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Probing Interactions between Electron Donors and the Support in MgCl₂-Supported Ziegler–Natta Catalysts

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INTRODUCTION

Ziegler–Natta catalysts (ZNCs) play an important role in the worldwide production of polyolefins. Modern catalysts are composed of a disordered MgCl₂ support with co-adsorbed TiCl₄ and an organic electron donor. This system is activated by an Al-alkyl, often together with a second donor (in most cases, an alkoxysilane). Still, these catalysts hold many secrets at the molecular level. The important surface structures are not well understood, due to the complexity of the system and the absence of significant experimental studies. Yet, fundamental understanding of the active constructs is crucial for further catalyst design.

The last decade yielded a significant number of theoretical contributions aimed at finding the most stable surface constructs for MgCl₂–donor or MgCl₂–TiCl₄ binary adducts. Thermodynamically, (110)-surface sites have been found to be the most stable. However, coordination of electron donors can reverse the relative stabilities so that the (110)-surface sites become more stable than the (104)-surface. Some computational studies go one step further and look at the role that the donors play in the whole catalytic cycle.

Recent years have seen more experimental studies that focus on structure–function relationships, for both traditional MgCl₂-based ZNCs and new MgCl₂-derived support materials. Still, many studies try to investigate the produced polymer in intricate ways to learn more about these elusive catalysts via an indirect approach. It is our belief that the final answers about the working mechanisms of ZNCs will primarily be found when studying the catalysts themselves.
This calls for a wide range of experimental studies making use of the strengths of different spectroscopic techniques, including solid-state NMR spectroscopy. A few recent studies have shown the potential of a combined 1H and 13C solid-state NMR/density functional theory (DFT) approach for the study of the organic donors on the catalysts’ surface, giving valuable experimental proof for standing hypothesis about preferred coordination modes. The surface structures in Ziegler–Natta catalysts can be studied from two sides. Besides the donor, the support can be studied. One of the strengths of NMR spectroscopy is its ability to study interactions between different components, such as donor–support interactions, making it a suitable tool for the study of heterogeneous catalysis. Such insight into donor–support interactions should give a more complete picture of the coordination of donors on the MgCl2–support. In this article, we will present a detailed investigation of the MgCl2 nanoparticles’ surface. Subsequently, we will present an in-depth study of the interactions between the donors and the surface. To this end, we make use of correlation experiments, such as cross-polarization (CP), rotational-echo double-resonance (REDOR), and transfer of populations in double resonance (TRAPDOR).

In a previous study, we showed the feasibility of 25Mg and 35Cl solid-state NMR for the study of the neat support material MgCl2 (α-MgCl2) as well as the ball-milled equivalent (β-MgCl2). The results indicated that the bulk of MgCl2 nanoparticles is readily observed; however, more advanced schemes are necessary to study the catalytic relevant surfaces because of their large quadrupolar interactions. Here, we will use 1H, 25Mg, and 35Cl solid-state NMR to study the support with its surfaces and support–donor interactions in Ziegler–Natta catalyst model systems. We will make use of a variety of sensitivity enhancement schemes and correlation experiments to yield information about the surface structures. The interpretation of the NMR results is supported by DFT calculations of both 25Mg and 35Cl quadrupolar interaction parameters.

### RESULTS AND DISCUSSION

A series of ball-milled binary adducts between MgCl2 and industry-relevant electron donors and an adduct between MgCl2 and TiCl4 are studied. The investigated samples have been introduced by us elsewhere and studied with 13C NMR spectroscopy to identify the preferences for particular surfaces depending on the donor type. The samples contain donors that are part of the families of 2,2-dialkyl-1,3-dimethoxypropanes and phthalates: 2,2-dimethyl-1,3-dimethoxypropane (DMDO, Do1), 9,9-bis(methoxymethyl)-9H-fluorene (DMFluo, Do2), and disobutyl phthalate (DiBP, Do3) used in fourth- and fifth-generation ZNCs. The binary adducts are coded as Do, where Do refers to the donor type and y refers to the donor loading (in percentage). Table 1 gives the sample characteristics showing the surface particle size as determined from powder X-ray diffraction (XRD), where ⟨L⟩ and ⟨L⟩ are the average particle dimensions perpendicular and parallel to the basal (ab) plane, respectively. Ball milling MgCl2 in the presence of electron donors yields nanoparticles with much smaller dimensions. On the basis of previous results, we printed the most likely surface type for each sample in bold.

The MgCl2 nanoparticles can be studied by 25Mg and 35Cl NMR. We compare the binary adducts to neat MgCl2 as well as the ball-milled equivalent (MgCl2 DCM) for quantitative measurements of the 35Cl NMR signal intensity. Despite large surface areas, these particles still have a dominant “bulk” phase, which will be the predominant species in 25Mg and 35Cl spectra. Therefore, we will first characterize the bulk phase in detail before performing dedicated NMR experiments that are necessary to look at the surfaces. With the surface sites revealed, correlation experiments can be performed to probe interactions between donor and support.

In studies of Ziegler–Natta catalysts, there are two types of surfaces of the MgCl2 nanoparticles that are most commonly considered: the (104)- and (110)-surfaces. The (104)-surface is supposedly the most stable lateral surface of MgCl2 in the absence of donors. It exposes pentacoordinated magnesium sites as well. The average size could not be determined because of the stabilizing electron donors, also the (110)-type of surfaces might become inclined to bind in a bridging mode. In the presence of chloride sites as well.

### Table 1. Sample Properties

| samples code | donor loading | ⟨L⟩ (nm) | ⟨L⟩ (nm) | Cl surf. frac. (%) | rel. int. (%) | Mg surf. frac. (%) |
|--------------|---------------|----------|----------|-------------------|---------------|--------------------|
| dry MgCl2    | n.d.          | n.d.     | 100      |                   |               |                    |
| MgCl2 DCM    | 12.6          | 13.0     | 5.3/6.2  | 96                | 10.5/6.2      |                    |
| MgCl2/TiCl4  | 4.3           | 6.34     | 8.4/10.2 | 92                | 16.8/10.0     |                    |
| Do1          | 4.0           | 4.24     | 8.6/10.3 | 94                | 17.0/10.0     |                    |
| Do1_10       | 10.0          | 2.84     | 14.3/17.2| 93                | 28.3/17.0     |                    |
| Do2_2.5      | 2.5           | 4.98     | 8.0/9.3  | 91                | 15.8/9.5      |                    |
| Do3_2        | 2.1           | 7.35     | 8.5/10.3 | 87                | 16.9/10.0     |                    |
| Do3_7        | 10.0          | 2.84     | 14.3/17.2| 93                | 28.3/17.0     |                    |
| Do3_8        | 10.0          | 2.84     | 14.3/17.2| 93                | 28.3/17.0     |                    |

a(% mol adsorbate/mol mg). bThe fraction of surface sites is given for particles exposing either (104)- or (110)-surface sites, see text. c55Cl intensities from solid-state NMR experiments are an average between magic-angle spinning (MAS) and static relative intensities, where the difference between MAS and static was never more than 3%. dSee ref 42. eThe average size could not be determined because the XRD resonances were too narrow (dry MgCl2) or too broad (Do3_7). fNumbers in bold face indicate most probable exposed surface.
The results of solid-state $^{35}$Cl NMR measurements will be dominated by signal from the bulk or bulklike presence of larger distributions in quadrupolar parameters than smeared out. The spectra of the binary adducts show the isotropic chemical shift position is present in all samples, (Figure 1B), in which it can be seen that the discontinuity at neg. This is most obvious examining the static experiments

Line Shape. For neat ball-milled MgCl$_2$, we previously described the distribution in quadrupolar parameters of the bulk-phase signal to be induced by surface effects (i.e., lack of long-range order) and fitted its line shape using the extended Czjzek distribution. The much larger surface areas of the smaller particle dimensions. Along the sample series, as shown in Figure 1, there is a gradual increase in the distribution in quadrupolar parameters. The smallest particles with the highest donor loading (Do1$_{10}$ and Do3$_{7}$) give rise to the largest distribution in quadrupolar parameters.

$^{35}$Cl and also $^{25}$Mg) experiments were performed with long relaxation delays ($5 \times T_{1}$) and in the weak radio frequency (RF) regime ($\nu_{RF} \ll \nu_{Q}$) to ensure quantitative conditions and avoid line shape distortions. Quantification of the spectral intensities (see Table 1) shows that the spectra of some samples lack a significant fraction of the anticipated signal. This is most prominent for the DMFluo (Do2) and DiBP (Do3) adducts, for which 10–20% of the $^{35}$Cl signal is not detected. For Do3$_{7}$, a sample with a high donor loading and the smallest particle size, the largest fraction of $^{35}$Cl signal escaped detection. It is also the sample with the least-defined line shape and thus the largest distribution in quadrupolar parameters. This loss of signal can pertain to sites with large quadrupole interactions, which consequently yield resonances that are broadened beyond detection (at least under the experimental settings used to acquire the spectra in Figure 1).

In general, there is a correlation between particle size (in the lateral dimension) and intensity loss in the chlorine Hahn-echo spectra (see Table 1). This strongly suggests that the surface sites in the lateral dimension are missing from the spectra. Such an observation is in agreement with the results from DFT calculations (vide infra) that predict large quadrupolar parameters for these surface sites, even after binding of donors. Remarkably, the samples containing DMDOMe (Do1) fall outside this trend (Figure 2). In particular, the spectrum of Do1$_{10}$ shows only a relatively low fraction of signal loss, despite a large surface area (small particle size), high donor loading, and a line shape showing a large distribution in quadrupolar parameters.

Figure 1. $^{35}$Cl NMR Hahn-echo spectra of MgCl$_2$ binary adducts (A) at 15.625 kHz MAS, rotor-synchronized and (B) under static conditions, $B_0 = 20$ T.
smaller nanoparticles of the adducts explain the larger distribution in quadrupolar parameters observed.

The Czjzek model\(^{46,49}\) can be used to describe a distribution in quadrupolar parameters for a disordered system. For systems with an intrinsic quadrupole moment, such as MgCl\(_2\), a more elaborate model is necessary that can describe long-range disorder around a locally ordered site. For such situations, the so-called extended Czjzek model has been introduced.\(^{46,47}\) Here, \(C_{Q,0}\) and \(\eta_0\) are the quadrupolar parameters for the well-defined first-order coordination sphere and, similar to the Czjzek model, the distribution in quadrupolar parameters caused by structural variations in the higher coordination spheres is described by the parameter \(\sigma\).

A distribution in quadrupolar parameters as the result of ball milling was observed earlier by Bureau et al.\(^{50}\) for GaF\(_3\) and by Scholz et al.\(^{51}\) for Al\(_2\)O\(_3\). In both studies, the particle size is around 13 nm, very similar to what we obtain for neat ball-milled MgCl\(_2\). In contrast to our \(^{35}\)Cl spectra, bicomponent line shapes are observed, in particular for GaF\(_3\). Because of a weak quadrupolar interaction in the \(^{71}\)Ga spectrum prior to ball milling, the authors model their experimental spectra using two Czjzek distributions, with different \(\sigma\)-values. The site with the lowest \(\sigma\) is attributed to "crystalline grains" (i.e., bulk sites that are slightly more distributed than crystalline GaF\(_3\)), while the site with the largest \(\sigma\) is attributed to "grain boundaries" (i.e., surfaces). The latter corresponds to 70% of the intensity, showing that ball-milling impacts much more than just the outer shell. For Al\(_2\)O\(_3\), Scholz et al. used a combination of Czjzek distribution and well-defined resonance to describe their spectra, again assigning the two components to grain boundaries/surfaces (referred to as "amorphous phase" in their contribution) and crystalline grains/bulk. The fraction of the amorphous phase even reaches 80%, again showing the far-reaching impact of ball milling. Just like MgCl\(_2\)/Al\(_2\)O\(_3\), already has a quadrupolar interaction before ball milling and we therefore believe that an extended Czjzek model (which had not yet been introduced at that time) would be better suited to model the spectra of ball-milled Al\(_2\)O\(_3\) in particular because the experimental spectrum shows no sign of two components (which clearly is the case in GaF\(_3\)). It is important to realize for our study that the ball milling affects a significantly larger fraction of the Mg and Cl sites in the nanoparticle than just those in the outer shell. This is something which becomes apparent in the analysis of our relaxation data (vide infra).

We tried to describe our experimental line shapes using extended Czjzek distributions. Using the EGDecon program,\(^{52}\) the MAS spectra could be modeled reasonably well with a single component exhibiting an extended Czjzek distribution, as can be seen in Figure 3. The overall experimental line width (in both the static and MAS spectra) does not increase along the sample series, despite the increasing distribution in quadrupolar parameters. The fitting results show that a larger distribution is compensated by a somewhat smaller \(C_{Q,0}\), e.g., while the \(^{35}\)Cl sites in neat MgCl\(_2\) have a quadrupolar coupling constant, \(C_{Q,0}\) of 4.61 MHz, adduct Do3_2 gives \(C_{Q,0} = 4.36\) MHz and Do3_7 \(C_{Q,0} = 4.16\) MHz (see Table 2). The decrease in \(C_{Q,0}\) can be attributed to the increased contribution of (001)-surface sites, which have slightly smaller quadrupolar coupling parameters compared to the bulk (see Table 3). For robustness, the fitting routine has a lower limit of 0.5 for the \(\sigma\) parameter. As a consequence, the actual distribution is slightly overestimated for some of the least disordered samples, in particular MgCl\(_2\) DCM. The best agreement is found for the most disordered samples Do1_10 and Do3_7. Unfortunately, the static spectra could not be satisfactorily simulated using the parameters following from the MAS fit, nor could they be fitted properly to the extended Czjzek model (see Figure S2). It could be that some CSA is present in the static spectra, which prevents fitting them to a model only taking into account the quadrupolar interaction. Alternatively, even the extended Czjzek model may not be sophisticated enough to describe

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**Figure 2.** Missing intensity in quantitative \(^{35}\)Cl NMR spectra vs fraction of Cl surface sites. \(^{35}\)Cl intensities from solid-state NMR experiments are an average between MAS and static relative intensities, where the difference between MAS and static was never more than 3%.

**Figure 3.** Fit of the \(^{35}\)Cl MAS spectra \((B_0 = 20\) T\) to the extended Czjzek model.

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**Table 2. Results from Fitting to the Extended Czjzek Distribution**

| samples code          | \(C_{Q,0}\) (MHz) | \(\eta_0\) | \(\sigma\) (MHz) |
|-----------------------|-------------------|------------|-----------------|
| MgCl\(_2\) DCM        | 4.34 ± 0.10       | 0.0        | 0.50 ± 0.05     |
| MgCl\(_2\)/TiCl\(_4\) | 4.46 ± 0.10       | 0.0        | 0.51 ± 0.05     |
| Do2_2.5               | 4.36 ± 0.10       | 0.0        | 0.51 ± 0.05     |
| Do3_2                 | 4.36 ± 0.10       | 0.0        | 0.54 ± 0.05     |
| Do3_7                 | 4.16 ± 0.10       | 0.0        | 0.65 ± 0.05     |
| Do1_4                 | 4.40 ± 0.10       | 0.0        | 0.51 ± 0.05     |
| Do1_10                | 4.22 ± 0.10       | 0.0        | 0.68 ± 0.05     |

*Lower limit of the fitting routine is \(\sigma = 0.5\) MHz.*
the distribution that results from the effects causing both variation in first and higher coordination spheres of the chlorines. Although it would undoubtedly give a better fit, we do not think it is justified to include a second component into the fitting procedure, as was done in the studies of GaF₃ and Al₂O₃ because we see no features of a well-defined crystalline fraction (with pronounced quadrupolar features) in the spectra.

Relaxation. A strong reduction in the 35Cl T₁ relaxation times is found for the binary adducts with respect to neat MgCl₂ (see Table S1). The relaxation times show a correlation with the relaxation behavior of neat MgCl₂. Therefore, the relaxation behavior of our binary adducts would suggest the presence of two phases, such as surfaces and bulk, each having its own typical relaxation. However, in the discussion about the distributed line shapes, we argued against such a distinction in two different phases because we find no evidence for a crystalline fraction. In analogy to a distribution in quadrupolar parameters to describe the observed line shape, a distribution in relaxation times seems more appropriate, and this can be modeled using a Weibull distribution (“stretched exponential”), as can be seen in Figure S3. Ideally, both distributions would even be connected, as 1/T₁ ∝ ωQ. Along the samples series, the distribution in ωQ does not change dramatically, but T₁ times decrease drastically. Quadrupolar relaxation is often overwhelmingly dominated by fluctuating electric field gradients. This suggests that motion-driven relaxation processes play a crucial role and we hypothesize that defect-induced dynamics govern the fast relaxation. Surface sites have largest ωQ (vide infra) and probably highest dynamics as well, resulting in the fastest relaxation. To fully understand the relaxation behavior, extensive field- and/or temperature-dependent relaxation measurements have to be performed, which is beyond the scope of this contribution.

The relaxation times of 25Mg and 35Cl appear to be strongly correlated. This again suggests that their relaxation is influenced by the same defect-induced dynamics. Mobility of donor molecules could also contribute to enhanced relaxation at the surfaces, but the reduction of T₁ for sample MgCl₂ DCM indicates that there is already enhanced relaxation in the absence of a donor.

DFT Calculations of 35Cl Sites. The surfaces are, at least partially, covered by donor molecules. Intuitively, it would be expected that coordination of these molecules to the unsaturated (104)- and (110)-surfaces would have a large impact on the quadrupolar parameters. To interpret the quadrupolar NMR parameters, we calculated quadrupolar coupling constants (C_Q) and asymmetry parameters (η) for the binary adduct systems. As a test case to see if this hypothesis is true, we first calculated the 25Mg and 35Cl quadrupolar parameters for adsorbed water on the surface. We choose water because it is a small molecule with few degrees of freedom, as well as because water adsorption is known to occur in these kinds of samples. For the (110)-surface, binding of both a single water and a full coordinative saturation by the binding of two water molecules was considered (see Figure 4).

Table 3. DFT Calculations of the 35Cl and 25Mg Quadrupole Parameters for Various Neat MgCl₂ Species and MgCl₂·H₂O Adducts, at B3LYP-D2/pob-TZVP Level

| species            | atom | 35Cl C_Q (MHz) | η | atom | 25Mg C_Q (MHz) | η |
|--------------------|------|----------------|---|------|----------------|---|
| MgCl₂ bulk        | Cl   | 4.4            | 0 | Mg   | 1.62           | 0 |
| MgCl₂(001)        | Cl   | 4.9            | 0 | Mg   | 1.51           | 0 |
| MgCl₂(104)        | Cl   | 15.0           | 0.7 | Mg   | 11.2           | 0.3 |
| Cl₁               |      | 6.7            | 0 |      |                |   |
| MgCl₂(110)        | Cl₁  | 18.3           | 0.5 | Mg   | 6.6            | 0.4 |
| MgCl₂(104)·H₂O    | Cl₁  | 10.5           | 0.7 | Mg   | 2.3            | 0.8 |
| Cl₁,2             |      | 5.7            | 0.9 |      |                |   |
| MgCl₂(110)·H₂O    | Cl₁  | 19.7           | 0.4 | Mg   | 10.5           | 0.1 |
| Cl₂               |      | 16.7           | 0.6 |      |                |   |
| MgCl₂(110)·2H₂O   | Cl₁  | 13.6           | 0.3 | Mg   | 6.5            | 0.6 |
| Cl₂               |      | 13.6           | 0.3 |      |                |   |

Figure 4. Optimized structures of H₂O (A) on the (104)-surface surfaces of MgCl₂ and (B, C) on the (110)-surface; Mg atoms are colored in yellow, Cl atoms in green, O atoms in red, H atoms in white. Cl-2 on the (104)-surface is in the Cl₁ position.
Furthermore, we calculated quadrupolar parameters for MgCl$_2$(110)−TiCl$_4$, MgCl$_2$(104)−DMDOME, and MgCl$_2$(110)−DMDOME adducts using periodic calculations. We used cluster models that were introduced in ref 34, for the calculations of the quadrupolar parameters for DiBP adducts and for a high-coverage model of DMDOME. In the calculations, the donor molecules are coordinated in either the “bridge” or the “chelate” mode (see Figures S5, S8, and S9).

As expected, the quadrupolar parameters of the bare surface sites differ strongly from those of the bulk sites. The coordination of water has little effect on the $^{35}$Cl quadrupole parameters of the surface sites, however. It does not really matter whether a pentacoordinated or hexacoordinated Mg site is formed or whether the (104)- or the (110)-surface is considered; in all situations, the $^{35}$Cl C$_Q$ of the surface sites remains very close to the values found for the bare surfaces. Only a small reduction in C$_Q$ is observed for the Cl$_a$ sites.

Figure 5 shows structures of DMDOME on MgCl$_2$. On the (104)-surface of MgCl$_2$, binding takes place via both oxygen in a bridging coordination and this restores the coordinative saturation of two surface magnesium sites, although no perfect octahedron is formed. The calculated quadrupole parameters at the B3LYP-D2/TZVP level are shown in Table 4. We note that for the bulk phase, slightly better agreement with experimental results was obtained at the B3LYP-D2/pob-TZVP level, although the results at the B3LYP-D2/TZVP level were comparable to this computational more demanding calculation. Moreover, the coefficients of the TZVP basis set were specifically optimized for MgCl$_2$ adducts$^{11}$ and hence we performed the calculations at the B3LYP-D2/TZVP level.

Considering that we used slightly different approaches, we will mainly look at trends in the calculated C$_Q$ values and do not focus too much on their absolute values. The results for the $^{35}$Cl C$_Q$ in the bridging coordination mode show no significant effect for Cl−4−Cl−6, while Cl−1−Cl−3 (Cl$_a$) have again a reduced, bulklike C$_Q$ value. For binding of water, the most pronounced effect was observed for these Cl$_a$ sites as well. Also the coordination of DMDOME to the (110)-surface does not affect the chlorine C$_Q$. There is hardly any difference between a monodentate and a chelating binding mode, similar to the case where water was considered.

The presented periodic calculations have some conceptual problems, as the small MgCl$_2$ nanoparticles lack long-range crystalline order. In ref S6, an alternative cluster description has been presented that should be better suited to describe such disordered systems. On the basis of this cluster approach, we proposed some high-coverage models$^{34}$ that were indeed found to better describe the MgCl$_2$−DMDOME adducts as far as $^{35}$C chemical shifts of the donor are concerned. Quadrupole parameters have been calculated for the optimized cluster model with three donors on the surface that has been shown in ref 34 and is reproduced in Figure S6. Two different conformers, namely, Do1A and Do1C, are considered and their presence have been indicated by $^{13}$C NMR. For both conformations considered, this high-coverage cluster model does not result in significant changes in the chlorine quadrupole parameters and we report only the average $^{35}$Cl C$_Q$. The conformation considered in the periodic calculation (chelate binding mode) corresponds to conformer Do1C from the cluster calculations.

Optimized cluster models for the DiBP donor in different conformation on both (104)- and (110)-surfaces were presented in ref 34 as well. The structures of these models are reproduced in Supporting Information Figure S7. The five different models consider a symmetric and an asymmetric conformation of the DiBP molecule on the two different surfaces. However, in none of the considered models, we find a significant effect of donor coordination on the $^{35}$Cl C$_Q$ for the surface sites (Cl−4−Cl−6) (see Table S). These results are in line with the other calculations and indicate that the quadrupolar parameters of surface chlorines are insensitive to
binding of molecules. After binding, the chlorines in the Cl\textsubscript{1} position (Cl\textsubscript{1}−Cl\textsubscript{3}) have their \( C_Q \) reduced from 6.7 MHz toward the bulk value, in agreement with the other calculations. The chelating coordination of DiBP on the (110)-surface of MgCl\textsubscript{2} also restores the coordinative saturation for magnesium. However, the surface chlorines Cl\textsubscript{1}−Cl\textsubscript{2} again yield \( C_Q \) values close to the bare surface chlorines and appear to be only marginally influenced, in both the symmetric and asymmetric conformers.

| species atom | \( 35\text{Cl} \) \( C_Q \) (MHz) | \( \eta \) | atom \( 25\text{Mg} \) \( C_Q \) (MHz) | \( \eta \) |
|---------------|-----------------|-----|-----------------|-----|
| MgCl\textsubscript{2}(104)−DMDOMe | Cl-1 | 6.1 | 0.3 | Mg-1 | 2.81 | 0.3 |
| | Cl-2 | 4.2 | 0.0 | Mg-2 | 2.91 | 0.3 |
| | Cl-3 | 6.0 | 0.3 |        |        |        |
| | Cl-4 | 11.1 | 1.0 |        |        |        |
| | Cl-5 | 12.1 | 1.0 |        |        |        |
| | Cl-6 | 11.2 | 0.1 |        |        |        |
| | Cl-1 | 13.5 | 0.4 | Mg-1 | 11.9 | 0.2 |
| | Cl-2 | 15.2 | 0.5 |        |        |        |
| | Cl-3 | 14.9 | 0.6 |        |        |        |
| | Cl-4 | 15.1 | 0.6 |        |        |        |
| | Cl-1 | 13.5 | 0.5 | Mg-1 | 3.42 | 0.7 |
| | Cl-2 | 13.4 | 0.6 |        |        |        |
| | Cl-3 | 14.9 | 0.5 |        |        |        |
| | Cl-4 | 14.8 | 0.6 |        |        |        |
| high-coverage cl\textsubscript{27}u\textsubscript{110} 3Do1A | Cl | 13.1 | 0.6 | Mg-l | 2.1 | 0.7 |
| | | | | Mg-m | 1.8 | 1.0 |
| | | | | Mg-r | 2.2 | 0.9 |
| high-coverage cl\textsubscript{27}u\textsubscript{110} 3Do1C | Cl | 13.5 | 0.6 | Mg-l | 3.2 | 0.6 |
| | | | | Mg-m | 2.9 | 0.9 |
| | | | | Mg-r | 3.2 | 0.6 |

Table 5. DFT Calculations of the \( 35\text{Cl} \) and \( 25\text{Mg} \) Quadrupole Parameters for MgCl\textsubscript{2}−DiBP Adducts, from Cluster Calculations

| species atom | \( 35\text{Cl} \) \( C_Q \) (MHz) | \( \eta \) | atom \( 25\text{Mg} \) \( C_Q \) (MHz) | \( \eta \) |
|---------------|-----------------|-----|-----------------|-----|
| cl\textsubscript{24}u\textsubscript{110} Do3S | Cl-1 | 6.1 | 0.4 | Mg-1 | 1.8 | 0.4 |
| | Cl-2 | 3.2 | 0.7 | Mg-2 | 1.8 | 0.4 |
| | Cl-3 | 6.1 | 0.4 |        |        |        |
| | Cl-4 | 10.8 | 1.0 |        |        |        |
| | Cl-5 | 13.3 | 0.4 |        |        |        |
| | Cl-6 | 10.8 | 1.0 |        |        |        |
| cl\textsubscript{24}u\textsubscript{110} Do3A | Cl-1 | 5.4 | 0.2 | Mg-1 | 2.0 | 0.8 |
| | Cl-2 | 4.9 | 0.8 | Mg-2 | 2.1 | 0.6 |
| | Cl-3 | 5.9 | 0.3 |        |        |        |
| | Cl-4 | 11.6 | 1.0 |        |        |        |
| | Cl-5 | 12.6 | 0.8 |        |        |        |
| | Cl-6 | 11.0 | 0.9 |        |        |        |
| cl\textsubscript{24}u\textsubscript{110} Do3A1 | Cl-1 | 5.7 | 0.4 | Mg-1 | 2.5 | 0.9 |
| | Cl-2 | 5.6 | 0.6 | Mg-2 | 1.7 | 0.9 |
| | Cl-3 | 5.5 | 0.2 |        |        |        |
| | Cl-4 | 11.4 | 1.0 |        |        |        |
| | Cl-5 | 12.0 | 0.8 |        |        |        |
| | Cl-6 | 12.0 | 0.9 |        |        |        |
| cl\textsubscript{27}u\textsubscript{110} Do3S | Cl-1 | 13.3 | 0.5 | Mg-1 | 2.5 | 0.6 |
| | Cl-2 | 13.9 | 0.4 |        |        |        |
| | Cl-1 | 13.9 | 0.5 | Mg-1 | 2.6 | 0.5 |
| | Cl-2 | 13.4 | 0.5 |        |        |        |

Table 6. DFT Calculations of the \( 35\text{Cl} \) and \( 25\text{Mg} \) Quadrupole Parameters for MgCl\textsubscript{2}(110)−TiCl\textsubscript{4}, at the B3LYP-D2/pob-TZVP Level

| species atom | \( 35\text{Cl} \) \( C_Q \) (MHz) | \( \eta \) | atom \( 25\text{Mg} \) \( C_Q \) (MHz) | \( \eta \) |
|---------------|-----------------|-----|-----------------|-----|
| B3LYP-D2/TZVP | Cl\textsubscript{surf-1} | 8.9 | 0.6 | Mg-1 | 2.05 | 0.7 |
| | Cl\textsubscript{surf-2} | 8.9 | 0.6 | Mg-2 | 2.05 | 0.7 |
| | Cl-1 | 17.8 | 0.1 |        |        |        |
| | Cl-2 | 17.8 | 0.1 |        |        |        |
| | Cl-3 | 21.1 | 0.8 |        |        |        |
| | Cl-4 | 21.1 | 0.8 |        |        |        |

Some effects on the chlorine quadrupolar parameters are seen for the binary system MgCl\textsubscript{2}−TiCl\textsubscript{4} (see Table 6). In particular, the two chlorine surface sites that are directly involved in TiCl\textsubscript{4} coordination (see Figure 6) are calculated to have a reduced \( C_Q \) (from 18 to 9 MHz), although it remains significantly large. The other chlorine atoms (Cl\textsubscript{1}−Cl\textsubscript{4}) are exclusively bound to Ti. They are calculated to have \( C_Q \) values of 18 and 21 MHz, which are in the same order of magnitude as, or even larger than, the exposed MgCl\textsubscript{2} surfaces. The observation of the titanium-bonded chlorines with solid-state NMR suffers therefore from the same difficulties as observation of the surface sites: both belong to diluted species and will give very broad lines and hence are difficult to observe in the bulk MgCl\textsubscript{2}-dominated spectrum. Johnston et al.\textsuperscript{57} showed a \( 35\text{Cl} \) solid-state NMR spectrum for TiCl\textsubscript{4} grafted on SiO\textsubscript{2}, an experiment that obviously benefits from the lack of a chlorine-containing substrate. They observed a ~400 kHz broad pattern and simulated that with \( C_Q = 14.3 \) MHz and \( \eta = 0.15 \), which seem in line with our calculations for the titanium-bonded chlorides. However, it should be noted that the coordination mode of TiCl\textsubscript{4} on SiO\textsubscript{2} is different from the coordination mode on MgCl\textsubscript{2}.

Our calculations of the \( 35\text{Cl} \) quadrupolar coupling parameters show that they are hardly affected by various
donor molecules and coordination modes. In some cases, \( \eta \) changes slightly, but in all considered structures (for both (104)- and (110)-surfaces), the \( ^{35}\text{Cl} \) \( C_Q \) appears to be unperturbed by surface binding of donor molecules, with the exception of chlorines coordinating to TiCl\(_4\) and chlorines in the Cl\(_{ss}\) position. In our previous study, the Cl\(_{ss}\) position was not primarily considered as a surface site because it has, in first approximation, a bulklike coordination. Similar to the (001)-surface, it should therefore have quadrupole parameters similar to the bulk. In the case of an uncoordinated surface, its parameters are calculated as \( C_Q = 6.7 \) MHz and \( \eta = 0 \). After coordination of donors, the quadrupolar parameters for the Cl\(_{ss}\) sites are almost restored to bulk values. The \( ^{35}\text{Cl} \) \( C_Q \) for the real surface sites are hardly influenced by absorption of a donor on either the (104)- and (110)-surface and still yield large \( C_Q \) (≤ 12 MHz). Hence, these chlorine sites remain “invisible” also after coordination of a donor. Consequently, the loss of intensity in the chlorine spectra could therefore still pertain to distorted surface sites, similarly to what has been found for the bare surfaces in MgCl\(_2\) DCM. The low signal loss for Do1_10 suggests the formation of surface sites with a smaller \( ^{35}\text{Cl} \) \( C_Q \). However, the calculations of the \( ^{35}\text{Cl} \) \( C_Q \) for the proposed chelating binding mode on a (110)-surface give large \( C_Q \) values, suggesting that different structural models should be considered, e.g., relating to specific defects generated as a result of the ball-milling process.

\textbf{\( ^{35}\text{Cl} \) NMR Spectra of Surface Sites.} The single resonance that is observed in \( ^{35}\text{Cl} \) spectra is assigned to the bulk phase of the MgCl\(_2\) nanoparticles, although it might also include contributions from well-defined surface sites such as (001)-terminations. The signal from surface sites is not observed in Figure 1A or B because it is broadened beyond detection as follows from the calculated quadrupolar parameters. In an attempt to observe and characterize these surface sites with large \( C_Q \), we acquired rotor-synchronized sideband-selective double-frequency sweep quadrupolar Carr–Purcell–Meiboom–Gill (ssDFQS-QCPMG) (MAS) and QCPMG (static) spectra to increase sensitivity. In the case of \( ^{25}\text{Mg} \) spectra (vide infra), these methods allowed the detection of additional signal, but in \( ^{35}\text{Cl} \), we did not observe a second signal, while we did get some line shape distortions (see Figures S4 and S5).

In a previous publication\(^{18}\) we showed that the use of high-RF fields, which enable broadband excitation, makes broad resonances visible for Do1_10. Using a static home-built probe with a 1.2 mm inner diameter coil, we reached an RF field strength of 500 kHz for \( ^{35}\text{Cl} \) at a static magnetic field strength of 18.8 T (\( \nu_L = 78.3 \) MHz). We showed that this led to the detection of part of the satellite transitions from the MgCl\(_2\) bulk, but also to the observation of signal from the surface sites, which will be discussed in more detail here. Using nutation NMR and variable offset cumulative spectra, we showed the absence of other, much broader, components for Do1_10. The high RF experiment is now also applied for Do3_7 and MgCl\(_2\) DCM. Figure 7 compares the spectra of Do1_10 and Do3_7, where clearly a ~350 kHz broad resonance is detected for both adducts. The control experiment for MgCl\(_2\) DCM gives a flat baseline.

For both samples, the resonances show a somewhat asymmetric line shape, but they do not show well-defined quadrupolar features. This suggests the presence of a distribution in quadrupolar parameters, which is expected given the supposed heterogeneous nature of the surfaces. The two samples do give distinctly different spectra, where Do1_10 appears to give additional signals compared to Do3_7. The experiments at high-RF field are not performed under quantitative conditions, prohibiting the ability to retrieve absolute intensities. Nevertheless, the spectra in Figure 7 can still be interpreted semiquantitatively, given that the sample amount (± 1 mg) and relative MgCl\(_2\) content of the samples are very comparable. This shows that Do1_10 has more intensity in the broad signals. For Do3_7, there are two signals: besides the bulk phase signal, there is one broad resonance spanning about 350 kHz that should result from a surface site. After comparison with Do3_7, it becomes clear that the spectrum of Do1_10 actually has three resonances. Besides the bulk phase signal and the ~350 kHz broad resonance, there is also a less intense resonance spanning about 170 kHz. From the span of this resonance, a \( C_Q \) of ~8 MHz is estimated, which is significantly smaller than any of the calculated \( C_Q \) values.

An ~350 kHz broad resonance corresponds to a \( C_Q \) of ca. 10−11 MHz. Although a bit lower, this is in the range of calculated \( C_Q \)s for the surfaces (ca. 12−14 MHz, whether coordinated with donors or not, Tables 3−5). As none of the adducts have a full surface coverage of the donor, uncoordinated surface sites remain present for both Do1_10 and Do3_7. We can therefore not be certain whether the signal in the spectrum of Do3_7 originates from exposed or coordinated surface sites or both. For Do1_10, the ~350 kHz broad resonance corresponds most likely to exposed surface sites. A \( T_1 \) measurement for Do3_7 under the high \( \nu_{RF} \) conditions shows that the ~350 kHz broad surface site has a...
coordination on the $^{35}\text{Cl}$ quadrupolar parameters and observed for MgCl$_2$ DCM at all, as this has surface sites (dynamics at the surface can explain this short relaxation time of C that their visibility in the static spectra (see Figure 8B) the signal is rather similar but the line shapes look rather comparable for all samples. Also quadrupolar parameters. This is in contrast to the $^{35}\text{Cl}$ measurements, where there was a clear difference in the level of distribution in quadrupolar parameters for the different samples. The larger the distribution, the less well-defined the line shapes get and the longer the observed tailing of the signal. However, the $^{25}\text{Mg}$ C$_Q$ ($\approx 1.65$ MHz) is much smaller than the $^{35}\text{Cl}$ C$_Q$.

The $^{25}\text{Mg}$ MAS spectra indicate the presence of additional site(s), which show up as a pronounced tailing on the right-hand side and actually differ significantly between the samples. The strongest tailing, and thus the largest distribution in quadrupolar parameters, is observed for Do$_3$\_7 and it stretches out as far as $-8$ kHz ($-150$ ppm), as is shown in the blown-up top trace in Figure 8A. A significant tailing is also observed for Do$_3$\_2 and MgCl$_2$/TiCl$_4$ stretching to ca. $-5$ kHz ($-100$ ppm). For MgCl$_2$ DCM and Do$_1$\_10, the asymmetric line is more narrow and slopes down to $-2.5$ and $-4$ kHz (ca. $-50$ and $-75$ ppm), respectively. In the static spectra, there are clues for the presence of a broader component as well, as can be seen in the rescaled top trace in Figure 8B. Again, this underlying component is broadest for Do$_3$\_7.

Spectral overlap makes it difficult to exactly identify this second component. An experiment that might help to alleviate this issue is the multiple-quantum MAS (MQMAS) experiment thanks to its ability to separate overlapping quadrupolar broadened resonances in a two-dimensional fashion. Unfortunately, we were not able to observe the second site in MQMAS experiments (see Figure S8) due to the limited RF field strength ($\nu_{RF}$), which hampers the excitation and conversion of the triple-quantum coherence.

Similar to the fraction of chlorine surface sites, the fraction of magnesium surface sites can be estimated from the particle dimensions. In contrast to the chlorine case, the fraction of magnesium surface sites differs a lot between the (104)- and (110)-surfaces. Particles having mostly (104)-surfaces expose 60–70% more surface sites than the equisized particles (see Table 1). For example, if it would exhibit (104)-surfaces, the Do$_3$\_7 adduct would feature 31% surface sites, compared to 19.5% in case it exhibits (110)-surfaces. The difference between both surfaces might therefore seem to be an easy handle to interpret the $^{25}\text{Mg}$ spectra. However, the quadrupolar couplings of the coordinated surfaces are much closer to the bulk value (vide infra), meaning that surface sites should not be broadened beyond detection in $^{25}\text{Mg}$ spectra and they might significantly overlap.

![Image](image-url)
The extent to which comparison of the 13C chemical shifts allowed for a better description of the system, based on a models and coordination modes. For example, the interaction quadrupolar parameters of the high-coverage model to a single mode. The monodentate binding of DMDOMe on (110) gives reduced as well, but only in the case of a chelating binding surface, giving a pentacoordinated magnesium, also has an reduced. The consequence of the bridging coordination of DiBP (Do3) on the (104)-surface of MgCl2 also coordinative saturation is restored. This is directly reflected in the quadrupolar parameters for the two involved surface magnesium sites (see Table 5). Remarkably, conformer A1 appears to induce a difference between the two Mg surface sites, while conformer A does not. All in all, in both the symmetric and asymmetric conformers, CQ is strongly reduced to values close to the bulk CQ. The chelating coordination of DiBP on the (110)-surface of MgCl2 leads to a reduction of 25Mg CQ as well. Again octahedral coordination is restored and thus the corresponding CQ shows a significant reduction, but appears to be slightly larger than at the (104)-surface (see Table 5). Also in this case there is no significant difference between the symmetric and asymmetric conformers.

The MgCl2–TiCl4 binary adducts show pronounced effects on the 25Mg CQ as well (see Table 6). Binding of TiCl4 generates magnesium surface sites with an octahedral coordination by chloride ligands, very similar to the bulk, although this is only true for a high TiCl4 loading. At lower loadings, the resulting Mg sites will be pentacoordinated. Alternatively, TiCl4 molecules might coordinate on steps or holes with structures locally resembling the structural donor model shows interesting differences for 25Mg CQ (Table 4) again in contrast to the chlorides where no effect was observed. We focus on the central Mg site (Mg-m) as this should be most representative, although the results are actually rather comparable to the left- and right-hand-side Mg sites. Interestingly, the exact conformation considered in the high-coverage model is of significant influence on the 25Mg CQ. On the basis of 13C chemical shifts, Do1A was identified as the sole conformer in Do1_10 and the major component in Do1_4. This conformer yields a CQ that is very close to the bulk value of 1.65 MHz. Do1C, which was found to be present as a minor component in Do1_4, gives a CQ of 2.9 MHz, again a strong reduction compared to the bare surface, but significantly larger than Do1A. These differences should result in significant differences in the line widths of the respective resonances.

In the case of the bridging coordination of DiBP (Do3) on the (104)-surface of MgCl2, also coordinative saturation is restored. This is directly reflected in the quadrupolar parameters for the two involved surface magnesium sites (see Table 5). Remarkably, conformer A1 appears to induce a difference between the two Mg surface sites, while conformer A does not. All in all, in both the symmetric and asymmetric conformers, CQ is strongly reduced to values close to the bulk CQ. The chelating coordination of DiBP on the (110)-surface of MgCl2 leads to a reduction of 25Mg CQ as well. Again octahedral coordination is restored and thus the corresponding CQ shows a significant reduction, but appears to be slightly larger than at the (104)-surface (see Table 5). Also in this case there is no significant difference between the symmetric and asymmetric conformers.

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motive, as shown in Figure 6, so that for at least one of the two magnesium sites octahedral coordination is restored. $C_Q$ for the octahedral magnesium sites comes down to approximately 2 MHz, which is very close to the bulk value. The results are in line with the results from the donors, but this is the only case where the binding does not take place to an oxygen, but to a chlorine.

Our calculations of the $^{25}\text{Mg}$ quadrupolar parameters show that they are affected to a different extend by various coordination modes. Coordination of one oxygen to the (110)-surface (a single H$_2$O or monodentate coordination of a donor), leading to pentacoordinated magnesium, already lowers $^{25}\text{Mg} C_Q$, but it remains significantly higher than in the case of hexacoordinated magnesium. In all considered structures (for both (104)- and (110)-surfaces), $^{25}\text{Mg} C_Q$ reduces strongly after restoration of the octahedral surrounding with both oxygen and chlorine ligands. In the case of MgCl$_2$−H$_2$O and MgCl$_2$−donor adducts, $^{25}\text{Mg} C_Q$ generally becomes 2−6 MHz, but only when octahedral coordination is restored. Despite a clear reduction compared to the exposed surfaces, the resulting $C_Q$ generally remains somewhat larger than the bulk. The high-coverage model 3D01A on the (110)-surface results in the largest reduction of $C_Q$ for the covered surfaces and it almost reaches bulk values.

$^{25}\text{Mg}$ NMR Spectra of Surface Sites. The calculated quadrupole coupling constants of coordinated magnesium surface sites (2−4 MHz) correspond to resonances with line widths (3−18 kHz at 20.0 T) that should be detectable under regular conditions. However, sensitivity could be an issue because only a small fraction (2−10%) of the spin pool is a covered surface site. $^{25}\text{Mg}$ Hahn-echo experiments already showed the presence of additional components. To increase the sensitivity of $^{25}\text{Mg}$ NMR experiments, we obtained static QCPMG and ssDFS-QCPMG spectra under MAS. The ssDFS sequence$^{61}$ gave enhancements in the S/N ratio of up to $\sim$2.7. The ssDFS-QCPMG experiments actually emphasize the broad signal on the right-hand side over the bulk phase signal. Moreover, the spikelet spectrum allows for an easy differentiation between baseline and the broad components of the signal. Due to increased sensitivity, the tailing is observed to span an even larger frequency range compared to the spectra in Figure 8. For TiCl$_4$ and DiBP adducts, the signal extends beyond $\sim$10 kHz ($\sim$200 ppm). For the Do1_10 sample, it only tails to $\sim$5 kHz ($\sim$100 ppm, see Figure 9). The broad signal lacks well-defined features, and the asymmetric featureless tailing is again indicative of a distribution in quadrupolar parameters reflecting disorder.

Also in static QCPMG experiments, the additional broader component can easily be detected in the spikelet spectrum. The sensitivity for static QCPMG experiments could be boosted with a double-frequency sweep (DFS) pre-pulse, giving enhancements of $\sim$2.9 for DCM, Do1_10, and Do3_7 with line shapes similar to the experiments without DFS (see Figure S9). Clearly, this second broad component is detected for most samples, but not for Do1_10 (see Figure S10). Generally, the relative intensities in the QCPMG spectrum are the same as in a spectrum obtained by a Hahn echo, with the exception of Do1_10, where the QCPMG spectrum is actually narrower than that obtained by Hahn echo. For that sample, the Hahn echo shows some broadening due to a distribution in quadrupolar parameters, but this is not very apparent in the QCPMG spectrum.

The DiBP adduct with the smallest particles (Do3_7) gives the broadest QCPMG spectrum, spanning almost 25 kHz (from $\sim$200 to $\sim$250 ppm). Additional QCPMG experiments were performed at higher $\nu_B$ of 20 kHz for this sample. This is no longer in the low $\nu_B$ nutation regime for the signal of the bulk phase ($C_Q \approx 1.65$ MHz). Therefore, it led to some line shape distortions as well as signal loss for the narrow signal. The signal intensity of the broader component is very similar in both experiments. Importantly, the higher $\nu_B$ did not lead to the excitation of further, even broader, resonances (see Figure S11). QCPMG experiments were also performed at a second magnetic field strength of 14.1 T. At the lower field, the line widths naturally increase due to stronger quadrupolar broadening. However, after scaling the axis for the field difference, the spectra for 14.1 and 20.0 T can be overlaid and show identical line shapes. This proves that the line shapes of the resonances are purely of quadrupolar origin.

The additional resonances that are detected have significant intensities, which impose some problems. Due to the potential difference in $T_2$ between different components, QCPMG experiments are in first approximation no longer quantitative. However, comparison between the first echo and the sum of all echoes shows only small difference in the line shape and thus relative intensities comparable to a single Hahn echo. The high intensity of the broad resonances can therefore not completely be explained by $T_2$ effects. For Do3_7, the broad component corresponds to a much larger fraction of the signal than can be accounted for by the donor loading. Also, calculated $C_Q$’s of ca. 2−2.5 MHz are actually too small to account for the observed span of the resonance, in particular if we consider that larger $\nu_B$ might give somewhat broader lines. This is also true for the TiCl$_4$ adduct, the $C_Q$ of the surface magnesium for the TiCl$_4$ adduct is calculated as 2 MHz (Table 6). This value underestimates the width of the experimental spectrum, which indicates a $C_Q$ of up to $\sim$3.5 MHz. These differences might be related to the accuracy of the calculations. Also here, the second site represents much more spins than the 8% that can account for TiCl$_4$-bound sites (since per TiCl$_4$ there are two surface chlorine sites involved in the bonding). On the basis of relaxation data, we concluded earlier that the surfaces might affect a much larger fraction of the spins than just the outer shell, e.g., due to defects caused by the milling process.

For Do1_10, no broad component is detected, suggesting that the quadrupolar parameters of covered surface sites are very close to the bulk and those sites will (practically) overlap. This is in agreement with the $C_Q$ value (1.8 MHz) calculated for Do1A, which is the main surface structure, as followed from $^{13}\text{C}$ experiments. However, $^{35}\text{Cl}$ NMR results suggest a different surface construct. For Do1_4, on the other hand, a second surface structure was identified using $^{13}\text{C}$ NMR: Do1C, for which a larger quadrupole parameter of 2.9 MHz is predicted. The presence of Do1C can explain the second site that is indeed found in the QCPMG experiments for this sample. In fact, the calculated quadrupolar parameters match the experimental span, although the accuracy of the calculations does not allow for such a specific agreement. Again, there is a problem with the intensities though. The $^{13}\text{C}$ NMR results indicate that Do1C is only a minor component$^{34}$ and it can therefore not account for such an intense signal.

Donor−Surface Interactions. Since the surfaces are covered with organic donors and thus with protons, this should offer the possibility to do correlation experiments between the donors and the surface sites. To this end, we
performed $^1$H–$^{35}$Cl and $^1$H–$^{25}$Mg double-resonance experiments to probe potential interactions.

$^1$H–$^{35}$Cl Correlation Experiments. $^1$H–$^{35}$Cl cross-polarization (CP) experiments were employed with the aim to selectively get signal for those sites in the vicinity of donors (i.e., surface sites) and suppress the signal from the bulk phase. However, the resulting $^1$H–$^{35}$Cl CP spectra showed signals very comparable to the direct excitation (see Figure S12). Moreover, these measurements proved to be very time-consuming because of low CP efficiencies and also because $^1$H $T_1$ times (2–3 s) are significantly longer than the $T_1$’s of the quadrupolar nuclei (150 ms for smallest nanoparticles).

$^{35}$Cl–($^1$H) REDOR and $^1$H–($^{35}$Cl) TRAPDOR experiments have been performed to get a deeper insight into the donor–surface interactions. The REDOR sequence has been combined with signal enhancement schemes to give an ssDFS-REDOR-QCPMG pulse sequence for enhanced sensitivity. $^{35}$Cl–($^1$H) REDOR experiments show a clear Cl–H interaction (see Figure 10). The REDOR fraction reaches 40% for most of the samples after a dephasing time of ~65 ms. This includes the MgCl$_2$ DCM sample, which has no donor protons. Previously, we did observe that this sample contains Mg–OH groups. The other donor-free adduct, MgCl$_2$–TiCl$_4$, only reaches a REDOR fraction of 11%, thus clearly having less or weaker Cl–H dipolar interactions.

Due to the relative high natural abundance (75%) of $^{35}$Cl, it should be possible to perform the reverse experiment, $^1$H–($^{35}$Cl) REDOR, to get more insight into the protons responsible for the observed Cl–H REDOR effect. Due to the strong $^{35}$Cl quadrupole interaction, the REDOR-type experiment is not feasible, but alternatively a $^1$H–($^{35}$Cl) TRAPDOR can be used as shown in Figure 11. The $^1$H spectrum of MgCl$_2$ DCM shows a sharp signal at 1.66 ppm, which has been assigned to a Mg–OH surface group. This signal shows a clear TRAPDOR effect. After 12.5 ms of chlorine irradiation, the TRAPDOR effect, $\Delta S/S_0$, is 95%. The broad signal around 4 ppm, most likely related to some H$_2$O, has a much shorter $T_2$ but shows a TRAPDOR effect as well. In MgCl$_2$–TiCl$_4$ there is also a pronounced TRAPDOR effect, again for the signal at 1.66 ppm as well as the signal at 3.8 ppm (most likely some H$_2$O-related signal), as shown in Figure S13.
The proton spectrum shows two resonances at 1.26 and 0.84 ppm that can be assigned to hydrocarbons physisorbed to the MgCl₂ particles. These narrow signals have a long T₂ and dominate the 1H spectrum at longer echo times, but clearly do not show any TRAPDOR effect.

The signals from physisorbed hydrocarbons and Mg–OH are also the relevant proton signals in the TRAPDOR experiments of the DMDOMe (Do1) adducts. The signals from the donor have a short T₂ and are therefore not visible in the spectra for Do1_10 in Figure 11) as they have decayed before any TRAPDOR effect could be observed. What is left at longer dephasing times are again hydrocarbon signals that do not show any TRAPDOR effect and a Mg–OH peak with a relatively strong TRAPDOR effect (see Figure 11). Similar reasoning applies to the TRAPDOR experiment for Do3_7, although the hydrocarbon peaks show up at slightly lower ppm values and also the intensity of the hydrocarbons as well as the Mg–OH group appears to be much lower.

The TRAPDOR effect was monitored as a function of the offset of the chlorine transmitter to probe the strength of the quadrupolar parameter of the site that couples to the Mg–OH protons (Figure S14). From 2.25 MHz onward, no detectable dephasing occurs anymore, indicating the TRAPDOR cutoff frequency, ν_C, which equals ν_S in the case of a spin S = 3/2 nucleus. From this, the C_0 of the coupled 35Cl can be determined, which is found to be 4.5 MHz. This matches perfectly with the 35Cl of MgCl₂, indicating that the Mg–OH protons have an interaction with bulk or bulklike chlorine atoms. Our TRAPDOR experiments fail to show an interaction between the donor and MgCl₂. Due to the short T₂ of the donor resonances, the peaks have already dephased completely at longer echo times and potential TRAPDOR effects cannot be observed.

**1H–25Mg Correlation Experiments.** Static 25Mg QCPMG experiments yield better signal with 1H decoupling. In particular for Do3_7 and Do1_10, significantly more echoes can be acquired using decoupling (Figure S15). The line shape, on the other hand, does not seem to be influenced by the decoupling. Also MQMAS experiments performed better using 1H decoupling. These are the first, rudimentary, proofs of an interaction between 25Mg and protons in these systems. To further investigate this, we attempted to perform 1H–25Mg CP measurements (see Supporting Information (SI)) initially on samples MgCl₂ DCM, Do1_10, and Do3_7. The 1H–25Mg CP spectra of the adducts look very comparable to the bulk, although the S/N ratio is too low to warrant that there are no additional broader signals present. For MgCl₂ DCM, a signal could only be detected after 68 h of experimental time (because proton relaxation times were found to be very long (~1 min)), in which 4096 scans were acquired using 20 ms of contact time (see Figure 12A). The spectral quality is poor. Nevertheless, it is remarkable that this intrinsic proton-free sample is able to give a CP signal that looks quite similar to the direct excitation spectrum.

An 1H–25Mg CP spectrum of Do3_7, acquired in 91.5 h at −40 °C, is shown in Figure 12B. While the line shape of the bulk signal appears slightly broader than the QCPMG echo, the overall line shape agrees very well with the QCPMG echo. Both the CP and QCPMG spectrum show the broad component between −200 and 200 ppm with the same relative intensities (see also Figure S16A). All in all, this correspondence in line shape and long relaxation times discouraged us to continue with CP experiments. However, the similarity between DP and CP spectra requires an explanation. Also, the observation of CP signal for MgCl₂ DCM is unexpected due to the low proton content in this sample. Clearly, bulklike sites are in the vicinity of some source of protons. These bulklike sites could either be the layers just below the surface or perhaps the (001)-surfaces. The latter surface sites have quadrupole parameters close to the bulk, yet no donors or −OH groups should coordinate to these (001)-surfaces. The protons that are involved in the CP were further probed using correlation experiments.

Correlation experiments such as 25Mg–{1H} ssDFS-REDOR-QCPMG, 1H–{25Mg} REDOR, and 1H–25Mg HETCOR experiments have been performed to study the H–Mg interaction(s) (see SI). Similar to the 35Cl–{1H} REDOR experiment, the 25Mg–{1H} REDOR experiments show clear X–H interactions (Figure S17), while for technical reasons, no interactions could be seen in 1H–{25Mg} REDOR and HETCOR experiments (Figures S18 and S19).

For the 25Mg–{1H} REDOR experiments, there is quite a difference between the samples, with some showing a pronounced REDOR effect, while for others, the effect is only small. The REDOR fraction, ΔS/S₀, goes up to 17 and 24% for Do1_10 and Do3_7, respectively. For MgCl₂ DCM and MgCl₂–TiCl₄ adduct, the REDOR effect is only marginal, showcasing a much weaker 1H–25Mg dipolar interaction.

Remarkably, MgCl₂ DCM showed a significant effect in the 35Cl–{1H} REDOR experiment. Owing to the ssDFS and
QCPMG elements, the $^{25}\text{Mg}$ spectra show both the bulk signal and the surface site for Do1_4, Do3_7, and the TiCl$_4$ adduct. This clearly shows that only REDOR effects are observed for the signal from the bulk phase, and the surface sites are never influenced by the refocusing pulses on the proton channel. Also in $^{35}\text{Cl}$−{1H} REDOR experiments (vide supra), an X−H interaction (resulting from −OH groups) with the bulk was found. As the surface sites could not be observed in the $^{33}\text{Cl}$ REDOR experiments, we cannot establish if there is an interaction between protons and chlorines at the surface.

**Implications.** The analysis of $^{25}\text{Mg}/^{35}\text{Cl}/^{1}\text{H}$ correlations experiments gives some intriguing results. An H−X interaction between Mg−OH protons and the bulk of MgCl$_2$ is detected, while interactions between the donor and the support could not be established. Only in the case of $^{1}\text{H}−^{25}\text{Mg}$ CP experiments, there is a correlation between the surface sites and protons, which was not found in the $^{25}\text{Mg}−{^{1}\text{H}}$ REDOR experiments.

Most intriguing results have been obtained for sample Do1_10. Both $^{25}\text{Mg}$ and $^{35}\text{Cl}$ show interesting differences compared to the other adducts. The absence of surface sites in $^{25}\text{Mg}$ QCPMG experiments can still be explained by the formation of surface sites with low $C_Q$ (of similar value as the bulk), in agreement with computational results for the suggested model, which was identified based on $^{13}\text{C}$ NMR results. However, the spectrum of Do1_4 is significantly different, which is unexpected since $^{13}\text{C}$ NMR results suggest that both samples have predominantly the same surface structure for the donor, with Do1_4 only having a minor contribution of an additional conformer. The high $^{35}\text{Cl}$ visibility of Do1_10 is not in line with its large surface area, suggesting the formation of surface sites with lower $^{35}\text{Cl}$ quadrupolar coupling parameters that are indeed detected using $^{35}\text{Cl}$ Hahn echoes at high RF power. These findings do not conform to the calculated quadrupolar coupling parameters from the suggested surface structure. All in all, there are some inconsistencies in the results from quadrupolar NMR studies that do not allow us to either confirm or reject the proposed surface model for DMDOMe. One explanation for this might lie in the dynamics at the surface. This is very demanding to accommodate into DFT calculations, but it could have pronounced influence on some spectral aspects.

Considering the other adsorbates, the $^{35}\text{Cl}$ NMR results are in agreement with the large $C_Q$ values for the exposed surface sites (either coordinated or not). However, the unresponsiveness of the $^{35}\text{Cl}$ C$_Q$ to donor adsorption makes it impossible to detect coordinated and bare surface sites independently. The observation of surface sites in $^{25}\text{Mg}$ QCPMG experiments is interesting and confusing at the same time. In particular, the span of these resonances indicates larger quadrupole coupling parameters than what have been calculated. Also, the high relative intensities of these resonances do not conform to the fraction of coordinated surface sites. It could very well be that also magnesium sites in the next shell contribute to the broader signals. Surface deformations can change the local symmetry of these otherwise coordinatively saturated sites, increasing their quadrupolar coupling parameters. Moreover, there may well be many defects in the sample induced by the ball milling.

Despite different approaches, we have not been able to measure interactions between the donor and the support. Although protons have shown interactions, the observed effects did not originate from the donors. Low resolution and short $T_2$ hamper the further application of proton NMR, and more demanding experiments, involving, for example, $^{13}\text{C}$, are required. Intrinsically, $^{13}\text{C}−^{25}\text{Mg}/^{35}\text{Cl}$ correlation experiments sound very appealing; unfortunately, they are not feasible. The main limitation for this is the sensitivity, due to the dilution of the relevant species, low natural abundance of the involved nuclei ($^{13}\text{C}$, $^{25}\text{Mg}$), and their low gyromagnetic ratio leading to low receptivity. Although costly, a boost in the sensitivity could be obtained by (selective) isotope labeling of $^{13}\text{C}$ and/or $^{25}\text{Mg}$.

**CONCLUSIONS**

We showed DFT calculations of the $^{25}\text{Mg}/^{35}\text{Cl}$ electric field gradient (EFG) tensor and $^{25}\text{Mg}/^{35}\text{Cl}$ solid-state NMR spectra for a series of binary adducts between MgCl$_2$ and TiCl$_4$ or MgCl$_2$ and electron donors. 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 to find experimental evidence for suggested models. Correlation experiments clearly show X−H interactions, but they ultimately involved the Mg−OH surface group as source of the proton polarization. The interactions were found to occur between the OH group and bulklike sites.

In general, for magnesium, DFT calculations show pronounced reduction of the quadrupolar interaction ($C_Q$) for each case, where octahedral coordination is restored at the surface. In some cases, the resulting $C_Q$ becomes almost the same as the bulk value. For chlorine surface sites, on the other hand, the coordination of adsorbates has only a minor effect, which means that chlorine surface sites will continue to give broad lines also after coordination of a donor. This is in line with the visibility of Hahn echoes of the central transition (low $v_Q$), in which up to 20% of the expected signal intensity is missing. Echo experiments, obtained using high RF fields, indeed show the presence of chlorine sites with low local symmetry, i.e., large quadrupole parameters ($C_Q > 10$ MHz) for the small-particle DiBP adduct (Do3_7).

The DMDOMe adduct behaves quite differently compared to the other adducts. In $^{25}\text{Mg}$ QCPMG and ssDFS-QCPMG experiments, the spectra of all adducts clearly indicate the presence of a second component for most samples, but this is absent in Do1_10. Also, it has a surprisingly high $^{35}\text{Cl}$ visibility given its small particle size. Besides sites with large quadrupole parameters, echo experiments obtained at high RF power show an additional signal with an intermediate large quadrupole parameter ($C_Q \sim 8$ MHz) for this sample. This is not in line with calculated NMR parameters from the suggested model. We should therefore consider a notably different surface structure for Do1_10, in which both $^{25}\text{Mg}$ and $^{35}\text{Cl}$ $C_Q$ are affected by the donor coordination.

We found that it is not feasible to use $^{35}\text{Cl}$ $C_Q$ for the interpretation of specific structural models. In that respect, the $^{25}\text{Mg}$ quadrupolar interaction parameters seem much more promising as they are strongly influenced by donor binding, both experimentally and computationally, and also show significant structural variations. Further research employing solid-state NMR should focus on $^{25}\text{Mg}$ NMR as a very valuable source of structural information.

Identifying specific surface structures by comparing NMR results to DFT calculations proved to be difficult in all cases. This is partly attributed to the existence of many defect structures caused by the ball-milling process used to prepare the samples. The existence of such defect structures both at the surface and in the interior of the MgCl$_2$ particles is obvious from $T_1$ relaxation studies of the adducts, which display large
difference in relaxivity as a function of particle size/ball-milling time.

### EXPERIMENTAL SECTION

#### Sample Preparation.

The preparation of the samples studied in this contribution is described elsewhere. In short, dried MgCl₂ and the respective donors were ball-milled for 8 h. 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.

#### Computational Details.

Quadrupolar parameters were calculated by means of a well-known periodic ab initio software package, namely, the CRYSTAL09 suite, which uses atom-centered (Gaussian) basis sets. Geometry optimizations and electric field gradient (EFG) calculations were carried out at the B3LYP level of theory, including Grimme’s (D2) semiempirical correction for dispersion (with the modification proposed by Civalieri and co-workers), using the TZVP basis set for Mg, Cl, and Ti, and Ahlrichs VTZ plus polarization basis set for the C, H, and O atoms (optimized in a previous work). In the case of MgCl₂·nH₂O, the EFG calculations were carried out using the p6-TZVP basis set for Cl atoms. The positions of all atoms were fully relaxed along with the cell parameters. With reference to the CRYSTAL09 user manual, in the evaluation of the Coulomb and Hartree–Fock exchange series, the field energy was set to 10⁶ Ha for the geometry optimizations. The reciprocal space was sampled according to a regular sublattice with shrinking factor equal to 6.

In the case of the DiBP adducts and the high-coverage model of the DMDOMe adduct, we adopt the cluster approach described elsewhere.

The optimized cluster structures are reproduced in the SI. The EFG calculations were carried out at the TPSS functional level using the 6-31+G(2d,p) basis set for Mg and Cl, and the IGLO-II basis set for H, C, and O atoms.

#### NMR.

Mg and Cl spectra were recorded at room temperature on a Varian VNMRS 850 MHz spectrometer (20 T, 52.0 MHz for ²⁵Mg, 83.25 MHz for ³⁵Cl) using a triple-resonance 4.0 mm Varian T3 MAS probe at 15.625 kHz MAS. Mg and Cl spectra have been obtained using a Hahn echo with short echo times: 1 rotor period (64 μs) or 16 μs (static). Recycle delays were long enough (3–5 times T₁) to ensure quantitative measurements. Shifts were referenced to solid NaCl (δ NaCl = −45.37 ppm with respect to infinitely dilute solution of NaCl(aq) (δ NaCl = 0.00 ppm)) or a saturated solution of MgCl₂(aq) (set to 0.00 ppm).

We used the sideband-selective double-frequency sweep (ssDFS) pulse scheme to transfer population from the satellites into the central transition to increase the signal. A theoretical maximum enhancement of 2f can be obtained using this technique. We also used the QCPMG detection scheme. A series of echo pulses is applied with signal detection between the echoes. This leads to the so-called spikelet spectrum, in which the regular Hahn-echo signal is split into a manifold of sharp lines (spikelets), which resembles the envelope of the echo spectrum. Since the intensity of the echo is distributed over a few spikelets, the signal-to-noise ratio increases significantly. As shown before, we combined ssDFS and QCPMG to get maximum enhancement.
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