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CH_3-ReO_3 on γ-Al_2O_3: understanding its structure, initiation and reactivity in olefin metathesis.**

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Understanding the structure of catalytically active sites at a molecular level is still a challenge in heterogeneous catalysis. Surface Organometallic Chemistry (SOMC) has investigated ways to generate well-defined heterogeneous catalysts through a molecular approach to better understand these systems.[1] This has already yielded several efficient catalysts for olefin conversion processes (polymerization, hydrogenation, metathesis),[1-3] and even processes to convert alkanes at low temperatures.[4] In the specific field of olefin metathesis, we have developed a series of well-defined silica supported metal alkylidene complexes,[5] which have shown unprecedented performances compared to both homogeneous and heterogeneous catalysts. Yet, industrial processes typically rely on simpler catalytic systems, and one of the simplest and highly efficient heterogeneous catalysts for olefin metathesis derived from SOMC is based on CH_3ReO_3[6] supported on Lewis acidic supports such as silica alumina,[7, 8] alumina,[9] nobia[10] or zeolithes.[11] Recent investigations have shown that CH_3ReO_3 is grafted to silica alumina mainly through coordination via Lewis acid – Lewis base interaction.[8] However, the structure of the so-called "active site" remains elusive, and the mechanism of formation of the expected propagating carbene species is unknown. Despite numerous studies, a question remains : is the methyl group of CH_3ReO_3 involved or not in the formation of the initial carbene ? [10, 12, 13]

Through a combined use of spectroscopic (IR, NMR and EXAFS), reactivity and molecular modeling studies,[14, 15] we show below that CH_3ReO_3 reacts with γ–alumina partially dehydroxylated at 500 °C, γ–$Al_2O_{3\text{-}(500)}$, to produce mainly a coordination adduct onto the Lewis acid sites of this support through its oxo ligand. Yet, this species is not active and the active sites correspond to a minor species, which results from the C-H activation of the methyl ligand of CH_3ReO_3 onto reactive Al_s-O sites of alumina yielding surface hydroxyl (Al_sOH) and a methylene Re surface complex, [$Al_sCH_2ReO_3$] (the initiating center for the olefin metathesis carbene propagating species).

IR spectroscopy. Under static vacuum, CH_3ReO_3 sublimed on γ–$Al_2O_{3\text{-}(500)}$ at room temperature, and the solid turned to deep red. The IR spectrum (Fig. 1) shows the appearance of two bands at 2995 and 2910 cm^{-1}, associated with the symmetric and anti-symmetric ν(C-H_3), along with two bands at 1390 and 1204 cm^{-1} assigned to δ(C-H_3). Moreover, the original Al-OH bands have been replaced by a large band centered at 3531 cm^{-1} (spanning between 3759 and 3184 cm^{-1}), which probably correspond to OH in a new environment (interaction with CH_3ReO_3).[15] Finally, a weak band at 1958 cm^{-1} attributed to (Re=O) harmonics is also observed.

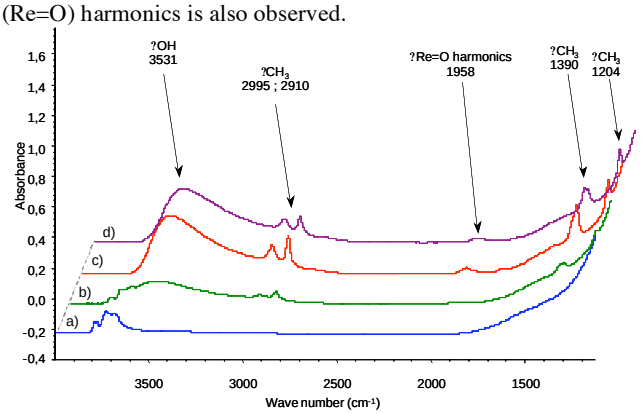

Figure 1. Monitoring the grafting of CH_3ReO_3 on γ-Al_2O_3 by IR spectroscopy. a) γ-$Al_2O_{3\text{-}(500)}$ after calcination and treatment at 500 °C under vacuum (10^{-5} Torr), b) 5 min after breaking the seal isolating CH_3ReO_3 from γ-$Al_2O_{3\text{-}(500)}$, c) after sublimation of CH_3ReO_3 on γ-$Al_2O_{3\text{-}(500)}$ and desorption, and d) after evacuation at 10^{-5} Torr for 2 h.

Mass balance analysis. Rhenium elemental analysis of CH_3ReO_3/γ-$Al_2O_{3\text{-}(500)}$ is 3,8 ± 0.1 $\%_{wt}$, which corresponds to 1.2 Re/nm². Therefore, Re coverage is much lower than the amount of OH groups present on a γ-$Al_2O_{3\text{-}(500)}$ (4 OH/nm²). Note that 1) no CH_4 evolved upon grafting and 2) reaction of CH_3ReO_3/γ-$Al_2O_{3\text{-}(500)}$ with H_2O does not give CH_4; these data show that the Re-C bond of CH_3ReO_3 has not been cleaved upon grafting.

Extended X-Ray fine structure spectroscopy (EXAFS). The EXAFS data are consistent with a Re center surrounded by four direct neighbors : 1 C at 2.16(2) Å and 3 O at 1.718(4)Å. The fit is improved by adding 1 O at a relatively short distance, 2.47(5) Å, along with 4 O at 3.47(4) Å and 2 Al at 3.11(3) Å. Considering the four direct neighbors, the Re-O and the Re-C distances are elongated by about 1 and 5%, respectively compared to these in free CH_3ReO_3, for which they are 1.704(3) and 2.063(2) Å, respectively.[16] The structure of CH_3ReO_3 supported on γ-$Al_2O_{3\text{-}(500)}$ is thus largely unchanged compared to this of free CH_3ReO_3.

Table 1. Re-X bond distances for CH_3ReO_3 supported on γ-Al_2O_3 as measured by EXAFS (S_0^2=1, ΔE_0 = 5(1) eV).

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Neighbor	# of Neighbors	Distance (Å)	σ^2 (Å^2)
O	2.8(2)	1.718(4)	0.0031(4)
CH_3	1	2.16(2)	0.006(2)
O	1	2.47(5)	0.013(3)
Al	2	3.11(3)	0.013[a]
O	4	3.47(4)	0.013[a]

[a] Constrained to equal the preceding variable

Solid state NMR spectroscopy. A quantitative single pulse proton decoupled ^{13}C MAS solid state NMR spectrum of 100% ^{13}C labeled CH_3ReO_3 on γ-Al_2O_3 clearly shows one large signal at 30 ppm (78%) along with three other signals at 64 (12%), 19 (2%)[17] and 10 (8%) ppm, which indicates clearly that several surface species are in fact present in contrast to what is suggested by the EXAFS data, which point towards the presence of a single species.

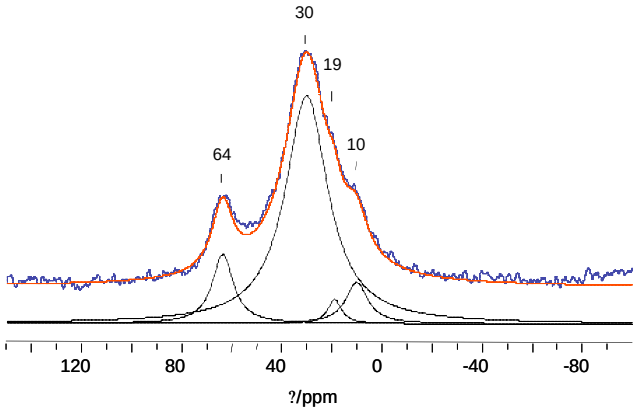


Figure 2. Direct proton decoupling MAS solid state NMR spectrum of ^{13}C labeled CH_3ReO_3 on γ-Al_2O_3 under MAS of 10 kHz, pulse angle of 45°. The number of scan was 5000, and the recycle delay was set to 10 s.

Modeling studies through periodic calculations of chemisorbed CH_3ReO_3 on Lewis acid sites of γ–Al_2O_3. The bulk of γ-Al_2O_3 is composed of Al_{Oh} (75%) and Al_{Td} (25%), and the bare surface of a fully dehydroxylated alumina is therefore composed of Al_{III} (Fig. 3a) and troncated octahedral aluminum (Al_{Oh}, Fig. 3b-c).[18-20] γ-Al_2O_3 pretreated at 500°C is partially hydroxylated and shows various types of OH groups (4 OH/nm^2) and Al_V Lewis acid sites. It was shown from the reactivity of H_2 and CH_4 that the hydration is not uniform and that low coordination dehydrated Al_{III} (from bulk Al_{Td}, Fig. 3a) and Al_{IV} (from bulk Al_{Oh}, Fig. 3b) are present as surface defects:[20] Al_{III} (0.03/nm^2) reacts with H_2 and CH_4, Al_{IV} (0.04/nm^2) only with H_2, while regular Al_V Lewis acid sites (~ 4/nm^2) react with neither of these molecules. We have therefore studied the structure and the associated spectroscopic properties of surface species resulting from the reaction of CH_3ReO_3 on various Lewis acid sites (Fig. 3d-i).

First, coordination of CH_3ReO_3 through an oxo ligand on these Lewis acid sites is exoenergetic, with reaction energies ranging from –97 (Al_{III}) to –33 (Al_V) kJ.mol^{-1} (Fig. 3d-f). Coordination has only a small effect on the geometries at Re and Al: the Re–C and Re–O bond distances, not involved in the coordination, remain unchanged, and the Re–O bond length of the Re=O bound to Al is only slightly elongated by 2%. Moreover, the calculated ^{13}C chemical shifts for the methyl ligand range from 27 to 37 ppm, slightly downfield from free $MeReO_3$ (δ_{exp} = 17 ppm and δ_{calc} = 15 ppm).

Second, $MeReO_3$ can also react with these Lewis acid sites through the C-H bond activation of its methyl group, and the resulting surface species are more stable than the separated reactants independently of the coordination at Al, with energies ranging from -114 to -29 kJ.mol^{-1} (Fig. 3g-i). The calculated chemical shift δ_{calc} of $MeReO_3$ activated on Al_{III} is 43 ppm (Fig. 3g) and close to δ_{calc} of the coordinated compounds (see above). In contrast, δ_{calc} of surface species resulting from the C-H activation on Al_{Oh} are shifted down field in the 78-88 ppm range (Fig. 3h-i), so that the peak observed at 64 ppm can be attributed to Al_{Oh}-CH_2ReO_3 species. Note that the Re–C and Re=O bond distances in [Al_S-CH_2ReO_3] are also close to those in free CH_3ReO_3, which probably explains why, despite the presence of numerous surface species, the observed EXAFS data are consistent with a unique Re environment. Additionally, grafting via C-H bond activation generates surface hydroxyls, hydrogen-bonded to surface Al-O species, which is also consistent with the appearance of Al_sOH bands at lower wave number in the IR spectrum (Fig. 1).

Considering the surface density of the various types of Al Lewis acid sites, the integration of the observed NMR signals and the δ_{calc} of various possible surface species, the major surface species (1.05/nm^2), associated with NMR signals observed around 30 ppm, are mainly $MeReO_3$ coordinated on Lewis acid sites, and the minor species (0.15/nm^2) correspond to [Al_{Oh}-CH_2ReO_3].

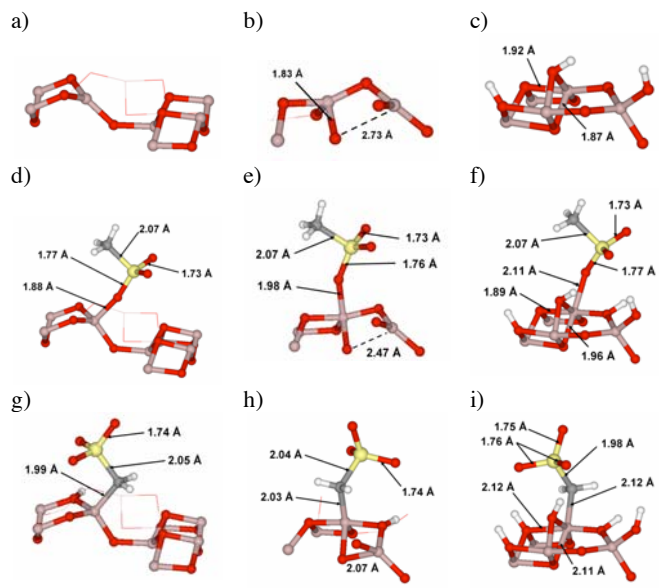
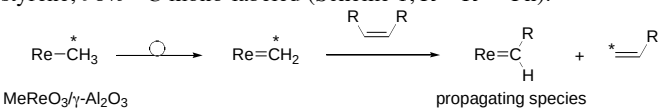


Figure 3. Structures of representative aluminium Lewis sites (a, b, c), of the corresponding different stable CH_3ReO_3 coordinated to the Al sites (d, e, f) and of the corresponding complex resulting from the heterolytic splitting of the methyl of CH_3ReO_3 on the Al sites (g, h, i) (δ_{Me} = calculated chemical shift and ΔE = adsorption energy):a) A_{III} from bulk Al_{Td} ; b) Al_{IV} from bulk Al_{Oh} ; c) A_{IV} (from hydration of Al_{IV}) d) δ_{Me} = 37 ppm and ΔE = -97 kJ.mol^{-1}; e) δ_{Me} = 33 ppm and ΔE = -33 kJ.mol^{-1}; f) δ_{Me} = 27 ppm and ΔE = -33 kJ.mol^{-1}; g) δ_{Me} = 43 ppm and ΔE = -114 kJ.mol^{-1}; h) δ_{Me}= 78 ppm and ΔE = -43 kJ.mol^{-1}; i) δ_{Me} = 88 ppm and ΔE = -29 kJ.mol^{-1}. Only a small number of atoms of the periodic surface slab in the vicinity of the grafting site are shown for clarity.

Olefin metathesis activity and active site of CH_3ReO_3 supported on γ-Al_2O_3. CH_3ReO_3/γ-Al_2O_3 rapidly transforms 500 equiv of propene into a thermodynamic mixture of ethene and 2-butenes in less than 1h with an initial TOF of 11 mol of propene/Re/min, but the structure of the active site and the importance of the methyl ligand remains to be understood at a molecular level.[10, 12, 13] We have therefore investigated the reaction of several olefins with CH_3ReO_3 supported on alumina in order to understand the initiation step.

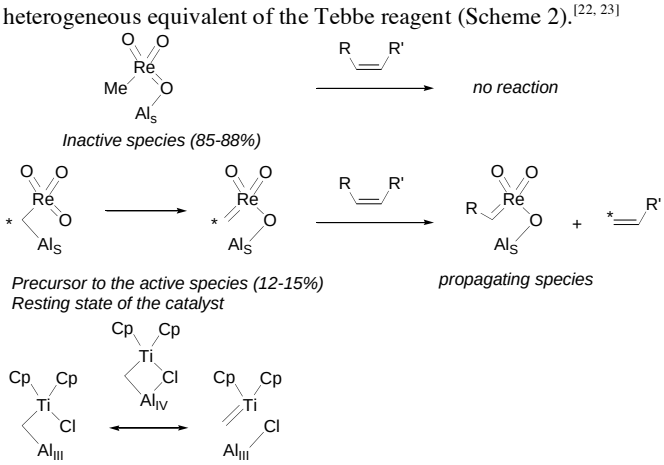
First, after reaction of CH_3ReO_3/Al_2O_3 with 0.53 equiv of ^{13}C di-labeled ethene for 15h, 0.40 equiv of ethene is detected, of which 28%

is ^{13}C mono-labeled. Besides ethene, 0.015 equiv of a mixture ^{13}C labeled propene isotopomers is formed, probably by decomposition of the metallacyclobutane intermediate.[21] Considering a mass-balance of 80% and the non-quantitive exchange due to the small amount of ethene/Re active site, CH_3ReO_3/Al_2O_3 contains *ca*. 14-15% of active site. Reverse titration of active sites by contacting CH_3ReO_3/Al_2O_3, previously treated with di-labeled ethene, with un-labeled ethene gives ^{13}C mono-labeled ethene, in an amount which also corresponds to *ca*. 14-15%. This shows that *ca*. 14-15% of the methyl groups are involved in the formation of the carbene propagating species (Scheme 1, R = R' = H). The involvement of the methyl of CH_3ReO_3 has been further confirmed by contacting 99% ^{13}C labeled CH_3ReO_3/Al_2O_3 with 11 equiv of *Z* stilbene, which gives *E* stilbene and 0.10 equiv of styrene, 98% ^{13}C mono-labeled (Scheme 1, R = R' = Ph).



Scheme 1.

Furthermore, the solid state ^{13}C CP MAS NMR spectrum of CH_3ReO_3/Al_2O_3 contacted with 0.8 equiv of 100% ^{13}C di-labeled ethene shows that the major signal results from a sharp increase of the peak at 66 ppm, previously attributed to $[Al_{Oh}CH_2ReO_3]$ (Fig. S2a-b). Other signals have also appeared, and they are attributed to physisorbed olefins (144 ppm) and olefin oligomers (31, 21 and 11 ppm), because the same signals appear upon contacting γ-Al_2O_3 with ^{13}C di-labeled ethylene (Fig. S2c). Noteworthy, the integration of the signal at 66 ppm in the ^{13}C NMR spectrum of the ^{13}C labeled CH_3ReO_3/γ-Al_2O_3 (12%, Fig. 2) is fully consistent with the titration of this site with ^{13}C labeled ethene (14-15%). Note that no signal at low fields (150-400 ppm range), typical of carbene ligands, has been observed. Therefore $[Al_{Oh}CH_2ReO_3]$ is the stable form of the active site of the catalyst, which probably generates the necessary carbene *in situ* during metathesis, and thus this system corresponds to a Re-based heterogeneous equivalent of the Tebbe reagent (Scheme 2).[22, 23]



Scheme 2. Proposed active sites for CH_3ReO_3 supported on γ-Al_2O_3.

In conclusion, for CH_3ReO_3 on γ-Al_2O_3, a highly efficient olefin metathesis catalyst, the major surface species (85-88%) correspond to the interaction of the oxo ligand of CH_3ReO_3 with surface Lewis acid sites of alumina, but these are inactive fro olefin metathesis. The active site, $[Al_{Oh}CH_2ReO_3]$, is in fact a minor species (12-15%), and results from the C-H bond activation of the methyl ligand of CH_3ReO_3 on alumina. Overall, this study also shows that the major observed surface species is not responsible for the catalytic event, and therefore that a careful combined use of several techniques (in particular careful modeling and labeling experiments) is required in order to understand the structure of working catalysts at a molecular level.

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Olefin metathesis

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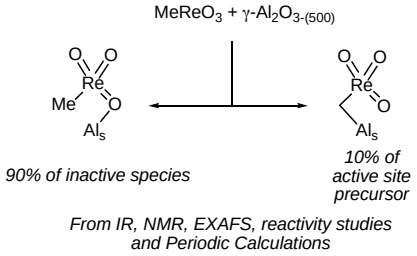
Me-ReO_3 on γ-alumina: understanding the structure, the initiation and the reactivity of a highly active olefin metathesis catalyst

Heterolytic splitting of the C-H bond of the methyl group of CH_3ReO_3 on Al_sO reactive sites of alumina as a way to generate the active site of CH_3ReO_3 supported on γ-Al_2O_3.



Supplementary materials.

CH_3-ReO_3 on γ-Al_2O_3: understanding its structure, initiation and reactivity in olefin metathesis.

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Experimental section.

General procedure. All experiments were conducted under strict inert atmosphere or vacuum conditions using standard Schlenk techniques. CH_3ReO_3 was prepared according to the literature procedure.[1] Elemental analysis were performed at the CNRS Central Analysis Service of Solaize (Re). Gas-phase analysis was performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and an KCl/Al_2O_3 on fused silica column (50 m X 0.32 mm).

IR spectroscopy. Infrared spectra were recorded on a Nicolet 550-FT by using an infrared cell equipped with CaF_2 windows, allowing *in situ* studies. Typically 16 scans were accumulated for each spectrum (resolution, 2 cm^{-1}).

Extended X-Ray Fine Structure Spectroscopy (EXAFS). Data were obtained at Stanford Synchrotron Radiation Laboratory on beam-line 11-2. Data acquisition and analysis were performed as previously described (ref. 9).[2]

Solid state NMR spectroscopy. All solid-state NMR spectra were recorded under MAS (ν_R = 10 kHz) on a Brüker Avance 500 spectrometer equipped with a standard 4-mm double-bearing probe head and operating at 500.13, 125.73 MHz for ^1H and ^{13}C, respectively. The freshly prepared samples were immediately introduced in the 4 mm zirconia rotor in a glove box and tightly closed. Compressed air was used for both

bearing and driving the rotors. Chemical shifts are reported in ppm downfield from $SiMe_4$ (± 0.1 and 1 ppm for ^1H and ^{13}C NMR spectra, respectively). The typical cross-polarization sequence was used for the ^{13}C CP MAS NMR spectra : 90° proton pulse, cross-polarization step to carbon spins and detection of the carbon magnetization under proton decoupling TPPM-15.[3] For the CP step, a ramp radio frequency (rf) field centered at ν^{CP} = 60 kHz was applied on protons, while the carbon rf field was matched to obtain optimal signal. The contact time for CP was set to 2 ms. An exponential line broadening of 80 Hz was applied before Fourier transform. All other details are given in the caption of figures.

Grafting of CH_3ReO_3 supported on partially dehydroxylated alumina at 500 °C, $Al_2O_{3\text{-}(500)}$, monitored by IR spectroscopy. γ-Al_2O_3 from Degussa C Aerosil® was calcined at 500 °C under N_2/O_2 flow overnight (18 h) and then partially dehydroxylated at 500 °C under high vacuum (1.34 Pa) for 18 h to give γ-$Al_2O_{3\text{-}(500)}$ having a specific surface area of 105 m^2/g.

Preparation of CH_3ReO_3 supported on partially dehydroxylated alumina at 500 °C, $Al_2O_{3\text{-}(500)}$. A γ-$Al_2O_{3\text{-}(500)}$ (1 g) was contacted, while stirring, with 100 mg of CH_3ReO_3 at 25°C. After 3 hours of reaction, removal of the excess of molecular complex was carried out by reverse sublimation, and the resulting solid was then treated under vacuum (0.13 mPa) for 3 h. Elemental analysis: 3.8 $\%_{wt}$ of Re.

Preparation of ^{13}C labeled CH_3ReO_3 supported on partially dehydroxylated alumina at 500 °C, $Al_2O_{3\text{-}(500)}$. This sample was prepared as described above by replacing unlabeled $MeReO_3$ by 100% ^{13}C labeled $MeReO_3$ (See Figures 2 and S1).

Reactivity of $CH_3ReO_3/Al_2O_{3\text{-}(500)}$ with ^{13}C di-labeled ethene followed by contact with unlabeled ethene. In a 22 mL batch reactor was introduced under Ar, $CH_3ReO_3/Al_2O_{3\text{-}(500)}$ (330 mg, 67.6 μmol of Re). After evacuation of Ar, 30 Torr of ^{13}C di-labeled ethene (0.53 equiv) was added. After 15 h, the gas phase was analyzed by GC and GC/MS, and then evacuated from the reactor under high dynamic vacuum for 1 h at 25 °C. Part of the solid (71 mg) was employed to prepare the NMR sample (See Fig S2-3), and the remaining

amount (259 mg, 53 μmol of Re) was contacted with unlabeled ethene (35 Torr, 0.78 equiv). After 15 h, the gas phase was analyzed by GC and GC/MS.

Reactivity of γ-$Al_2O_{3-(500)}$ with ^{13}C di-labelled ethene. In a 22 mL batch reactor was introduced 300 mg of γ-$Al_2O_{3-(500)}$ under Ar. After evacuation of Ar, 30 Torr of ^{13}C di-labeled ethene (1.2×10^{-4} mol/g of alumina) was added. After 15 h, the gas phase was evacuated from the reactor under high dynamic vacuum for 2 h at 25 °C, and the solid was analyzed by solid state NMR (See Fig S2b).

Reactivity of ^{13}C labeled $CH_3ReO_3/Al_2O_{3-(500)}$ with *Z* stilbene. In a 22 mL batch reactor was introduced 100 mg of ^{13}C labeled $CH_3ReO_3/Al_2O_{3-(500)}$ (20 μmol of Re) and 3 mL of a 7.5×10^{-2} M solution of *Z* stilbene in cyclohexane (224 μmol). The reaction was monitored by GC and GC/MS. Besides the isomerization of *Z* into *E* stilbene, 2 μmol of styrene (0.098 equiv./Re), > 98 % ^{13}C mono-labeled, was formed.

Computational methods and systems.

The calculations were performed on the framework of density functional theory (DFT) using a periodic description of the system as implemented in the VASP code.[4,5] The generalized gradient approximation was used in the formulation of Perdew and Wang PW91.[6] Atomic cores were described with the projected augmented wave method (PAW) which is equivalent to an all electrons frozen core approach.[7,8] The wave functions are developed on a basis set of plane waves. With the selected PAW potentials, a cutoff energy of 275 eV is adequate and yields a converged total energy. Brillouin zone integration was converged with a 331 k-point mesh generated by the Monkhorst-Pack algorithm.[9] Vibrational frequencies were calculated in the harmonic approximation by a numerical evaluation of the Hessian matrix. Chemical shifts have been evaluated with the GIAO method[10] implemented in the Gaussian03 code[11] at a DFT/B3LYP level.[12-15] The IGLO-II basis set[16] has been used for carbon and hydrogen. For other atoms, Hay and Wadt effective core potential[17-19] have been used with the adapted LANL2DZ basis set. The chemical shift calculations have been performed on selected clusters as previously discussed.[20] These clusters are extracted from the periodic surface taking at least the second oxygen layer as limit and saturated with hydrogen atoms such as the total

charge is zero. It generates clusters of approximately 60 atoms, depending on the site on which the cluster is centered. This ensures that the carbon atom of the grafted complex has at least all its fourth neighbors included in the chemical shift calculation.

The thickness of the model slab representing the surface has been sampled from 8 two 4 atomic layers with no significant changes. Thus a 4 layers slab has been used has a standard model. With such an asymmetric representation of the surface, some dipole correction may be necessary. Some tests reveal only infinitesimal changes in geometries and energetic corrections below 5 $kJ.mol^{-1}$ which are coherent with the large vacuum zone between the slabs (≈ 17 Å). Thus such corrections have not been applied.

The periodic cell of the slab contains 8 Al_2O_3 units in a 8.1 x 8.4 $Å^2$ cell. The vacuum zone upon the slab being approximately 17 Å, the cell is 23 Å high. Al_{III} and Al_{IV} sites are studied on the dehydrated (110) termination of the γ-Al_2O_3 bulk model (non hydrated unit cell) while Al_V is taken from the trihydrated unit cell.[21-24]

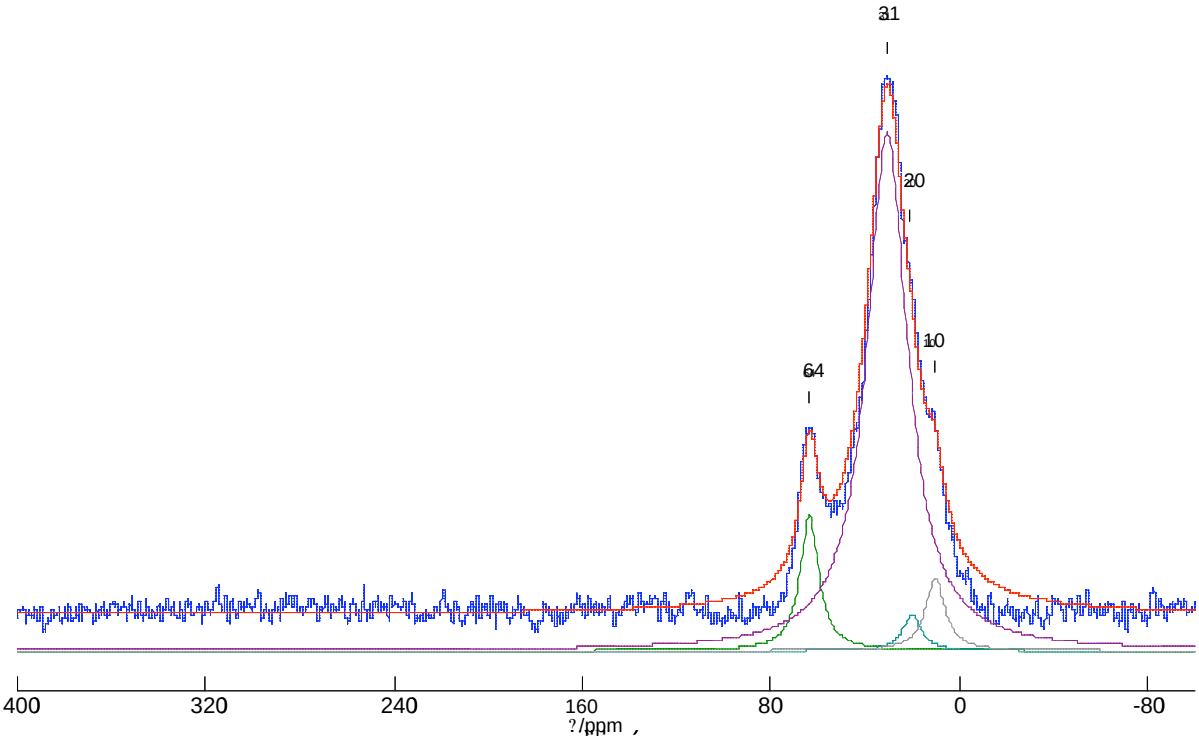
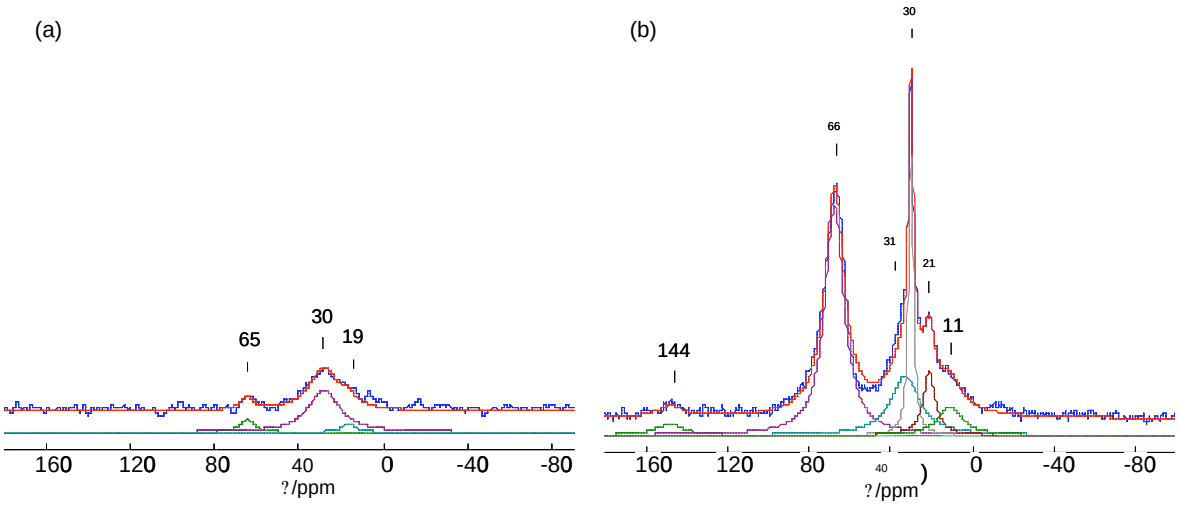


Figure S1. ^{13}C CP-MAS solid state NMR spectrum of ^{13}C labelled CH_3ReO_3 on γ-alumina under MAS of 10 kHz. The number of scan was 5120 and the recycle delay was set to 1 s.



c)

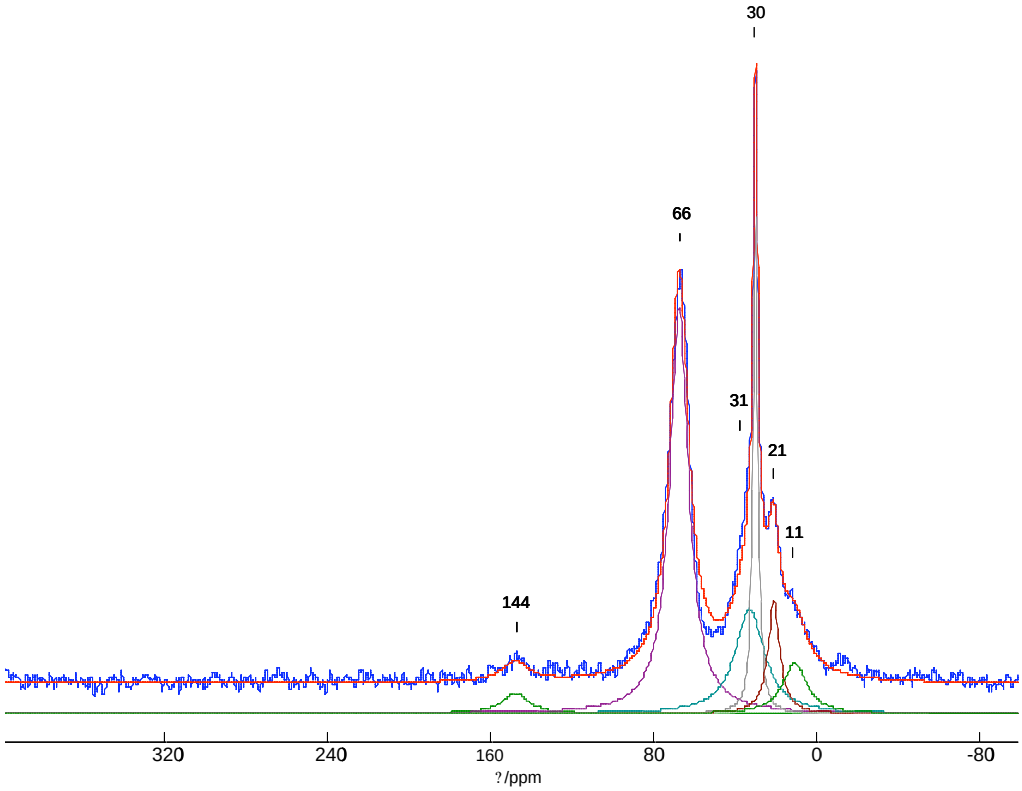


Figure S2. ^{13}C CP MAS solid state NMR spectrum (10 kHz): a) unlabeled CH_3ReO_3 on γ-alumina. The number of scan was 136000, CP = 1ms, and the recycle delay was set to 1 s. b) CH_3ReO_3 on γ-alumina after contact with ^{13}C di-labeled ethene. The number of scan was 1000, the CP = 2ms, and the recycle delay was set to 2 s. c) Same spectrum but full spectral window.

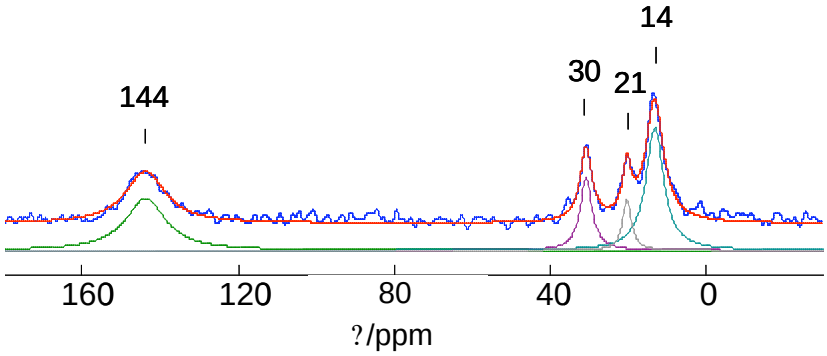


Figure S3. γ-alumina contacted with ^{13}C di-labeled ethane. The number of scan was 3600, CP = 2ms, and the recycle delay was set to 2 s.

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