

Supporting Information

Tetrahydrofuran in $\text{TiCl}_4/\text{THF}/\text{MgCl}_2$: a Non-Innocent Ligand for Supported Ziegler-Natta Polymerization Catalysts

Etienne Grau,^{1,2,3} Anne Lesage,⁴ Sébastien Norsic,²

Christophe Copéret,^{*1} Vincent Monteil,^{*2} Philippe Sautet^{*3}

* ccoperet@inorg.chem.ethz.ch, monteil@lcpp.cpe.fr, philippe.sautet@ens-lyon.fr

1: Department of Chemistry, ETH Zurich, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland,

2: Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, Chimie Catalyse Polymères et Procédés (C2P2), LCPP team, 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France,

3 : Université de Lyon, CNRS, Ecole Normale Supérieure de Lyon, Laboratoire de Chimie, 46 Allée d'Italie, 69364 Lyon Cedex 07, France,

4 : Université de Lyon, CNRS, Ecole Normale Supérieure de Lyon, Centre de RMN à Très Hauts Champs, 5 rue de la Doua, 69100 Villeurbanne, France.

Experimental section

All chemicals were handled using standard Schlenk procedures under argon atmosphere. Solvents were distilled from drying agents. Pure triethylaluminium (TEA) was purchased from Wacko chemical. Ethylene (purity 99.95%) was purchased from Air Liquide and used without any further purification.

Polyethylene characterizations

Molecular weights of polyethylenes were determined by size exclusion chromatography (SEC) using a Waters Alliance GPCV 2000 instrument (columns: PLgel Olexis); two detectors (viscosimeter and refractometer) in trichlorobenzene (flow rate: 1 mL/min) at 150°C. The system was calibrated with polystyrene standards using universal calibration.

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1 at a heating rate of 5 K/min. Two successive heating and cooling of the samples were performed. We have considered data (T_m values) obtained during the second heats.

ZN Pre-catalyst characterizations

Small-Angle X-ray diffraction (XRD) on powder was carried out on a Bruker D8 Avance diffractometer (33 kV & 45 mA) with Cu K α radiation ($\lambda = 0.154$ nm) in the “Centre de diffractometrie H. Langchambon”, UCBL, Lyon, France. The diffraction patterns were collected in the 2θ angle range [5°-70°] at a scanning rate of 0.1°/min. Analysis of air-sensitive samples were performed using an airtight PMMA dome filled in a glove-box.

GC-MS were performed on Agilent 5973/6890 system using electron impact ionization 70eV, He carrier, 30mx0.25mm HP-INNOWAX capillary column.

EPR analyses were performed in the “Laboratoire de Chimie” at Ecole Normale Supérieure de Lyon on a Bruker Elexys E500 X-Band (9.4 GHz) spectrometer with a standard cavity. The magnetic field is measured on time by a gaussmeter. Analyses of air-sensitive products are performed using quartz Young tubes.

Titanium, Magnesium, Carbon, Hydrogen contents of precatalysts were determined by elemental analysis, performed at the CNRS SCA (Service Central d'Analyse) laboratory in Solaize (France).

Synthesis of pre-catalysts

- **(MgCl₂/THF/TiCl₄):** The Ziegler-Natta pre-catalyst was prepared as follows: first MgCl₂ was stirred in boiling THF (1g of MgCl₂ for 10 mL of THF) for 4 h. Then after cooling down the suspension, heptane was added dropwise. After decantation the filtrate was removed and remaining solid was washed 4 times with heptane. A white powder of MgCl₂(THF)_x with x≈1.5 was obtained. The compound was then treated with an excess of liquid TiCl₄ (1g of MgCl₂(THF)_x for 10 mL of TiCl₄) at 90°C for 2 h. Toluene was added dropwise, and the mixture cooled down. After decantation, the solid was washed 3 times with hot toluene and 4 times with heptane yielding a yellow powder.

- **(MgCl₂/ClBuOH/TiCl₄) and (MgCl₂/EtOH/TiCl₄):** The procedure is similar to the (MgCl₂/THF/TiCl₄) case replacing THF by 4-Chlorobutanol or ethanol.

Standard polymerization procedure of ethylene

Caution, all polymerizations involve high pressure and explosive gas.

Ethylene polymerizations were carried in a 1 L stainless steel autoclave (equipped with safety valves, stirrer, oven) from Sotalem Co.. Before each polymerization, the reactor was washed using a millimolar solution of TEA in heptane. A suspension of few milligrams of pre-catalyst was then prepared in 250 mL of a 3 mM solution of TEA in heptane in a Schlenk tube under argon. The mixture was introduced through cannula into the cooled reactor. Then 1 bar of H₂ was introduced with 7 bars of ethylene. The mixture was heated at 80°C under stirring (500 rpm). During the polymerization the total pressure was maintained constant. After 1 hour of polymerization the reactor was slowly cooled down and degassed. The slurry of polymer was then filtrated, washed with ethanol and dried under vacuum at 90°C.

Solid-State NMR Spectroscopy

All NMR experiments were carried out on a Bruker AVANCE III wide bore spectrometer operating at a ¹H Larmor frequency of 800.13 MHz. The proton spectra were referenced to the single resonance observed in adamantane for protons at 1.87 ppm with respect to neat TMS. ¹³C chemical shifts were referenced with respect to the CH₂ resonance of adamantane at 38.48 ppm with respect to neat TMS.¹

Heteronuclear correlation spectroscopy

The two-dimensional (2D) proton carbon-13 correlation spectrum of Figure 1 was recorded using a double resonance 2.5 mm probe at a magic angle spinning (MAS) frequency of 22 kHz. A conventional solid-state heteronuclear correlation (HETCOR) experiment was

applied, which consists first in a 90° proton pulse, followed by a t_1 evolution period under proton isotropic chemical shift and a cross-polarization (CP) step to transfer magnetization on the neighboring carbon-13 spins. For the spectrum of Figure 1, a total of 128 t_1 increments of 50 μs with 512 scans each were recorded. The total experimental time was 28 hours. The contact time was 500 μs and the repetition delay was 1.5 s. SPINAL-64² heteronuclear decoupling (during t_2) and e-DUMBO-22³ homonuclear decoupling (during t_1) were applied at radio-frequency (RF) fields of respectively 100 kHz and 120 kHz. A ramped CP was used with a proton RF field of 90 kHz at the top of the ramp while the RF field on carbon-13 was adjusted for optimum transfer efficiency. Quadrature detection was achieved using the TPPI method⁴ by incrementing the phase of the proton spin-lock pulse during the CP step. A scaling factor of 0.57 was applied to correct the proton chemical shift scale.

The one-dimensional (1D) carbon-13 spectrum displayed on the top of the 2D map in Figure 1 was recorded using the same experimental conditions and with 18432 scans. For the spectrum of Figure S6, the contact time was 2000 μs . All other experimental parameters were the same as for Figure 1.

Proton Double-Quantum Spectroscopy

The 2D proton double-quantum (DQ) single-quantum (SQ) correlation spectrum of Figure S4 was recorded at a spinning frequency of 60 kHz using a 1.3 mm triple resonance probe. DQ excitation and reconversion were achieved using the BABA⁵⁻⁷ pulse sequence. A proton 90° pulse of 2.5 μs was used. The length of the excitation and reconversion periods was set to 33.33 μs . Quadrature detection in ω_1 was achieved using the States-TPPI method.⁸ A recycle delay of 1.5 s was used. A total of 300 t_1 increments of 16.67 μs with 128 scans each were recorded. The total experimental time for the DQ experiment was 17 hours.

- (1) Morcombe CR, Zilm KW (2003) Chemical shift referencing in MAS solid state NMR. *J. Magn. Reson.* 162:479-486.
- (2) Fung BM, Khitritin AK, Ermolaev K (2000) An improved broadband decoupling sequence for liquid crystals and solids. *J. Magn. Reson.* 142:97-101.
- (3) Elena B, de Paepe G, Emsley L (2004) Direct spectral optimisation of proton-proton homonuclear dipolar decoupling in solid-state NMR. *Chem. Phys. Lett.* 398:532-538.
- (4) Marion D, Wüthrich K (1983) Application of phase sensitive two-dimensional correlated spectroscopy (COSY) for the measurements of ^1H - ^1H spin-spin coupling constants in proteins. *Bioch. Biophys. Res. Com.* 113:967-974.
- (5) Graf R, Demco DE, Gottwald J, Hafner S, Spiess HW (1997) Dipolar couplings and internuclear distances by double-quantum nuclear magnetic resonance spectroscopy in solids. *J. Chem. Phys.* 106:885-895.
- (6) Schnell I, Lupulescu A, Hafner S, Demco DE, Spiess HW (1998) Resolution enhancement in multiple-quantum MAS NMR spectroscopy. *J. Magn. Reson.* 133:61-69.
- (7) Brown SP (2007) Probing proton-proton proximities in the solid state. *Prog. Nucl. Magn. Reson. Spectrosc.* 50:199-251.
- (8) Marion D, Ikura M, Tschudin R, Bax A (1989) Rapid recording of 2D spectra without phase cycling. *J. Magn. Reson.* 85:393-399.

VASP calculation

The DFT calculations were performed in periodic boundary conditions in the Generalized Gradient Approximation (GGA) using Perdew-Wang (PW91) functional, as implemented in the VASP code (version 5.2.11). The Projected Augmented Wave (PAW) method was adopted for the description of atomic cores. In order to take into account Van der Waals interaction (especially between MgCl_2 layers), Grimme method was also implemented. An 10-layer thick slab was used, with an inter-slab distance of approximately 10 Å. The Brillouin zone integration is performed with 1 x 1 x 1 k-point grid generated by the Monkhorst-Pack algorithm. In order to reproduce the properties of extended surfaces, the bottom 5 layers were kept fixed during the calculations at bulk coordinates, while the top layers were allowed to relax.

INCAR file:

```
System = MgCl2+TiCl4+THF

LCHARG = .FALSE.
LVDM = .TRUE.

Grimme method for VdW
VDW_RADIUS = 30.0
VDW_SCALING = 0.75
VDW_D = 20.0
VDW_C6 = 5.71 5.07 10.80 0.70 1.75 0.14
VDW_R0 = 1.364 1.639 1.562 1.342 1.452 1.001

Electronic minimization
PREC = ACCURATE
GGA = 91
EDIFF = 1E-6
ALGO = Fast
LREAL = Auto

Ionic relaxation
EDIFFG = -0.01
NSW = 400
IBRION = 2
POTIM = 0.5
ISIF = 2

DOS related values
ISMEAR = 0
SIGMA = 0.1
```

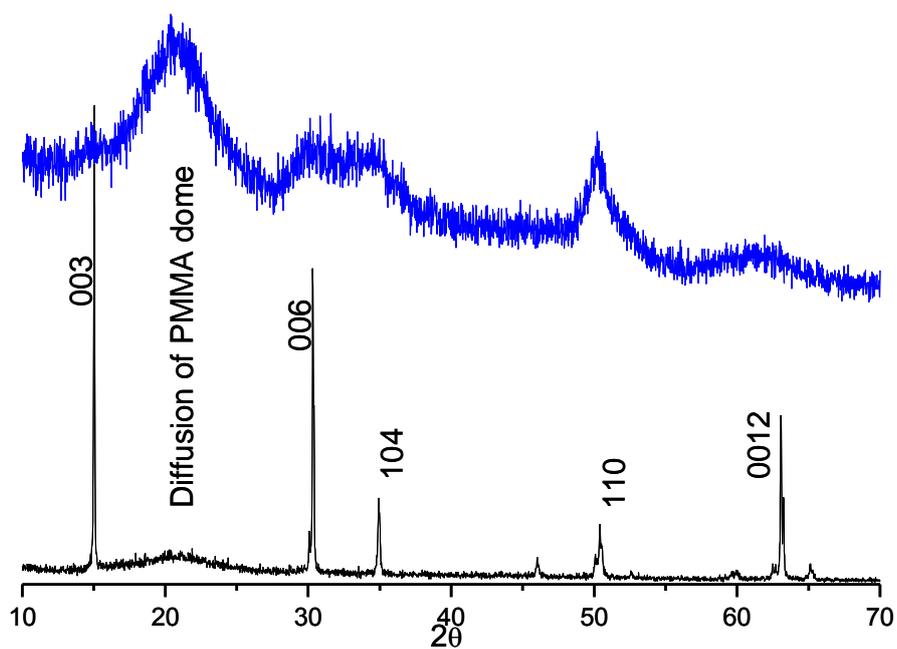


Figure S1. X-rays powder diffraction pattern of MgCl_2 (black bottom curve) and ZN pre-catalyst (blue top curve).

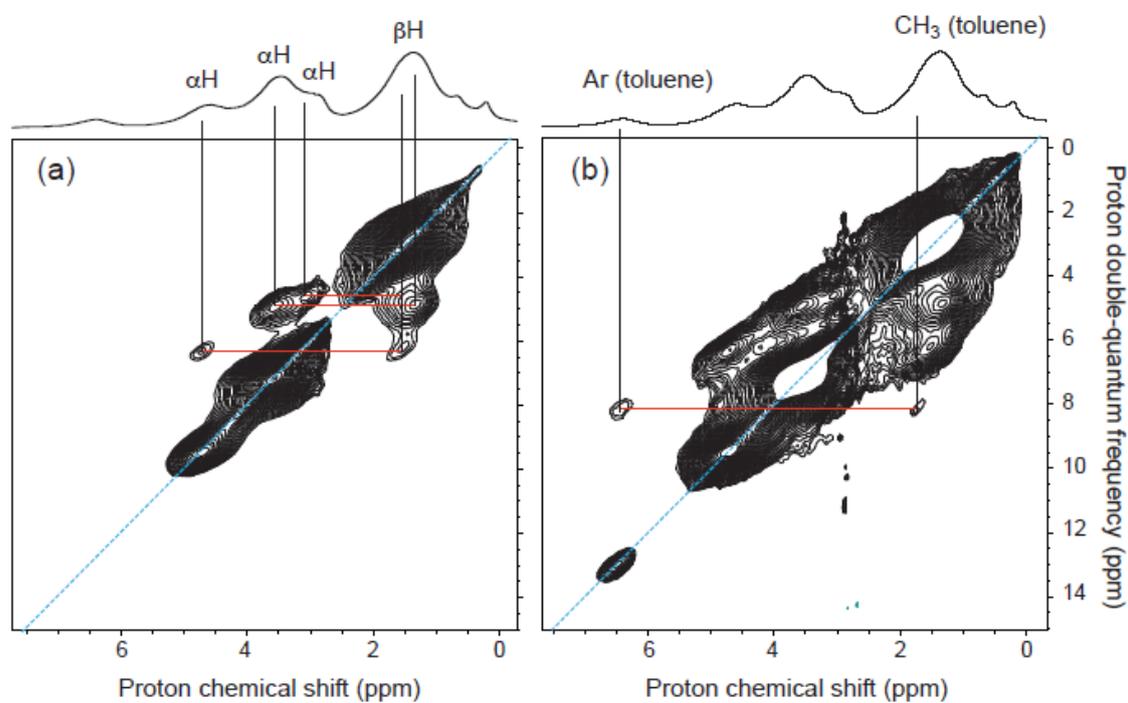


Figure S2. Solid state NMR of $\text{MgCl}_2/\text{TiCl}_4/\text{THF}$ Ziegler-Natta pre-catalyst: Double Quanta ^1H - ^1H 2D-NMR at two different level contour.

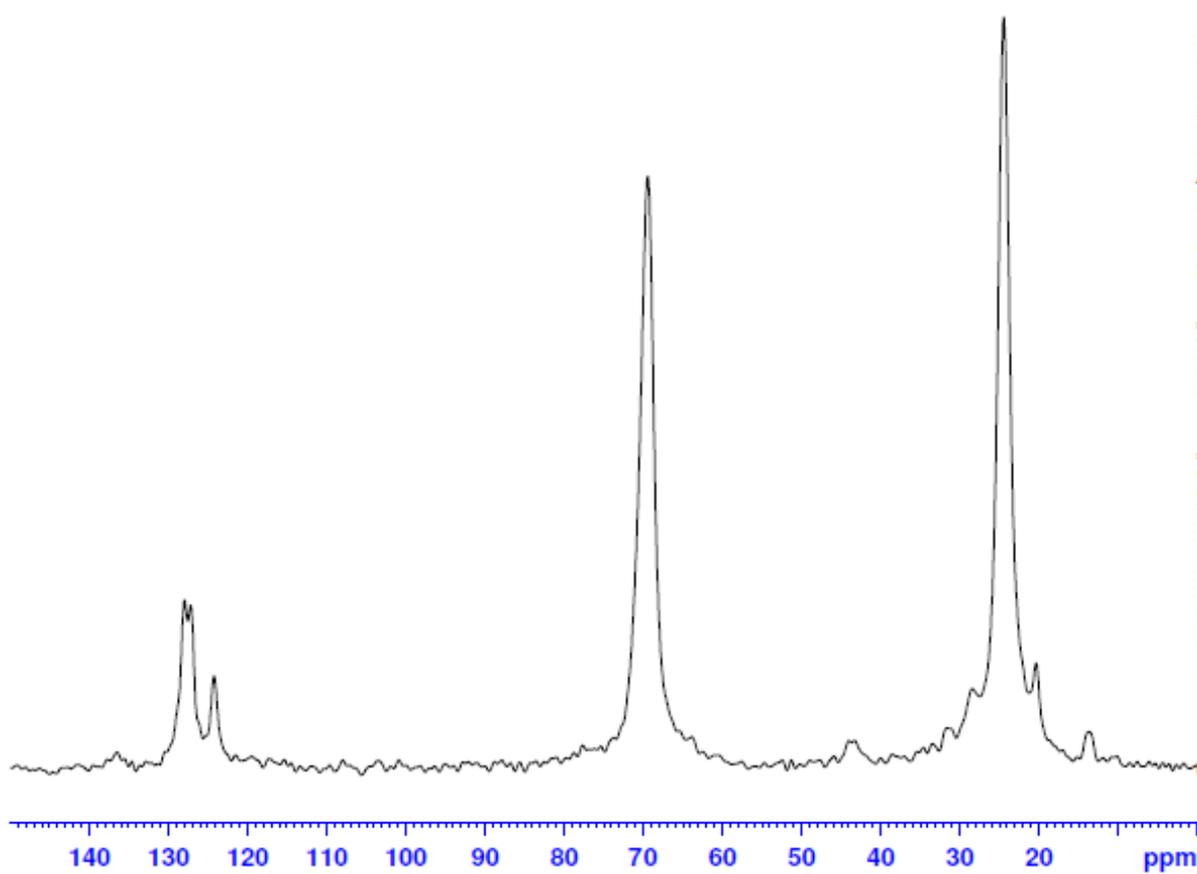


Figure S3. Solid State ^{13}C CP-MAS NMR of $\text{MgCl}_2/\text{TiCl}_4/\text{THF}$ Ziegler-Natta pre-catalyst with additional toluene. Spectrum recorded using 4mm probe at a spinning rate of 10 kHz on a 300MHz Bruker spectrometer.

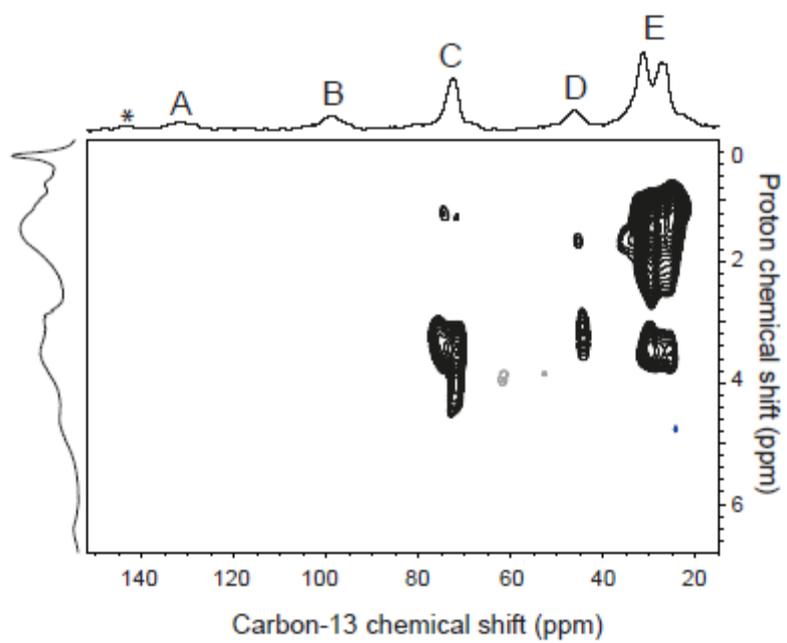
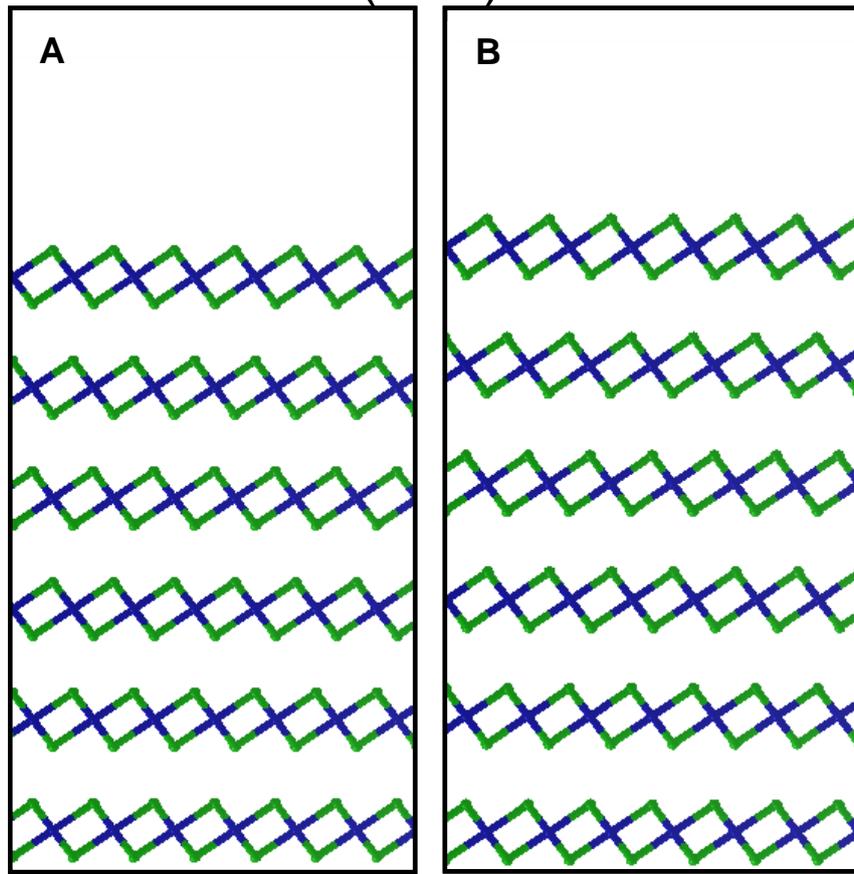
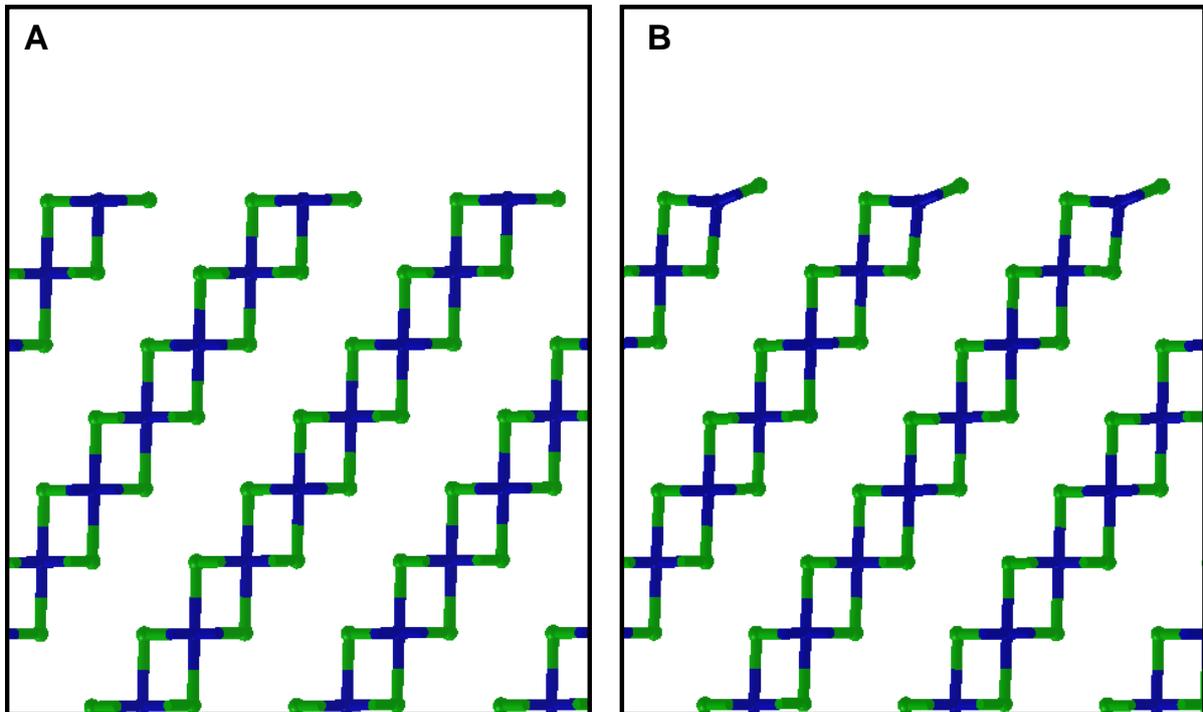


Figure S4. Two-dimensional ^{13}C - ^1H HETCOR spectrum using a cross-polarisation contact time of 2 ms.

(0 0 1)



(1 0 4)



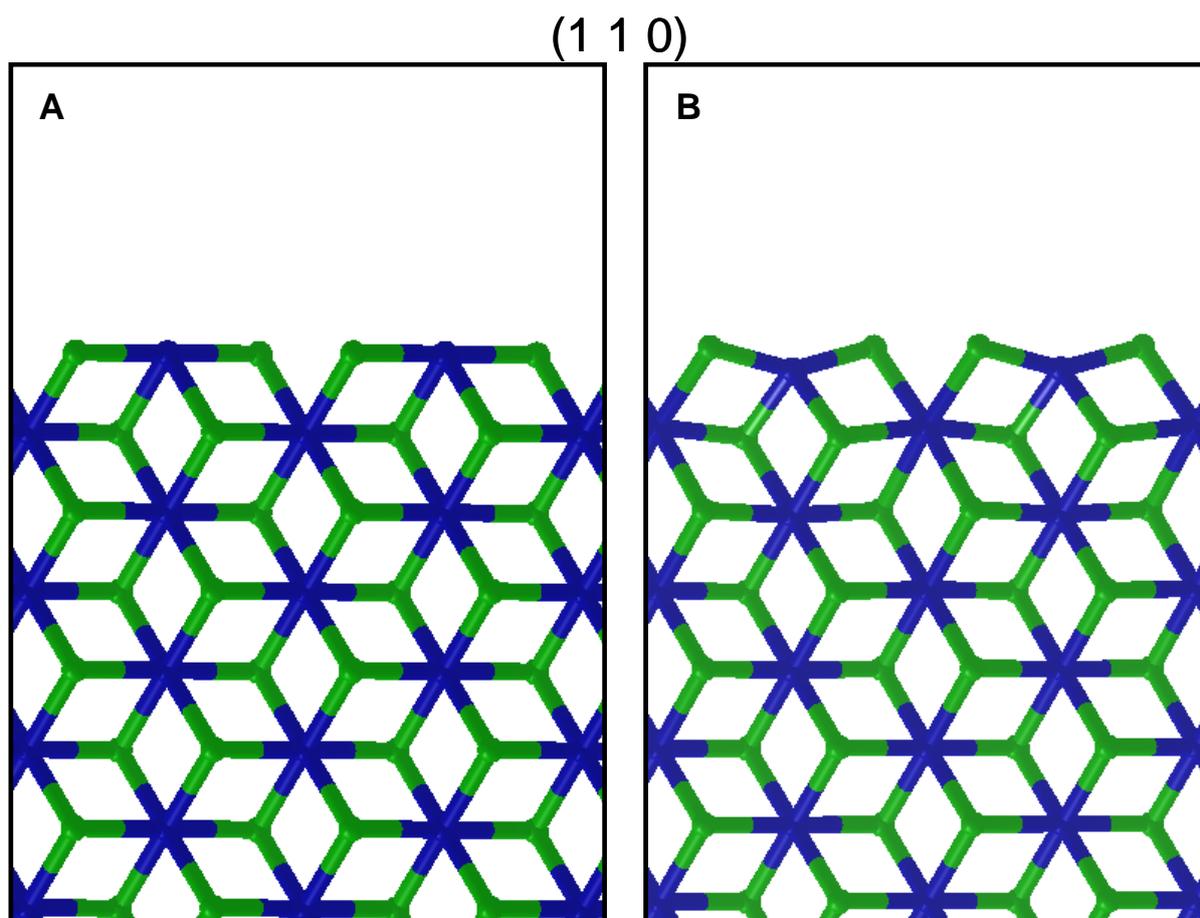


Figure S5. Orthographic view of the structures of the main MgCl₂ crystal surfaces considered in this work: (A) as cut from the bulk, (B) after relaxation.

Table S1: Periodic DFT-calculated surface Energies, γ_{hkl} , of MgCl₂ slab models.

Surface	(0 0 1)	(1 0 4)	(1 1 0)
γ_{hkl} before ionic relaxation (J.m ⁻²)	0.194	0.790	1.51
γ_{hkl} after ionic relaxation (J.m ⁻²)	0.115	0.312	0.460

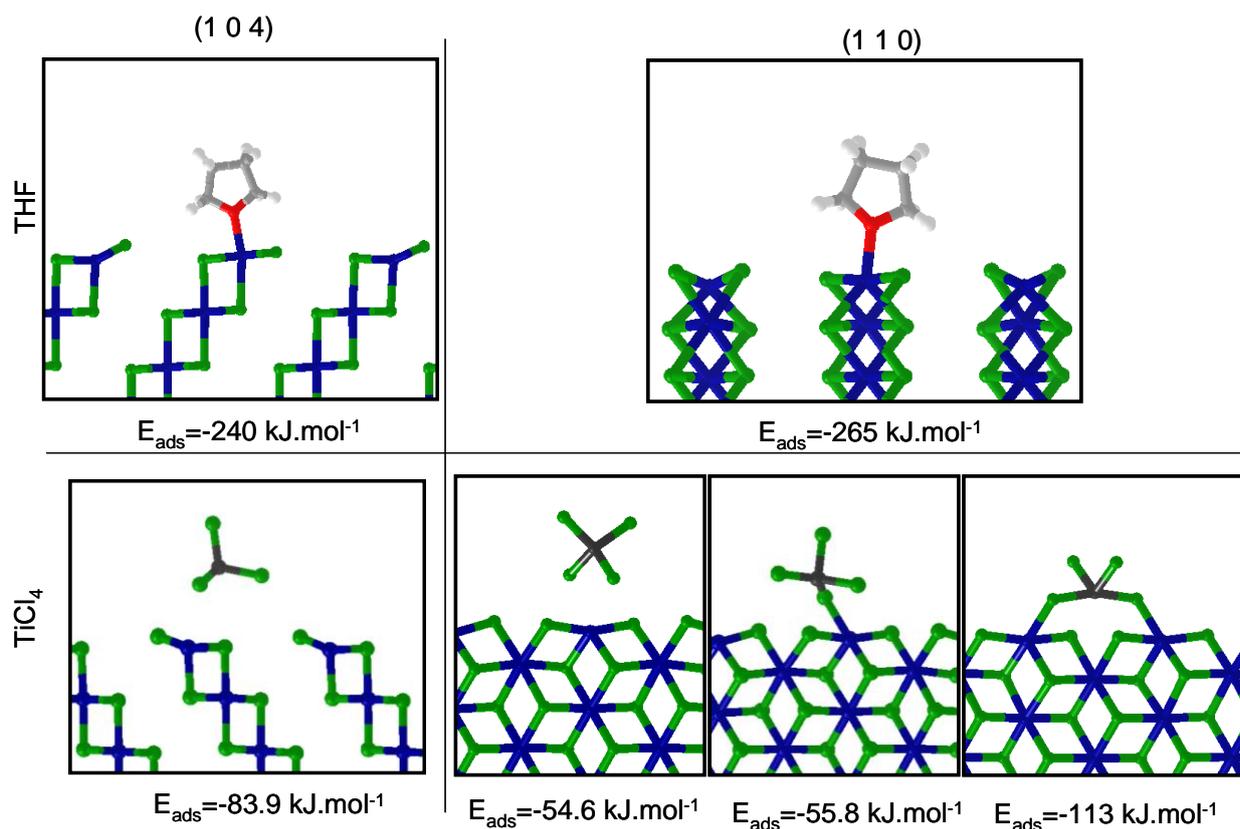


Figure S6. Orthographic view of the structures of the main THF and TiCl_4 adsorption site on MgCl_2 crystal surfaces considered in this work.

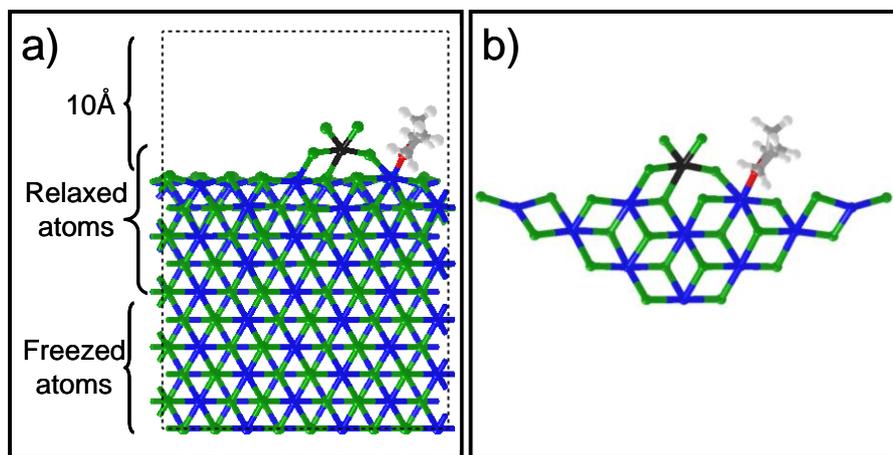
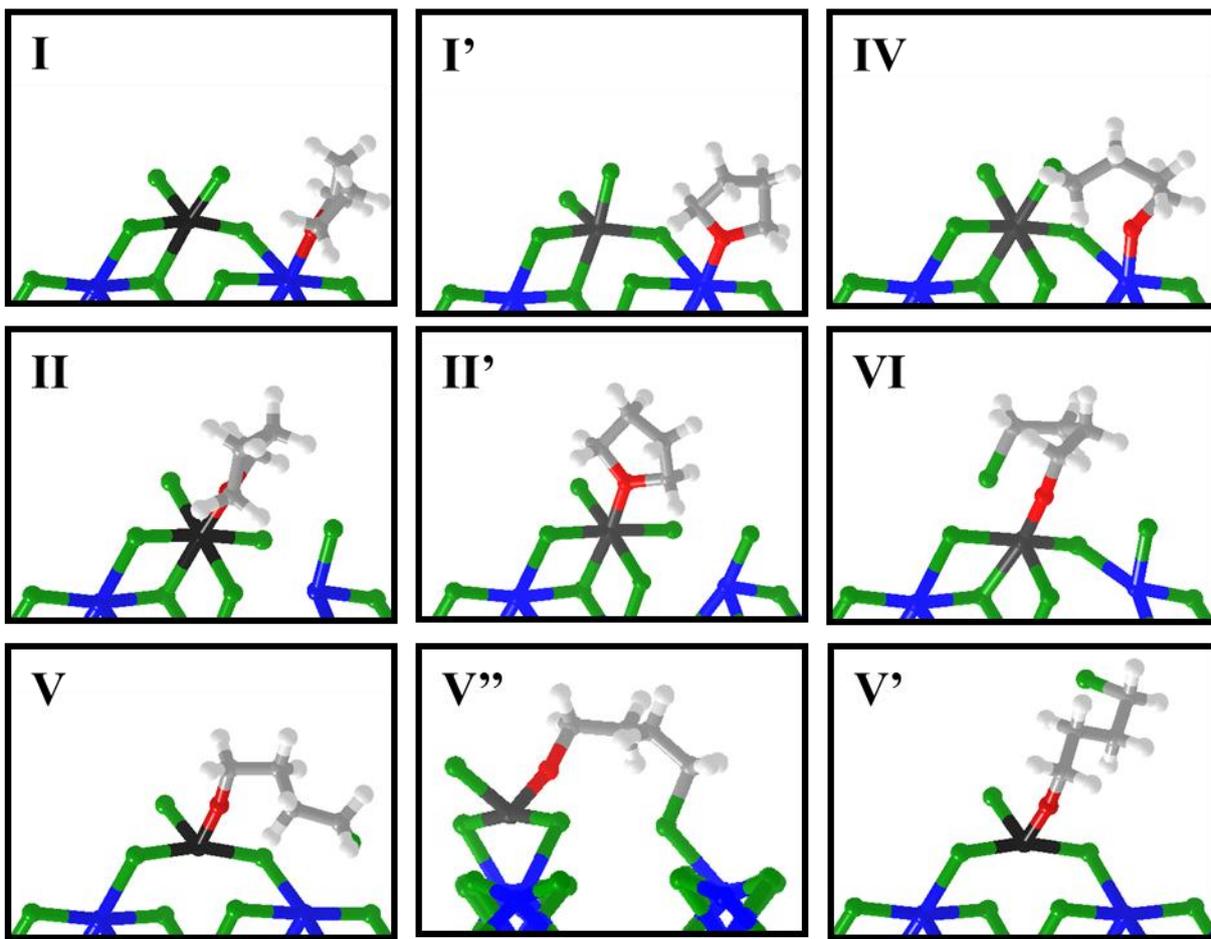
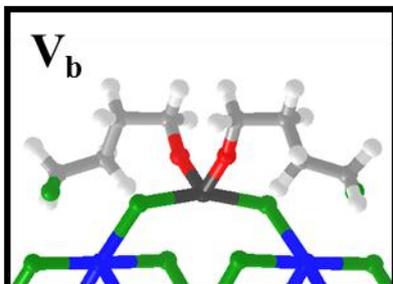
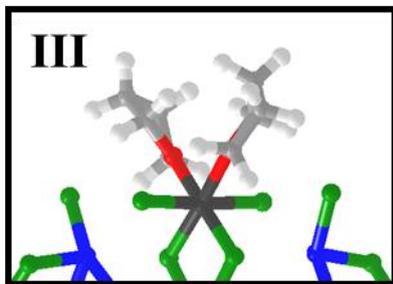
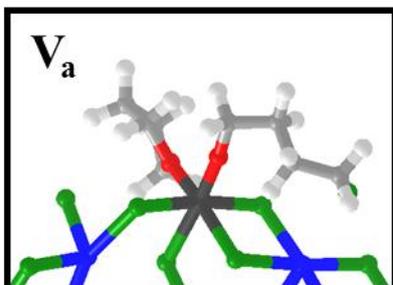
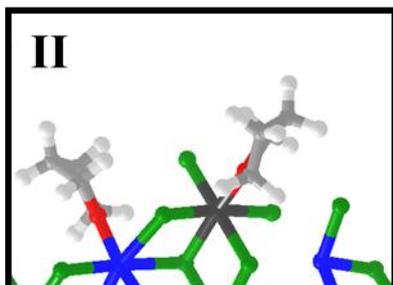
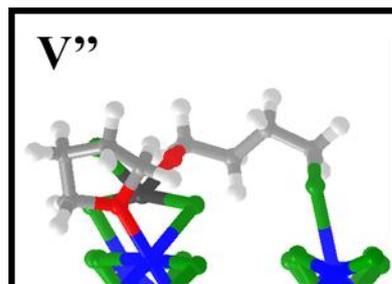
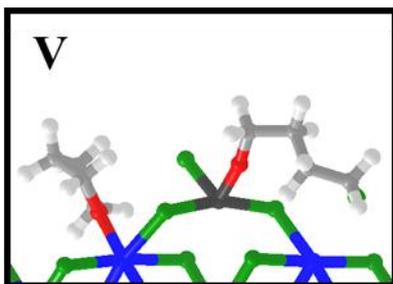
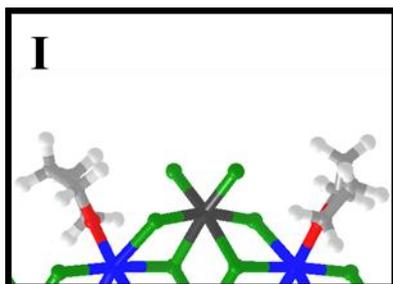


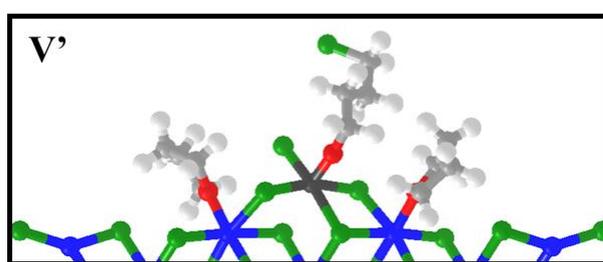
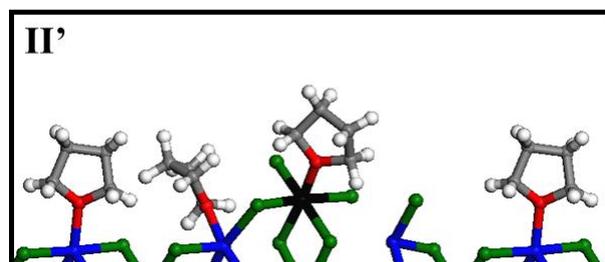
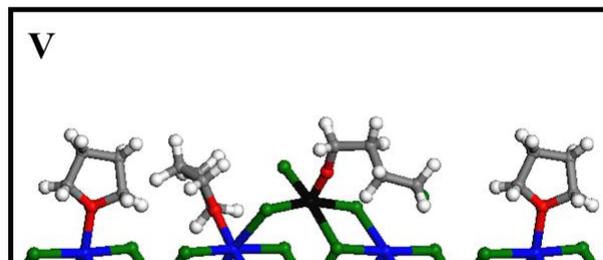
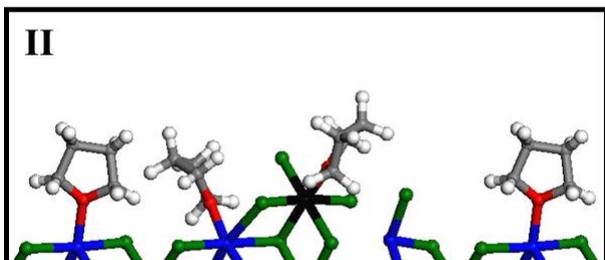
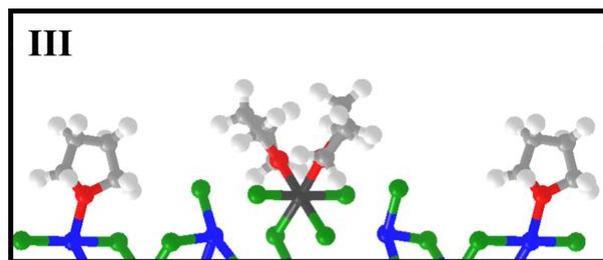
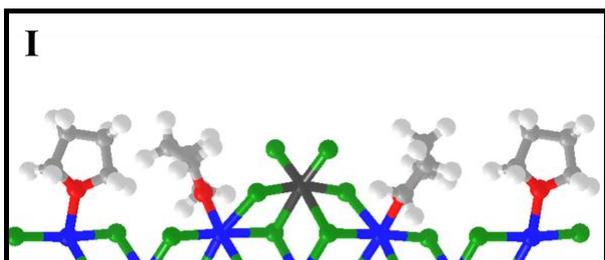
Figure S7. Example of cell (a) and the extracted cluster (b) considered for the calculation of TiCl_4 and THF co-adsorption on MgCl_2 (110) surface (in blue Mg atom, green Cl, black Ti, red O, gray C, pale gray H).



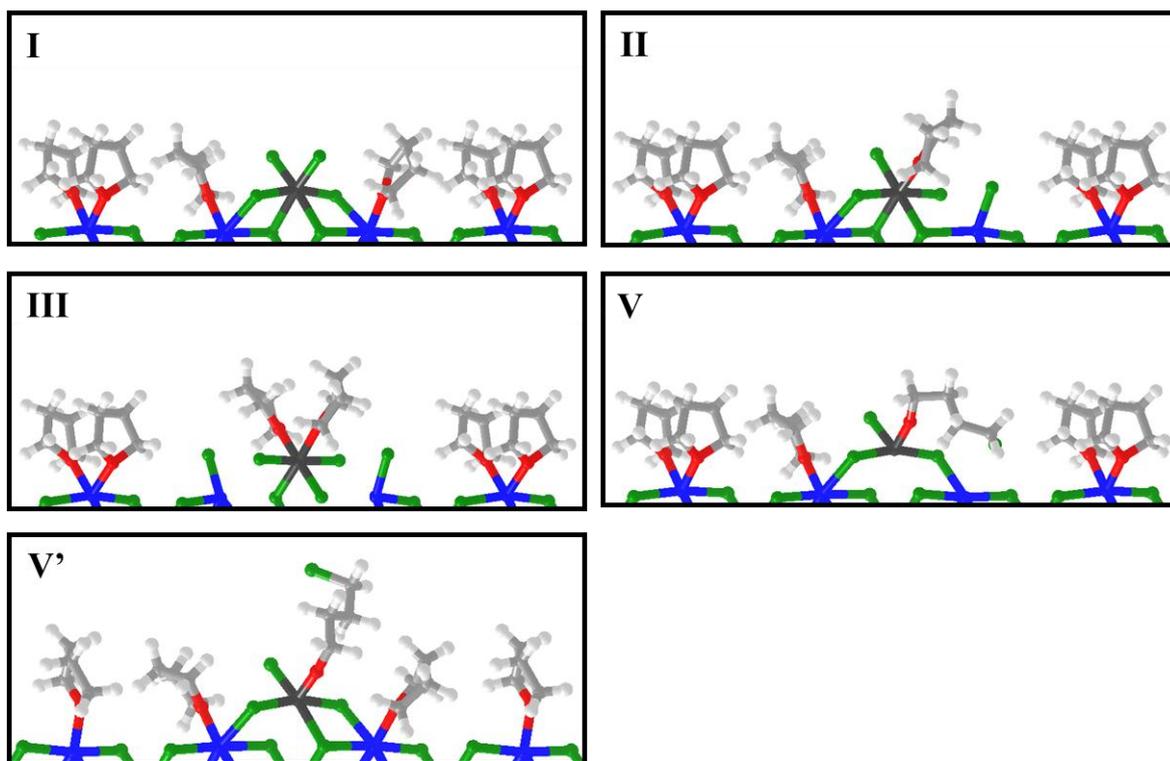
a) 1THF / cell



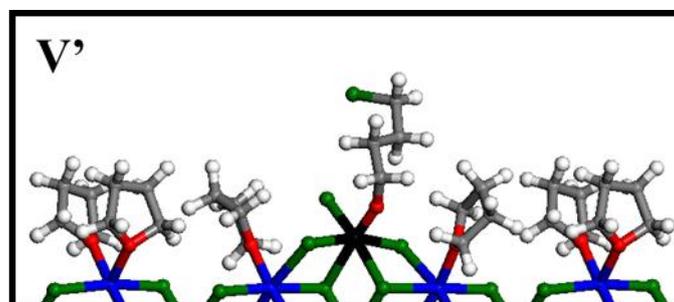
b) 2THF / cell



c) 3THF / cell



d) 4THF / cell



e) 5THF / cell

Figure S8. Orthographic view of the structures of the main THF/TiCl₄ adsorption site on (110) MgCl₂ crystal surfaces considered in this work.

Table S2: Calculated ^{13}C (**A**) and ^1H (**B**) NMR chemical shifts of different THF derivate species vs free THF.

A: ^{13}C NMR

Species	α -O (ppm)	α -Cl (ppm)	β -O (ppm)	β -Cl (ppm)
1 THF: I	+2.6		+1.7	
1 THF: II	+22.5		+2.5	
1 THF: V	+21.4	-13.6	+3.4	+2.9
1 THF: V'	+24.3	-19.2	+6.1	-5.9
1 THF: I'	+7.3 / +5.5		+1.2 / +1.0	
1 THF: II'	+25.0 / 20.5		+2.1 / +1.4	
1 THF: IV	+11.4	+6.6	+12.0	+8.7
1 THF: V''	+22.4	-12.8	+4.7	+2.4
1 THF: VI	+22.3	-11.2	+4.4	-0.3
<hr/>				
2 THF: I	+2.1		+1.6	
2 THF: II	+21.6 (+2.0)		+2.6 (+1.5)	
2 THF: III	+17.1		+2.3	
2 THF: V	+20.6 (+1.7)	-13.7	+2.9 (+1.1)	+2.4
2 THF: V_a	+20.6 (+15.9)	-14.8	+2.8 (+1.4)	+2.3
2 THF: V_b	+15.8	-13.6	+2.8	+1.8

B: ¹H NMR

Species	α -O (ppm)	α -Cl (ppm)	β -O (ppm)	β -Cl (ppm)
1 THF: I	+0.6		+0.3	
1 THF: II	+1.8		+0.7	
1 THF: V	+1.3	+0.1	+0.7	+0.0
1 THF: V'	+1.1	+0.0	+0.6	+0.6
1 THF: I'	+0.8 / +0.7		+0.2 / +0.2	
1 THF: II'	+2.0 / 1.3		+0.6 / +0.3	
1 THF: IV	+1.8	+1.1	+0.5	+0.2
1 THF: V''	+1.4	+0.1	+0.6	+0.1
1 THF: VI	+1.3	+0.5	+1.6	+0.1

2 THF: I	+0.6		+0.4	
2 THF: II	+1.8 (+0.8)		+0.5 (+0.4)	
2 THF: III	+1.7		+0.5	
2 THF: V	+1.4 (+0.6)	+0.1	+0.4 (+0.4)	+0.3
2 THF: V_a	+1.6 (+1.7)	+0.1	+0.5 (+0.5)	+0.1
2 THF: V_b	+1.1	+0.2	+0.4	+0.0

Table S3: Differential adsorption energies of different THF derivate species vs. **I** in $\text{kJ}\cdot\text{mol}^{-1}$.

Species	1 THF / TiCl_4	2 THF / TiCl_4	3 THF / TiCl_4	4 THF / TiCl_4
I	0	0	0	0
II	76	74	73	61
II'	106	108	105	95
III	not stable	157	152	138
IV	231	nd	nd	nd
V	39	42	44	41
V'	63	60	56	32
V''	51	36	nd	1
V_a	-	117	nd	108
V_b	-	86	nd	82
VI	147	nd	nd	nd

nd means not determined

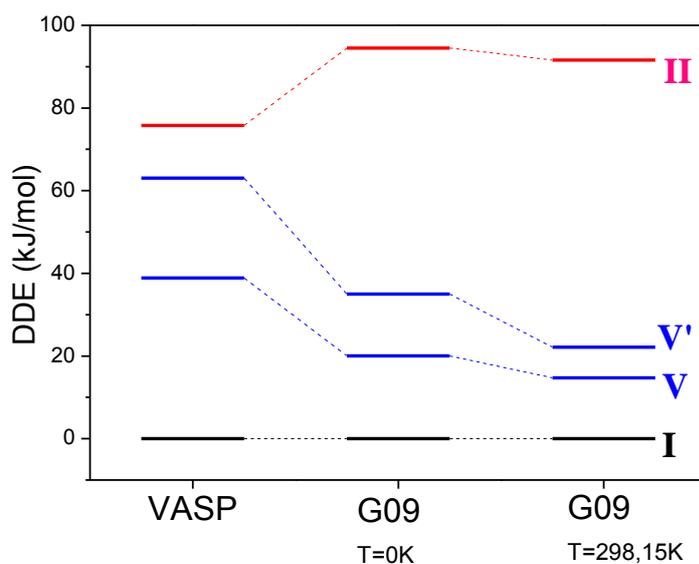


Figure S9. Relative energy of the THF/TiCl₄ species on MgCl₂ (110) using VASP calculation on cell or Thermochemie module of Gaussian09 on cluster at 0K or taking into account vibrational entropy at 298.15K. (It should be noted that the entropy associated to the gain in mobility of the pendant chain is not included in these calculations).

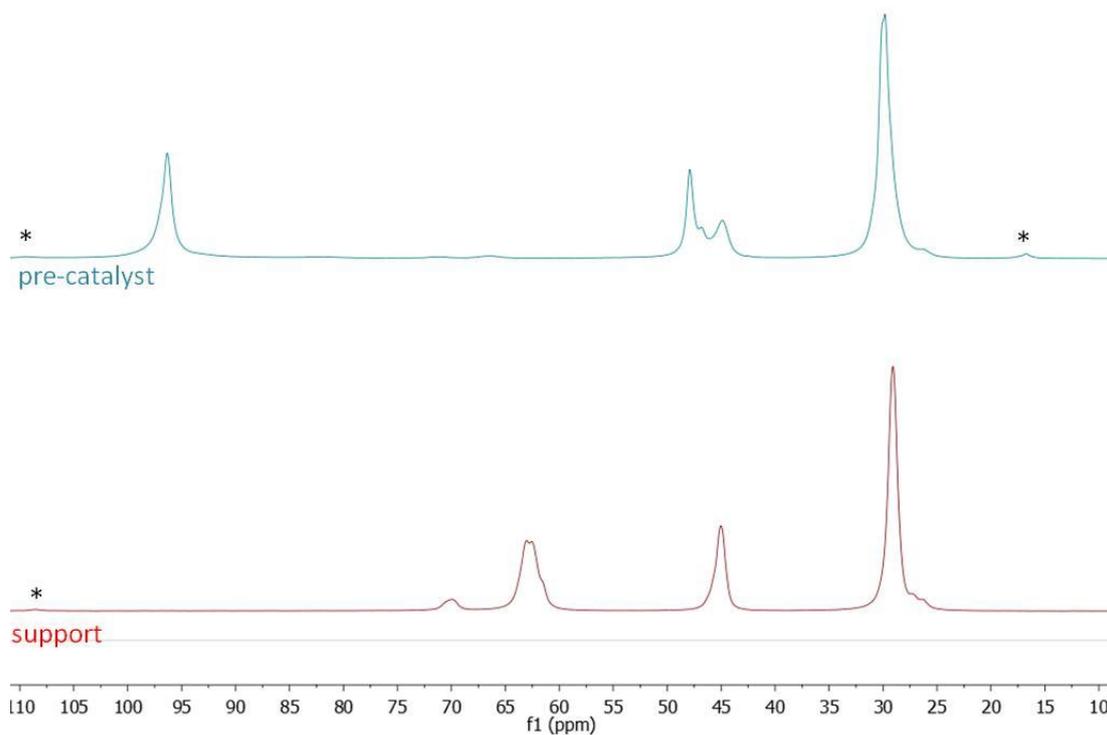


Figure S10. Solid State ^{13}C CP-MAS NMR of solid support $\text{MgCl}_2/\text{ClBuOH}$ (1) and precatalyst $\text{MgCl}_2/\text{TiCl}_4/\text{ClBuOH}$ (2): Spectra recorded using 4mm probe at a spinning rate of 10 kHz on a 500 MHz Bruker spectrometer. Principal peaks are: 63, 45, 29 ppm for $\text{MgCl}_2/\text{ClBuOH}$ (smaller peaks at 27 and 70 ppm corresponds to THF which is present in small amounts in 4-chlorobutanol) and 96, 48, 45, 29 ppm for $\text{MgCl}_2/\text{TiCl}_4/\text{ClBuOH}$.

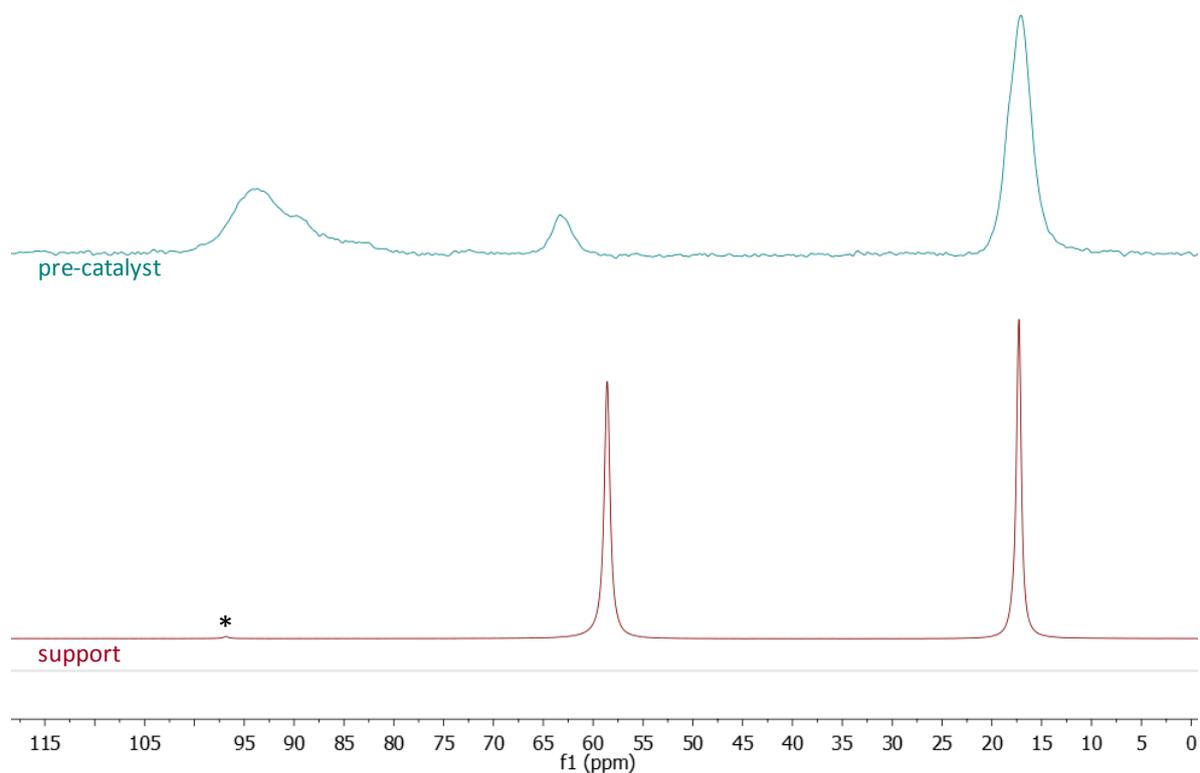


Figure S11. Solid State ¹³C CP-MAS NMR of solid support MgCl₂/EtOH (1) and precatalyst MgCl₂/TiCl₄/EtOH (2): Spectra recorded using 4mm probe at a spinning rate of 10 kHz on a 500 MHz Bruker spectrometer.

Principal peaks are:

- 59 and 17 ppm for MgCl₂/EtOH (corresponding to methylene carbon in α to oxygen (59 ppm) and to methyl carbon in β (17 ppm) of ethanol adsorbed at MgCl₂ surface);
- 94, 63 and 17 ppm for MgCl₂/TiCl₄/EtOH (corresponding to methylene carbon in α to oxygen (94 ppm) of titanium ethoxy species, to methylene carbon in α to oxygen (63 ppm) of ethanol adsorbed at precatalyst surface and to methyl carbon in β (17 ppm) of ethanol adsorbed at MgCl₂ surface and of titanium ethoxy species).

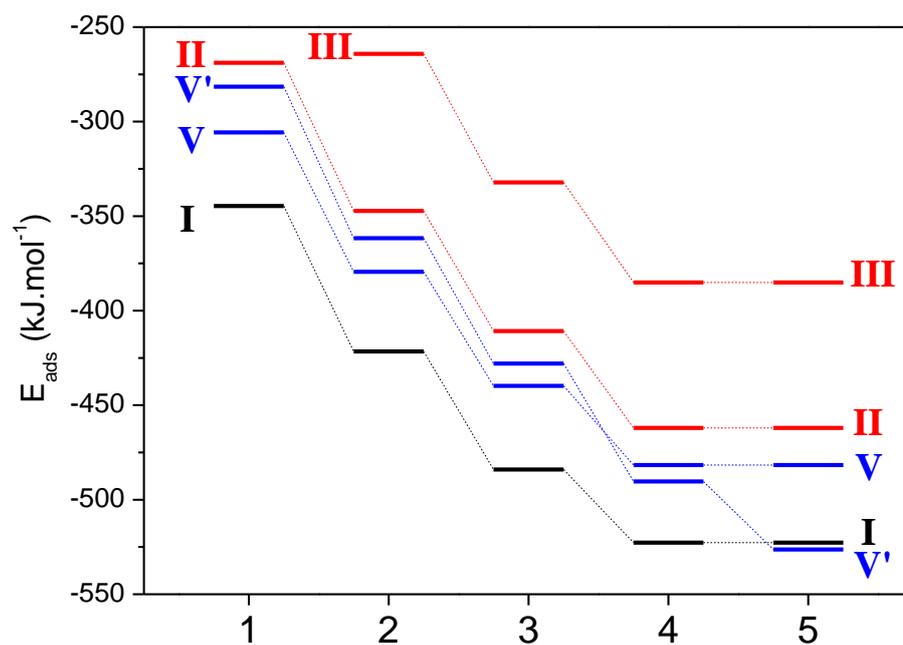


Figure S12. Total adsorption energies of the THF species on MgCl_2 (110) surface for 1, 2, 3, 4 or 5 THF per cell. The energy references are THF in $\text{TiCl}_4(\text{THF})_2$ and TiCl_4 in gas phase for THF and TiCl_4 respectively.