coordination vacancy, and the anion was  $MeB(C_6F_5)_3^{-15}$  The latter is convenient from the computational standpoint; since the anion is always in the second coordination sphere, it is representative of other competent counterions (including the ill-defined anion of MAO) for the catalysts of interest, as found in previous experimental studies.<sup>15</sup> The geometries of both facfac (C2) and mer-mer (C2x) isomeric cations were optimized, with the anion in the positions identified in previous studies (Figure 2).<sup>13,15</sup> Not surprisingly, in the *fac-fac* geometry in general the isobutyl group turned out to interact with the Zr center through a  $\beta$ -agostic interaction; this is not feasible in the mer-mer geometry, where the vacant site is trans to the isobutyl moiety. The structures of all isolated  $M_C 1-M_C 10$  cations were optimized as well, starting from the respective ion pair structures and removing the anion. The main results of the calculations are summarized in Tables 2 and 3. Table 2, in particular, lists the values of the four  $C\alpha$ -Zr-X angles (where  $C\alpha$  is the  $\alpha$  carbon of the isobutyl and X represents a N or O atom of the ligand) for the C2x isomers of all cations; these values represent the only appreciable differences between the

Table 2. Values of the C $\alpha$ -Zr-X Angles (in deg) in the DFT-Optimized Geometries of the Cations in *mer-mer* Geometry for Ion Pairs ("M") and Isolated Cations ("Mc") (See Text)

	X = O1	X = N1	X = N2	X = O2
M1_C2x	98.7	105.1	97.7	102.1
Mc1_C2x	101.8	109.8	100.2	107.1
M2_C2x	101.2	105.2	97.6	104.6
Mc2_C2x	103.7	107.8	99.3	107.6
M3_C2x	99.8	105.2	96.6	104.1
Mc3_C2x	103.2	108.6	99.1	107.9
M4_C2x	100.7	107.9	97.0	106.0
Mc4_C2x	101.6	109.2	98.2	107.9
M6_C2x	99.7	106.2	97.3	103.6
Mc6_C2x	104.4	104.3	99.6	110.0
M7_C2x	96.7	104.5	96.2	100.4
Mc7_C2x	100.2	110.2	99.8	106.7
M8_C2x	98.2	109.6	100.4	107.0
Mc8_C2x	101.5	110.0	100.2	107.1
M9_C2x	97.1	104.3	100.5	96.7
Mc9_C2x	101.6	109.9	100.2	107.1
M10_C2x	97.2	104.4	100.9	96.4
Mc10_C2x	101.7	109.8	100.3	107.0

 Table 3. DFT-Calculated Energy Differences between the C2

 and C2x Isomers for the Studied Complexes

ion pairs	$\Delta E_i$ (kcal mol <sup>-1</sup> )	isolated cations	$\Delta E_{i,c}$ (kcal mol <sup>-1</sup> )
M1	9.73	M <sub>c</sub> 1	8.37
M2	10.08	M <sub>c</sub> 2	10.28
M3	9.17	M <sub>c</sub> 3	5.38
M4	12.31	M <sub>c</sub> 4	12.37
M5	10.25	M <sub>c</sub> 5	10.34
M6	5.87	M <sub>c</sub> 6	12.26
<b>M</b> 7	6.90	<b>M</b> <sub>c</sub> 7	5.54
M8	9.52	<b>M</b> <sub>c</sub> 8	5.10
M9	7.05	<b>M</b> <sub>c</sub> 9	5.79
M10	9.48	M <sub>c</sub> 10	8.00

computed geometries of the cations in the two cases (ion pairs vs isolated cations). In the absence of the anion, the [ONNO] ligand in the mer-mer conformation appears to "relax", and all four C $\alpha$ -Zr-X angles (in the range between 98° and 110°) systematically increase by  $2^{\circ}-10^{\circ}$ ; this is an indication that the ion pairing interaction, while being an important element of stabilization, introduces some strain in the six-membered Zr-O-C-C-C-N ring. We believe that this is the reason why, when all the C $\alpha$ -Zr-X angles are forced to approach 90° following the coordination of a nucleophile (e.g., THF, an olefin, but also the methyl group of the  $MeB(C_6F_5)_3^-$  anion) to the sixth Zr coordination site, the mer-mer geometry is no longer the most stable one, as found before;<sup>13,15</sup> in fact, it appears that the strain introduced by the interaction with the nucleophile is not compensated by its binding energy, and when the nucleophile does bind, the preferred structure has the fac-fac geometry. Importantly, the effect of the anion on the values of the C $\alpha$ -Zr-X angles turned out to be vanishingly small for structures M4 and M8, that is, when  $R_3 = ethyl$  (rather than methyl); this can be traced to the fact that in such cases the anion, which is located at the back of the ligand frame, is practically prevented from interacting with the cation due to the larger steric demand of R<sub>3</sub>. We will come back to this later.

The energy differences between the C2 and C2x isomers for the M1-M10 ion pairs ( $\Delta E_i$ ) as well as the isolated M<sub>C</sub>1-M<sub>C</sub>10 cations ( $\Delta E_{ic}$ ) are collected in Table 3.

Plots of ln  $R_X$  (X = E or P; Table 1) vs  $\Delta E_i$  (Table 3) for ion pairs **M1–M10** (Figure 3) show a nice linear correlation. This



**Figure 3.** Plot of catalyst productivity for polyethylene (ln  $R_{\rm E}$ ,  $\blacksquare$ ) and polypropylene (ln  $R_{\rm P}$ ,  $\bullet$ ) for catalysts derived from precursors **P1–P10** (Table 1) vs  $\Delta E_i$  for ion pairs **M1–M10** (Table 3). The straight lines through the data points represent the best linear fits, with correlation coefficients of 0.952 and 0.938, respectively.

supports our hypothesis that for the considered [ONNO]Zr-(IV)-based catalysts the activity is mainly governed by the relative stabilities of the C2x (dormant) and C2 (active) isomers. As already noted before, from this one should not conclude that the C2x-C2 isomerization is the ratedetermining step, but rather that the energetics of the subsequent steps in the reaction path (i.e., olefin uptake and insertion, see Figure 1) are rather similar for all catalysts, i.e., relatively insensitive to the specific substitution pattern of the ancillary ligand, at least as far as the impact on the reaction rate is considered. The most active catalysts in the set (namely, P6 and **P7**) feature values of  $\Delta E_i < 7$  kcal mol<sup>-1</sup>, whereas at the other extreme catalysts with very poor activity (namely P1, P2, **P4**, **P8**) all have  $\Delta E_i > 9.5$  kcal mol<sup>-1</sup>. While the correlation is not perfect, it accommodates all screened substituent effects, both steric and electronic ones, independent of whether or not a specific substituent is close to or far from the active pocket. Of course, second-order effects are present which are not taken into account by this simple scheme, as indicated by the minor scattering of the data points in Figure 3.

It would be convenient if the relative stabilities of the isolated cations followed those of the ion pairs; in such a case, the DFT modeling would be much less demanding in terms of computational time/resources. Unfortunately, plots of  $\ln R_X$  vs  $\Delta E_{i,c}$  for  $M_C 1 - M_C 10$  show a large scatter and no significant correlation (Figure 4), which indicates that the anion must be included explicitly for a meaningful prediction of catalyst activity. This may look somehow surprising, because—as noted repeatedly—for these systems the anion is not at the catalyst front; we conclude that ion pairing impacts on the complex summation of interactions defining cation energetics to different extents for different geometrical isomers.

Two cases are specially paradigmatic in this respect. For the **M6** ion pairs ( $R_1 = 9$ -anthracenyl) the value of  $\Delta E_i$  (= 5.87 kcal mol<sup>-1</sup>) is the lowest in Table 3, whereas for the  $M_C6$  cations that of  $\Delta E_{i,c}$  (= 12.26 kcal/mol) is one of the highest. This can be understood on inspection of the DFT-optimized structures.



**Figure 4.** Plot of catalyst productivity for polyethylene ( $\ln R_{\rm E}$ ,  $\blacksquare$ ) and polypropylene ( $\ln R_{\rm P}$ ,  $\bullet$ ) for catalysts derived from precursors **P1– P10** (Table 1) vs  $\Delta E_{ic}$  for isolated cations **M**<sub>C</sub>**1–M**<sub>C</sub>**10** (Table 3). The straight lines through the data points represent the best linear fits, with correlation coefficients of 0.26 and 0.13, respectively.

In M6\_C2x (Figure 2) the distance between the Zr atom and the nearest F atom of the anion is 3.94 Å (to be compared, e.g., with 3.23 Å for M1\_C2x, with  $R_1$  = methyl); this is due to the orientation of the anthracenyl moiety, which points directly toward the anion, pushing it away, weakening the anion–cation interaction, and ultimately destabilizing the ion pair. In M6\_C2, on the other hand, the anion and the anthracenyl do not interact at all. The net result is a peculiarly low value of  $\Delta E_i$  for this complex. For the isolated cations the situation is reversed; in fact, the M<sub>C</sub>6\_C2x model species turned out to be very stable because the two nearly parallel anthracenyl moieties do not cause the steric congestion typical of complexes with closeto-spherical  $R_1$ 's. This justifies the large value of  $\Delta E_{i,c}$ .

A much more subtle case is that of **M4** and **M8**, with  $R_3 =$  ethyl. Both feature large  $\Delta E_i$  values, which correlates well with the very low productivities of the catalysts based on them. Their methyl-substituted homologues **M3** and **M7**, in turn, have lower  $\Delta E_i$  values and, consistently, yield catalysts with higher productivities. Why this is so, however, is hard to understand by visual inspection of the optimized structures;<sup>20</sup> the substituent effects here are more diffuse, which makes them difficult to identify.

# CONCLUSIONS

On the basis of the results of the previous section, we conclude that the correlation between  $\Delta E_i$  and activity for the investigated catalyst class holds and can be used as a simple and convenient predictive tool, regardless of whether or not a detailed structural interpretation of the DFT-calculated  $\Delta E_i$ value can be found. This means that, although the approach was inspired by a precise element of mechanistic understanding, the search for improved catalysts through a systematic exploration of the substituent effects remains largely empirical (albeit carried out in silico). What differentiates our model from a typical QSAR one<sup>21'</sup> is that one single parameter with a welldefined molecular kinetic meaning (namely,  $\Delta E_i$ ) is adequate to describe the property of interest, whereas less fortunate cases require a "black-box" treatment with complex "cocktails" of descriptors whose individual relationships with the targeted variable(s) can be obscure. In the investigated case, in fact, the correlation between catalyst structure and activity is dominated by one key element, that is, the energy gap between a dormant species representing the catalyst resting state and the active

one. On the other hand, modulating this gap by means of a rational design of the ancillary ligand remains difficult, as discussed above, and even in case of success major drawbacks can show up; productivity is only one of several properties of interest, and other important features of catalyst performance may vary in an undesired manner. The catalyst derived from precursor **P6** is once again a good example; with its low  $\Delta E_i$  it is exceedingly active but yields polymers of very low average molecular mass and in the case of polypropylene practically atactic.

Until now, we have not yet identified  $R_1/R_2/R_3$  combinations ending up with well-balanced properties. In spite of this, the calculation of  $\Delta E_i$  is highly recommended before the actual synthesis of a similar catalyst with a new combination of substituents. If the calculated  $\Delta E_i$  is higher than 8 kcal/mol, the catalyst is probably not worth trying, and valuable laboratory time is saved.

Of course, changing other structural features of the ligand is also an option, but then the possibility that the structure/ activity correlation changes in nature should be considered. For the investigated [ONNO]Zr(IV)-R cations, the root of the problem is that the two six-membered M-N-C-C-C-O rings tend to adopt the inactive mer-mer geometry. The literature demonstrates that proper modifications can be very beneficial; in particular, ("salalen")Ti(IV)-22 and bis(phenoxy ether)M-(IV)-based catalysts<sup>23</sup> with high activities and selectivities have been disclosed. We are currently looking at these and other formally related systems with [OYYO] or [YYYY] ligands (Y = heteroatom) to find out if the mechanism elucidated for [ONNO]M(IV) species is more general. We believe that this can be the case as long as the role of inner-sphere ion pairs (ISIP)<sup>24</sup> in the catalytic cycle is marginal; as a matter of fact, whenever an ISIP is the most stable product of precatalyst activation, as is the case with metallocenes<sup>25,26</sup> and a number of "post-metallocene"<sup>12</sup> catalysts, the activity is crucially and directly affected by the cation-anion interaction, which makes general interpretation schemes less likely.

## EXPERIMENTAL SECTION

All experiments were performed under an atmosphere of dry argon or in a argon-filled glovebox. Solvents were purchased by Aldrich as HPLC grade. Toluene and diethyl ether were previously purified in a MBraun SPS unit. n-Hexane was dried on metallic Na by standard procedures. Tetrabenzylzirconium was synthesized according to the literature.<sup>27</sup> NMR samples of complexes were prepared in oven-dried J-Young NMR tubes. NMR spectra for ligands and metal complexes were recorded on Bruker Avance DRX 400 spectrometer and referenced to residual protons in benzene- $d_6$  ( $\delta$  7.15) and chloroform- $d_1$  ( $\delta$  7.26) and to <sup>13</sup>C chemical shift of benzene ( $\delta$  128.0). The following abbreviations were used for describing NMR multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. MAO (10% w/w solution in toluene) was purchased from Chemtura. <sup>1</sup>H NMR analysis revealed it to contain 38% of Al as "free" AlMe<sub>3</sub>. TBP and 4-methyl-2-(1-methyl-1-phenylethyl)phenol were purchased from Aldrich. Propene (polymerization grade) was purchased from SON and used as received. Complexes P1,<sup>14a</sup> P2,<sup>14a</sup> P3,<sup>14c</sup> P5,<sup>14f</sup> P6,<sup>14c</sup> and P7<sup>28</sup> were synthesized according to the literature.

**Synthesis of the (ONNO) Ligands.** The tetradentate [ONNO] ligands L1–L10 were prepared by reacting *N*,*N*'-dimethylethylenediamine or *N*,*N*'-dimethylethylenediamine with formaldehyde and the appropriate phenol, as described in the literature.<sup>14</sup> 10 mmol of *N*,*N*'-dimethylethylenediamine, 10 mmol of formaldehyde (37% solution in water), and 10 mmol of the appropriate phenol were added to 30 mL of methanol and kept under reflux for 3 h. The precipitated product was filtered off, washed with cold methanol, and dried in an oven, at 65

°C under vacuum for 3 h. A second crop of product could be obtained by keeping the methanol solution in a fridge for several days. Total yields were ca. 60%.

L4 ( $R_1$  = Cumyl,  $R_2$  = Me,  $R_3$  = Et). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 300 K): δ 0.48 (t, 6H, N-CH<sub>2</sub>-CH<sub>3</sub>), 1.84 (s, 12H, C(CH<sub>3</sub>)<sub>2</sub>), 1.90 (m, 4H, N-CH<sub>2</sub>-CH<sub>3</sub>), 1.93 (s, 4H, NCH<sub>2</sub>), 2.28 (s, 6H, CH<sub>3</sub>), 3.05 (s, 4H, NCH<sub>2</sub>Ar), 6.71 (d, 2H, Ar), 7.08 (t, 2H, Ar), 7.18 (t, 4H, Ar), 7.29 (d, 2H, Ar), 7.37 (d, 4H, Ar), 10.46 (bs, 2H, OH). <sup>13</sup>C NMR (100.62 MHz,  $C_6D_6$ , 300 K): δ 11.1 (N-CH<sub>2</sub>-CH<sub>3</sub>), 21.1 (CH<sub>3</sub>), 29.5 (C(CH<sub>3</sub>)<sub>2</sub>), 42.2 (C(CH<sub>3</sub>)<sub>2</sub>), 47.5 (N-CH<sub>2</sub>-CH<sub>3</sub>), 50.0 (NCH<sub>2</sub>), 58.3 (NCH<sub>2</sub>Ar), 122.0 ( $C_{ipso}$ ), 124.9 (C-H), 126.0 (C-H), 126.9 ( $C_{ipso}$ ), 151.5 ( $C_{ipso}$ ), 154.4 ( $C_{ipso}$ ). Anal. Calcd for C<sub>40</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub>: C, 81.04; H, 8.85; N, 4.73. Found: C, 81.22; H, 8.95; N, 4.66.

**L8** ( $R_1 = R_2 = Cl$ ,  $R_3 = Et$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 300 K): δ 1.11 (s, 6H, N–CH<sub>2</sub>–CH<sub>3</sub>), 2.60 (q, 4H, N–CH<sub>2</sub>–CH<sub>3</sub>), 2.73 (s, 4H, N–CH<sub>2</sub>), 3.73 (s, 4H, NCH<sub>2</sub>Ar), 6.85 (d, 2H, Ar), 7.27 (d, 2H, Ar), 10.8 (br, 2H, OH). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K): δ 11.1 (N–CH<sub>2</sub>–CH<sub>3</sub>), 47.9 (N–CH<sub>2</sub>–CH<sub>3</sub>), 50.3 (NCH<sub>2</sub>), 57.4 (NCH<sub>2</sub>Ar), 121.7 ( $C_{ipso}$ ), 123.7 ( $C_{ipso}$ ), 126.8 (C–H), 128.9 (C–H), 152.9 ( $C_{ipso}$ ). Anal. Calcd for C<sub>20</sub>H<sub>24</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>: C, 51.52; H, 5.19; N, 6.01. Found: C, 51.54; H, 5.26; N, 6.00.

**L9** ( $R_1 = Cl$ ,  $R_2 = R_3 = Me$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 300 K): δ 2.23 (s, 6H, CH<sub>3</sub>), 2.32 (s, 6H, N–CH<sub>3</sub>), 2.73 (s, 4H, N–CH<sub>2</sub>), 3.69 (s, 4H, NCH<sub>2</sub>Ar), 6.68 (d, 2H, Ar), 7.08 (d, 2H, Ar), 10.6 (br, 2H, OH). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K): δ 20.3 (CH<sub>3</sub>), 41.9 (N–CH<sub>3</sub>), 54.3 (NCH<sub>2</sub>), 61.4 (NCH<sub>2</sub>Ar), 120.5 ( $C_{ipso}$ ), 122.3 ( $C_{ipso}$ ), 127.7 (C–H), 129.1 ( $C_{ipso}$ ), 129.7 (C–H), 154.1 ( $C_{ipso}$ ). Anal. Calcd for C<sub>18</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 58.54; H, 6.00; N, 7.59. Found: C, 58.50; H, 6.05; N, 7.55.

**L10** ( $R_1 = Me, R_2 = Cl, R_3 = Me$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 300 K):  $\delta$  2.20 (s, 6H, CH<sub>3</sub>), 2.29 (s, 6H, N–CH<sub>3</sub>), 2.66 (s, 4H, N–CH<sub>2</sub>), 3.65 (s, 4H, NCH<sub>2</sub>Ar), 6.80 (d, 2H, Ar), 7.04 (d, 2H, Ar), 10.6 (br, 2H, OH). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  15.7 (CH<sub>3</sub>), 41.7 (N–CH<sub>3</sub>), 53.9 (NCH<sub>2</sub>), 61.4 (NCH<sub>2</sub>Ar), 122.2 ( $C_{ipso}$ ), 123.2 ( $C_{ipso}$ ), 125.8 (C–H), 127.1 ( $C_{ipso}$ ), 129.8 (C–H), 154.5 ( $C_{ipso}$ ). Anal. Calcd for C<sub>18</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 58.54; H, 6.00; N, 7.59. Found: C, 58.55; H, 6.03; N, 7.60.

**Synthesis of Zr Complexes.** The synthesis was done according to the literature procedure.<sup>14</sup> 5 mmol of ligand was weighted in a Schlenk flask and dissolved in 10 mL of dry toluene (heating the mixture helps the dissolution of the compound). The resulting solution was added to another Schlenk flask containing a solution of 5 mmol of  $Zr(Benzyl)_4$  in 10 mL of the same solvent, under an argon atmosphere. The mixture was kept at 65 °C for 2 h, and then the solvent was evacuated to give the product as a pale yellow powder. Recrystallization from diethyl ether afforded the product in 60% yield.

Complex **P4.** <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  0.20 (*t*, 6H, N–CH<sub>2</sub>–CH<sub>3</sub>), 1.35 (*d*, 2H, N–CH<sub>2</sub>), 1.84 (*s*, 6H, CH<sub>3</sub>), 1.94 (*m*, 2H, N–CH<sub>2</sub>–CH<sub>3</sub>), 2.02 (*s*, 6H, CH<sub>3</sub>), 2.10 (*m*, 2H, overlapped, N–CH<sub>2</sub>–CH<sub>3</sub>), 2.10 (*d*, 2H, overlapped, NCH<sub>2</sub>), 2.19 (*d*, 2H, Zr–CH<sub>2</sub>), 2.20 (*s*, 6H, CH<sub>3</sub>), 2.71 (*d*, 2H, Zr–CH<sub>2</sub>), 2.76 (*d*, 2H, N–CH<sub>2</sub>Ar), 3.20 (*d*, 2H, N–CH<sub>2</sub>Ar), 6.43 (*d*, *J* = 2.3 Hz, 2H, Ar), 6.79 (*t*, 2H, Ar), 6.95 (*d*, 4H, Ar), 7.08 (*t*, 2H, Ar), 7.09 (*t*, 4H, Ar), 7.23 (*t*, 4H, Ar), 7.34 (*d*, 2H, Ar), 7.50 (*d*, 4H, Ar). <sup>13</sup>C NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  4.3 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 29.2 (CH<sub>3</sub>), 32.6 (CH<sub>3</sub>), 42.7 (C(CH<sub>3</sub>)<sub>2</sub>), 43.4 (N–CH<sub>2</sub>), 44.6 (NCH<sub>2</sub>), 56.8 (NCH<sub>2</sub>Ar), 72.1 (Zr–CH<sub>2</sub>), 120.9 (C–H), 125.5 (C-H), 125.9 (C<sub>ipso</sub>), 126.5 (C–H), 126.8 (C-H), 127.1 (C<sub>ipso</sub>), 127.9 (C–H), 128.1 (C–H), 129.6 (C–H), 129.9 (C–H), 137.0 (C<sub>ipso</sub>), 149.8 (C<sub>ipso</sub>), 151.6 (C<sub>ipso</sub>), 156.9 (C<sub>ipso</sub>). Anal. Calcd for C<sub>52</sub>H<sub>60</sub>N<sub>2</sub>O<sub>2</sub>Zr: C, 74.68; H, 7.23; N, 3.35. Found: C, 74.60; H, 7.28; N, 3.30.

Complex **P8.** <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 300 K):  $\delta$  0.28 (t, 6H, N–CH<sub>2</sub>–CH<sub>3</sub>), 1.27 (d, 2H, N–CH<sub>2</sub>), 1.91 (d, 2H, N–CH<sub>2</sub>), 1.98 (d, 2H, Zr–CH<sub>2</sub>), 2.34 (d, 2H, Zr–CH<sub>2</sub>), 2.35 (m, 2H, N–CH<sub>2</sub>–CH<sub>3</sub>), 2.53 (d, 2H, N–CH<sub>2</sub>Ar), 2.78 (m, 2H, N–CH<sub>2</sub>–CH<sub>3</sub>), 3.33 (d, 2H, N–CH<sub>2</sub>Ar), 6.47 (d, 2H, Ar), 6.86 (t, 2H, Ar), 7.07 (t, 4H, Ar), 7.14 (d, 4H, Ar), 7.30 (d, 2H, Ar). <sup>13</sup>C NMR (100.62 MHz,  $C_6D_6$ , 300 K):  $\delta$  5.2 (CH<sub>3</sub>), 44.9 (N–CH<sub>2</sub>), 45.7 (NCH<sub>2</sub>), 56.5 (NCH<sub>2</sub>Ar), 64.1 (Zr–CH<sub>2</sub>), 123.2 (C–H), 123.5 ( $C_{ipso}$ ), 124.0 ( $C_{ipso}$ ), 128.8 (C–H),

129.3 (C–H), 129.4 (C–H), 129.7 (C–H), 145.5 ( $C_{ipso}$ ), 154.4 ( $C_{ipso}$ ). Anal. Calcd for  $C_{34}H_{36}Cl_4N_2O_2Zr$ : C, 55.28; H, 5.05; N, 3.79. Found: C, 55.38; H, 5.25; N, 3.71.

Complex **P9.** <sup>1</sup>H NMR (400 MHz,  $C_6D_{6r}$  300 K):  $\delta$  0.79 (*d*, 2H, NCH<sub>2</sub>), 1.82 (*s*, 6H, CH<sub>3</sub>), 1.99 (*s*, 6H, NCH<sub>3</sub>), 2.02 (*d*, 2H, ZrCH<sub>2</sub>), 2.25 (*d*, 2H, NCH<sub>2</sub>Ar), 2.36 (*d*, 2H, NCH<sub>2</sub>), 2.40 (*d*, 2H, ZrCH<sub>2</sub>), 3.83 (*d*, 2H, NCH<sub>2</sub>Ar), 6.28 (*d*, 2H, Ar–H), 6.87 (*t*, 2H, Ar–H), 7.09 (*t*, 4H, Ar–H), 7.15 (*d*, 2H, Ar–H), 7.25 (*d*, 4H, Ar–H). <sup>13</sup>C NMR (100.62 MHz,  $C_6D_{6r}$  300 K):  $\delta$  20.2 (CH<sub>3</sub>), 44.6 (NCH<sub>3</sub>), 53.0 (NCH<sub>2</sub>), 62.4 (NCH<sub>2</sub>Ar), 63.2 (ZrCH<sub>2</sub>), 122.9 ( $C_{ipso}$ ), 123.0 (C–H), 126.6 ( $C_{ipso}$ ), 128.78 ( $C_{ipso}$ ), 129.1 (C–H), 129.3 (C–H), 129.6 (C–H), 130.5 (C–H),145.7 ( $C_{ipso}$ ), 153.6 ( $C_{ipso}$ ). Anal. Calcd for  $C_{32}H_{34}Cl_2N_2O_2Zr$ : C, 59.98; H, 5.35; N, 4.37. Found: C, 60.08; H, 5.39; N, 4.34.

Complex **P10.** <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 300 K):  $\delta$  0.71 (*d*, 2H, NCH<sub>2</sub>), 1.6 (*s*, 6H, NCH<sub>3</sub>), 1.92 (*d*, 2H, NCH<sub>2</sub>), 2.12 (*d*, 2H, NCH<sub>2</sub>Ar), 2.13 (*d*, 2H, ZrCH<sub>2</sub>), 2.20 (*s*, 6H, CH<sub>3</sub>), 2.24 (*d*, 2H, ZrCH<sub>2</sub>), 3.70 (*d*, 2H, NCH<sub>2</sub>Ar), 6.62 (*d*, 2H, Ar–H), 6.86 (*t*, 2H, Ar–H), 7.00 (*d*, 4H, Ar–H), 7.07 (*t*, 4H, Ar–H), 7.11 (*d*, 2H, Ar–H). <sup>13</sup>C NMR (100.62 MHz,  $C_6D_6$ , 300 K):  $\delta$  16.9 (CH<sub>3</sub>), 44.2 (NCH<sub>3</sub>), 52.7 (NCH<sub>2</sub>), 62.6 (ZrCH<sub>2</sub>), 62.7 (NCH<sub>2</sub>Ar), 122.8 (C–H), 123.4 ( $C_{ipso}$ ), 126.0 ( $C_{ipso}$ ), 127.6 (C–H), 128.7 (C–H), 128.8 (C–H), 130.6 (C–H), 146.0 ( $C_{ipso}$ ), 156.7 ( $C_{ipso}$ ). Anal. Calcd for  $C_{32}H_{34}Cl_2N_2O_2Zr$ : C, 59.98; H, 5.35; N, 4.37. Found: C, 60.03; H, 5.36; N, 4.40.

Polymerization Runs. All ethene and propene homopolymerization runs were carried out at 25 °C, in a 250 mL magnetically stirred jacketed Pyrex reactor with two necks (one of which capped with a silicone rubber septum, the other connected to a Schlenk manifold), according to the following procedure, unless otherwise specified. The reactor was charged under nitrogen with 150 mL of toluene (toluene HPLC, Aldrich, previously purified in an MBraun SPS unit) containing 5.0 mL of MAO (Chemtura, 10% w/w solution in toluene) and 1.7 g of 2,6-di-tert-butylphenol (Aldrich, 99%) and thermostated at 25 °C. After 1 h, 5.0 mL of the liquid phase was syringed out and used to dissolve the proper amount of precatalyst in a glass vial. The reactor was then evacuated to remove nitrogen and saturated with the monomer (SON, polymerization grade) at a partial pressure of 0.8-1.6 bar for ethene and 2.0 bar for propene. The polymerization was started by syringing in the catalyst solution, left to proceed at constant monomer pressure for the appropriate time, and quenched with 5 mL of methanol/HCl(aq, conc) (95/5 v/v). The polymer was coagulated with excess methanol/HCl, filtered, washed with more methanol, and vacuum-dried. Results of polymerization experiments are given in Table 4 (ethene) and Table 5 (propene).

#### Table 4. Ethene Polymerization Results

Cat	$\begin{bmatrix} C_2 H_4 \end{bmatrix}$	[Zr]	t (b)	yield	$R_{\rm E} (\rm kg_{\rm PE}/\rm mol ~ h [C H ]))$
Cat.	(141)	(µmor)	$\iota_p$ (II)	(g)	$(\Pi Ol_{cat} \Pi [C_2 \Pi_4]))$
P1	0.17	38	0.17	0.3	270
P2	0.17	42	0.05	0.14	400
P3	0.17	5.1	0.25	1.0	4600
P4	0.21	30	1.5	0.02	2
P5	0.17	3.8	0.12	0.19	2400
P6	0.11	0.135	0.067	0.56	560000
<b>P</b> 7	0.21	0.51	0.083	0.52	58000
P8	0.21	9	0.5	0.35	460
P9	0.21	1.2	0.083	0.89	42000
P10	0.21	4.6	0.25	0.69	2900

**Computational Details.** Density functional calculation were performed with the Turbomole program<sup>29</sup> (version 5.8) in combination with the OPTIMIZE routine of Baker and co-workers.<sup>30</sup> All geometries were fully optimized at the restricted  $RI^{31}$ -BP86<sup>32</sup> level, using the SV(P)<sup>33</sup> basis set (small-core pseudopotential on  $Zr^{34}$ ). The cations in these systems have well-defined geometries, but for the ion pairs the movement of the anion relative to the cation is very soft. A number of plausible starting geometries were explored for the basic system, and the "best" optimized structures were then used to

Table 5. Propene Polymerization Results

Cat.	[C <sub>3</sub> H <sub>6</sub> ] (M)	[Zr] (µmol)	<i>t</i> <sub>p</sub> (h)	yield (g)	$\begin{array}{c} R_{\rm p} \; ({\rm kg}_{\rm PP} / \\ ({\rm mol}_{\rm cat} \; {\rm h} \; [{\rm C}_{3} {\rm H}_{6}])) \end{array}$
P1	1.32	37	3.5	1.1	6.2
P2		63	2	0.42	2.5
P3		9	0.5	0.45	76
P4		50	4	0.05	0.2
P5		18	2	0.35	7.4
P6		3.5	0.08	3.3	8900
<b>P</b> 7		4.6	0.5	1.9	600
P8		46	4	0.25	1
P9		37	2	2.4	260
P10		37	2	3.2	33

construct starting geometries for the substituted systems. These systems, in particular the ion pairs, are so large that calculation of the Hessian is impractical; with computer times of weeks this would also defeat the purpose of using the calculations as an efficient tool for prediction of catalyst performance. Finally, the ion pairs are so "floppy" that thermal corrections arising from a vibrational analyses would not be very meaningful. Therefore, no vibrational analyses were carried for any of the substituted systems, and energy values cited in the text are pure electronic energies.

Single-point solvent corrections were calculated using the conductor-like screening model  $(COSMO)^{35}$  with  $\varepsilon = 2.37$  to model an nonpolar solvent (e.g., toluene). All energies mentioned in the text include this solvation correction, unless noted otherwise. To check for the sensitivity of the results to details of the calculation method, we also carried out single-point calculations with a larger basis set (def-TZVP<sup>36</sup>) and calculated the nonelectrostatic solvation terms separately.<sup>37</sup> These results are discussed in the Supporting Information, where we conclude that the simple recipe described here is preferable as a prescreening method.

Initial geometries and reasonable starting Hessians were obtained from PM3 computations with the Spartan package from Wavefunction  ${\rm Inc.}^{38}$ 

# ASSOCIATED CONTENT

# **Supporting Information**

Summary and discussion of TZVP results and nonelectrostatic solvent corrections; DFT-optimized structures of all species studied as a zipped archive of pdb files usable with various molecule viewers. This material is available free of charge via the Internet at http://pubs.acs.org.

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# Notes

The authors declare no competing financial interest.

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