Structural Characterization of Electron Donors in Ziegler–Natta Catalysts

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Supporting Information

ABSTRACT: Ziegler–Natta catalysis is a very important industrial process for the production of polyolefins. However, the catalysts are not well-understood at the molecular level. Yet, atomic-scale structural information is of pivotal importance for rational catalyst development. We applied a solid-state NMR/density functional theory tandem approach to gain detailed insight into the interactions between the catalysts’ support, MgCl₂, and organic electron donors. Because of the heterogeneity of the samples, large line widths are observed in the carbon spectra. Despite this, good agreement between experimental and computational values was reached, and this shows that 1,3-diether based donors coordinate at (110) surface sites, while phthalates are less selective and coordinate at both (104) and (110) surface sites.

INTRODUCTION

Modern Ziegler–Natta catalysts (ZNCs) for the industrial production of isotactic polypropylene are complex formulations, consisting of a highly disordered MgCl₂ support, on which TiCl₄ and an organic donor (e.g., an ester or an ether) are co-adsorbed. Activation entails reaction with an Al-trialkyl (e.g., AlEt₃), usually complexed with a second donor (in most cases, an alkoxysilane). Ever since their discovery, improvements on the catalytic system have been made, giving different generations of catalysts with varying electron donors and increasing performance. Despite their long-term industrial use, many questions still remain about the active constructs and the exact working mechanism of the catalyst. As a result of this, catalyst development has been primarily empirical. A fundamental understanding of the catalysts’ inner workings is key to a more rational catalyst design. One of the long-standing discussions concerns the question on which surface site the active titanium coordinates. Closely related to this are questions concerning electron donors and how they control or influence the stereospecificity of the active sites.

Seminal work in this field has been performed by Corradini and coworkers. The past years have seen a large number of theoretical studies aimed at revealing the surfaces sites of the activated MgCl₂ support that are bound by donors and TiCl₄ with results contradicting earlier models in the literature. The (104) and (110) surfaces have been identified as those relevant for catalysis, although some recent publications suggest that surface defects on those surfaces are the real adsorption sites. Consensus has been reached about (104) surfaces, exposing pentacoordinated magnesium sites, as being thermodynamically more stable than (110) surfaces, exposing tetracoordinated magnesium sites. The (015) surface has recently been proposed as an alternative relevant surface. The addition of donors to the surface can significantly change the picture to favor the (110) sites, especially for 1,3-diethers. Traditionally, TiCl₄ was believed to form Ti₂Cl₈ dimers on the (104) surface, while donors would cover the more acidic and nonstereoselective (110) sites.

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### Table 1. Properties of All the Samples Investigated in This Study

<table>
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<tr>
<th>samples code</th>
<th>donor</th>
<th>loading [% mol adsorbate/mol Mg]</th>
<th>(L_p) [nm]</th>
<th>(L_a) [nm]</th>
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</thead>
<tbody>
<tr>
<td>MgCl₂ DM³⁰</td>
<td>DMDOMe</td>
<td>4.0</td>
<td>12.6</td>
<td>13.0</td>
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<td>Do1_4</td>
<td>DMDOMe</td>
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<td>12.6</td>
<td>13.0</td>
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<td>DMDOMe</td>
<td>10.0</td>
<td>12.6</td>
<td>13.0</td>
</tr>
<tr>
<td>Do2_2.5</td>
<td>DMFluo</td>
<td>2.5</td>
<td>12.6</td>
<td>13.0</td>
</tr>
<tr>
<td>Do3_2</td>
<td>DiBP</td>
<td>2.1</td>
<td>12.6</td>
<td>13.0</td>
</tr>
<tr>
<td>Do3_7</td>
<td>DiBP</td>
<td>6.7</td>
<td>12.6</td>
<td>13.0</td>
</tr>
</tbody>
</table>

\(L_p\) and \(L_a\) are the average particle dimension perpendicular and parallel to the basal \((ab)\) plane, respectively. See ref 40. “The average size could not be determined because the XRD diffraction peaks were too broad.”

### EXPERIMENTAL SECTION

#### Sample Preparation

The preparation of anhydrous MgCl₂ is described elsewhere. Dried MgCl₂ and the respective donors were ball-milled using a Retsch PM-100 planetary ball mill. Operating inside a glovebox, the samples (2–12 g) were loaded inside an air-tight and chemically inert ceramic jar (Y-stabilized ZrO₂), along with 87 g of grinding ceramic balls (3 mm diameter). The jar was then transferred to the mill. The rotational speed was set to the maximum value (650 rpm), and the rotational motion was inverted at 20 min intervals to prevent as far as possible encrustations on the inside walls of the jar. A milling time of 8 h turned out to be adequate to reach the lower limit of the crystallite size. The resulting solid was then washed with one or more aliquots of dry heptane and pentane under vigorous stirring at room temperature and finally dried under vacuum at 50 °C overnight.

The particle size of the MgCl₂ support follows from powder X-ray diffraction (XRD), following the procedure described by Giunchi and Allegra. The XRD profile were recorded using a Philips PW 1830 diffractometer equipped with a custom-made airight cell with PVC windows and able to maintain a static atmosphere with negligible O₂ and moisture contamination for at least 8 h. The cell was loaded in a glovebox and transferred to the diffractometer, where the diffraction profile was collected using Ni-filtered Cu Kz radiation (30 mA, 35 kV) with a step scanning procedure (2θ range between 5° and 70°, 0.1° step, 20 s counting time per step). The donor content of the samples has been quantified by solution-state \(^1\)H NMR using a Bruker ADVANCE DRX 400 MHz spectrometer, after dissolving the adducts in deuterated methanol and quantification versus an internal standard (acetonitrile).

#### Computational Details

All chemical shielding calculations were carried out with a cluster approach using the Gaussian 09 package. For single-adsorbate models, optimization and frequency calculations were carried out at the R\(^3\)15,44–47, TPSSTPSS\(^6\)-6-31+G(2d,p)\(^5\) level, while single-point energy corrections were carried out at R\(^3\)15,44–47, TPSSTPSS\(^6\)-6-31+G(2d,p)\(^5\) and R\(^3\)15,44–47, TPSSTPSS\(^6\)-6-31+G(2d,p)\(^5\) levels. \(^1\)C chemical shielding calculations were performed at the TPSSTPSS level of theory, exploring different basis sets, including the basis set suited for chemical shielding calculations, such as aug-pVTZ-J\(^5\), IGLO-II\(^5\), and IGLO-III.\(^5\) Comparable results were obtained for all basis sets, so we only discuss IGLO-II results for the sake of simplicity. Chemical shifts (\(\delta\)) of the neat donors were calculated relative to tetramethylsilane, and the correlation between these computational results and the experimental reference shifts have been used to correct the calculated shifts for the adducts.

The increased computational demand for higher coverage systems with multiple adsorbate molecules forced us to carry out the optimization and frequency calculations at the R\(^3\)15,44–47, TPSSTPSS level, with a smaller basis set, namely, def2-SVP\(^4\), correcting the electronic energy with the Grimme’s D3 dispersion correction.\(^4\) NMR. \(^1\)C CPMAS and \(^1\)H–\(^1\)C HETCOR measurements were recorded at room temperature on a Varian VNMRS 400.
MHZ spectrometer (9.4 T, 104.6 MHz for $^{13}$C) using a triple resonance 3.2 mm Varian T3MAS probe at 15 or 20 kHz MAS using 75 or 100 kHz $^1$H decoupling. Additional $^{13}$C CPMAS experiments were performed on Varian VNMR 600 and 850 MHz spectrometers (14.1 T, 156.9 MHz for $^{13}$C and 20.0 T, 221.4 MHz for $^{13}$C) using triple resonance 3.2 and 4.0 mm Varian T3MAS probes. Fast MAS $^1$H measurements and $^1$H SQ–DQ measurements were performed on the 850 MHz machine using triple resonance 1.2 and 3.2 mm Varian T3MAS probes.

### RESULTS AND DISCUSSION

The binary adducts studied in the paper are prepared by ball milling of anhydrous MgCl$_2$ and the respective donor. They are coded as Do$x$y where Do$x$ refers to the donor type and -y refers to the donor loading (in percentage); see Table 1. The structures of the neat donors are represented with the $^1$H spectra, as shown in Figure 1. The structure of the adducts is studied by a combination of solid-state NMR and DFT calculations. Table 1 gives the characteristics of the samples as determined by XRD and solution-state NMR (see the Experimental Section). Indeed, co-milling of MgCl$_2$ with a donor leads to binary adducts with much smaller MgCl$_2$ nanoparticles compared to neat ball-milled MgCl$_2$ without additives as a result of the stabilization of the surfaces by the electron donor. The smallest particles are, on average, only a few nm thick, corresponding to just a few MgCl$_2$ layers and thus have large surface areas.

$^1$H NMR of Organic Donors. Figure 1 shows the $^1$H spectra of selected adducts (Do1.4, Do2.2.5, and Do3.7). The assignment of the spectra is shown in the figure. The spectra of Do10 and Do3.2 (not shown) conform to the results shown. Reasonably well-resolved $^1$H NMR spectra can be obtained from the Do3.7 adduct using fast MAS. Figure 1C shows the 50 kHz proton MAS spectrum of the Do3.7 adduct. The resolution is sufficient to resolve different proton resonances at 7.7, 4.0, 2.1, and 0.9 ppm which can be assigned to the aromatic, –OCH$_2$–, –CH, and –CH$_3$ protons, respectively. However, the resolution is not high enough to be able to differentiate between coordination modes or to assign these resonances to a particular surface structure. Proton resolution is often hampered by strong homonuclear dipolar interactions, yet the line widths reduced only marginally, going from 15 to 50 kHz MAS. Homonuclear DUMBO decoupling experiments$^{56}$ did not lead to improved resolution either, indicating that in this case, the heterogeneity of the sample is most likely the limiting factor for the line width. The spectra of the other adducts are recorded at lower spinning speed, still the resolution is sufficient to resolve different proton resonances. However, again, this does not permit assignment to particular surface sites. The spectra suffer from a strong rotor background signal around 7 ppm, overlapping with the aromatic resonances from DMFluo. An additional background signal at −2.5 ppm is shown in Figure 1A.

Despite the limited resolution, $^1$H NMR can still be used to inspect the H$_2$O content, which is always a concern when studying such samples. On a first inspection, we find no evidence for the presence of water in the $^1$H spectra of the adducts. In a previous publication, we showed that even thoroughly dried neat MgCl$_2$ samples are not completely water-free.$^{40}$ In fact, a full surface coverage of water or otherwise protonated species (–OH surface groups) was found. The binary adducts presented in this study have significantly larger surfaces areas (Table 1) and might potentially take up large quantities of water. From the 1D spectra, this can be ruled out; however, it cannot be excluded that some minor water signals are hidden under the resonances from the donors, as might be indicated by the shoulder around 5 ppm in the spectrum of Do3.7.

Water uptake is observed when samples are stored for a longer time or when they are deliberately exposed to ambient atmosphere for a few minutes; see Figure 1A. In that case, a pronounced signal appears at 5.1 ppm, which can be straightforwardly detected in a 1D spectrum. This demonstrates the ability to detect the presence of H$_2$O in such catalyst samples and at the same time also showcases the low H$_2$O content before exposure. We propose that these results show that the organic donors, which coordinate in situ to the formed nanoparticles, successfully protect the surface from H$_2$O uptake. The latter is something which inevitably happens with exposed surfaces, even when working under a controlled glovebox atmosphere.

Similar to the detection of H$_2$O, $^1$H NMR also detects the presence of other impurities in the sample. This mainly concerns the presence of residual signals from physisorbed hydrocarbons that have been used in washing steps during the adduct preparation stage (see the Experimental Section) and
apparently survived the subsequent drying steps; see Figure 1B. These signals of pentane and/or heptane are found at δ 0.88, 1.27, and 1.30 ppm. Such signals are, in particular, detected in the 1D spectrum of Do2_2.5 because of the absence of aliphatic protons for the DMFluo donor. However, they are also found in the other donors; see Figures 1A and 2.

Overlap of the proton signals is alleviated in 2D proton single quantum−double quantum (SQ−DQ) experiments. Figure 2 shows the SQ−DQ spectrum of Do1_4 in which the −OCH2− and −OCH3 groups are separated. The cross-peak at 0.96/3.78 corresponds to the interaction between the methyl group and the −OCH2− protons of the donor. The −OCH3 group lacks a cross-peak with the methyls. On top of the broad methyl signal, there are narrow and strong signals from hydrocarbons, as a result of the long T2 of these signals. In the 2D SQ−DQ experiment, a weak signal around 5 ppm is detected, showing the presence of small amounts of water that could not be resolved in a 1D spectrum. However, it is clear that the water signal is significantly lower than that of the donor, thus implying that the surfaces are mostly water-free. A strong H2O signal is found in the SQ−DQ spectrum of the hydrated sample; see Figure S1. In both SQ−DQ spectra, there is a weak signal at 2.1 ppm. The 1D spectrum (red trace) also shows a small shoulder at 1.6 ppm that could point to some −OH surface groups, but again this signal is much smaller than the peaks from the donor. Interestingly, this −OH group is not found in the 2D SQ−DQ spectrum, neither as a diagonal nor as a cross-peak, indicating that these Mg−OH groups are isolated on the surface.

13C NMR of Organic Donors. Compared to 1H NMR, 13C NMR generally yields enhanced resolution because of its larger chemical shift dispersion, and it is therefore a valuable tool to study the organic donors. 1H−13C cross polarization (CP) experiments have been performed at fields of 9.4, 14.1, and 20 T. The latter could potentially yield the highest resolution, but the relative slower spinning speed causes overlap between spinning sidebands from the aromatic resonances and center bands from other resonances. The final line shape and line width (in ppm) are very comparable at all fields, again proving that structural heterogeneity is the main source of line broadening. Reference spectra are obtained in the solution state for the DMDOMe and DiBP donors (solvent CDCl3, Figure S2), whereas a solid-state reference spectrum has been obtained for DMFluo. The 13C CPMAS spectra of the adducts are shown in Figure 3. Tables 2−4 compare the experimental 13C chemical shifts of the organic donors in the binary adducts to reference data.
Computational Results Are for a High-Coverage Model (See Text)

Table 2. Experimental Isotropic 13C Chemical Shifts (in ppm) of Do1_4 and Do1_10 Adducts

<table>
<thead>
<tr>
<th>carbon #</th>
<th>𝑑exp DMDOMe</th>
<th>𝑑exp Do1_4</th>
<th>𝑑exp Do1_10</th>
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<tr>
<td>−OCH3− (C6, C7)</td>
<td>78.9</td>
<td>84.2</td>
<td>84.5</td>
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<td>Cquat (C4)</td>
<td>35.9</td>
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<tr>
<td>−CH3 (C1, C2)</td>
<td>21.9</td>
<td>23.1</td>
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<td>−OCH3 (C1, C2)</td>
<td>58.9</td>
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Neat donor, measured in (CDCl3).

Table 3. Experimental and Computational Isotropic 13C Chemical Shift (in ppm) for DMFluo and DMFluo Adducts on MgCl2; Computational Results Are for a High-Coverage Model (See Text)

<table>
<thead>
<tr>
<th>carbon #</th>
<th>𝑑exp DMFluo</th>
<th>𝑑exp Do2_2.5</th>
<th>𝑑ΔΔ, clu27u110 + 3Do2A</th>
<th>𝑑ΔΔ, clu27u110 + 3Do2C</th>
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<td>57.8</td>
<td>62.3</td>
<td>64.0</td>
<td>64.7</td>
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</table>

Neat donor, measured as a solid powder, blue trace in Figure 3B.

Table 4. Experimental Isotropic 13C Chemical Shifts (in ppm) of Do3_2 and Do3_7 Adducts

<table>
<thead>
<tr>
<th>carbon #</th>
<th>𝑑exp DMDOMe</th>
<th>𝑑exp Do3_2</th>
<th>𝑑exp Do3_7</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbonyl (C1, C2)</td>
<td>167.3</td>
<td>173.4, 176.8, 181.0</td>
<td>172.5, 175.8, 182.0</td>
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<tr>
<td>aromatics (C3, C4)</td>
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<td>134.4</td>
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<td>(C5, C6)</td>
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<td>(C7, C8)</td>
<td>128.5</td>
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<td>−OCH3− (C9, C10)</td>
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<td>−CH (C11, C12)</td>
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<tr>
<td>−CH3 (C13−C16)</td>
<td>18.9</td>
<td>18.1</td>
<td>18.9</td>
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</table>

Neat donor, measured in (CDCl3).

DMDOMe. Figure 3A shows the 13C spectra of adducts of DMDOMe with MgCl2. Both donor loadings yield distinct resonances for the four carbons in the system. The quaternary carbon (C4) gives a sharp singlet at 36.9 ppm; see Table 2. The other carbons give significantly broader lines. Both the methyl (C6, C7, ~21 and 23 ppm) and the methoxy (C3, C4, ~64.5 and 66.5 ppm) resonances are composed of at least two components. The −OCH3− and −OCH2− resonances for the four carbons in the system. The quaternary carbon (C3) gives a sharp singlet at 36.9 ppm; see Table 2. The ppm values of the other two resonances are shifted a little bit (~0.5 ppm) with respect to Do1_10; see Table 2 and Figure S3. The third component is found at a lower chemical shift, δ = 20.0 ppm.

- The −CH3 resonance for Do1_4 shows an additional line. It is composed of three components; two of them are in close agreement with the values found for Do1_10; see Table 2 and Figure S3. The third component is found at a lower chemical shift, δ = 20.0 ppm.
- The −OCH3 resonance for Do1_4 also shows an additional line at lower ppm values (δ = 62.5 ppm). The ppm values of the other two resonances are shifted a little bit (~0.5 ppm) with respect to Do1_10; see Table 2 and Figure S3.

In general, the line widths in both spectra are the same, yet the −OCH3− resonance for Do1_4 is slightly broader than it is for Do1_10. It cannot satisfactorily be fitted with a single component. A bicomponent deconvolution cannot be performed unambiguously; however, satisfactory two-component fits can be obtained with a shift difference between 0.5 and 1.2 ppm for the two lines. In contrast, for Do1_10, the −OCH3− resonance can be fitted well with a single component, yet bicomponent deconvolution yields plausible results when the chemical shift difference is limited to <0.9 ppm.

Do1_10 shows hydrocarbon impurities similar to the 13C spectrum of Do2_2.5 (vide infra). Although 1H SQ–DQ of Do1_4 also shows hydrocarbons, they are not observed in the 13C spectrum. This is probably because of the high mobility and thus low CP efficiency.

It comes as a surprise that Do1_4 gives additional signals in the 13C spectrum, as it may point to the presence of an additional surface construct (see the next section), which is more likely expected for a high donor loading. However, different loadings cannot directly be interpreted as different surface coverages. Indeed, the two samples have quite different particle sizes as well; with ⟨L ⟩ = 4.24 nm and ⟨L ⟩ = 7.70 nm for Do1_4, and ⟨L ⟩ = 2.84 nm and ⟨L ⟩ = 4.37 nm for Do1_10.
Do1_10; see Table 1. Under the assumption of hexagonal particles exposing solely (110) surfaces, an estimation of the exposed Mg surface sites can be made and correlated to the donor content. This gives the surface coverage, which is given as the fraction of Mg surface sites that coordinate a donor (see Figures S8 and S9 as an example for full coverage). This back-of-the-envelope calculation indicates a surface coverage of about 60% for Do1_10 and 40% for Do1_4. The surface coverages for Do1_4 is thus of the same order as that for Do1_10, which is therefore not a plausible explanation for the additional signals for Do1_4. Interestingly, both adducts have a large fraction of surface sites that are not covered by the donor, but still the H2O or −OH content is low.

DMFluo. The solid-state 13C CPMAS spectrum of neat DMFluo shows narrow lines with a splitting for some of the resonances, as shown in Figure 3B. The 13C CPMAS spectrum of the corresponding binary adduct (Do2_2.5) shows much broader lines originating from the heterogeneity of the donor’s local environment over the sample. The absence of narrow lines also means that all donor molecules coordinated to the support. Most resonances can be assigned straightforwardly, but additional interrupted decoupling experiments were performed to make the final assignment for the peaks around 63 and 53 ppm, which correspond to the methoxy groups (C16−C17) and quaternary carbon C18 respectively. Additional minor signals at 14, 22, 29, and 31 ppm can be assigned to hydrocarbons. Small amounts of the solvent (heptane and pentane) apparently remain trapped in the catalyst after the washing steps, as was also witnessed from the 1H solid-state NMR spectra. This has been observed before by others.57-58 Another impurity at 44 ppm remains unassigned. The −OCH3− (C1−C2) and −OCH2− (C16−C17) peaks show significant shifts with respect to the reference spectrum: both shift more than 5 ppm toward higher ppm values, similar to what was observed for Do1 adducts. Other peaks display much smaller shifts and sometimes shift toward lower ppm values. The large shifts of the −OCH3− resonances are a clear indication that the adducts are strongly attached to the surface and bind via the oxygen atom.

Analyzing the carbon spectrum of Do2_2.5 in more detail, it appears that some resonances might be composed of multiple resonances. The deconvoluted experimental shifts can be found in Table 3. The quaternary carbon has an asymmetric line shape that suggests multiple components. The −OCH3− resonance is clearly composed of two peaks which are found at 78.3 and 81.5 ppm, and the −OCH2− carbon resonance is also composed of two peaks. The presence of multiple resonances might contain valuable information about the coordination mode (vide infra).

DIBP. The resonances in the 13C CPMAS spectra of Do3 adducts, shown in Figure 3C, can be straightforwardly assigned. The spectrum shows relatively narrow resonances for the aliphatic carbons; the aromatic region is broader. The line widths obtained for the Do3 adducts are significantly lower than those reported by Sormunen et al.59 and Heikinen et al.60, who synthesized binary adducts by adding a donor to already ball-milled MgCl2. Clearly, co-milling of the components leads to a support that is more heterogeneous, which is also in agreement with the much smaller particles obtained when co-milling (see Table 1). These findings are in agreement with the results of Sormunen et al.61 who obtained adducts following both co-milling of the components as well as mixing DIBP to pre-ball-milled MgCl2. The broad aromatic region contains multiple peaks, with shifts that correspond to the solution state reference. The −OCH3− resonance is significantly shifted (~5 ppm) compared to the solution-state reference. Also, the resonances in the carbonyl region are shifted considerably (>5 ppm) with respect to solution-state spectra; see Table 4, again clearly proving the coordination to the support.

When comparing the different donor loadings, the following is apparent:

- The aliphatic region has slightly broader lines for Do3_2. Minor chemical shift differences are observed. In Do3_2, there appears to be some additional resonances originating from physisorbed hydrocarbons, as was also observed in Do1_10 and Do2_2.5. Because of overlap with the isobutyl protons, this is not directly clear from the 1H spectrum of Do3_2.
- The carbonyl resonance is composed of multiple components, as shown in Figure S4. The spectrum of Do3_2 displays three resonances at 173.4, 176.8, and 181.0 ppm. The latter signal is much weaker for Do3_7. In the 20 T spectrum, it cannot be observed because of overlap with a spinning sideband. In the 9.4 T spectrum, there is a weak signal for this third component that shows up as a low-intensity foot (~182 ppm) besides the two main resonances. The peaks in the carbonyl region for Do3_7 are shifted a bit to lower ppm values, 172.5 and 175.5 ppm.
- The −OCH3− resonance shows up as a single component for both loadings. Again, a minor chemical shift difference is observed.

Heterogeneity. The 13C spectra of the binary adducts display some characteristic shifts of resonances involved in the coordination of the donor to the support. Besides shifts, some of the resonances also show the presence of multiple peaks such as the aliphatic resonance in the spectrum of DIBP adducts and the methyl and methoxy resonances in the spectra of DMDOMe adducts. In an attempt to get more information about the multiple peaks, we performed 1H−13C HETCOR experiments. Also, we hypothesized that magnetic susceptibility effects giving inhomogeneous broadening could be alleviated using HETCOR experiments.62-63 The 2D HETCOR spectra can be found in Figures S5 and S6, but they are unfortunately not too informative. The splitting of some of the carbon resonances is very clear (Figure S6), but this was already found in the 1D spectra. The resolution in the 1H dimension is low. Unique 1H/13C shift pairs for the multiple resonances can therefore not be obtained.

Note that the HETCOR spectra show broad correlation peaks. If inhomogeneous broadening from anisotropic bulk magnetic susceptibility was the dominant line broadening mechanism, these should show up as tilted peaks because of correlated inhomogeneous broadening for carbons and protons. The same effect (elongated/tilted correlation peaks) should be observed in 1H SQ−DQ experiments.64,65 This is clearly not the case, and susceptibility broadening is thus not the main cause of line broadening. Broadening due to disorder in and/or heterogeneity of the donor’s coordination on the surface is the determining factor for the line width (vide infra).

Multiple peaks can point toward an asymmetric coordination and/or the presence of several conformations, thus giving insight into the surface constructs. Such observations have been made in the early literature. Back then, the focus was on the donor ethylbenzoate used in third-generation ZNCGs.57,60,61,66-67
although alkoxysilanes and phthalates were already in the picture.59–61,68 However, the spectra were never assigned to particular surface structures. To interpret the observed shifts in terms of surface structures, we employ chemical shift calculations as described in the next section.

Chemical Shift Calculations. To help the molecular interpretation of the experimental spectra, we employed chemical shift calculations for structural models. This should give insight into the coordination mode of the different donors on MgCl₂ surfaces. To this end, we considered coordination modes to different surfaces, including bridging and chelating coordinations on both (104) and (110) surfaces.

DMDOMe. DMDOMe is a small donor, yet it is a conformationally dynamic molecule. We carried out a conformational analysis of the isolated (gas phase) molecule and studied the chemisorption of the molecule on MgCl₂ clusters (mimicking crystal lateral terminations) via a cluster DFT approach. The free molecule can adopt multiple coordinations which have very similar Gibbs free energies; see Table S1. On inspection of these conformations (Figure 4), Do1A and Do1C were identified as the only conformers suited to coordinate to the MgCl₂ lateral terminations in a chelating or bridging coordination mode and were therefore selected for chemisorption modeling. Monodentate coordination has been excluded to be the prevailing coordination mode by us and others previously,11,16,17,20,29,69 and given the relative low surface coverage (40–60%), we have not taken this coordination mode into consideration. Two model cluster systems serve as surrogates for MgCl₂ nanocrystals, namely, clu_27u_110 (containing 27 units of MgCl₂) and clu_24u_104 (containing 24 units of MgCl₂) for the (104) and (110) surfaces, respectively.

The results of Table S2 indicated a strong preference (~11–15 kcal/mol) of DMDOMe for chelate binding to four-coordinated Mg sites (clu_27u_110) over pentacoordinated ones (clu_24u_104); this is in line with previous literature claims.70,71,72 Moreover, conformer Do1A binds stronger to both surfaces than conformer Do1C (3–4 kcal/mol), as opposed to the relative stability of the isolated molecule (see Table S1).

Table 5 shows the calculated chemical shifts of the adducts of the two DMDOMe conformers with the two clusters; the values have been adjusted by subtracting the mean absolute deviation obtained from the free molecule calculations. The calculated shifts are generally within 3 ppm from the experimental shifts. These deviations are within the accuracy that can be expected for such calculations.71 Therefore, we look in particular for trends and differences between the models, rather than looking at absolute values. Focusing on Do1_10, the following can be noted:

- A combination of the two conformations on one surface or of all the conformations on both surfaces should give rise to a large split or broadening (up to 6 ppm) of the −OCH₂− group (C₃–C₄), which is not in agreement with the experiment.
- Both clusters show quite different chemical shifts for the quaternary carbon (C₃). This allows us to exclude a distribution of the molecule over both surfaces because if this was the case, we should observe a significant splitting or broadening (up to 3 ppm) of the signal of this carbon, which is clearly not the case (see Figure 3A). The chemical shift difference between conformer Do1A and Do1C on a particular surface, on the other hand, is negligible.
- Only binding of conformer Do1A leads to a surface-induced asymmetry, both upon coordination on (104)–as well as (110)–like clusters. The Do1A conformation shows a chemical shift difference (Δδ) for the methyl (C₄) and methoxy (C₆ and C₇, 0.2 ppm) carbons, which is in agreement with the experiment; but it also shows a large Δδ (~3 ppm) for the −OCH₂− carbons (C₅ and C₆), which is not observed experimentally. For conformer Do1C, each pair of carbons has (almost) the same shift. From Table S3, it can be seen that the dihedral angles of the left side of the molecule are quite different from the right-side ones in Do1A. This implies that, for example, the OCH₃(C₁−C₂) and methoxy(C₆ and C₇, 0.2 ppm) fragments have a different orientation with respect to the cluster, which explains the observed chemical shift difference. Do1C, on the other hand, remains symmetric, explaining the absence of chemical shift differences (Δδ).
The remaining possibility is that only one conformation on one surface produces the observed spectrum, and the results in Table S5 indicate that the thermodynamically most stable donor−surface interaction (conformer Do1A on the (110) surface) should indeed show the experimentally observed multiple peaks, albeit the magnitude of the shift differences deviates from the experiment. The additional resonances observed for Do1_4 indicate the presence of a second species. Energetically, conformer Do1C on the (110) surface would be the most realistic candidate, which is also in agreement with a single, narrow resonance for C3. However, the calculations do not support the observation of lower chemical shift values for the additional peaks compared to the resonances in Do1_10.

We are the first to admit that the model clusters investigated so far are only rough approximations of real-world adducts, which are characterized by a larger degree of surface coverage and multiple structural layers. Fully relaxed multilayer models are still prohibitively expensive in terms of necessary computational time and resources. On the other hand, monolayer models at a higher degree of coverage are feasible, and evaluating the effect of this parameter on calculated 13C chemical shifts, both on the absolute shift as well as on the shift differences between pairs of carbons, was our next step. We focused on the (110) lateral termination because the ΔG suggests a strong preference for this surface (Table S2). Two structural models were considered: (i) three molecules (both Do1A or Do1C) on clu_27u_110; (ii) five molecules on a larger cluster, clu_39u_110, containing 39 MgCl2 units. Because of the higher computational demand, we carried out structure optimizations and frequency calculations with a smaller basis set than for the single-molecule adducts. Moreover, full relaxation was only possible for the smaller basis set than for the single-molecule adducts.

Figures S8 and S9 show the optimized structures of the high-coverage clu_27u_110 and clu_39u_110 models, and Table S4 reports their average binding energies (ΔH and ΔG average), and for the clu_27u_110 system, also the energies of the last entering molecule (chemisorption of the third molecule on a preformed cluster containing already two chemisorbed molecules). Finally, in Tables S5–S7, we report the calculated chemical shifts. Table 6 reports the chemical shift difference between the chemical shifts of each couple of carbon atoms for the fully relaxed cluster for 3Do1A and 3Do1C. The middle donor molecule in all these models can be considered to have a chemical environment comparable to a donor in a highly loaded system.

Looking at the results, the following facts can be noted:

- Thermodynamically (Table S4), only small effects of increased coverage are found for both surfaces. The relative stability between conformer Do1A and Do1C does not change, favoring conformer Do1A in all cases (by ~4 kcal/mol). The coordination of the third molecule is only slightly weaker than binding of the first and second molecule. This suggests little steric hindrance which rationalizes why the chemical shifts are very comparable to the single-molecule model; compare Tables S5 and S6.

- A high coverage does not lead to any shift difference for the middle donor(s) for conformer Do1C, neither within the frozen cluster approximation nor in the fully relaxed model. We therefore ultimately exclude this binding mode for Do1_10. The lack of a splitting supports the assignment of this species as the second component in Do1_4.

- All high-coverage models give a reduced Δδ for C4 and C3 (−CH3 carbons), while experimentally, the methyl region shows multiple peaks with a significant shift difference. The frozen cluster approximations, especially for clu_39u_110 + 3Do1, give a larger Δδ for C1 and C2. The fully relaxed structure clu_27u_110 with 3Do1A shows enhanced Δδ for C4 and C3 and a reduced Δδ for carbon C1 and C3 with respect to the single-donor model, bringing the predicted shift differences closer to the experiment.

All in all, we can conclude that a high-coverage model can improve the description of the MgCl2/Do1 system. Experimental and computational results strongly point to conformer Do1A on the (110) surface being the observed species in the Do1_10 adduct. A second species is observed for the Do1_4 adduct, most probably conformer Do1C on the (110) surface.

DMFluo. DMFluo is significantly bigger than DMDOMe, thus making it computationally more demanding. On the other hand, it has a rigid skeleton without mobile aliphatic side chains and is thus conformationally more restrained on the surface. Reducing the number of potential surface structures saves the computational time. Following the same procedures as for the DMDOMe, we again found two conformers Do2A and Do2C that are suited to interact with the surface; see Figure S10. Both conformers have a strong preference for binding to the (110) surface (~10−12 kcal/mol), with conformer A being slightly more stable than conformer C on both surfaces (~1.5 kcal/mol). These results are in line with the results for DMDOMe, albeit with a slightly lower energy difference.

The calculated shifts are summarized in Table S9 and generally match with the neat donor, but in agreement with the experimental results for the adduct, they show a pronounced higher chemical shift for both OCH3 groups. However, the calculated shift differences between the different conformers and surfaces are only small. Generally, the calculated chemical shifts for the aromatic carbons are underestimated by ~5 ppm. The match for the relevant carbons (C1−C2 and C16−C17) is much better. The quaternary carbon (C9) falls in between the two situations, with calculated shift differences of 2−4 ppm. Its shift seems conserved in all models, which does not explain the apparent multiple resonances detected experimentally. Computationally, most shift variation is found for the −OCH3− carbons (C4−C5). The results can be summarized as follows: the (110) surface induces slightly higher chemical shifts compared to the same conformer on the (104) surface (~1−2 ppm). Conformer Do2A has a slightly higher induced shift than conformer Do2C (~1−3 ppm). A shift difference for pairs
of carbons, such as observed for Do1A, is only seen in conformer Do2A on the (110) surface and not on the (104) surface. Moreover, Δδ is much smaller (1 ppm) than that is found experimentally (~3 ppm) or in the case of Do1A. Although conformer Do2A on the (110) surface is energetically the most favored species and the only one with a shift differences for pairs of carbon, the absolute chemical shifts for the −OCH3 carbons deviate most from the experimental ones (~2.5 ppm).

With a >5 ppm difference between the neat donor and the adducts, the methoxy group seems clearly indicative of an interaction with the surface. Despite this, it is not sensitive to the exact coordination mode. The chemical shifts calculated for the different models are all within 1 ppm of each other. Experimentally, the methoxy signal is found to be composed of multiple resonances, but the calculated Δδ of the −OCH3 carbons (C16−C17) is negligible. For DMDOMe, these features were found to change in a high-coverage model. The high-coverage model is applied to the (110) surface because of its energetic favoredness, and the results are given in Figure S11 and Table 3. Indeed, similar effects as found for DMDOMe are observed for DMI fluo; the chemical shift difference for the −OCH3 carbons increases to ~1 ppm for Do2A (compare Tables S9 to 3). At the same time, the Δδ for the −OCH2− carbons also increases (1.5 ppm). Conformer Do2C, on the other hand, remains fully symmetric. The absolute chemical shifts changes only little.

As DMI fluo is a 1,3-diether, literature dictates a strong preference for tetracoordinated magnesium surfaces, and this was also experimentally confirmed by infrared spectroscopy for the specific case of DMI fluo. Our DFT calculations also confirm these results. However, our experimental 13C NMR results can only partially support these findings. Do2A on the (110) surface is the only one with a shift difference in the −OCH3 carbons, which is in agreement with the experiment, albeit the magnitude is much lower than that obtained experimentally.

**DIBP.** Structure optimization for DIBP adducts yields a symmetric conformer (S) and an asymmetric conformer (A), where the asymmetric conformer has two different surface constructs (A and A1) on the (104) surface. The conformations A and A1 just differ in the orientation of the donor with respect to the cluster. This yields in total five constructs divided over the two surfaces; see Figure S12. Table S10 gives the adsorption energies for the different models, which show that DIBP can coordinate in different fashions to both surfaces with comparable energies. The only exception being conformer Do3S on the (104) surface, which has a slightly weaker adsorption energy (6–8 kcal/mol). Chemical shifts have been calculated using a cluster DFT approach, and the results are shown in Table 7. Interestingly, for DIBP, a significant difference in the chemical shift between the two different coordination modes is found for the carbonyl carbon: coordination to the (110) surface results in a considerable lower chemical shift (~4 ppm) than coordination to the (104) surface. In the asymmetric coordination modes, the carbonyl resonances have a split difference (1–3 ppm) on both the surfaces, while the symmetric conformers give no Δδ for the carbonyl resonances. Experimentally, we observed multiple resonances for the carbonyl carbons, which can be interpreted as a proof of the binding to both the (110) surface (~173 ppm) and the (104) surface (~176 ppm). Despite a larger shift difference, the peak at 181 ppm can also most likely be attributed to a site coordinating on the (104) surface. These results are in agreement with the literature. It is predicted that phthalates are not very selective for particular surfaces. A Fourier transform infrared study has also provided experimental evidence for the coordination of DIBP on both (104) and (110) surfaces.

The different relative intensities of the peaks (see below) argue against splitting of a resonance, so that symmetric conformers (Do3S on the (110) and the (104) surface) are most likely responsible for the peaks at 173 and 176 ppm. Thermodynamic considerations corroborate the assignment of the 173 ppm resonance to Do3S on the (110) surface seems, but Do3S on the (104) surface is less stable, and hence, the 176 ppm peak could be an asymmetric conformer as well.

Most other carbons seem insensitive to the coordination mode in terms of the absolute chemical shift. It is not possible to separate the (110) surface from the (104) surface based on the shifts of the aromatic carbons or the isobutyl fragment. Except for the −CH carbons (C11−C12), there is a good agreement between computational and experimental shifts. There is one interesting aspect for the −OCH3− carbons. They

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*a*(104) and (110) refer to clu_24u_104 and clu_27u_110, respectively.
show a shift difference between C\textsubscript{9} and C\textsubscript{10} but this time, this asymmetry is not indicative of a particular conformer, but rather to a particular surface. Both conformers on the (110) surface give a significant difference in the chemical shift between C\textsubscript{9} and C\textsubscript{10} with Δ\textdelta\textsubscript{\textell} being largest for the asymmetric conformer Do3A. All conformers on the (104) surface give (almost) equal chemical shifts for the said carbons. Experimentally, we observe a single resonance for Do3\textsubscript{7}. Bicomponent deconvolution yields plausible results when Δ\textdelta\textsubscript{\textell} is confined below 1 ppm. Alternatively, the –OCH\textsubscript{2}– resonance could be composed of three lines, two of which correspond to the (110) surface and one to the (104) surface. The quality of the spectrum does not permit such a detailed deconvolution for Do3\textsubscript{2}, but it seems unlikely for Do3\textsubscript{7}. The –OCH\textsubscript{2}– carbon resonance, therefore, seems to indicate coordination to the (104) surface, which is in disagreement with the results from the carbonyl resonances and with the literature.

\(^1^3\text{C} \text{CPMAS} \) experiments are generally not quantitative because of the different contact time dependency of the various chemical groups (e.g., carbonyl resonances require a longer build-up time because of the absence of directly bonded protons). However, the relative intensities of the different carbonyl signals can be approximately analyzed, assuming comparable nearest-neighbor proton distances. From the different structural models, these distances are indeed found to be very similar; see Table S12. Further assuming the absence of significantly different dynamics between varying conformations allows a semiquantitative interpretation of the carbonyl signal. The two dominant signals for Do3\textsubscript{7} (172.5 and 175.5 ppm) have an approximate relative intensity of 2:1, indicating that the (110) surface is favored. The foot at 182 ppm only contributes to about 5% of the total carbonyl intensity. In Do3\textsubscript{2}, the peak at 181 ppm corresponds to almost 40% of the carbonyl intensity. The ratio between the 173.4 and 176.8 ppm peaks is 4:1, which gives an equal distribution of the (104) and (110) surfaces overall. This semiquantitative interpretation is further corroborated by CP measurements at a second magnetic field of 14.1 T, where again, a 4:1 ratio is found for the peaks around 173 and 176 ppm. The peak at 181 ppm contributes to 30% of the carbonyl intensity.

A rather good agreement between experimental results and calculations was reached for all donors, in particular, for the carbons closest to the binding site. Generally, the aromatic moieties show slightly larger deviations, potentially arising from interactions of the aromatic ring with the surface\textsuperscript{72} or neighboring donors.\textsuperscript{73} However, the high-coverge models give little difference in the chemical shifts with respect to the clusters with a single donor.

\section{CONCLUSIONS}

We presented \(^1^H \) and \(^1^3\text{C} \) solid-state NMR spectra for a series of binary adducts between MgCl\textsubscript{2} and EDs. These samples have been investigated as model systems to Ziegler–Natta catalysts. In particular, we have been looking into the surface structures formed by different donors using \(^1^3\text{C} \) solid-state NMR and DFT calculations. All in all, the results from \(^1^3\text{C} \) NMR and DFT calculations are in good harmony. High-coverge models bridge the gap between experimental results and the clusters with a single donor. The match between the experiment and calculations allows us to infer the preferred coordination modes of these donors. In agreement with standing hypotheses, \(^1^3\text{C} \) chemical shifts and thermodynamic considerations prove that DMDOMe and DMFluo coordinate (predominantly) on the (110) surface, while DiBP coordinates on both (104) and (110) surfaces.

Secondly, our \(^1^H \) analysis clearly shows the absence of significant H\textsubscript{2}O or –OH surface groups, which we propose to be resulting from a shielding effect of the donors. They successfully prevent hydration of the unsaturated surfaces.

\(^1^3\text{C} \) resonances are quite broad for the binary adducts, and from 2D experiments, we concluded that susceptibility broadening is not the main cause for this line width. The disorder and heterogeneity of the sample is clearly more important than susceptibility broadening, resulting from the MgCl\textsubscript{2} surface. In this respect, we could consider surface defects that have been recently proposed as a source of heterogeneity. Steps and kinks can generate structures of which the coordination locally resembles the (104) surface on an otherwise (110) surface, or the other way around. However, such a defect structure is inherently less defined, which might explain the heterogeneity of the sample and hence the large distribution in chemical shifts. The heterogeneity of the samples also follows from \(^2^H\text{Mg} \) and \(^3^5\text{Cl} \) solid-state NMR studies of the support material, MgCl\textsubscript{2}, which will be the subject of a forthcoming publication.

\section{ASSOCIATED CONTENT}

\subsection{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b12667.

Additional 2D NMR spectra (\(^1^H \) SQ–DQ and \(^1^H\text{–}^1^3\text{C} \) HETCOR) and optimized structures with calculated energies and detailed chemical shifts (PDF)

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\subsection{Notes}

The authors declare no competing financial interest.

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\section{REFERENCES}


(3) Corradini, P.; Barone, V.; Fusco, R.; Guerra, G. A Possible Model of Catalytic Sites for the Stereospecific Polymerization of \(\alpha\)-Olefin on
Surface Defects by Mono- and Bidentate Donors.


